HANDBOOK OF EXPLORATION GEOCHEMISTRY

G.J.S GOVETT (Editor)

1. ANALYTICAL METHODS IN GEOCHEMICAL PROSPECTING
2. STATISTICS AND DATA ANALYSIS IN GEOCHEMICAL PROSPECTING
3. ROCK GEOCHEMISTRY IN MINERAL EXPLORATION
4. REGOLITH EXPLORATION GEOCHEMISTRY IN TROPICAL AND SUB-TROPICAL TERRAINS
5. REGOLITH EXPLORATION GEOCHEMISTRY IN ARCTIC AND TEMPERATE TERRAINS
6. DRAINAGE GEOCHEMISTRY

Handbook of Exploration Geochemistry

VOLUME 6

Drainage Geochemistry

Edited by

M. HALE

International Institute for Aerospace Survey and Earth Sciences
Department of Mineral Exploration
Delft, The Netherlands

J.A. PLANT

British Geological Survey
Keyworth, Nottinghamshire, UK

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EDITOR'S FOREWORD

As readers of earlier volumes in the Handbook of Exploration Geochemistry will know, the concept of the Series arose for a number of practical reasons. As the utility of geochemistry in mineral exploration became widely appreciated, geologists with little or no formal training in exploration geochemistry became increasingly responsible for its application. At the same time the scope and complexity of exploration geochemical techniques were becoming so great that it was not possible to encompass all the necessary information within a single text. The decision to produce a series of separate volumes, each devoted to a particular aspect of exploration geochemistry and compiled by the best qualified specialists, was designed to remedy these difficulties. The underlying theme of all volumes is ore-finding, and the objective is to present information in a practical "how to" form for use by field geologists, to provide a theoretical framework to allow an understanding and development of interpretations, and to also provide a reference source for researchers.

This is the sixth volume in the Series, and the fourth on field operational procedures. The question I have been asked most frequently as the volumes of the Handbook of Exploration Geochemistry have slowly emerged is "When can we expect the drainage volume?". I suspect that this is because even amateur prospectors feel that they can understand the application of drainage sampling to mineral exploration (by analogy to gold panning), and also because it has been, in one form or another, one of the most widely used of the exploration geochemical techniques. As my own Ph.D. topic was concerned with its application in the Zambian Copperbelt nearly 40 years ago, I must confess a definite affection for the technique.

Drainage geochemistry may indeed be superficially one of the easiest of the techniques to apply but, as is evident from modern work, it is also one of the most complex to fully understand and from which to derive the maximum useful information. For this reason I was concerned to find authors who also appreciated the full depth and breadth of drainage geochemistry in both its theoretical basis and practical application.

I think that I was fortunate in persuading the powerful team of Dr. Jane Plant and Professor Martin Hale to undertake the task of bringing together the diverse talent (including their own) necessary to produce this major work on drainage geochemistry. It has been a long task (about 10 years in all) but the result amply fulfils my objective of all volumes.

The content of the book falls naturally into four sections of four chapters each that informally can be regarded as introductory stage-setting, sample media, climatic and geomorphological zones, and specific topics.

The Editors (in various partnerships with J. Tarney and R. Raiswell) set the stage in the first four chapters with a brief history and explanation of the layout of the book, the classification of ore deposits and their primary geochemical signatures, the processes of formation of secondary signatures, and the broad strategic choices of sample media, sample preparation and analytical methods, and logistical and budget constraints on the choices.

Chapters 5–8 examine in detail the theoretical and practical aspects of the main media — stream sediments, heavy mineral concentrates, lake sediments, and waters. In the third part (Chapters 9–12) applications in glaciated, tropical rain-forest, arid, and young folded mountain terrains are described. In the final section (Chapters 13–16) special topics of contaminated terrains, gold exploration, uranium exploration, and selective extractions and contrasting media are examined.

I read all chapters at least twice in manuscript form before completion of the volume. On a third reading before writing this foreword I am still impressed by the scope and depth the Editors and individual authors have achieved, the clarity of the illustrations, and the wealth of reference material. I am confident that this volume will provide a guide for the use of drainage geochemistry in virtually any environment, and will be the definitive source book on the technique for many years.

G.J.S. GOVETT
Sydney, Australia
October 1994

PREFACE

Drainage geochemistry can trace its origins to panning stream gravels for visible signs of mineralization — especially gold — at least to Roman times. It was the middle of this century, however, when it was first applied as a modern geochemical exploration technique based on rapid and sensitive trace element analyses. Soil geochemistry had begun to be used in the former USSR in the 1930's and several successful demonstrations of biogeochemistry had been made in the 1940's before drainage geochemistry was investigated. Initially stream sediment surveys were used for mineral reconnaissance, particularly for base metal exploration in deeply-weathered tropical terrains. The main advantage of the method was shown to be the identification of target areas for more detailed exploration, upstream of sample sites with anomalous geochemistry. Subsequently other drainage media were found to have similar advantages in solving new exploration challenges: lake sediments and waters were used for reconnaissance mapping in northern Canada; methods based on well and spring waters were developed; and the time-honoured procedure of panning heavy mineral concentrates was refined to provide a modern technique now widely employed in gold exploration.

Innovation in drainage sampling methods has been paralleled by the introduction of new techniques in geochemical analysis. In its early years, the success of exploration geochemistry owed much to the speed and simplicity of colorimetric analyses performed in a field laboratory using basic laboratory glassware and a few reagents. Such simplicity, however, has not been an enduring requirement. Advances in laboratory analytical instrumentation and methodology, such as atomic absorption spectrophotometry, neutron activation, plasma emission and mass spectrometry, have provided outstanding improvements in analytical sensitivity and multi-element capability, and have led to more quantitative multi-element geochemical mapping programmes.

Whilst these developments in analytical methods generated much larger quantities of drainage geochemical data, computers revolutionised the ways in which these data were processed and mapped. Even the simple procedure of calculating a threshold at the mean plus two standard deviations of a normal distribution is now rarely performed manually. Moreover, it is usually only the first step in a series of electronic statistical and geostatistical computations which would be impossible in the absence of suitable hardware and software! The worm and point source symbol maps are still used to highlight drainage geochemical anomalies, but are now also used to represent derivative data such as regression residuals or factor scores. The value of automated cartography is increasingly recognised, and in some applications it is now commonplace to filter or smooth drainage geochemical data and present them as continuous tone maps based on areas of sample influence or catchment basins. Geochemical maps are frequently available in digital form on geographical information systems for integration with other spatially-related information, including geological, geophysical and remotely-sensed data.

Not only have drainage geochemical methods been honed and refined over the past several decades, but also their applications have been extended. Drainage geochemistry has been increasingly used to delineate regions of anomalously high or low levels of chemical elements — whether related to natural geochemical variations or to pollution — that are potentially damaging to the health of man, animals or crops. The same information is important for land use planning. Demonstrations that geochemical maps have both environmental and economic applications have prompted governments worldwide to initiate national drainage geochemical mapping projects. The resulting maps are of particular value in developing countries, indicating possible toxicities and deficiencies of elements in regions where diets comprise mainly food of local origin, and stimulating investment in mineral exploration.

This volume is essentially a status report on drainage geochemistry in mineral exploration. It begins by showing that it is a discipline based on the sound fundamentals of mineral deposit geochemistry and the geochemical behaviour of minerals and elements in the near-surface weathering zone. Then different, often overlapping, perspectives are offered: the range of drainage sample media is considered; the approach to drainage geochemistry in different surface terrains is reviewed; and some elements — notably gold and uranium — are singled out for special attention. The overall picture is one of a dynamic subject that has been continuously evolving and adapting to meet new challenges, and seems likely to continue to do so.

This picture took a great deal of time to assemble. As editors we set out to produce a volume on drainage geochemistry with the appropriate scope and balance, and to achieve this we asked 25 experts to contribute. All of them did so. They reside in Australia, Europe and North America, but their expertise is rooted not only in their work in their home countries but also in their professional activities elsewhere in the world, ranging from Greenland to the Gambia, Malaysia to Malawi. They include three Distinguished Lecturers of the Association of Exploration Geochemists and four of its past Presidents. To those amongst them who persevered with pandering to our demands for additions and revisions to their contributions, and to those who demonstrated endless patience after speedily completing their contributions, we can only express our boundless appreciation. Many whose names do not appear in the list of contributors have assisted in the preparation of this volume; we extend our thanks to all of them, and in particular to Ella Ng Chieng Hin for her artwork and John Carranza for his assistance in compiling the indexes.

MARTIN HALE, Delft
JANE A. PLANT, Keyworth
October 1994

LIST OF CONTRIBUTORS

J. Donald Appleton, B.Sc. (geology) University of Durham, Ph.D. (geochemistry), University of Edinburgh. Dr. Appleton joined the British Geological Survey in 1970 and has been involved in mineral exploration and environmental geochemical projects in Bolivia, Colombia, Great Britain, Malawi, Peru, Zambia and Zimbabwe.

Dominique Artignan, Ing. (geochemist), E.N.S. Geology, Nancy. After fifteen years of mineral exploration in the field (Africa, Saudi Arabia, ..., France), D. Artignan is now in charge of the "Exploration Support" unit which provides specialized services in geochemistry, geophysics, remote sensing and data processing within BRGM's Department of Exploration.

Alf J. Björklund, Ph.D. (geology) University of Helsinki. Following a period of teaching in economic geology at the Technical University of Helsinki and a Post-Doctoral Fellowship at Queen's University in 1971–1973, Dr. Björklund worked as a geochemist in the Department of Geochemistry at the Geological Survey of Finland until 1977. During 1977–1979 he held a visiting professor's position at the Federal University of Bahia, Brazil, whereafter he returned to the Geological Survey of Finland, first as a geochemist and from 1980 as the head of the Department of Geochemistry. In 1986 he joined the Abo Akademi University as an associate professor in geology.

Eion M. Cameron, Ph.D., University of Manchester. Joined the Geological Survey of Canada in 1957 and was Head of the Geochemistry Subdivision of the GSC from 1967 to 1981. Editor-in-Chief of the Journal of Geochemical Exploration since 1971 and Adjunct Professor at the University of Ottawa since 1983. Main scientific interests since 1981 have been: isotopic geochemistry of Precambrian oceans and of Archaean gold deposits; petrogenesis of mantle-derived magmas related to gold; and processes for the extraction of gold from the lower crust.

J.S. Coats is a geochemist working for the British Geological Survey in mineral exploration, mainly in Scotland. He graduated from Bristol University in 1965 and obtained his Ph.D. from the same institution in 1970. His main research interests are in exploration within areas of glaciated terrain for stratabound base-metal and volcanic-hosted gold deposits. Recently he has become increasingly involved in the application of relational database systems to geochemical exploration data.

Derek C. Cooper, B.Sc., Ph.D. (geology) C. Geol., University of Nottingham. Following research for his doctorate in Norway, Dr. Cooper joined the British Geological Survey where he was engaged initially in a uranium exploration programme. It was in the course of this work that he first encountered the problems of mineral exploration in contaminated terrains. Subsequently he was involved in lithogeochemical and metallogenetic studies, particularly in the Lower Palaeozoic rocks of the English Lake District, and a number of projects concerned with the search for metalliferous mineral deposits in Britain, often in contaminated terrains. He is currently working on a mineral occurrences database for Britain and is coordinator of the DTI-funded Mineral Reconnaissance Programme.

W.K. Fletcher received both his B.Sc. in Geology and Ph.D. in Applied Geochemistry at Imperial College of Science, Technology and Medicine, University of London. He joined the Department of Geological Sciences, University of British Columbia, in 1968, where he is now a Professor. During leaves of absence he has been Chief Geochemist to MINDECO (Zambia) and Geochemist and Team Leader to the United Nations project at the Southeast Asia Tin Research and Development Centre in Malaysia. His principal research interest is the transport and behaviour of heavy minerals in streams. He is an author of more than fifty scientific papers and of the first volume in this series, Analytical Methods in Geochemical Prospecting. He is a former Distinguished Lecturer and President of the Association of Exploration Geochemists.

Angela M. Giblin, B.Sc. (chemistry) University of Sydney, M.Sc. (chemistry) Macquarie University. Mrs. Giblin joined the British Solomon Islands Geological Survey as analytical chemist where she was involved in geochemical exploration projects until 1968. She then joined the Australian Commonwealth and Industrial Research Organisation where she has worked on mineral exploration research until the present. During the last 15 years her research has focused on techniques for collecting and interpreting groundwater geochemical data for mineral exploration.

Martin Hale, B.Sc. (geology) University of Durham, Ph.D. (applied geochemistry) University of London, FIMM, CEng, was successively an exploration geologist with the Anglo American Corporation in central Africa, a minerals economist in a firm of consultants in London, and a lecturer and the Assistant Director of the Department of Geology at Imperial College, London. Since 1990 he has been Professor of Mineral Exploration at the International Institute for Aerospace Survey and Earth Sciences in Delft, The Netherlands.

R.C. Leake is a geochemist who has worked since 1968 for the British Geological Survey, mostly on mineral exploration in southern Scotland and southwest England. He holds a B.Sc. in geology and a Ph.D. from Durham University. His main interests are in geochemical exploration methodology and in metallogenesis. Recently he has worked on the identification of inclusion assemblages in detrital gold as an aid to source characterisation.

Pasi Lehmuspelto, Lic. Phil. (Quaternary geology) University of Turku. After a short period of teaching at the University of Turku he joined the Geological Survey of Finland in 1973, and has since been involved in geochemical mapping and exploration geochemistry. In 1991 he was appointed Head of Technical Services, Regional Office of North Finland, Geological Survey of Finland. He is responsible for technical field activities, sampling and geophysical field measurements.

Richard H. Mazzucchelli, B.Sc. (geology major) University of Western Australia, Ph.D. (applied geochemistry) University of London. Dr. Mazzucchelli was employed by Western Mining Corporation Ltd. for nearly twenty-five years, with lengthy appointments as Chief Geochemist and Regional Exploration Manager. This period included extensive experience with the development and application of geochemical techniques for a wide variety of metallic commodities in Australian environments. Since 1986, Dr. Mazzucchelli has practised as an independent consulting geochemist trading as Searchtech. Pty. Ltd.

Ian Nichol graduated with a B.Sc. from the University of Durham in 1956, an M.A. from Queen's University in 1958, and Ph.D. from Durham in 1962. From 1961 to 1969 he was a Research Associate with the Applied Geochemistry Research Group at Imperial College, London. In 1969 he returned to Queen's University as Professor of Exploration Geochemistry to establish research activity in exploration geochemistry based on Canadian problems. His attention has focused on lithogeochemistry, glacial overburden, stream and lake sediments applied to base metal, uranium and gold exploration; and on the development of analytical procedures, computer-based data-processing and interpretational methods. His current research emphasis is on the development of more effective geochemical exploration methods for gold deposits. He has supervised over forty M.Sc. and Ph.D. programmes, authored or co-authored over eighty scientific papers, and has acted as advisor on the application and interpretation of geochemical exploration programmes throughout the world, both with the United Nations and the private sector. He was the first Secretary of the Association of Exploration Geochemists from 1970–1972, and is a former President and Distinguished Lecturer of the Association.

Rolf Tore Ottesen, Cand. Real. (geochemistry) University of Bergen and University of Helsinki, joined the Geological Survey of Norway in 1976, where he has been involved in developing improved methodologies for regional geochemical surveys (multi-media surveys, overbank sediments). In 1983 he was appointed Head of the Section for Geochemistry and Hydrogeology. In 1992 he was appointed Director of the Environmental Department in the City of Trondheim.

D. Peachey worked as a geochemist with the British Geological Survey from 1968 until his retirement in 1989. He is a Licentiate of the Royal Society of Chemistry and holds a B.A. degree from the Open University. He has worked extensively on the application of techniques of analytical chemistry to a range of geological problems including geochemical exploration, environmental studies and geological mapping.

Jane A. Plant, B.Sc. (geology) University of Liverpool, Ph.D. (geochemistry) University of Leicester, FGS, FIMM, CEng. Dr. Plant joined the British Geological Survey in 1967 where she has led the Geochemical Survey Programme, several studies of metallogeny with particular reference to granites and sedimentary basins, and studies of environmental geochemistry. In 1991 she was appointed Assistant Director and Head of the Minerals and Geochemical Surveys Division of BGS. She is a Council member of the Institution of Mining and Metallurgy, a former Council member of the Geological and Mineralogical Societies and has held several temporary appointments including Visiting Professor at Strathclyde University. She was appointed Distinguished Lecturer of the Association of Exploration Geochemists 1992–94.

Robert W. Raiswell, B.Sc. (chemistry), M.Sc., Ph.D. (geochemistry) University of Liverpool. In 1973 Dr. Raiswell joined the School of Environmental Sciences, University of East Anglia. Since 1983 he has worked in the Department of Earth Sciences, University of Leeds and now holds the posts of Reader in Sedimentary Geochemistry and Research Director of the Leeds University Environmental Centre. His research interests are mainly concerned with the low temperature geochemistry of sulphur.

J. Ridgway graduated with B.Sc. and Ph.D. degrees from Liverpool University and joined the BGS in 1972 after a short period at the University of Keele. Since then he has worked mainly overseas and conducted regional geochemical exploration programmes in terrains ranging from tropical rain forest to semi-desert.

Arthur. W. Rose, B.S. (geology), Antioch College, Ph.D. (geology and geochemistry), California Institute of Technology. Dr. Rose spent seven years in exploration and exploration research on porphyry copper deposits for Kennecott Copper Co. and three years as a geologist with the Alaska Division of Mines and Minerals before joining Penn State University where, as Professor of Geochemistry, he teaches and does research in economic geology, geochemical exploration and environmental geochemistry. He was president of the Association of Exploration Geochemists in 1980–81.

Agnete Steenfelt, Cand. scient. (geology) University of Copenhagen. Joined the Geological Survey of Greenland in 1972, and has since been responsible for geochemical mineral exploration and reconnaissance geochemical mapping. She has been regional council member of the Association of Exploration Geochemists since 1992 and member of the editorial board of Journal and Geochemical Exploration since 1989.

Henrik Stendal, M.Sc. (geology), Ph.D. (applied geochemistry) University of Copenhagen. Dr. Stendal joined the University of Copenhagen in 1975 and has been involved in improving methodologies for drainage geochemical surveys. During the last ten years his research has shifted towards lithogeochemistry and ore geological investigations, especially on a regional scale. The main research areas are Greenland, Norway and Turkey. He teaches geochemical exploration and ore geology.

John Tarney, B.Sc., Ph.D. (geology) University of Durham, spent 16 years teaching an M.Sc. Course in Mineral Chemistry at Birmingham University before being appointed to the F.W. Bennett Chair of Geology at Leicester University in 1980. His research interests have been divided equally between the oceans and the continents, but are presently centred on Greece, Labrador and the Colombia/Caribbean area, and are concerned with petrogenetic problems of igneous rocks and their associated mineralisation.

Paul K. Theobald, B.Sc. (geology) Stanford University, California, has been a geologist with the U.S. Geological Survey since 1951 and now enjoys an emeritus status with that organisation. He has been active in exploration geochemistry since 1955, primarily involved with the application of data from stream sediments and particularly with the development and application of techniques using heavy minerals.

Iain Thornton, Ph.D., D.Sc, DIC, University of London. Following a period of 6 years as Soil Scientist in the Gambia, Professor Thornton joined the Applied Geochemistry Research Group at Imperial College of Science, Technology and Medicine in 1964. He is at present Director of the Environmental Geochemistry Research Group and the Global Environment Research Centre, both within the College's Centre for Environmental Technology. His main research interests concern the applications of geochemistry in agriculture, rural and urban pollution and global contamination from mining and mineral processing. He was President of the Society for Environmental Geochemistry and Health for 1988 and 1989.

E. Wilhelm, Ph.D. (geochemistry) University of Strasbourg (France). Following a period of exploration in Africa, Dr. Wilhelm worked in the scientific centre of BRGM as head of the geochemistry unit; during this period he was involved in developing methodologies for geochemical exploration and data processing. In 1981 he was appointed Head of the Department of Exploration. He is now in charge of mining investments of BRGM in Africa.

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Chapter 1

INTRODUCTION: THE FOUNDATIONS OF MODERN DRAINAGE GEOCHEMISTRY

JANE A. PLANT and MARTIN HALE

The systematic collection and analysis of drainage samples has become an established method of mineral exploration at both the reconnaissance and more detailed scales in many parts of the world. The importance of stream sediment samples in preparing geochemical maps of large areas rapidly and at low cost was first recognised in the 1950's (Lovering et al., 1950; Hawkes and Bloom, 1956; Boyle, 1958; Webb, 1958b). Stream sediments provide a robust sample that is easy to collect and analyse, suitable drainage systems exist in most terrains and useful results can be obtained in many different climatic regimes (Plant et al., 1988a). More recently other types of drainage media have been developed for geochemical mapping which extend the range of the method. For example, in glaciated basement terrains, stream networks are frequently replaced by extensive networks of lakes linked by only short, poorly developed streams, and initially regional geochemical exploration was considered impractical in such areas. Since the late 1960's, however, the development of lake sediment sampling methods in Canada and Finland has enabled regional geochemical exploration to be extended over such important metalliferous provinces as the Canadian and Fennoscandian shields (Chapter 7, this volume). The basic methods of stream and lake sediment sampling can be modified readily by the collection of different size fractions or heavy mineral concentrates, according to the type of terrain to be covered or to enhance anomalies for particular ore deposit types.

Two other types of sampling media — water and overbank samples — have recently become important. The importance of water in exploration has increased as a result of the improved understanding of the chemistry of natural waters, the need to explore for buried ore deposits and especially great improvements in the sensitivity of analytical methods (particularly the introduction of ICP-MS techniques). Groundwater sampling may be of particular value in arid terrains (Chapter 8, this volume). Preliminary studies suggest that overbank samples are representative of larger regions than stream sediments and hence may be of value for low density surveys (Ottesen et al., 1989). Moreover, as in the case of lake sediment samples, it may be possible to collect overbank samples from varying depths or older terraces or floodplains, so that they can be used to distinguish the effects of anthropogenic contamination from natural geochemical variation. However, the use of overbank samples for regional geochemistry remains controversial.

Overall it is the representativity of drainage samples which distinguishes them from other sample media. Stream sediment samples, for example, approximate to composite samples of soil, weathering products and rocks upstream from sampling sites and are representative at the scale of drainage basins. This property provides the means of preparing systematic geochemical datasets over large regions of the Earth's crust at relatively low cost. Such data give a unique picture of trace element distribution that reflects not only the presence of anomalies related directly to the leaching and erosion of orebodies but also to the geochemical characteristics of host rocks which can be used to identify the setting in which the deposits occur. High resolution systematic regional geochemical data are increasingly used with remotely sensed and digital geological and geophysical data for exploration, resource evaluation and mineral deposit modelling studies. It is our aim in this volume to provide up-to-date information not only on direct methods of geochemical exploration for a wide range of ore deposit types but also on applications of regional geochemical data for identifying the tectono-magmatic and tectono-stratigraphic settings of different mineral deposit types.

In this chapter a brief review is given of the development of regional geochemistry based on drainage samples from a simple qualitative tool for exploration for base metals to the development of quantitative methods of sampling and analysis for the preparation of systematic multi-element geochemical surveys and databases. Finally the application of geochemistry based on drainage samples for sophisticated exploration and resource evaluation programmes based on mineral deposit models is discussed.

DRAINAGE GEOCHEMISTRY IN EXPLORATION AND MAPPING

Historical reviews of the development of exploration geochemistry have been given by Boyle (1967a), Boyle and Garrett (1970), Bloom (1971), Hawkes (1976b), Thomson (1982) and Govett (1986), and only a brief summary is presented here.

Exploration geochemistry developed from basic research in geochemistry in the USSR and Scandinavia during the 1930's. In the USSR primary and secondary dispersion halos associated with ore deposits were described (Fersman, 1939a), while in Norway and Finland the secondary dispersion of anomalous levels of chemical elements in soils, waters and vegetation around sulphide deposits was demonstrated (Vogt, 1939; Rankama, 1940). Elsewhere, geochemistry and its adoption as an exploration tool did not attract much attention until after the Second World War, when programmes were initiated in Canada, the USA, Britain and France between 1945 and 1955. At that time metal prices were high, reflecting the reconstruction of the Western European economies in the post-war era, and the major sources of supply were the developing countries, South Africa, Australia and Canada. Very extensive areas remained relatively unprospected, and new techniques of exploration, particularly for application in tropical terrains, were developed. Scientifically, the understanding of ore deposits remained essentially descriptive; but geochemical methods of exploration gained impetus from progress in chemistry (and the physical sciences generally) during the war, which led to the widespread development and application of improved analytical (especially colorimetric) methods, such as the dithizone tests for heavy metals (Huff, 1948, 1951). The collection and analysis of the <80-mesh (BSI) size fraction of stream sediments, which is well suited to exploration in areas of predominantly chemical weathering, was applied to exploration in the southwestern USA (Lovering et al., 1950) and at the same time hydrogeochemical surveys were tested in Africa (Webb and Millman, 1950).

Drainage geochemistry met with early success and proved highly cost-effective thanks to technical developments that led to low-cost, high-productivity analytical methods (Table 1-I). During the early 1950's, three mineral deposits were discovered in Gaspé and New Brunswick, eastern Canada, through the collection and analysis of less than 5000 samples at a cost of $150,000 (Hawkes and Bloom, 1956; Hawkes et al., 1960; Govett, 1986). By the late 1960's high metal prices and pessimistic forecasts of shortages of supply in the long term had combined to create a worldwide expansion in exploration geochemistry

TABLE 1-I

Factors in the development of regional geochemistry (compiled with reference to Boyle and Smith, 1968)

Period	Innovation
1930's	Recognition and understanding of dispersion halos associated with mineral deposits (USSR and Scandinavia). Development of emission spectrography as a rapid, accurate analytical method (USSR).
1940's	Development of colorimetry as a rapid, accurate analytical method (USA).
1950's	Development of polythene field and laboratory equipment. Development of atomic absorption spectrophotometry (USA and Australia).
1960's	Application of statistical and computer methods (UK, Scandinavia, Canada and Australia). Improved sampling procedures to provide reproducible data (Canada and UK).
1970's	Automation of multi-element analytical methods, providing low-cost, quantitative multi-element data. Introduction of rigorous error control procedures (Canada and UK).
1980's	Application of advanced interactive computer graphical methods to integrate geochemical data with remotely sensed and other data sets (UK, Canada and Australia). Development of knowledge-based systems for exploration employing regional geochemical data sets (USA, UK (BGS), France).

(Govett, 1986). During this period, large, often low-grade deposits, such as Cu–Mo porphyries and nickeliferous laterites, which are particularly suited to geochemical exploration, were among the main exploration targets, reflecting the development of large, capital-intensive mining in a climate of cheap energy and increasing labour costs; exploration activity for gold was limited because the metal price was pegged at an artificially low level in US dollar terms until 1968. Notable discoveries in which drainage geochemistry played a prominent role included the Bougainville copper–gold porphyry deposit in Papua New Guinea, the Woodlawn copper–lead–zinc deposit in New South Wales, Australia, and the Casino copper–molybdenum porphyry deposit in Canada (R.W. Boyle, 1979a). The large quantities of geochemical data that were generated led to the widespread application of computers for data processing (Table 1-I). Whereas initially little interpretation of geochemical data had been carried out beyond the identification of the presence or absence of anomalies of ore metals, numerical statistical techniques, such as trend-surface and moving-average methods, were introduced to distinguish regional geochemical trends and anomalies, and the application of multivariate methods, such as principal component, factor and cluster analysis, became common (Howarth and Martin, 1979; Howarth and Sinding-Larsen, 1983; Howarth and Garrett, 1986).

The late 1960's and the 1970's saw the peak of exploration geochemistry based on the collection and processing of large quantities of low-cost data to prepare broad-scale reconnaissance maps and geochemical atlases (e.g., Webb et al., 1978). The 1:2,000,000 geochemical atlases of western Germany (Fauth et al., 1985) and England and Wales (Webb et al., 1978) are typical of maps that were prepared during this phase. Stream sediments collected at a density of about one/3 km^2 were analysed by high-productivity analytical methods and the data were smoothed to reduce the amount of random error by moving average or other statistical methods. Such maps are useful for showing areas that are broadly anomalous — for example, Ba, Cd, Cu, Pb and Zn background levels are shown to be high over the old mining districts of the Harz Mountains of Germany and over southwest England — and for environmental purposes, but they are of limited application in areas where the geology is well known. Nevertheless, the Wolfson Atlas of England and Wales was an important landmark in the presentation of geochemical maps and helped to promote the implementation of national geochemical mapping campaigns by geological survey organisations worldwide.

In the mid-1970's, following the sharp increase in energy costs, a general decline in base-metal prices and the introduction of a free market price for gold, emphasis in mineral exploration shifted increasingly to high unit-value deposits, such as those of massive sulphides and precious metals — in particular, gold. Anxiety about the vulnerability of the West's supplies of metals from the developing world followed the oil crisis in 1973; and later in the decade particular concern was focused on the "strategic metals" such as Cr, V and the platinum-group metals, as the political stability of the main source — the Republic of South Africa — was increasingly called into question. In addition, considerable exploration was carried out for U as an energy mineral until the early 1980's.

Overall, by the end of the 1970's the situation for most metals was one of marked excess of production over demand. Investment in developing countries and in South Africa declined, while the entry of international oil companies into the mining sector emphasised exploration for large, high grade deposits that could be worked profitably by large corporations. In exploration geochemistry generally, this period was one of retrenchment, with a decline in the annual publication rate on exploration geochemistry topics after 1976 (Govett, 1986). Publications were mainly case histories demonstrating alternative sampling strategies and refinements in analytical techniques. Emphasis was also on the extension of regional geochemical coverage in countries considered to offer a stable, secure supply of minerals, particularly those of strategic importance.

REGIONAL GEOCHEMISTRY AND RESOURCE EVALUATION

During the same period, there was a marked improvement in the understanding of metallogeny, partly as a result of investigations of extant geothermal fields and ocean-ridge hydrothermal systems, as well as of stable isotope and fluid inclusion studies of ore deposits. Moreover, advanced mineral deposit models (e.g., Cox and Singer, 1986), incorporating economic and scientific components, became increasingly available for many ore deposit types, although these use few geochemical or geophysical data. Petrogenetic data also became widely available, partly as a result of the increased use of methods such as instrumental neutron activation analysis for uranium exploration (e.g., Ferguson and Price, 1976) and, more recently, for gold (Hoffman, 1992).

These developments, and the introduction of highly sensitive ICP-MS methods, combined with an improved knowledge of geology, particularly in tectonics and basin analysis, provided a basis for regional geochemical mapping to embark on a new phase of expansion. Some of the advantages and limitations of regional geochemical mapping are compared with geophysical and conventional geological mapping in Table 1-II. The extent of regional geochemical mapping has recently been summarized by Plant et al. (1988a) and Darnley (1990). Xie and Ren (1991) have described the scope of regional geochemical mapping in China, where 4,000,000 km^2 has been mapped over the past decade. Although taking advantage of improved technical developments in sampling, analysis and data processing, realization of the full potential of regional geochemical mapping will depend on the application of fundamental scientific skills, especially those of geochemical data interpretation.

Exploration geochemistry, as Mazzucchelli (1986) has pointed out, has been through a period of negative thinking (that has resulted in the excessive use of drilling). A more positive approach is becoming evident, however, with an improved understanding of the geochemistry of surface processes (Butt and Zeegers, 1992; Chapter 3, this volume) and of ore formation and geochemi-

TABLE 1-II

Some advantages of regional geochemistry

Low cost per unit area compared with that of conventional geological mapping and most geophysical methods.

Basic data collected are numerical and, therefore, more objective than, for example, geological mapping.

Less skill required for sampling than in conventional geological mapping.

Data for 30–50 parameters (chemical elements) can be provided and used singly or in combination.

Concentrations of chemical elements — and hence, mineral deposits — are mapped directly, whereas indirect methods, such as geophysics or remote sensing, are based on measurement of primary or induced physical properties.

Genetic information provided on contemporaneous geological processes, whereas geophysical methods give information on present disposition of geological units.

cal zoning around mineral deposits (Chaffee, 1976; Beus and Grigorian, 1977; Govett, 1983; Chapter 2, this volume). This is paralleled by the development of a more fundamental scientific approach in regional geochemistry — in particular, improved understanding of the effects of surface processes on primary geochemical signatures and the use of geochemical data for mineral deposit modelling.

Metalliferous mineral exploration is increasingly based on the scientific understanding of the way in which ore deposits form, especially where concealed or blind deposits are sought (Woodall, 1984). Such an approach requires that regional geochemistry be used to investigate the processes of ore formation to provide mineral deposits models and derive exploration criteria that can be used to screen data. Evidence is accumulating that at least in cool temperate climates trace element plots based on stream sediment data can be used to summarise the geochemical characteristics of ore deposits and their host rocks (Plant et al., 1990). The importance of metallogenic provinces is also being re-evaluated (Bölviken et al., 1990a; Plant et al., 1990) and the role of crustal reservoirs, particularly for rare elements with average crustal abundance values of <10 ppm, is being considered. In this volume, therefore, attention is paid to the applications of regional geochemistry and other spatially related datasets for exploration or resource evaluation based on integrated GIS-IAS (e.g., Bonham-Carter et al., 1988; Gaál, 1988; Kuosmauen, 1988; Plant et al., 1988a).

MODERN METHODS IN DRAINAGE GEOCHEMISTRY

This volume is aimed at documenting current theory and practice in drainage geochemistry, including different sample media, alternative sampling methods and strategies and the interpretation of data according to specific exploration criteria for particular ore deposit types. In the introductory section, a new system of classification of ore deposit types suitable for regional geochemical exploration based in drainage samples is considered, and information on the primary lithogeochemical signatures of different ore deposits and their geological settings is reviewed. It is not possible to provide a comprehensive catalogue of the geochemical characteristics of all types of orebodies and their settings since relatively few systematic data are available on the geochemistry of the host rocks of ore deposits. Instead data on basalts and granites, which are frequently spatially associated with ore deposits, are used to indicate the type of approach which can be used to identify the tectono-magmatic settings for some of the most important types of ore deposits. The modification of the signatures of ore deposits and their host rocks in different surface environments is then discussed, and the development of optimum sampling strategies to achieve (1) representative sampling as a basis for geochemical mapping or (2) the enhancement of anomalies for different ore deposit types is considered. The final chapter in the introductory section is concerned with the strategic choices confronting the exploration geochemist/geologist according to the purpose of the survey, which can range from a large multipurpose, multi-element survey by a national government agency to a small exploration project for a single element such as gold.

The second section of the book is concerned with alternative sample media including water, stream and lake sediments, and heavy mineral concentrates. This is followed by a section dealing with different types of terrain with particular emphasis on areas requiring special methods of approach. These include arid, tropical and glaciated terrain as well as mountainous terrain and areas of heavy metal and other types of contamination. Overbank samples are briefly discussed in the chapters on strategic choices, stream sediments and exploration in glaciated terrain, but the development of the method for exploration is not yet sufficiently advanced to warrant an entire chapter.

In the last section, chapters concerned with exploration for uranium and gold, both elements of considerable economic importance but with unusual geochemical properties and requiring specialist exploration knowledge, are presented. These are followed by a chapter evaluating alternative sampling strategies for other ore deposit types.

Although largely concerned with mineral exploration and resource evaluation, an increasing number of regional geochemical surveys, particularly those carried out by government agencies, are designed to be multipurpose with a greater emphasis on environmental applications (Plant et al., 1988a). Programmes such as "International Geochemical Mapping" (Darnley, 1990), which is to be based mainly on the systematic analysis of drainage samples, are also primarily for environmental purposes. It is hoped that at least some of the information contained in this volume will be of value to these and similar programmes.

Drainage Geochemistry
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Chapter 2

MINERAL DEPOSIT MODELS AND PRIMARY ROCK GEOCHEMICAL CHARACTERISTICS

JANE A. PLANT and JOHN TARNEY

INTRODUCTION

Geochemical maps are being used increasingly to identify lithological variation which can be related to the geological history of large regions of the Earth's crust. Such studies form a basis for exploration and resource evaluation and metallogenic studies (Björklund, 1984; Plant et al., 1986, 1988a). The approach requires that, in addition to identifying geochemical anomalies directly related to orebodies undergoing leaching and erosion, geochemical features indicative of geological environments favourable for ore genesis are identified. For example the identification of rocks of tholeiitic basalt composition in a sedimentary basin succession can indicate the presence of a palaeo rift zone. Thermal anomalies and hydrothermal systems frequently occur in such settings, which are thus prospective for the discovery of base metal deposits (e.g. those of the Benue Trough of West Africa). Geochemical data for this type of study are increasingly available as a result of developments in automated methods of X-ray fluorescence analysis, instrumental neutron activation analysis and inductively coupled plasma emission spectrometry which can produce large quantities of high-quality multi-element data at low cost.

In this chapter we discuss the application of elements such as the rare earths (REE), the high-field strength (HFS) (Nb, Ta, Zr, Hf, Ti, Y), and low-field strength (LFS) groups such as the alkalis (Li, Na, K, Rb), alkaline earths (Mg, Ca, Sr, Ba) and heat-producing elements (U, Th, K, Rb) as well as the ore metals and pathfinder (B, As, Se, Sb, Tl) elements to mineral exploration, with particular reference to igneous rocks. Some of the most important mineral deposit models are reviewed first, and the effects of ore formation, commonly the result of fluid-rock interaction, are described. The geochemical characteristics of some of the igneous rock types frequently associated with ore deposits, including those which provide a direct source of metals and those which indicate favourable settings for ore deposition are then discussed. This information can be used where lithostratigraphical and structural information is sparse in areas of poorly known geology or to help understand the lithofacies of rock units in areas previously mapped in detail. Secular changes in the composition of the crust from Archaean to Phanerozoic times, which have a bearing on ore deposition, are also considered where they are relevant to particular ore deposit types.

The literature on rock geochemistry is voluminous, although relatively few authors have attempted to relate the information to ore genesis. A comprehensive review of litho-geochemistry is beyond the scope of this chapter (see Govett, 1983); instead emphasis is given to ore deposit types for which the metallogeny is relatively well understood and for which lithogeochemical studies have been carried out. The aim is to outline methods of approach and no attempt is made to provide comprehensive data on the primary geochemistry of different ore deposit types. Since this volume is primarily concerned with the use of drainage samples for mineral exploration, only methods which can be applied to the interpretation of large numbers of near-surface water, or lake- or stream-sediment samples are considered. Methods which are costly or inappropriate for drainage sampling, such as those based on the use of stable and radiometric isotopes or on the content or speciation of volatiles, are considered only where they have a bearing on mineral deposit models.

CLASSIFICATIONS OF ORE DEPOSITS AND THEIR SETTINGS

There have been many attempts to group ore deposit types, ranging from descriptive (e.g. Smirnov, 1976) to genetic (e.g. Lindgren, 1933) classifications and classifications based on associated host rocks (e.g. Stanton, 1972). However, it was the demonstration that late Proterozoic-Phanerozoic mineral deposits can be related to their geotectonic setting, first postulated by Bilibin (1955), and later related to plate tectonics by Sawkins (1972, 1990), Sillitoe (1972), Strong (1976) and Mitchell and Garson (1981), that provided the most useful basis for a modern understanding of ore deposits and their geochemistry. Hence porphyry Cu (Mo) and Kuroko Zn–Fe–Cu–Pb massive sulphide deposits are shown to be generally associated with island arc or Andean continental margin type subduction systems, whereas podiform chromite deposits occur in ophiolite complexes formed over depleted mantle at oceanic or back-arc spreading centres. Identification of igneous rocks with the composition of island arc or calc-alkaline magmas or of mid-ocean ridge basalts (MORB) and their associated ultramafic complexes provides information for regional resource evaluation. Moreover, detailed geochemical/petrogenetic studies are increasingly being used to identify the compositional characteristics of particular rocks likely to host economic ore deposits, e.g. Scott et al. (1983), Franklin (1986) and Plant (1986). Fewer data are available on the relationship between the geochemistry of sediments and their tectonic setting despite recent advances in basin analysis. Quantitative data on the geochemistry of metamorphic rocks in relation to ore deposits are also limited, although models for some types of U deposits involve metamorphic dewatering at the granulite-amphibolite boundary (Ryan, 1979) and some models for lode-Au deposits require decarbonation at the amphibolite-greenschist facies boundary (Groves et al., 1987).

TABLE 2-I

Clarke values and ore deposit mining grades, derived from Plant et al. (1990)

	Vinogradov (1962) (%)	Taylor (1964) (ppm)	Mineable grades (Non-placer) (approx. %)	Enrichment factor ×
"Common" elements				
Al	8.05	–	35.0	4.35
Fe	4.65	–	35.0[a]	7.53
Ti	–	5700.0	10.0	17.54
Co	–	25.0	0.2	80.00
Cu	–	55.0	1.03[c]	182.82
Ni	–	75.0	1.5	200.00
F	–	625.0	20.0	320.00
Ba	–	425.0	30.0	705.88
Zn	–	70.0	6.0[b]	857.14
P	0.003	–	5.0	1666.66
"Rare" elements				
Mo	–	1.5	0.3[d]	2000.00
Ag	–	0.07	0.015[e]	2142.86
Pt	–	0.002	0.0005[f]	2500.00
Cr	–	100.0	30.0	3000.00
Pb	–	12.5	5.0[b]	4000.00
Sn	–	2.0	1.0	5000.00
U	–	2.7	1.5	5555.00
W	–	1.5	1.0	6666.66
Au	–	0.0004	0.001	25,000.00
Hg	–	0.08	1.0	125,000.00
Cd	–	0.2	–	–

[a] 45% of Eastern block excluded; [b] USBM World figures, rounded; [c] Chile and C. Africa still over 1% (0.4% is below cut-off for North American porphyries); [d] Climax/Henderson grades; [e] Approximate value for main product Ag mines; [f] Merensky/UG2 grades.

In addition to the recognition of primary chemical signatures of rocks favourable for the formation of ore deposits, alteration associated with some types of mineralisation can also be identified geochemically. The formation of many types of ore deposits involves the concentration of elements to levels well above their average background value in normal rocks (Table 2-I) together with a change in mineralogy, frequently from silicates to oxides (e.g. Sn, U) sulphides (e.g. Ni, Pb, Zn) or sulphates (e.g. Ba). The process involves metal extraction from large volumes of rock and deposition in small volumes. In the case of magmatic deposits, such as those of chromite or Ni-sulphide, ore formation involves gravitational settling or extraction into an immiscible sulphide phase respectively. The majority of ore deposits, however, are formed by the interaction of rocks with aqueous fluids which, on the basis of oxygen and hydrogen isotope studies, comprise sea, meteoric, evolved connate or metamorphic waters or waters in isotopic equilibrium with primary

TABLE 2-II

Compositions of natural metalliferous hydrothermal solutions (mg/g), adapted from Lydon (1988)

	Salton Sea	Red Sea	Kuroko	East Pacific Rise	S. Juan de Fuca Ridge	Seawater
Temp (°C)	340	60	320	350	224	2
pH	5.5	5.5	4.5	3.5	3.2	8.0
Na	53,000	92,600	17,500	9800	18,300	10,790
K	16,500	1870	5000	1000	2020	395
Ca	28,800	5150	4400	860	3860	413
Mg	10	764	510	<1	<1	1280
SiO_2	400	60	?	960	1400	10
Cl	155,000	156,000	40,400	17,335	38,640	19,355
SO_4	10	840	?	<1	50	2745
H_2S	30	?	?	221	63	<1
ΣCO_2	500	140	8800	282	?	103
Fe	2000	81	6	100	1045	<1
Mn	1370	82	?	34	197	<1
Zn	500	5.4	3	7	59	<1
Cu	3	0.3	5	1	<0.1	<1
Pb	80	?	3	<1	?	<1
Ba	250	0.9	?	13	?	<1

magmas (White, 1974; H.P. Taylor, 1979). Data on ore-forming fluids (Table 2-II) are available from fluid inclusion studies (e.g. Sheppard et al., 1971; Poty et al., 1974; Roedder, 1977), studies of extant geothermal fields (e.g. White, 1965; Ellis, 1968) and studies of active metalliferous hydrothermal vents on the sea floor (Edmond et al., 1979). Together with isotopic, petrological and tectonic information, these data have led to the formulation of conceptual and fluid-dynamic geological models for different types of ore deposits, which provide a basis for classification and the development of systematic exploration criteria. This type of classification is preferred to ones based solely on tectonic setting since similar ore deposits can form in several different types of setting. Tin deposits associated with granites, for instance, can form in outer arcs, foreland thrust belts, back-arc basins or intracontinental rift systems.

The classification of mineral deposit types used in this chapter (Table 2-III) is based on that devised for Canadian mineral deposits (in: Eckstrand, 1984), but re-assembled into fewer groups, and arranged from low-temperature deposits formed by sedimentary processes, through to deposits formed at higher temperature in sedimentary basins by migrating fluids, on to deposits resulting from high-temperature water–rock interaction associated with volcanic and plutonic centres. High-temperature magmatic ores and deposits attributed to metamorphic dewatering are then described. Examples from each of the main groups are discussed below.

TABLE 2-III

Classification of mineral deposit types.

A. SEDIMENT/SEDIMENTARY BASIN ASSOCIATION

- 1. Contemporaneous with sedimentation or formed by surface weathering
  - 1.1 *Placer*
    - 1.1.1 Gold
    - 1.1.2 Tin
    - 1.1.3 Thorium
  - 1.2 *Pyritic palaeoplacer*
    - 1.2.1 Gold
    - 1.2.2 Uranium
  - 1.3 *Non-marine evaporites and laterites*
    - 1.3.1 Uranium
    - 1.3.2 Nickel

- 2. Associated with fluid flow in sedimentary basins
  - 2.1 *Red bed, sandstone-hosted uranium, copper, lead and deposits in post-orogenic basins*
    - 2.1.1 Sandstone uranium, including roll fronts
    - 2.1.2 Sedimentary copper
      - (a) Paralic marine (Kupferscheifer type)
      - (b) Continental (red bed type)
      - (c) Volcanic red bed
  - 2.2 *Unconformity and vein associated*
    - 2.2.1 Arsenide vein silver, uranium
    - 2.2.2 Vein uranium
    - 2.2.3 Unconformity-type uranium
    - 2.2.4 Vein copper
    - 2.2.5 Stratiform sediment-hosted (Sedex) lead–zinc–barium
    - 2.2.6 (a) Mississippi Valley lead–zinc replacement
      - (b) Mississippi Valley lead–fluorite vein type
  - 2.3 *Iron/manganese-rich sedimentary strata*
    - 2.3.1 Manganese nodules and layers
    - 2.3.2 Ironstone
    - 2.3.3 (a) Lake Superior type
      - (b) Algoma type

B. VOLCANIC/PLUTONIC IGNEOUS ASSOCIATION

- 3. Formed as a result of hydrothermal activity associated with high level (volcanic and plutonic) activity
  - 3.1 *Volcanic-associated massive sulphide*
    - 3.1.1 Copper–zinc (gold)
    - 3.1.2 Zinc–lead–copper (gold)
    - 3.1.3 Epithermal (adularia-sericite type) gold
  - 3.2 *Hydrothermal deposits associated with felsic plutons*
    - 3.2.1 Calc-alkaline associated Cu, Mo (incl. skarn Cu)
    - 3.2.2 Calc-alkaline associated Mo, W (incl. skarn W)
    - 3.2.3 Epithermal (acid sulphate type) gold
    - 3.2.4 Felsic intrusions associated Ag, Pb, Zn (incl. skarns)
    - 3.2.5 Akaline-sub-alkaline associated Sn, Li, Be, U

TABLE 2-III (*continued*)

4. Magmatic ore deposits
    - 4.1 *Mafic/ultramafic-hosted chromite*
        - 4.1.1 Stratiform
        - 4.1.2 Podiform
    - 4.2 *Magmatic nickel, copper, platinum group metals*
        - 4.2.1 Volcanic (komatiitic) lavas and intrusions in greenstone belts associated with nickel
        - 4.2.2 Ultramafic intrusive nickel–copper
    - 4.3 *Layered intrusive Ni Cu, PGM and gabbronorite stocks*
        - 4.3.1 Layered intrusive nickel–copper
        - 4.3.2 Layered intrusive PGM
        - 4.3.3 Stocks in orogenic belts
    - 4.4 *Mafic intrusion-hosted titanium–iron*
        - 4.4.1 Anorthosite-hosted titanium–iron
        - 4.4.2 Gabbro-anorthosite hosted Ti-magnetite
    - 4.5 *Carbonatite-hosted deposits*
        - 4.5.1 Nephelinite carbonatite
        - 4.5.2 Ultramafic carbonatite

5. Metamorphic ores
    - 5.1 *Lode gold deposits*
        - 5.1.1 Archaean greenstone belts
        - 5.1.2 Greywacke vein and shear gold
    - 5.2 *Some vein and pegmatite deposits*
        - 5.2.1 Some vein deposits
        - 5.2.2 Rare earth pegmatites

MINERAL DEPOSIT MODELS

Mineral deposit models can be used to derive geochemical criteria for exploration, ranging from the geochemistry of associated rock-types as indicators of tectonic setting to evidence of water rock interaction around particular deposit types.

Elements such as Sn, W, Mo, Hg, Ag and Au, which have very low average crustal abundances (<10 ppm, Table 2-I), require concentration prior to solution extraction (Skinner, 1979). In the case of Sn for example, highly evolved granites with elevated levels of Sn are necessary to provide the source of the metal. These granites have distinctive geochemical characteristics and can be identified readily using many different combinations of litho- or drainage-chemical data (Plant et al., 1986). For elements with a higher crustal abundance (>10 ppm), however, mass balance calculations (Krauskopf, 1979) and studies of geothermal systems (e.g. Ellis, 1968) suggest that adequate quantities of metals for ore formation can be extracted by the interaction of hydrothermal fluids with common silicate minerals in rocks containing only average concentrations of metals. For example, Pb can be released from K feldspar in rhyolite or greywackes to form Pb-bearing hydrothermal solutions leading, in conditions of highly focussed discharge and mineral precipitation, to the formation of

Pb deposits. In this case the ore metals may be acquired from large volumes of rock with an almost imperceptible decrease in overall metal concentration. Geochemical exploration is most appropriate for identifying changes in rock geochemistry in and around the ore deposits, and it may be useful in identifying favourable source rocks (see below).

Deposits contemporaneous with sedimentation: placers and palaeoplacers

These deposits are formed by concentration during weathering (e.g. Ni in gossans), by solution and re-precipitation of metals in surface waters (e.g. U in calcrete deposits as at Yeelirrie, Western Australia) or, in the case of placers, by physical separation of high density minerals in flowing waters.

The Phanerozoic (mainly Recent) Sn and Th placers in Malaysia and Thailand are frequently associated with highly evolved leucogranites already enriched in these elements. Similarly there may be an association between uraninite and evolved granites in the case of the late Archean-early Proterozoic Au–U and U palaeoplacers, such as those of the Witwatersrand. Evolved granite intrusions have been reported by Simpson and Plant (1984) to occur in the Kaapvaal craton around the edge of the Witwatersrand basin. These placer deposits contain concentrations of heavy minerals within oligomictic or polymictic conglomerates (Simpson and Bowles, 1977). The factors controlling the ore deposits are controversial, some authors relating their genesis to anoxic atmospheric conditions in the Precambrian, and others to their tectonic setting. Windley et al. (1984), for example, relate ore deposition and preservation to the formation of major intercontinental rift zones in the supercontinents that had formed by the late Proterozoic, or earlier in South Africa where cratonisation began in the Archaean. Geochemical associations appropriate for exploration include the recognition of appropriate granites in the provenance of the placers and the detection of heavy mineral concentrations (Chapter 6, this volume).

Deposits associated with fluid flow in sedimentary basins

This group includes U and Cu deposits (along with petroleum and natural gas) that can be related to the tectonic and thermal evolution of sedimentary basins. The deposits form as a result of the flow of sedimentary brines which transport and deposit the metals involved in ore formation (Lebedev, 1967; Carpenter et al., 1974; White, 1974). Fluid flow occurs in response to hydrostatic gradients related to topographic relief, compaction, osmotic pumping, thermal gradients, and deformation and tectonism.

Studies of intracratonic and marginal orogenic basin development (McKenzie, 1978; Royden et al., 1980; Dewey, 1982) provide a framework on which the processes can be considered. Studies of oilfields also provide information on fluid temperatures and composition, and on the processes of diagenesis and fluid transport (e.g. Hanor, 1979).

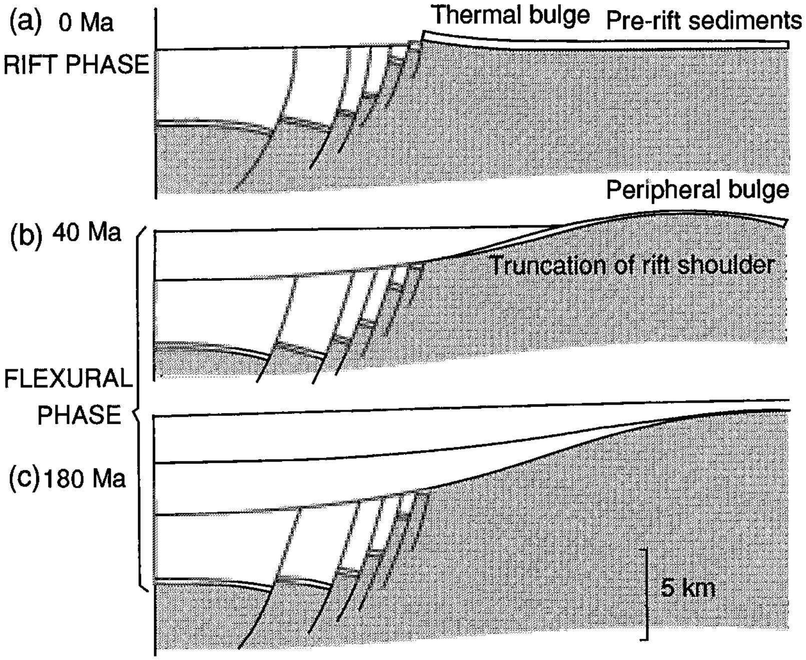


Fig. 2-1. Evolution of a sedimentary basin during rift and flexural phases assuming a lithospheric stretching model, modified after McKenzie (1978).

The McKenzie model (Fig. 2-1) is generally applicable to extensional intracratonic basins such as those that formed across North America and Europe from Devonian to Permian times. According to this model, lithospheric stretching of the crust initially produces rapid subsidence, extensional (listric) faulting and fissuring, accompanied by a high geothermal gradient associated with a rise in the Moho; typically faulting and bunching of isograds occurs at basin margins (Fig. 2-1a). Subsequently, thermal subsidence occurs, enhanced by the sediment load when a larger sediment overlap at basin margins develops following migration of a peripheral flexural bulge (Fig. 2-1b), to produce the classical "steer's head" configuration of the sedimentary sequence (Fig. 2-1c), while the thermal anomaly in the mantle decays. The model can be modified, following Royden et al. (1980), for high stretching rates (Fig. 2-2) — for example in orogenic marginal basins when large quantities of mafic magmas may be emplaced in the crust (Dewey, 1982). Orogenic marginal basins include, for example, those of Chile and Peru, parts of the W. Cordillera of the United States of America, the region between Harrison Lake and the Frazer Fault zone in British Colombia and the Scottish Dalradian. Other types of sedimentary basin include late- to post-orogenic basins, formed by thrust loading as in the Westphalian basin of Western Europe (Dewey, 1982) and those associated with transcurrent fault systems.

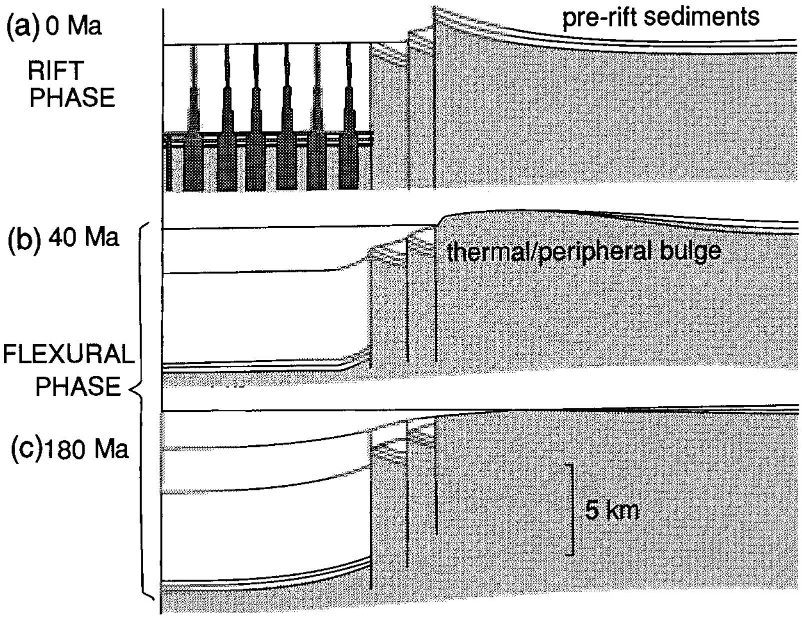


Fig. 2-2. Evolution of a sedimentary basin during dyking and flexural phases assuming lithospheric dyking model, modified after Royden et al. (1980).

The different tectono-volcanic regimes affect the nature of the ore forming processes and the types and proportions of sediments in-filling the basins exert strong control on the composition and migration of fluids. Hence the reduction in porosity in argillaceous sediments as a result of compaction and diagenesis with increasing depth of burial exceeds that of sandstones so that dewatering processes and phase transformations of clays will generally be most important in shale-rich basins. On the other hand, basins containing a high proportion of permeable clastic sediments tend to favour fluid circulation, as a result of thermal convection, particularly in the early stages of crustal extension when geothermal gradients are high, so that sedimentary exhalative (SEDEX) deposits tend to form over zones of isothermal bunching and fracturing. High permeability also favours gravity-driven fluid flow in late- to post-orogenic sedimentary basins. In general Pb–Zn–Ba deposits are formed by fluids derived from shale basins, whereas sedimentary Cu deposits are frequently associated with clastic red bed sequences in which fluids are SO_4-enriched (Gustafson and Williams, 1981). The relationship between temperature of mobilisation of ore and the percentage derivation of components from basinal fill is shown in Fig. 2-3, after Kissin (1988). The strong association between ore districts such as the Cobalt-Gowganda area, Canada and the Erzgebirge, Germany, which are characterised by hydrothermal veins containing Ni, Co, As, Bi, Ag and sometimes U and continental rift systems (Fig. 2-4) is suggested

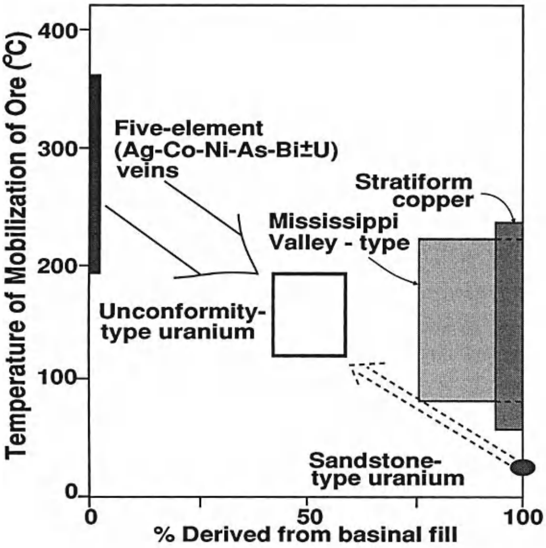


Fig. 2-3. Temperature of mobilisation of ore and the percentage derivation of components from basin fill, modified after Kissin (1988).

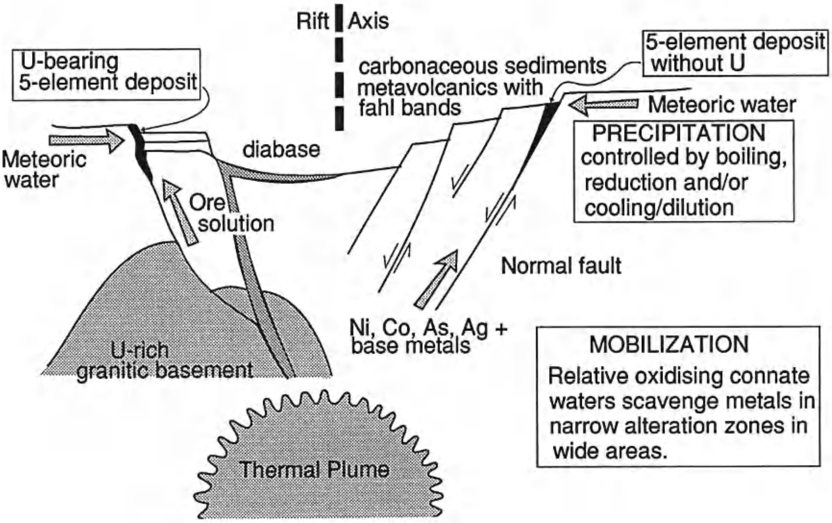


Fig. 2-4. Model for five-element veins, modified after Kissin (1988).

by Kissin (1988) to reflect mobilisation of high temperature (>400°C) high-salinity fluids generated in relatively oxidising conditions probably controlled by the magnetite–haematite buffer. Dyking associated with rifting may localise boiling.

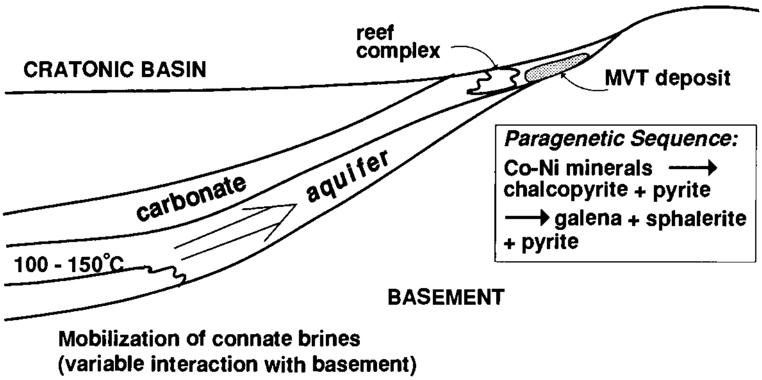


Fig. 2-5. Model for replacement Mississippi Valley Type lead–zinc–barium deposits, modified after Kissin (1988).

Basin analysis has been applied to carbonate-hosted deposits with particular reference to Britain and Ireland (Plant et al., 1988b). Hence SEDEX Zn–Pb–Ba "Irish style" deposits such as Navan, Silvermines and Tynagh have been related to the waxing phase of a regional cycle of basin formation in a regime of crustal extension and the rise of hot asthenosphere beneath the crust. The model developed is comparable to that described by Large (1983) for the Meggen and Rammelsberg SEDEX deposits of Germany.

In contrast, the main MVT replacement Zn–Pb–Ba deposits appear to be related to the waning phase of the cycle, with pervasive regional dewatering of basins following the decay of the thermal anomaly in the mantle and of isostatic readjustment of the crust (Fig. 2-5). The deposits are characterised by lower temperatures of formation (100–150°C) and very high-salinity fluids (>20 wt.% NaCl), and a considerably slower flow rate than in the case of SEDEX deposits (Anderson and MacQueen, 1982; Sangster, 1983). Moreover MVT deposits commonly show a close association with oilfields and fluid inclusions (which also contain hydrocarbons) are similar in composition to many oilfield brines (Carpenter et al., 1974).

Unlike SEDEX and replacement type MVT deposits, epigenetic Pb–Zn–F vein deposits, like those of the English Pennines and Kentucky in the USA, appear to be related to regional tectonism. In the case of the Pennines, catastrophic dewatering of shale basins, which had become overpressured beneath thick paralic sequences, occurred as a result of Hercynian deformation. The T–P–t evolution of the Edale Basin, thought to have been the source of the Pennine ore fluids, is shown in Fig. 2-6. Highly saline brines, carrying hydrocarbons, Pb, Zn, Ba and F, were driven into fracture systems in platform limestones with ore deposition occurring as a result of acid neutralisation and sulphate reduction reactions; in the northern Pennines buried, high heat production granites locally focused ore-fluids into hydrothermal convection cells

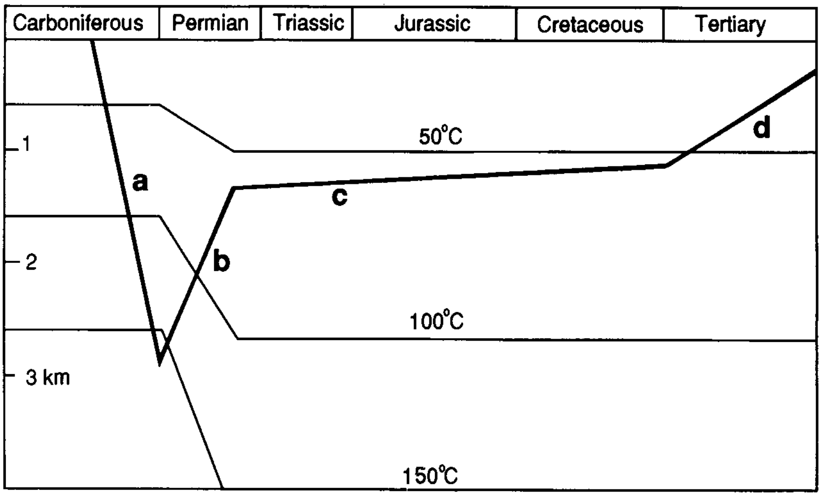


Fig. 2-6. Temperature–pressure–time evolution of the Edale Basin, the probable source of Pennine ore fluids.

so that the mineral zones are spatially related to the subcrop of the granites, despite the host rocks being younger.

Regional tectonism can also induce large scale gravitational fluid flow in sedimentary basins. Models for the generation of Pb–Zn deposits of the Upper Mississippi Valley Mineral district suggest that the orebodies were formed as a result of the flow of basinal brines through the Illinois Basin towards the Pascolar arc (Bethke, 1986). In the case of sediment hosted stratiform copper deposits, such as those of the Kupferschiefer and Zambian copperbelt, the Cu ores are suggested to have formed from sulphate rich brines with ore deposition occurring where the migrating fluids encountered organic rich shales (Gustafson and Williams, 1981; Kissin, 1988) (Fig. 2-7) or other hydrocarbon-rich fluids.

In late- to post-tectonic sandstone basins of Wyoming and Colorado in the Western USA, gravitational flow of oxidising meteoric waters has given rise to U deposits associated with Mo, Se and V concentrations where the descending water charged with these elements encounters reducing groundwater, sulphides or organic matter (Fig. 2-8). The uranium may have been derived from acid pyroclastics in the basinal fill and/or acid volcanics or granite in the provenance region, the presence of which may be detected geochemically. Other types of U deposits include the unconformity type (Fig. 2-9), exemplified by the Key and Rabbit Lake deposits of Canada and the Jabiluka Deposit of Northern Territory, Australia (Nash et al., 1981). These reflect convective fluid flow in sedimentary basins with deposition at redox barriers, but probably in response to magmatism, increased heat flow or tectonism, rather than to gravity (Fig. 2-9). Unconformity type uranium veins have variable amounts of Ni–Cu–As

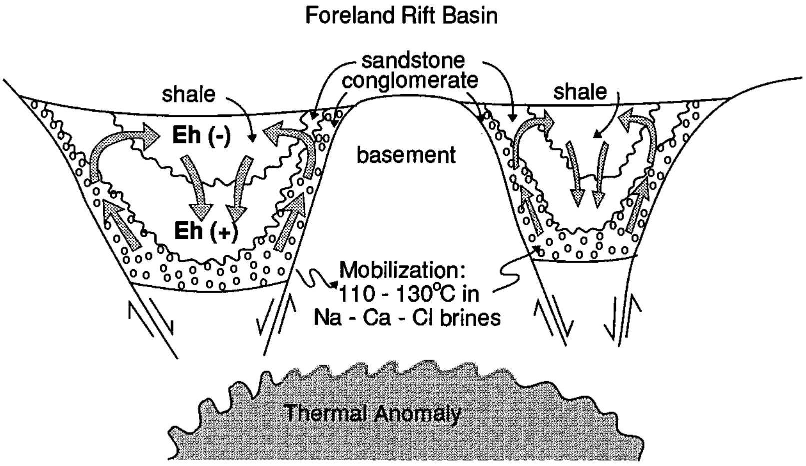


Fig. 2-7. Model for sediment-hosted stratiform copper deposits, modified after Kissin (1988).

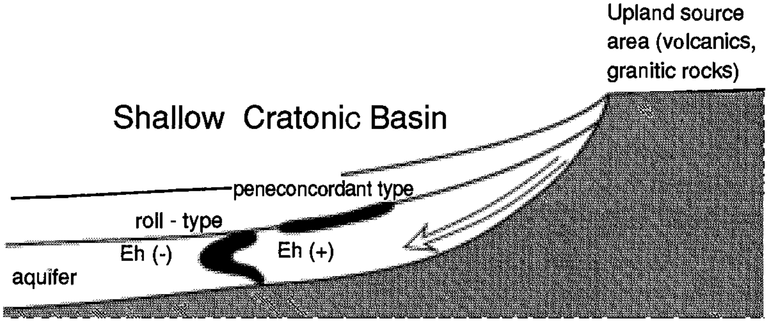


Fig. 2-8. Model for sandstone-type uranium deposits, modified after Kissin (1988).

mineralisation and sometimes base metal sulphides and Au. The presence of Ni and Co together with the presence of high As and low Fe contents is consistent with deposition from oxidising neutral- to slightly-alkaline fluids. The presence of U-rich felsic rocks is considered important for the generation of U deposits whereas basic and ultrabasic bodies are thought to supply Ni and Co.

Ore deposits in orogenic basins, such as the stratabound baryte–sulphide deposits which occur in the Dalradian Easdale Subgroup in Scotland and those of the Andean en-sialic basins of Chile and Peru can be related to the high geothermal gradients and high degree of tectonism in these basins, particularly along rift systems and bounding faults. Within these basins many listric-faulted basins and sub-basins may occur, together with extensive volcanic and volcano-sedimentary sequences. Cross basin lineaments may have originated as transform faults, separating zones in which crustal extension rates and

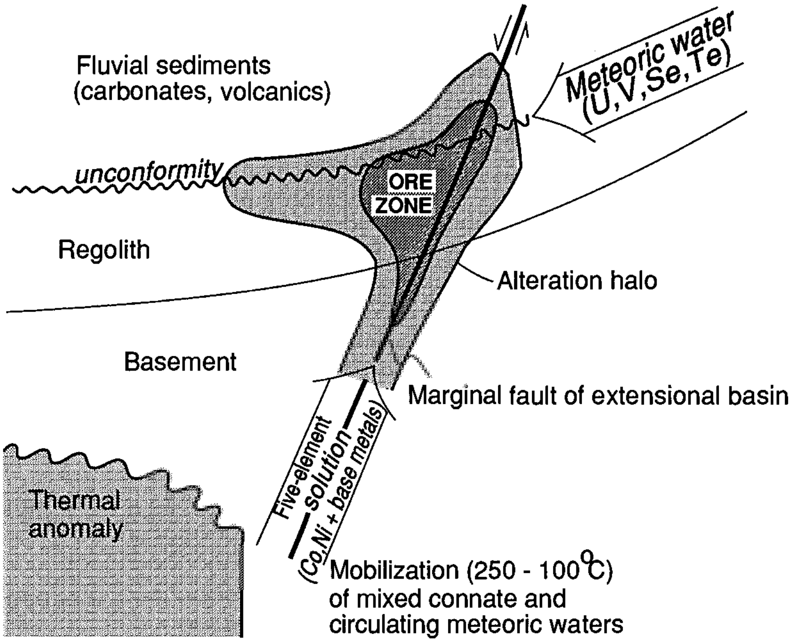


Fig. 2-9. Model for unconformity-type uranium deposits, modified after Kissin (1988).

metallogenic associations differed (Fettes et al., 1986). The basins may be identified by their high contents of elements such as B, Pb, Zn, and As and correspondingly low contents of elements such as Zr, Th and K_2O which are held in resistate minerals, and by the type of basalts which occur in them (which typically have back-arc characteristics).

The volume and chemistry of associated basic igneous rocks may give important information on basin development. In the early stages of basin evolution, and with low stretching rates, magmatism tends to be alkaline in character and of small volume. However, as stretching increases, less alkaline and more voluminous mafic dyke swarms and flood basalts are generated, giving way to tholeiites and, finally as complete rifting ensues, MORB-like basalts. Typically, volcanics tend to be associated with basin margin fault systems, but more complex patterns of volcanism occur where stretching is inhomogeneous.

The evolution of the volcano-sedimentary sequences of Archaean greenstone belts can also be modelled as zones of crustal extension having affinities with Phanerozoic en-sialic marginal basins (Tarney et al., 1976). Marginal basin models have been applied to the Abitibi greenstone belt in the Timmins and Kirkland Lake areas, which hosts massive sulphide and gold deposits (e.g. Jensen and Langford, 1983). Compared with post-Archaean volcanic sequences, Archaean greenstone belts typically have a high-Mg, -Cr, -Ni geochemical profile: a consequence of the presence of high-Mg ultramafic lavas (komatiites), which have few modern counterparts and can easily be recognised geochemically (Sun and Nesbitt, 1978). Komatiitic lavas frequently comprise the lower part of the volcanic succession, but there are also less Mg-rich basalts and high-Fe tholeiites and, particularly in the late Archaean belts, calc-alkaline lavas. The presence of iron-rich volcanics in greenstone belts has important implications for gold deposition (Simpson et al., 1989). Greenstone belts have many other features which make them important potential sites of mineralisation, including (1) thick predominantly submarine volcanic successions with the potential for Cu–Zn–(Pb) massive sulphide deposits, (2) thick sedimentary sequences deposited in tectonically controlled basins, with the possibilities for basin fluid migration, (3) presence of younger plutons with the heat potential to drive hydrothermal convective systems.

Sediment compositions

Unlike igneous rocks, there are relatively few studies of the relationship of the trace element chemistry of sedimentary rocks to tectonic setting and ore genesis, despite modern advances in basin analysis and the known relationship of deposition and diagenesis to rate of burial (Curtis, 1977). Models of ore genesis in sedimentary basins frequently involve migration of ore fluids from depth to palaeo-highs (e.g. Beales and Jackson, 1966), suggesting that geochemical studies could be of value in indicating basins with the potential to supply ore-forming fluids. In the UK, Old Red Sandstone sedimentary molasse-facies basins which are associated with U and Mo mineralisation and veins of Ba and Pb can be distinguished from unmineralised ORS basins by the higher contents of U, Mo and Zn, B in the rocks; similarly Carboniferous basins which supplied the ore fluids for the Pennine mineralisation of England contain sedimentary rocks enriched in As, Pb, Zn, P, B, Mo, having high calculated heat production (3.6–4.8 μW m^{-3}) reflecting high U contents (Jones and Plant, 1989).

The relatively low levels of trace elements over unmineralised arenaceous and carbonate sediments and the correspondingly high levels over shales, particularly those associated with organic detritus (black shales) are of particular significance for mineralisation. Limestones and sandstones are generally considerably more permeable than shales (they are frequently major aquifers) and oxidising conditions may persist to considerable depth due to the downward percolation of oxygen-bearing groundwaters. Limestones and other calcareous rocks promote acid neutralisation reactions, including those produced by the precipitation of sulphides from sedimentary (including neutral) brines. They thus commonly host a variety of ore deposits, although the metals themselves are likely to be derived from shales or other rocks containing organic detritus. Sulphur is also likely to be derived from shales, or other clastic sediments containing organic detritus, or from evaporites.

One of the most important controls of the potential of sedimentary basins to supply ore fluids may be the quantity of readily extractable metals bound in the organic or the carbonate fraction, and to a lesser extent on clays, in the sedimentary sequence. The distribution of chemical elements between the different fractions of the sediments largely reflects the importance of oxidation during weathering, transport and deposition and the diagenetic history of the sedimentary basin. The availability of sulphur may also be an important factor. This similarly reflects the extent to which sulphur is partitioned into metal sulphides, of which iron sulphides are most abundant (Chester, 1965; Dinur et al., 1980), or remains bound on organic compounds such as bitumen-kerogen. The presence of evaporites in sedimentary basins can also affect the activity of sulphur in basinal brines as well as their overall salinity.

Different suites of elements may be used in sedimentary rocks to characterise the detrital, carbonate, organic and alumino-silicate components. The elements, which are concentrated in the detrital fraction, are likely to be resistant to alteration during weathering, transport and deposition, and can be used to provide information on the provenance of the sediments. The elements which are most likely to be available for leaching into hydrothermal fluids are generally those which have a high seawater–upper crust partition coefficient (K_y) and long calculated residence times in sea water (see for instance Whitfield, 1979; Turner et al., 1980; Taylor and McLennan, 1985). Elements with a very high K_y and long sea water residence time, including most alkaline and alkaline earth elements, B and U, are strongly partitioned into natural waters and remain in solution for long periods of time. On the other hand, elements with very low K_y and short residence times, including Ti, Zr, the Al group, the REE (including Y) and Sc, Th, Nb and Be, are strongly excluded from natural waters and give the best information on source. Many relatively immobile elements are, however, difficult to use for deducing source. Some show marked changes in solubility as a result of changes in oxidation state (Fe, Mn) or are strongly chalcophile (Pb). Others such as Al have almost constant ratios with only limited dispersion in common igneous rocks; yet others tend to occur in heavy mineral concentrates (e.g. Zr). The distribution of REE, Y, Th, Sc and possibly Co are probably the most useful for determining sedimentary provenance (Taylor and McLennan, 1985). The REE, which form characteristic patterns, are a special case and their content in sedimentary rocks has been used by several authors to obtain information on average upper crustal compositions (see review in Taylor and McLennan, 1985).

As discussed above, black shales which tend to be highly enriched in organic, carbonaceous and phosphatic material, have particular significance for ore deposit modelling and geochemical exploration. Statistical analysis of chemical data from North American black shales showed that the detrital mineral fraction is characterised by Al_2O_3, TiO_2, Zr, Sc, and in some cases by Be, B, Ba, Na, K, Mg and Fe (Vine and Tourtelot, 1970). The carbonate fraction commonly includes Ca, Mg, Mn or Sr while the organic fraction tends to be enriched in Ag, Mo, Zn, Ni, Cu, Cr, V, and less commonly Co, Pb, Y and U. Carbonate-rich organic shales from the Namurian and Dinantian of Britain, considered to be the source of the mineralisation in the English Pennines, are enriched in P, Mo, As, B and U (Jones and Plant, 1989), elements which, together with S, U, Br, I, Zn and B, are also enriched in plants and their detritus in sedimentary rocks

(Perel'man, 1977). Hence sedimentary rocks, particularly shales and other rocks containing an important organic fraction, form important crustal reservoirs of bound H_2O, and S, F, P and B which have enrichment factors ranging up to 100 in plant ash compared to soil.

Deposits formed by hydrothermal activity associated with volcanism/plutonism

There is a continuum in the nature of ore deposition from extensional sedimentary basins, where fluid flow occurs as a consequence of thermal anomalies, to hydrothermal activity related to volcanism or high level plutons. In both cases ore deposits form as a result of the dissipation of the thermal anomaly, predominantly by fluid convection. However, in the case of hydrothermal activity associated with magmatism, a complex interplay of tectono-magmatic processes is required to generate fractures capable of transmitting fluids through otherwise impermeable rock. Such fractures may be generated semi-continuously and they are frequently the loci of multiple igneous intrusions or volcanic centres which overlap in time. Mathematical fluid flow models enable the temperature and fluid flow around igneous intrusions, or volcanics to be predicted (e.g. Cathles, 1981). Intrusion-related hydrothermal systems are generally more focussed and localised and the geochemical changes around ore bodies more readily detected than in the case of sedimentary basins where fluid flow is more pervasive and the amount of metal extracted relative to the bulk source is small.

Considerable controversy surrounds the genesis of felsic igneous rocks associated with ore deposits and the ultimate sources of the metals and fluids (Sawkins, 1982; Stanton, 1986). This partly reflects the inappropriate applications of models and classifications as well as difficulties in distinguishing the effects of high temperature water–rock interaction from primary magmatic characteristics. The S-type granite classification of Chappell and White (1974) for example is frequently applied to granites containing muscovite and biotite, although the muscovite may be secondary, and formed from biotite as a result of acid neutralisation reactions in hydrothermal systems (Eugster, 1985). Isotopic systems may also re-equilibrate in the presence of a fluid phase. Hence the high initial $^{87}Sr/^{86}Sr$ ratios used to support an S-type origin for the granites of Southeast Asia (Beckinsale, 1979) can be explained instead by a water–rock interaction event causing muscovitisation and Sn-mineralisation, which ended ca. 80 Ma after the emplacement of juvenile granites that had much lower initial $^{87}Sr/^{86}Sr$ ratios (E. Jager, pers. commun. to J. P., 1985). Moreover, the stable isotopic compositions of hot ^{18}O-shifted saline formation waters, metamorphic waters and magmatic waters overlap (H.P. Taylor, 1979), and boiling of hydrothermal systems can also increase their ^{18}O content. The isotope systems of fluid and magma may re-equilibrate, particularly at high temperatures and low water–rock ratios, to produce an apparent magmatic signature in the fluids. In the case of porphyry copper deposits, Norton (1982) has shown that a maximum of only 4 wt.% of total fluid in the hydrothermal system could be magmatic, the major fluid sources being the metamorphic host rocks.

Volcanic associated massive sulphides

These deposits are formed by the interaction of fluids (predominantly seawater) with volcanic rocks (Fig. 2-10), and are classified following Franklin et al. (1981) and Lydon (1984) according to their metal contents, into Cu–Zn, Zn–Cu(Pb), and Zn–Pb–Cu groups. Typically, such deposits have H, O and S isotopic compositions indicative of extensive seawater–rock interaction. They can generally be accounted for in terms of models of mass transfer in a subseafloor hydrothermal system involving large scale convective interaction with volcanics, probably in a single-pass convective system with high water–rock ratios (Fyfe and Kerrich, 1976). In the case of Cu–Zn (Cyprus-type) ores, formation temperatures are of the order of 400°C (Spooner and Fyfe, 1973), whereas in the case of Zn–Pb–Cu (Kuroko-type) deposits, temperatures of 300–250°C have been estimated on the basis of fluid inclusion and sulphur isotopic compositions (Ohmoto and Rye, 1974). Mineral stability fields in hydrothermally metamorphosed sea-floor rocks indicate exceptionally high (1000°C/km) geothermal gradients. The various alteration assemblages are shown in Fig. 2-10.

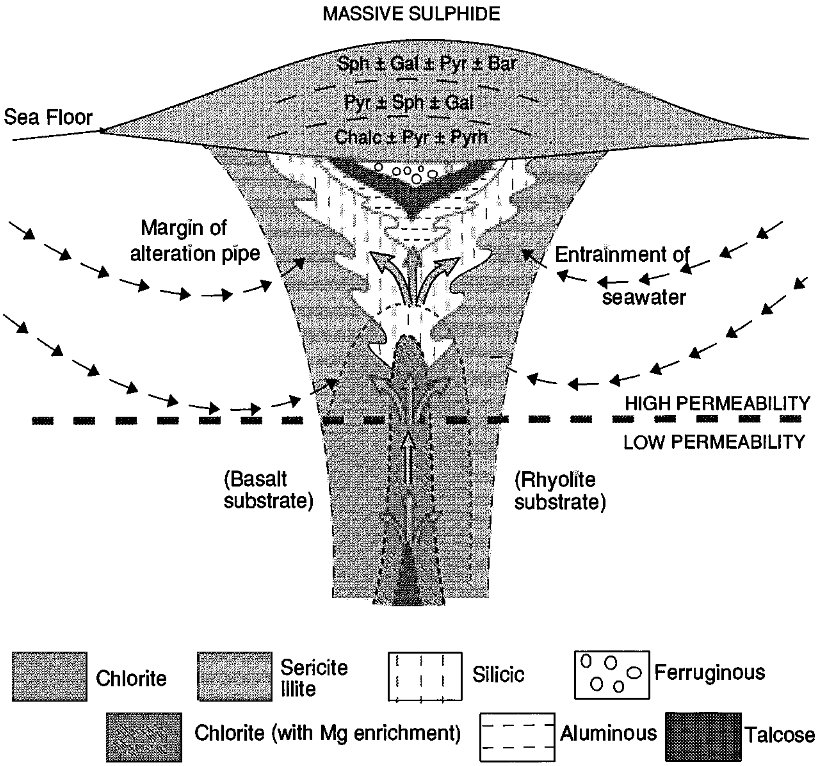


Fig. 2-10. Composite representation of the various alteration assemblages of alteration pipes of Volcanogenic Massive Sulphide (VMS) deposits, modified after Lydon (1984).

(1) Cu–Zn "Cyprus- and Besshi-type" ores and Zn–Cu (Pb) ores, associated with basalt. These deposits are formed at oceanic (including back-arc) spreading centres by the interaction of high temperature seawater with basalts at low water/rock ratios. The group includes, for example, Cu–Zn massive sulphide deposits formed in Precambrian greenstone belts, those in the Norwegian Caledonides, those associated with ophiolites in Cyprus, Oman and the Besshi district of Japan, as well as contemporary sea-floor deposits of the East Pacific Rise. Studies of active metalliferous vents on the sea-floor and of massive sulphide deposits in the geological record (Franklin, 1986), together with modelling (Cathles, 1981) indicate that the size of the deposits can be related to the tectono-magmatic setting. Thus abundant small deposits occur in volcanically active intermediate- to fast-spreading ridges; larger deposits (up to 1M tons of ore) are formed in volcanically inactive or mature ridge crests and the largest deposits (2M tons) in off-axis segments. Highly sedimented ridge crests have the potential for the largest deposits since the sediments prevent oxidative destruction of sulphides, and metals are more easily leached from sedimentary detritus than from volcanic rocks. In the Guyamas Basin, Gulf of California, the ridge axis is buried beneath ca. 500 m of biogenic and clastic sediments containing as much as 4% organic carbon. The associated hydrothermal solutions are alkaline, contain ammonium as a significant ion (300 ppm), and are depleted in ore metals (Edmond, 1985). It is thought that a sediment-hosted massive sulphide ore body is forming at depth, precipitation being induced by the reaction of ore fluids with biogenic carbonate and ammonia resulting from thermocatalytic breakdown of immature planktonic organic carbon. There is a wide range of hydrocarbons, from methane to asphalt, which may be the equivalent of graphite in mined bodies in older rocks (Edmond, 1985).

Formation of massive Cu–Zn sulphides requires tectonic stability with a substantial heat source at shallow depth (<2 km) in the oceanic crust (Franklin, 1986) so that they are generally associated with major mafic sub-volcanic intrusions. However in some Precambrian massive sulphide districts and in some back-arc environments the sub-volcanic intrusions are mainly felsic. A sub-group within the Cu–Zn group of massive sulphides includes deposits with atypically high Pb contents and high contents of Ag, such as those in the Mattabi and Kidd Creek deposits of the Canadian Shield. Such deposits have been attributed to formation in shallower water than is typical of Cu–Zn deposits associated with basalts generally (Franklin, 1986). Their association with felsic igneous rocks may provide an additional source of Pb.

(2) Zn–Pb–Cu deposits associated with calc-alkaline felsic volcanism. This group, associated with extrusive felsic volcanics or volcaniclastic sediments, includes the classic Kuroko deposits of the Green Tuff region of Japan (Fig. 2-11), the Iberian pyrite belt, deposits of the Bathurst district in Canada, the Tasman region of Australia, the Avoca district of Ireland and those in the English Lake District and North Wales. Such deposits occur in narrow time stratigraphic intervals within extensive volcanic sequences, frequently where

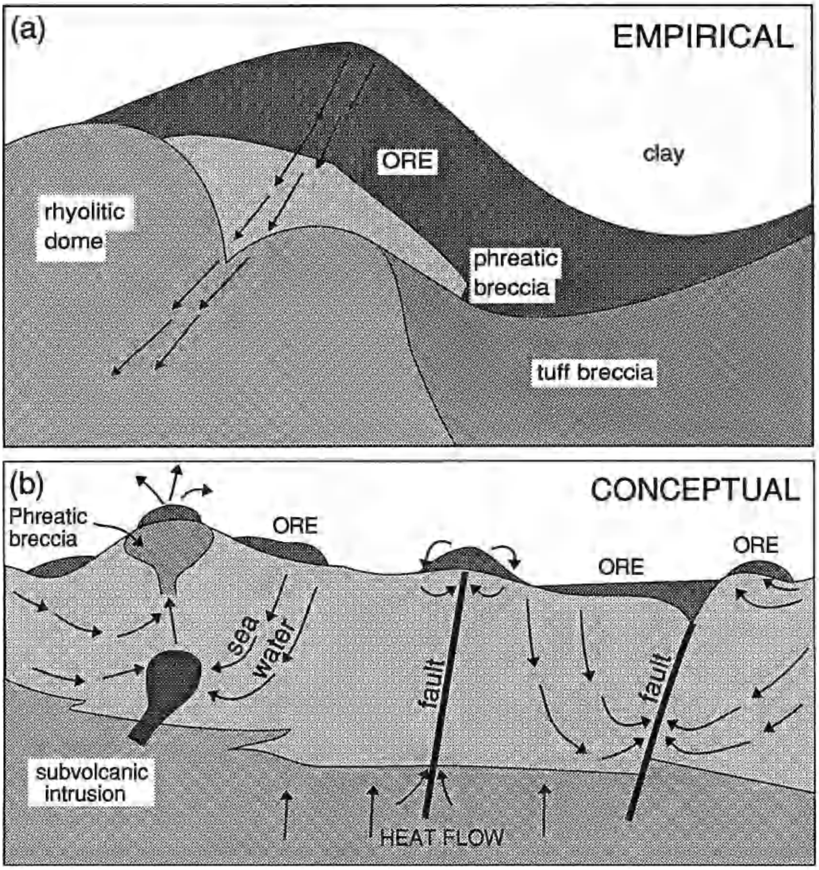


Fig. 2-11. (a) Idealised cross-section of a typical Kuroko Deposit, (b) main features of recent genetic models for Kuroko Deposits. Modified after Franklin et al. (1981).

there is a transition from lavas to volcaniclastic sediments, and they are commonly associated with pyroclastic rocks, caldera formation and/or faulting of rhyolite domes. Although there is abundant evidence of pervasive seawater–rock interaction, it has been suggested that the source of metals is magmatic fluids from intrusions emplaced beneath the volcanic sequences (Stanton, 1986); and a mixing model, involving a 1 : 9 mix of magmatic water and seawater, has been proposed (Sawkins, 1982) to account for their trace element and isotopic characteristics. However, reaction at high temperatures between sedimentary sub-seafloor formation water and igneous rock in systems with low water–rock ratios could account for these characteristics, and such a model is preferred to one involving juvenile fluids. The incursion of formational fluids, probably along deep fracture systems, may also have caused phreatic explosions, thereby accounting for the volcaniclastic rocks. Subvolcanic magma chambers are necessary however to maintain the hydrothermal systems for a sufficient length of time to produce economic concentrations of metals. Evidence of high-level crystal fractionation in the volcanic pile is thus important in indicating the existence of associated magma bodies and in identifying favourable horizons for massive sulphide deposits in basaltic or felsic volcanic-volcaniclastic sequences.

Reworking of early formed sulphide assemblages by evolved high pressure fluids has been proposed to explain the ore paragenesis and texture of Kuroko massive sulphides (Eldridge et al., 1983) and of Cyprus-type ores (Ixer et al., 1986). The involvement of a late sustained low T (<250°C) fluid has also been used to explain the association of some Archaean massive sulphides with Au mineralisation and to explain gold enrichment in seafloor polymetallic sulphide deposits generally (Hannington et al., 1986). In the latter setting gold enrichment is in low T sulphasalts of Pb, As, Sb, Ag and S.

(3) Epithermal Au–Ag deposits. These deposits are typically associated with late stage hydrothermal activity in regions of calc-alkaline felsic (andesitic to rhyolitic) volcanic or plutonic centres. They are formed by the convective circulation of heated low-salinity (1–3% NaCl; e.g. Nash, 1972) meteoric water (Taylor, 1973; O'Neil and Silberman, 1974). In certain types, very high water–rock ratios are involved, with deposition from long-lived circulation cells through fracture systems in which wall rocks have previously been depleted in ^{18}O so there is little shift in $^{16}O/^{18}O$ (cf. Archaean lode gold deposits). This group of deposits includes those of Western Nevada and the Western San Juan Mountains in Colorado, and several deposits in Southeast Asia and New Zealand. Two main types of epithermal precious metal deposits have been distinguished (Hayba et al., 1986) primarily on the basis of vein and alteration mineralogies. These are the *adularia sericite type* (Fig. 2-12a) which consists of illite-to-smectite clay minerals, quartz and pyrite, and the *acid sulphate type*. The adularia sericite type is thought to have formed in late- to post-magmatic hydrothermal systems, similar to those of the Taupo Volcanic Zone, New Zealand (Henley and Ellis, 1983), whereas the acid sulphate type (Fig. 2-12b), which shows a close spatial relationship with calc-alkaline volcanic domes and isotopic compositions close to volcanic host rocks, may be genetically related to porphyry Cu deposits (Hayba et al., 1986), The main features of the two deposit types of importance for geochemical exploration are described by Hayba et al. (1986).

Two hot spring systems active at the present day, namely Steamboat Springs, Nevada, and Broadlands, New Zealand, are presently depositing gold and silver and base metal sulphides. In the Broadlands field, which occurs along the east side of the Taupo volcanic zone, Zn, Pb and Cu sulphides are being deposited at depth with a near-surface element suite characterised by As, Sb, Hg, Tl, Au and Ag which is similar to that of epithermal deposits generally. The field occurs on an active seismic zone related to a graben system containing calc-alkaline silicic ash flows and rhyolites with minor basalts and lacustrine sediments and greywackes. At surface the ore-forming fluids are neutral. Seward (1973) showed that the Au was probably transported as $(Au(HS)_2)^-$, with S and B probably having been derived from sediments, particularly greywackes, at

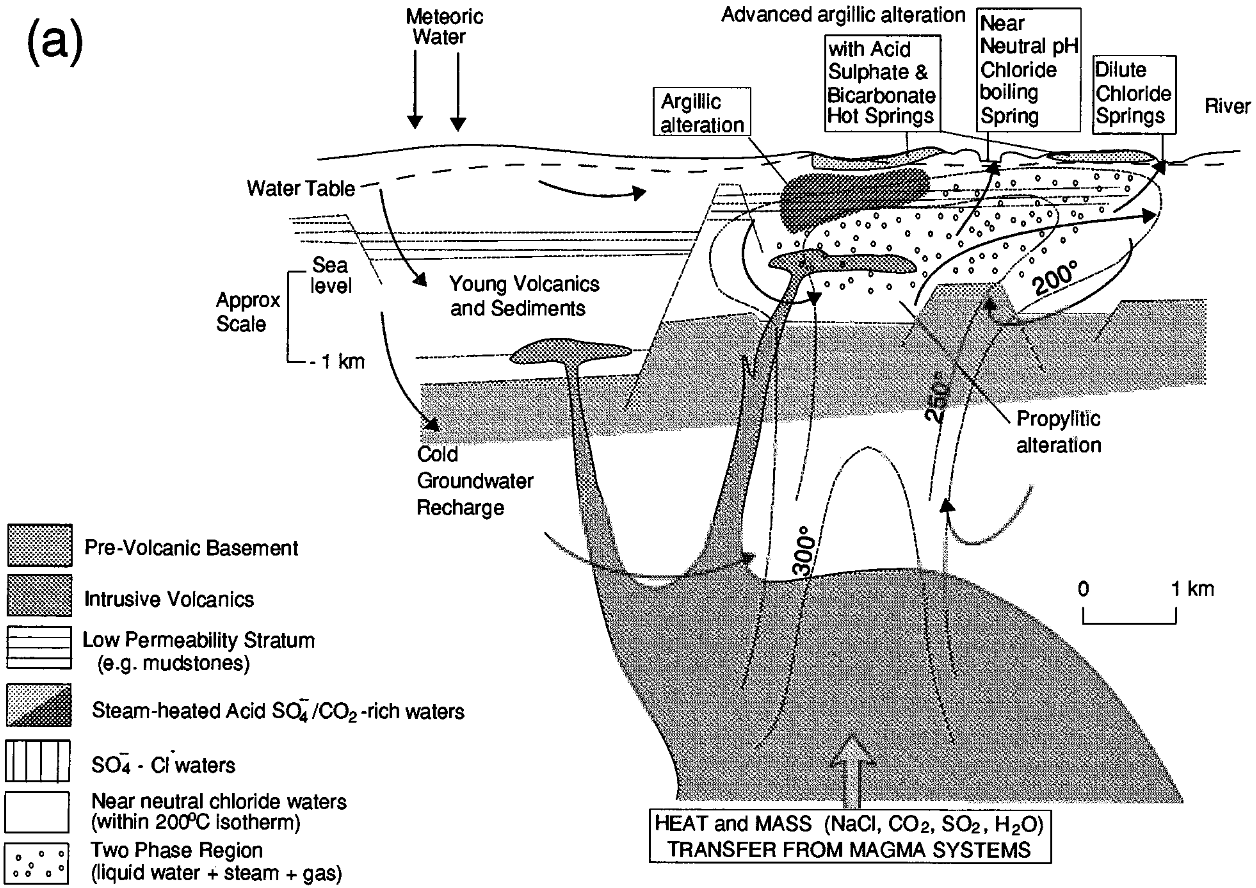


Fig. 2-12. (a) Generalised model for adularia-sericite epithermal gold system.

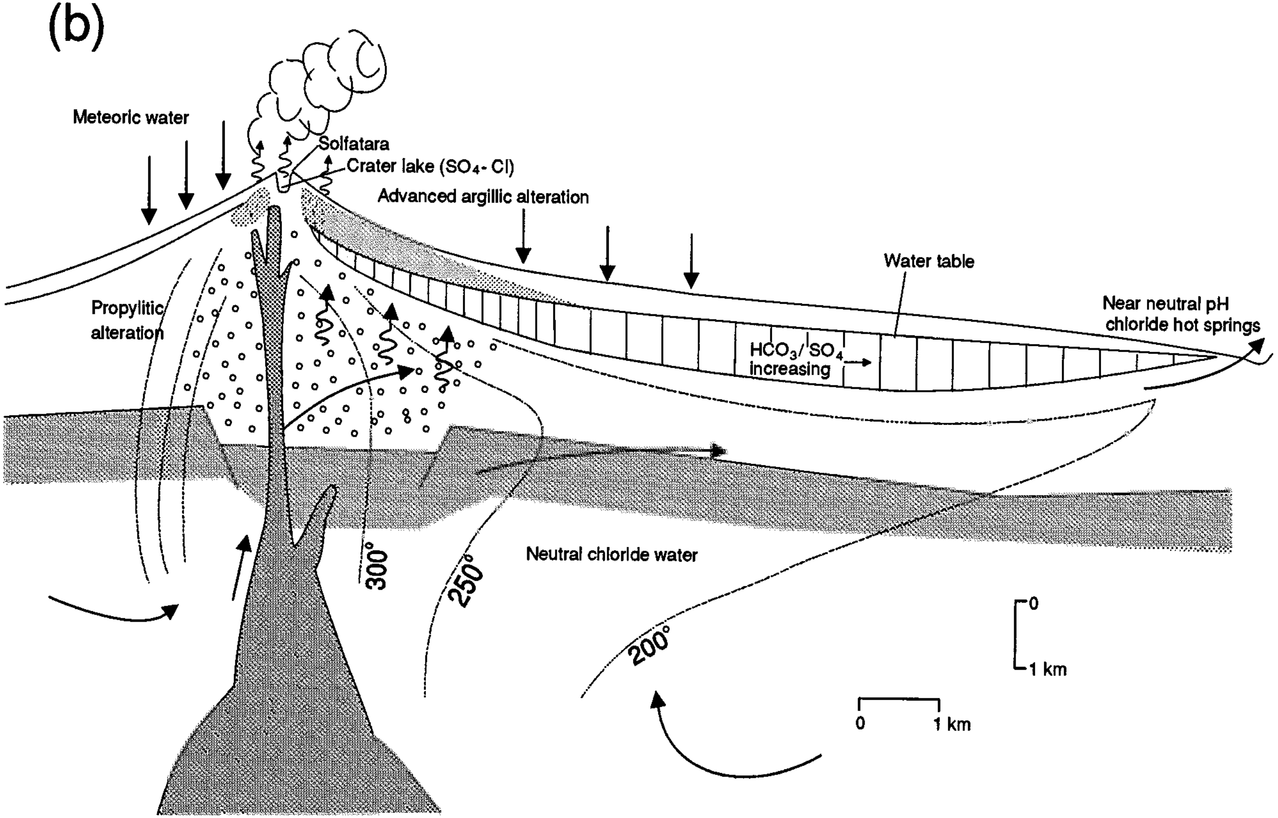


Fig. 2-12. (b) Generalised model for acid sulphate epithermal gold system. Both modified after Henley (1986).

depth (H.P. Taylor, 1979). Solubility of the $(Au(HS)_2)^-$ complex is greatest in alkaline conditions where the activity of Fe is low. Sorbtion of precious metals by SbS and other precipitates is thought to take place at the surface due to either a decrease in temperature from 250° to 100°C, the separation of steam in flashes with a loss of CO_2 and H_2S and a consequent increase in pH, or because of atmospheric oxidation of H_2S in the liquid phase.

Elements such as C, S, H, O, N, Fe, Mn, U, W, As, Sb, Bi, Cu, Ag, Au, Te and Sn participate in oxidation-reduction reactions in geothermal/epithermal environments. The first seven elements are the most abundant and interact to buffer the redox state; the remaining elements are usually less abundant and respond only to the chemical environment imposed by the dominant redox systems. Redox reactions are influenced by the interaction of organic matter with fluids, the oxidation of H_2S, the precipitation of native metals and pyrite and other sulphides, the destruction of sulphides by oxidation and the transformation of SO_2 into H_2S and SO_4^{2-} on cooling from high temperature.

The type of alteration in geothermal areas, together with features such as silica sinter and hydrothermal breccias are comparable to those described in several epithermal precious metal deposits (Hedenquist and Henley, 1985). In some hot spring systems ephemeral precipitates with ore grade Au and Ag form (Henley, 1986), and the suite of elements As, Sb, Hg and Tl, characteristic of epithermal Au deposits, is enriched.

Hydrothermal deposits associated with felsic plutons

Metalliferous mineral deposits associated with granites are frequently discussed in relation to the I- and S-type granite concepts of Chappell and White (1974) or the ilmenite- and magnetite-series granite terminology of Ishihara (1977). Cu and Mo porphyries are generally regarded as I-type, the calc-alkaline stocks around which mineralisation is centred being both temporally and spatially linked with subduction (e.g. Mitchell and Garson, 1981). The Bougainville Cu-porphyry is a typical example, being located ca. 100 km from the trench where oceanic lithosphere of the Soloman Sea is being subducted. Many major Cu-porphyry deposits of Mesozoic–Tertiary age are found in elevated positions in young Cordilleran or collision belts that were originally situated above subduction zones.

Copper and Mo porphyry style mineralisation, which consists of a metal–sulphide assemblage, sometimes with associated Au, is related to interaction between a high temperature “magmatic” fluid and formational or meteoric water (Fig. 2-13). The early-formed hydrothermal mineral assemblages, mainly of biotite and other K-rich silicates, have isotopic compositions compatible with the hypothetical field of magmatic water — although this may reflect low water–rock ratios and an approach to isotopic equilibrium between magma and ore fluids; co-existing quartz and K-feldspar commonly being out of isotopic equilibrium (H.P. Taylor, 1979). Beyond the innermost potassic zone, which mostly coincides with the low-grade core of the deposit, there is generally a phyllic zone, coincident broadly with the pyrite zone of mineralisation, a poorly

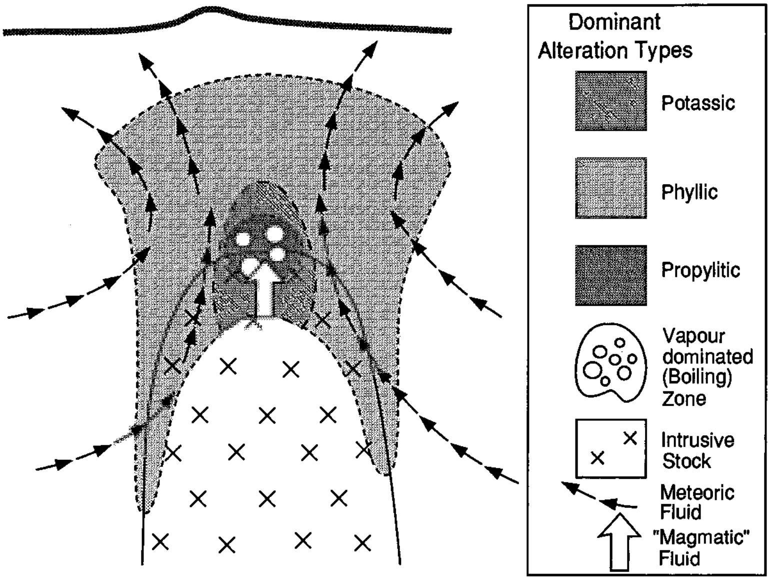


Fig. 2-13. Model of hydrothermal system for porphyry copper mineralisation, modified after Lydon (1984).

developed argillite zone, and a wider outer propylitic zone. The stable isotopic compositions of these zones indicate progressive influence of, and interchange with, meteoric water. Gold, if present, tends to be deposited in the cooler, outer (epithermal) parts of porphyry systems.

In contrast to porphyries, two-mica Sn–U granites are frequently considered as S-type in the sense of Chappell and White (1974), who attribute their formation to anatexis of upper crustal sedimentary protolith. Such models cannot account for the geochemical (Plant, 1986; Govett and Atherden, 1988), tectonic (R.G. Taylor, 1979; Watson et al., 1984) and experimental petrological characteristics of Sn granites however, and the model for Sn–W–U mineralisation associated with these granites first described by Simpson et al. (1979) and Plant et al. (1986) is preferred. According to this latter model, mineralisation is initiated as water-deficient granite magma rises to high levels in the crust. Hydration of the granite occurs initially by host-rock fluids at high (metamorphic) temperature. Reduction of silicate and primary accessory minerals is thought to commence at this stage, evolving into deuteric alteration of the granite magma and, finally, as the granite cools and cracks, hydrothermal convection with flow of formational and subsequently meteoric water through fracture systems. Such "S" type characteristics as the high initial $^{87}Sr/^{86}Sr$ ratios, ^{18}O enrichment and low ferric/ferrous ratios are attributed to interaction between the granite and its host rock through a fluid phase.

The ore assemblage associated with this type of granite is dominated by oxide (cassiterite, wolframite, uraninite) species. Gold may also occur, as in S.E. Asia and S.W. England. Cassiterite deposition occurs early in the development of the hydrothermal system, at temperatures of the order of 500°C (Rankin and Alderton, 1982), with U mineralisation occurring later at lower temperatures ($<150°C$). Uranium may also be re-mobilised to form pitchblende veins and these may post-date magmatism by tens or even hundreds of millions of years. This has been related to the high heat production capability of such granites (a consequence of their high U, Th and K levels) which, at times can re-initiate and sustain hydrothermal circulation systems (Fehn et al., 1978; Simpson et al., 1979).

Geochemical evidence of fluid rock interaction as a result of ore formation associated with high level igneous activity

Ore formation associated with high level igneous activity can involve fluxing of rocks with massive quantities of fluid. In the case of Cu–Zn ore bodies for example, it has been estimated that 1 km^3 of basalt magma can heat 3 km^3 of sea water to 300°C, as it cools (Spooner and Fyfe, 1973). Hence it is essential that the effects of water–rock interaction are distinguished from primary magmatic compositional variations. In the case of volcanic-associated massive sulphides, evidence of extensive interaction of seawater with the volcanic host rocks generally occurs around the ore bodies. Sea water, which is an oxygenated solution containing Na^+ and Mg^{2+} as major cations and Cl^-, Br^-, HCO_3^-, CO_3^- and SO_4^{2-} as major anions, reacts extensively with volcanic rocks at high temperature. Initially, as it descends into the volcanic pile and is heated, it becomes progressively reduced while the volcanics are pervasively oxidised. Magnesium is almost completely removed from solution into alteration products such as smectite, together with SO_4^{2-} which is removed by precipitation of anhydrite and reduction to sulphide (Mottl and Holland, 1978; Edmond et al., 1979; Mottl, 1983). In the recharge zone, oxidation occurs and calcite and anhydrite precipitation may be extensive, partly as a result of leaching of Ca from the volcanics.

With the progressive removal of oxidising species and with rising temperature the brines become increasingly reduced and Mn^{2+} and Fe^{2+} along with other transition metals, e.g. Cu, Zn, Ni, may pass into solution as chloride complexes (Helgeson, 1979) before being precipitated to form ore deposits. Above the ore zone chemical sediments enriched in Mn, Fe along with Ba, Co, Cu, Ni, Pb, V, Zn and Zr are formed as a result of oxidation of ore fluids and the deposition of the precipitates on the sea floor (Robertson, 1975; Govett, 1983). In areas of intense, long-lived hydrothermal convection associated with ore formation in basalts, the levels of the major elements SiO_2, Mg, Ca, Na, K, Mn and Fe and their ratios show a wide variability compared with those of unaltered basalt or basalt subjected only to hydrothermal weathering on the sea floor. The high field strength elements, including the REE Ti, V, Y, Zr, Hf, Nb and Ta will be relatively unaffected by such processes and these form the basis for some of the more robust classifications of basalt types (e.g. Pearce and Cann, 1973).

In the case of Kuroko massive sulphides, a detailed sequence of chemical reactions between progressively modified seawater and calc-alkaline volcanic rocks has been established (Pisuth-Arnond and Ohmoto, 1980). Fluid interaction is initiated during early diagenesis when pore fluid (seawater) reacts with rocks, increasing the total dissolved salt (mainly NaCl) and Ca content of the ore fluids and increasing the water and Mg contents of the country rocks. At this stage gypsum and calcite precipitation may deplete the CO_2 concentration in fluids but, with increasing temperature, the organic matter in marine sediments breaks down, increasing the CO_2 contents of ore fluids above the normal levels of seawater. In the discharge zone of Kuroko ore deposits, fluids at temperatures of about 200°C react with the early-formed zeolite facies minerals leaching Na and Cl, and at about 250°C, coincident with the deposition of the black ore assemblage, Ca-rich montmorillonite–illite mixed layer clays and sericite form. The continuous breakdown of plagioclase and the formation of sericite progressively increases the K/Na ratios (and K contents) of the ore fluids. Finally, at temperatures of about 300°C there is further depletion of Na and Ca, and increase in the K and Mg contents of the rocks.

Lithogeochemical studies of massive sulphides (see for example the review by Govett and Atherden, 1988) confirm the geochemical zonation corresponding to the progressive alteration zones in the recharge areas around such orebodies and to the discharge and supra ore zones. In most cases Fe, Mg and Zn are enriched and Na and Ca depleted. It is clear that, in the case of massive sulphides at least, the size of the exploration target can be greatly increased by searching for the entire area of alteration, particularly the pervasive recharge area, rather than by simply exploring for the ore deposit itself; such an approach is of particular value in regional geochemical exploration.

Particularly well defined zonation patterns in the ore forming elements have also been identified associated with mineralised plutons in Arizona (Chaffee, 1976) and elsewhere (Koval, 1984). However, as in the case of volcanic associated massive sulphides, it is essential that the primary characteristics of the magmas are distinguished from the effects of water rock interaction by the use of appropriate suites of elements or their ratios.

The general behaviour of elements in aqueous systems can be deduced from their ionic potential (Fig. 2-14). Those of low ionic potential (<3), for example, Li, Ba, Ca, and Mg, tend to form hydrated cations while those of high ionic potential (>12), for example B and S, form soluble complex oxyanions. The former group includes the important LIL elements which are commonly used as petrogenetic indicators, isotopes of Rb, Sr, K and Pb also being important in radiometric age dating. Ore deposits associated with high level igneous activity involve interaction with either seawater or, in continental settings, deep geothermal fluids, both systems being dominated by chloride brines. A classification of ore forming elements developed by Eugster (1985) on the basis of their behaviour in Cl-dominated aqueous systems, such as those associated with granites, is presented in Fig. 2-14 and Table 2-IV. The three main groups are: (a) the soluble cations, which can be further subdivided into elements

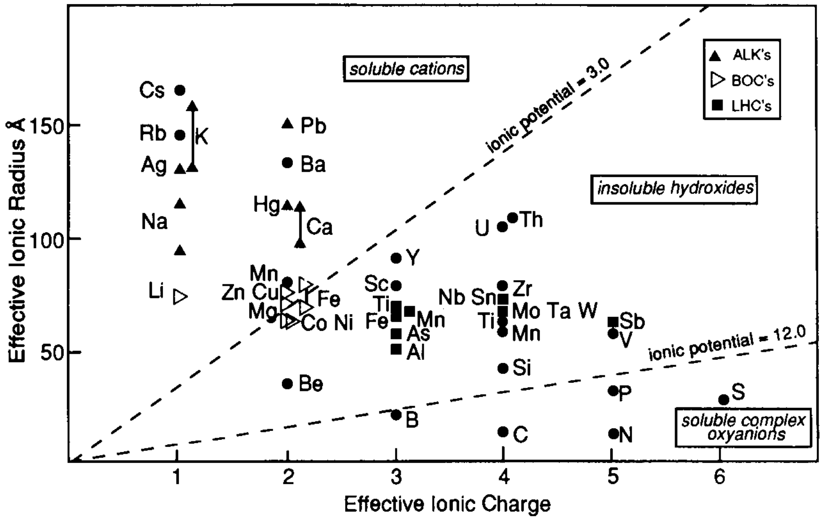


Fig. 2-14. General behaviour of elements in ore-forming solutions, categorised according to ionic potential and Eugster's (1985) classification of ore-forming elements.

showing behaviour comparable to alkaline elements ("ALC") or to ferrous iron (bivalent octahedral cations, "BOC"); (b) the large highly charged cations ("LHC"), which in Cl-dominated aqueous systems show behaviour comparable to Ti; and (c) a group of elements which form complex oxyanions in aqueous solution (B, C, N, P, S). The ALC's and their ratios are likely to show the most intense and widespread effects of alteration in hydrothermal systems (Fig. 2-14 and Table 2-IV), followed by the BOC elements, which include most of the elements enriched in massive sulphide and porphyry Cu deposits. The large highly charged cations which include the PGE, the Sn, W, Mo group and the REE, Y, Ti, Sc and V, are the least mobile in Cl dominated solutions. Boron, C, N, P and S are frequently enriched in mineralised igneous rocks, but in the crust the main reservoirs of these elements are shales and sediments that are particularly enriched in organic material such as kerogen or bitumen. Boron metasomatism has been suggested to represent the influx of fluids from sediment in the case of geothermal systems associated with granites (Lister, 1979; Simpson et al., 1979) and also in epithermal precious metal systems, for example at Broadlands, New Zealand. Sediments have also been suggested to be the source of S in porphyry and granite systems in China (Eugster, 1985).

In the case of ore deposits associated with water–rock interaction around igneous centres, the "LHC" element concentrations and ratios are normally the most dependable in deducing primary igneous characteristics related to tectonic environment. The "BOC" and "ALC" elements can be used to indicate widespread alteration and zonation around ore deposits, while increased levels of B, C, N, P and S associated with igneous intrusions may indicate fluid exchange between igneous systems and sediments.

TABLE 2-IV

Reactions releasing ore forming elements from silicates, modified after Eugster (1985)

Reaction type and condition	LHC	BOC	ALC
1. Congruent dissolution at low f_{O_2}	× × ×	× × ×	× × ×
2. Incongruent dissolution, no oxidation	×	× × ×	× ×
3. Incongruent dissolution, with oxidation	–	× × ×	× ×
4. Congruent exchange, neutral pH, no oxidation	×	×	–
5. Incongruent exchange with oxidation	–	× × ×	× ×
6. Melt–fluid exchange with HCl production	× ×	× ×	×

Continental porphyry- or andesite-related geothermal systems may evolve from high temperature acid reducing to neutral or alkaline systems, becoming less reducing as a result of declining temperature and the influx of meteoric fluid (Ellis and Mahon, 1977). In such systems the main ionic species may be reduced sulphur and carbonate species instead of chloride and a similar evolution in ore fluids may account for the formation of gold-enriched massive sulphides (Hannington et al., 1986). The presence of such an ore fluid may be indicated by enrichment of the chalcophile elements As, Se, Mo, Ag, Sb, Te, Hg, Bi and Tl. In epithermal deposits the particular suite of elements varies between the *acid sulphate association*, which has relatively high Cu and Bi values, and the *adularia sericite association* which is generally more enriched in Se (B and Mn). The former type shows a closer association with porphyry Cu igneous centres; the latter with more diffuse geothermal anomalies associated with andesitic volcanism and in some cases volcaniclastic sediments.

Geochemically one of the simplest criteria indicative of mineralisation associated with igneous rocks is the increased standard deviation of trace (and major) element contents (Beus and Grigorian, 1977; Simpson et al., 1979) although their mean content may remain unchanged. Hydrothermal activity also affects trace and major element variation diagrams such as Rb/Sr, Rb/Ba, K/Rb, Sr/Ba and U/Th and Mg/Li. These plots show relatively simple trends in rocks formed mainly by magmatic processes, reflecting diadochic substitution, but they are dispersed and scattered in mineralised intrusions whereas the HFS elements such as Ti and V retain their magmatic trends (Fig. 2-15).

Increased B/Ga, B/SiO_2 or even B/V ratios have been shown to be indicators of boron metasomatism (Fig. 2-15) as a result of high temperature interaction of granites with shale-derived fluids (Lister, 1979; Simpson et al., 1979; O'Brien et al., 1985). Chondrite normalised REE patterns generally reflect the magmatic history of the intrusions, but in areas affected by acid reducing fluids, REE patterns (Alderton et al., 1980), Zr/Sn and other element ratios may be affected. Dispersion of the Ga/Al ratio which is normally constant in igneous rocks may also occur as a result of deposition of high Al/Ga minerals such as topaz from highly acid solutions (Beus and Grigorian, 1977). It is at this stage, when

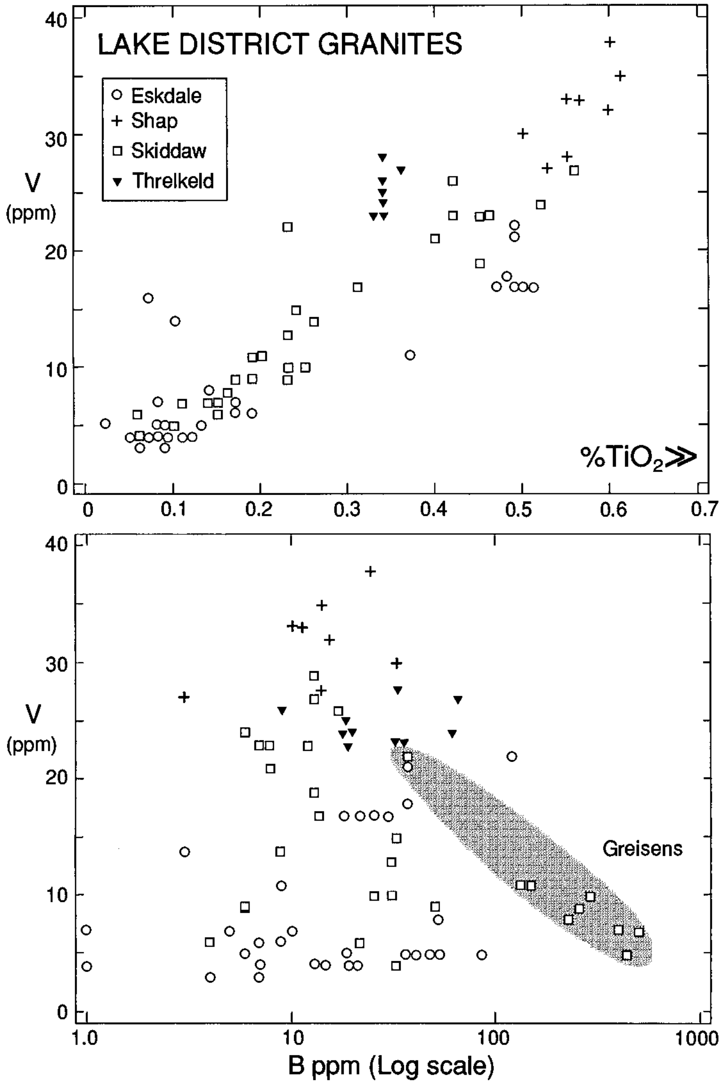


Fig. 2-15. Immobile and mobile elements in granitoids. The upper diagram shows a reasonably coherent trend for TiO2 vs. V for English Lake District granites, attributable to fractionation of mafic components. Comparable distribution of boron (lower diagram) shows incoherent scatter and much greater range, attributable to hydrothermal effects.

resistant primary accessory minerals such as zircon and monazite break down, that U is initially released into solution, and it can be subsequently remobilised from easily leachable sites because of the number and stability of its complexes (Langmuir, 1978).

Magmatic ore deposits

Magmatic deposits are those in which metal concentration is achieved in a relatively closed magmatic system and, in contrast to the deposits described above, sulphide or volatile activity (whether from juvenile or crustal sources), if any, takes place prior to or early in crystal fractionation. Mineral deposits in this group are mainly associated with ultramafic–mafic rocks, including chromites, Ni–Cu sulphides and PGE with Au (Naldrett and Cabri, 1976), and with some alkaline complexes.

Ultramafic–mafic rocks have been classified by Besson et al. (1979) following the work of Naldrett and Cabri (1976) into three main subdivisions: (A) synvolcanic bodies other than those related to intracratonic volcanism, (B) intrusions in cratonic settings, and (C) mafic complexes emplaced during orogenesis.

The first group, which includes komatiitic flows and sills and synvolcanic tholeiitic, picritic or anorthositic intrusions, is particularly important in Archaean greenstone belts where high-Mg komatiitic lavas are frequently associated with Ni, Au and PGE deposits. Primary Cu sulphides occur with orthopyroxenites in the important Caraiba Complex in Brazil (one of the few major Cu deposits in a Precambrian high grade terrain), and a similar association of Cu sulphides with pyroxenites occurs in the Koperberg Suite, a series of small late-Proterozoic plutons in South Africa (Naldrett, 1981; Conradie and Schoch, 1986).

The intrusions in intracratonic areas, particularly those related to flood basalts such as the Duluth Complex in the USA, the Noril'sk Talnakh Complex in Russia, and the large repetitively layered complexes such as Bushveld, South Africa, and Stillwater, USA, are the most important sources of nickel sulphides, PGE and chromite deposits. The Sudbury Igneous Complex of Canada is somewhat anomalous. It was emplaced about 1.8 Ga ago into the site of a large explosion crater (Naldrett et al., 1986a). The large layered mafic intrusions such as Bushveld and Stillwater, which apparently formed in an anorogenic setting, tend to be noritic rather than gabbroic.

Of the bodies emplaced during orogenesis, ophiolites may be associated with chromite or PGE deposits but there are no examples of significant Ni deposits. Large cumulate gabbro–ultramafic complexes also occur in active continental margin settings (Beard, 1986) and collision fold belts (Khan et al., 1989). Typically, they are noritic rather than gabbroic and are regarded either as the roots of island arcs or as manifestations of ensialic back-arc activity. Primary sulphides may occur in such intrusions, usually associated with orthopyroxenites (Himmelberg et al., 1987). A general model capable of explaining the formation of both sulphide and oxide mineralisation is based on magma mixing (Fig. 2-16). According to this model (Campbell et al., 1983) a jet of hot magma mixes with cooler resident magma of similar density causing sulphide precipitation (where one magma has a higher silica content), the formation of chromite horizons and PGE in layered intrusions.

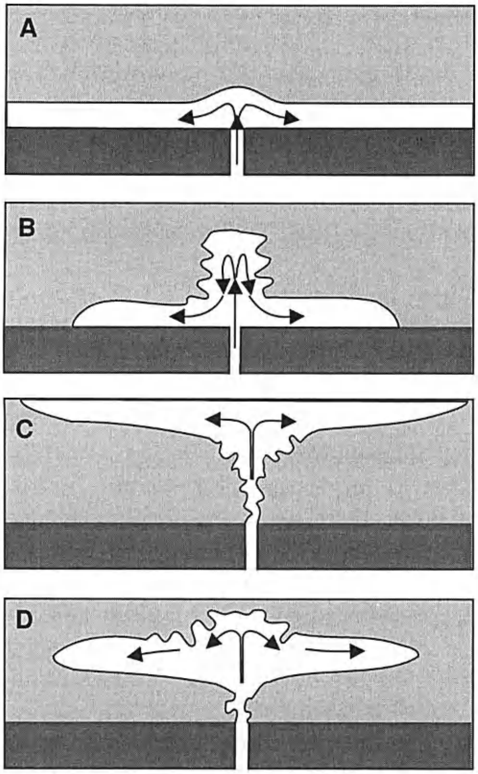


Fig. 2-16. Increasingly low-density magma injection plumes (A to C) into resident magma, each resulting in little mixing, and (D) where injection plume has similar density to resident magma. Situation D favours sulphide precipitation. Modified after Campbell et al. (1983).

Chromite ores

In ophiolites, minor chromite concentrations may occur in the lowest part of the cumulate sequence, usually associated with dunite, and normally no more than cm-size. The most important deposits however are podiform chromites (Dickey, 1975) which occur within the harzburgite tectonite (i.e. below the petrological Moho marking the base of the magma chamber); indeed they are usually concentrated in this zone. Commonly also associated with dunite, they occur in a variety of forms (lenticular veins, nodular, disseminated), sometimes with relict igneous textures. They most likely represent the initial precipitates of magmas rising through the mantle in the axial zone beneath a spreading ridge, Many of the morphological features of the deposits result from deformation however. Lava compositions in Tethyan ophiolites such as Troodos are rather siliceous and Cr-poor, indicating that significant chromite precipitation occurred before eruption.

Stratiform chromite deposits in large layered intrusions all appear to have formed as magmatic segregations during crystal fractionation. The layers extend over large distances and may be from a few cm to 1 metre thick. The precise reasons why massive chromite layers form are not well understood. In the case of the Bushveld and Stillwater complexes, Irvine and Sharpe (1986) have suggested that abundant chromite precipitation is the result of hybridisation of two separate magmas, one ultramafic, the other aluminous and anorthositic, with the solubility of Cr being abruptly decreased in the more aluminous siliceous liquid (see also Fig. 2-16).

Nickel sulphides

The deposition of nickel sulphides in stratiform and orogenic gabbroic complexes generally shows a concentration that appears to be related to igneous layering, although in some orogenic complexes, such as the giant Mascot Mine in British Colombia, the Ni sulphides occur along linear zones which may represent incipient fracture systems. The depletion of Ni in coexisting olivine (Duke, 1979) provides direct evidence of the existence of a sulphide phase during crystal fractionation, the liquid having become saturated with sulphur prior to, or during, crystallisation. The source of sulphur is controversial, and has been suggested to be either of mantle (Nesbitt, 1971) or crustal origin (see Naldrett (1981) for review). Se/S ratios have been used by Eckstrand and Cogulu (1986) as a means of distinguishing juvenile from crustal sulphur in mineral deposits associated with basic and ultrabasic rocks. Juvenile sulphur has Se/S ratios in the range 200–600 × 10^{-6} while crustal values are much lower.

Archaean Ni-sulphide deposits are commonly associated with komatiitic flows. Such flows often overlie sulphide facies iron formations which occur near to the top of underlying felsic volcanic and sedimentary sequences, or black shales. The high temperature high-Mg liquids have the potential for considerable thermal erosion and assimilation of such rocks suggesting that contamination by crustal sulphur was important in ore genesis (Groves et al., 1979). Others have suggested that komatiites are derived from sulphide rich portions of the mantle (Naldrett and Cabri, 1976).

Platinum group elements and gold

The large stratiform central complexes contain the world's most important PGE deposits. There is however considerable controversy concerning the role of magmatic (e.g. Naldrett et al., 1986a) and fluid (e.g. Stumpfl, 1986) processes in the concentration of PGE. It is now known for instance that Pt and Pd can be transported in ore-forming fluids as chloride complexes, and perhaps also as bisulphide or hydroxide complexes (Mountain and Wood, 1988). In Bushveld and Stillwater the PGE ores form thin stratiform layers in cumulate layers of anorthosite, norite and bronzitite. Evidence for a magmatic origin for the PGE in Stillwater has been summarised by Barnes and Naldrett (1985), and in the Bushveld complex. In contrast, Stumpfl (1986) has presented evidence for extensive volatile activity (C–OH–S–Cl phases) in the formation of the main PGE ore horizon in Stillwater, and a melt-fluid (C–OH–S–Cl) evolution path has also been proposed for the Bushveld Merensky Reef on the basis of petrological and fluid inclusion studies. The fluid inclusions contain CH_4CO_2 and $NaCl\cdot H_2O$. Whatever the relative importance of magmatic and fluid processes in concentrating PGE's, it has been argued, as in the case of Ni-sulphide deposits, that contamination took place before fractional crystallisation (Stumpfl, 1986).

The PGE concentrations in ophiolites tend to have less well defined layering, and to be of much lower grade — with ore grade sometimes attained only in placer concentrations (e.g. the Goodnews Deposit of Alaska) There are also differences in the relative abundances of the PGE between stratiform complexes and ophiolites. Stratiform deposits are enriched in Pt and Pd and the chondrite-normalised PGE patterns have positive slopes. Ophiolite PGE patterns generally have negative slopes, although that of the Unst Ophiolite (Prichard et al., 1986) is positive. The difference in the PGE patterns between stratiform and ophiolite complexes has been ascribed to the preservation of Os, Ir and Ru in laurite inclusions in early chromites (Talkington et al., 1984), the more incompatible PGE's having been lost to later-formed overlying gabbros, and/or removed during pervasive hydrothermal alteration and serpentinisation of ophiolites by fluids which may be rich in As and Sb. Several plots of metal ratios such as Pd/Ir against Ni/Cu and Ni/Pd against Cu/Ir (Fig. 2-17) have been developed for PGE exploration (Barnes et al., 1988). Plots of Pd/Ir versus Ni/Cu and Ni/Pd versus Cu/Ir are used to distinguish the effects of olivine and chromite fractionation from sulphide segregation and thus help to identify intrusions with potential for PGE deposits. Because Ir analyses are expensive, Rh and Pt can be used instead of Ir, but the results may be more ambiguous. The plots depend on the compatible behaviour of Ru, Ir and Os and incompatible behaviour of Pt and Pd during mantle melting and fractional crystallisation, and the fact that Ni is known to be compatible with olivine while Cu is probably incompatible with the structures of most mantle phases.

Metamorphic ores

Several deposit types, e.g. massive sulphides, are commonly found in metamorphic terrains and in some older ore classifications they are grouped with metamorphic ores. Metamorphism results in phase changes, for example hydrocarbons are changed to graphite and pyrite is reduced to pyrrhotite on progressive regional metamorphism, but only ore deposits formed by metamorphic processes which involve deposition from a metamorphic phase are considered here. Such ore-forming fluids are generated at high temperatures and pressures under conditions approaching equilibrium with their host rocks. Ore deposition occurs as fluids re-equilibrate at lower temperatures and pressures following their discharge along zones of high deformation and de-watering or de-carbonation of metasedimentary/metavolcanic sequences. The group includes some uranium vein deposits (Ryan, 1979) and probably some trace element enriched pegmatites but this discussion is concerned mainly with lode gold deposits.

Greenstone belts in Archaean cratons have produced approximately 18% of

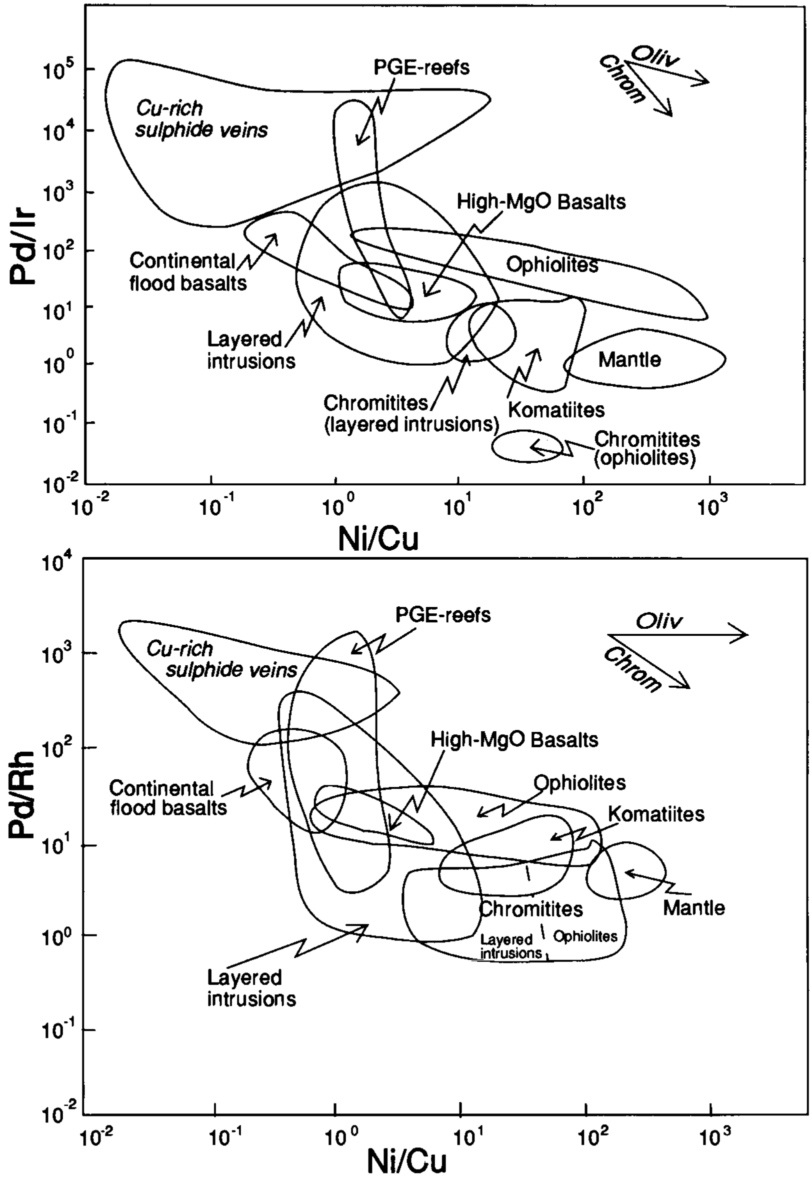


Fig. 2-17. Plots of metal ratios for PGE exploration, modified after Barnes et al. (1988).

the world's cumulative gold production, mainly from Canada, Australia, Zimbabwe, South Africa, Brazil and India (Woodall, 1985). The gold deposits are confined to the volcano-sedimentary sequences of the belts and do not normally occur in the enclosing paragneiss (Roberts, 1987). Mineralisation occurs in discrete quartz veins, pervasive micro-veins and tabular sulphide disseminations in structures that post-date most of the magmatic and metamorphic events (Colvine et al., 1988). Stratiform gold in veins and banded iron formations or iron-rich cherts, for example in the Murchison province of Western Australia, in Zimbabwe, and in Barberton, southern Africa, has also been related to a similar epigenetic model (Phillips et al., 1984). In the Abitibi belt of Canada the gold deposits can be related to steeply-dipping planar shear zones of brittle to ductile deformation, concentrated around regional fault systems, such as the Destor Porcupine break in the Timmins region (Roberts, 1987). Model lead ages (Thorpe, 1982) and ^{39}Ar/^{40}Ar cooling ages on the gold veins are close to those of the last stages of Abitibi greenstone belt igneous activity as determined by precise U–Pb isotopic ages on zircons (Colvine et al., 1988). Host lithologies include most of the rock types found in greenstone terrains (R.W. Boyle, 1979b). Replacement or metasomatic alteration around the deposits (mainly carbonate — commonly ferroan dolomite — alteration, silicification, sericification and/or tourmalinisation) reveals gross chemical disequilibrium between hydrothermal fluids and host rocks.

The nature of ore formation and particularly the source of the gold bearing fluids is controversial, with mantle degassing (Colvine et al., 1988) and metamorphic dewatering (Kerrich, 1983, 1989; Fyfe and Kerrich, 1984; and Groves et al., 1987) being alternatively proposed as the principal mechanism in the formation of Archaean lode gold deposits. In addition some deposits such as the Hemlo deposit have been suggested to represent volcanic-related epithermal deposits comparable to those of the Broadlands area of New Zealand (Cameron and Hattori, 1985).

According to the model of Colvine et al. (1988), mantle and lower crustal rocks, metasomatised by fluids generated at an underlying subduction zone, were the main source of gold, CO_2 and sub-crustal melts in the Archean greenstones of the Abitibi belt of Canada; magmatism was triggered from above by vertical and horizontal block movements along major crustal lineaments.

The alternative metamorphic model for Archaean gold deposits in Western Australia has been described by Groves et al. (1987) and for similar deposits in Canada by Fyfe and Kerrich (1984) based on earlier studies by Fyfe and Henley (1973) and R.W. Boyle (1979b). The model derives low salinity, moderate density, near neutral H_2O–CO_2 fluids, which carry Au as reduced S complexes, largely by de-volatilisation of the lower parts of greenstone successions and/or basement during metamorphism and synchronous late-stage deformation and granite emplacement. Phillips et al. (in Groves et al., 1987) have calculated that all of the components of a major gold deposit could be derived by devolatilisation of a 300 km^3 slab of greenstone containing only 2 ppb Au. As in the case of the mantle degassing model, fluid flow, probably driven by seismic pumping is considered to have been channelled via shear zones and other faults.

Although magmatic fluids (Burrows et al., 1986) cannot be ruled out on the basis of chemical and isotopic data, the spatial separation of some large deposits (e.g. Golden Mile, Kalgoorlie) from granites or abundant late stage porphyry intrusions suggests that magmatic processes are unlikely to have been critical in Au genesis. Some mantle contribution to the components of gold ore fluids is indicated by stable isotope data (R.E. Smith et al., 1987), but a direct mantle source is considered unlikely (Roberts, 1987).

The mantle degassing and metamorphic models suggest that the role of geochemistry in Au exploration is limited to the detection of anomalous levels of gold and its pathfinder elements such as As, Sb and Bi in the immediate vicinity of deposits. Recent studies (Plant et al., 1989b; Simpson et al., 1989) have suggested however that gold deposits are formed by the extraction of gold and sulphur species from large volume low grade crustal sources of these elements. Gold deposition in greenstone belts and certain types of Phanerozoic greywacke-shale basins is considered to represent the culmination of a sequence of events associated with orogenic basin development. Initially low level concentrations of gold, sulphur and the chalcophile pathfinder elements are suggested to accumulate in carbonaceous shale-greywacke sequences in listric faulted basins during the initial extensional phase of basin development. The gold, S and chalcophile pathfinder elements are remobilised when the f_{O_2} increases as a result of pervasive fluxing of the crust by CO_2 along deep fault systems and around rising felsic intrusions during cratonisation. Such a model (Fig. 2-18) suggests that the identification of regional As enrichment (and possibly Au or Sb depending on adequately low analytical detection limits) by regional geochemical mapping is important in identifying areas which merit detailed exploration for gold. Regionally anomalous As and sometimes Au have been shown to occur over the Goldenville formation of the Meguma group of Nova Scotia and the Dalradian belt of Scotland, both of which contain gold deposits. The gold deposits in these belts, as in the case of Archaean greenstone belts are

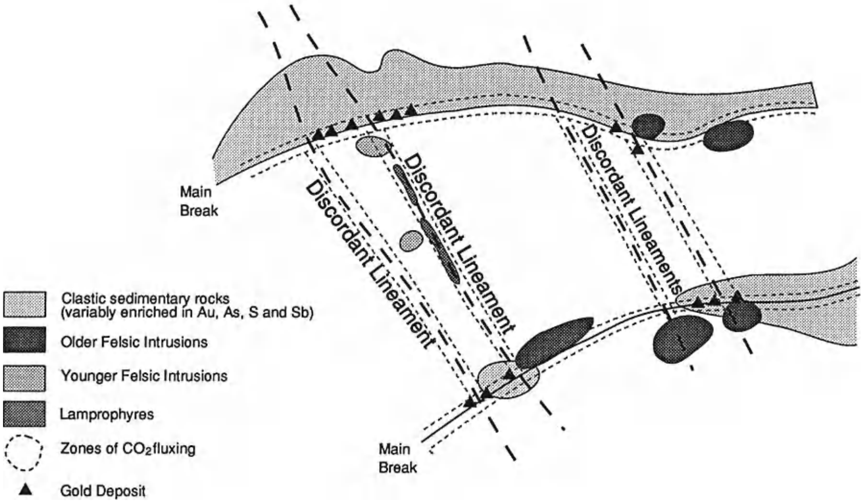


Fig. 2-18. General model for hydrothermal gold veins in greenstone belts and extensional basins, from Simpson et al. (1989), modified after Hodgson (1986).

spatially associated with major fault and shear systems. In Western Australia linear belts of enrichment in chalcophile pathfinder elements have been shown to be correlated with the presence of gold deposits in the Archaean Yilgarn craton where they are also spatially associated with major fault and shear systems cutting metasediments (R.E. Smith et al., 1987).

The situation for Au deposits is thus suggested to be analogous with that for Sn and some types of U deposits whereby the identification of crustal reservoirs is important for exploration/resource analysis.

PRIMARY GEOCHEMICAL SIGNATURES OF IGNEOUS ROCKS IN RELATION TO TECTONIC SETTING

There is generally a relationship between metalliferous mineral deposits and tectonic environment and several (particularly igneous) rock types have geochemical characteristics which can be used to distinguish different tectonic settings. These characteristics may be preserved to some degree despite metamorphism and hydrothermal alteration although identification of the tectonic setting becomes increasingly difficult in rocks which have suffered metamorphism, extreme deformation and tectonic disruption. Relationships can be quite complex, even in young terranes: for example along the western seaboard of North America a series of "suspect" or "displaced" terranes, formed in different environments, are juxtaposed. Moreover, whereas much Phanerozoic geology can be explained in terms of plate tectonics, the extension of uniformitarianist principles into the Precambrian is fraught with uncertainty. Nevertheless many clear geochemical patterns emerge, which can be used to identify geological settings as far back as the Archaean.

The most extensive use of geochemical data to identify tectonic setting has been for igneous rocks, particularly basalts and granites. The emphasis of such studies is increasingly on the use of trace rather than major elements. Basalts from the ocean floor, ocean islands, island arcs, continental margins, rift zones and flood provinces, for example, frequently have similar major element compositions but markedly different trace element characteristics and the same is true of granites. This discussion is therefore concerned mainly with trace elements.

There are several ways of presenting trace element patterns. Rare-earth element (REE) abundances are usually normalised against chondrites. The bulk Earth is broadly chondritic with respect to the REE, so that the REE patterns of igneous rocks reflect the sum of fractionation processes which have occurred during the evolution of the respective magmas, and in some cases of the magma source. For several elements the Earth is not chondritic, however, so that, patterns for a broader range of elements are generally displayed normalised to estimates of the primitive mantle (Wood et al., 1979a; Thompson et al., 1983; Sun and McDonough, 1989). Such multi-element diagrams are now used extensively to summarise element abundance variations in a wide range of rocks. Some elements are more useful than others in discriminating between

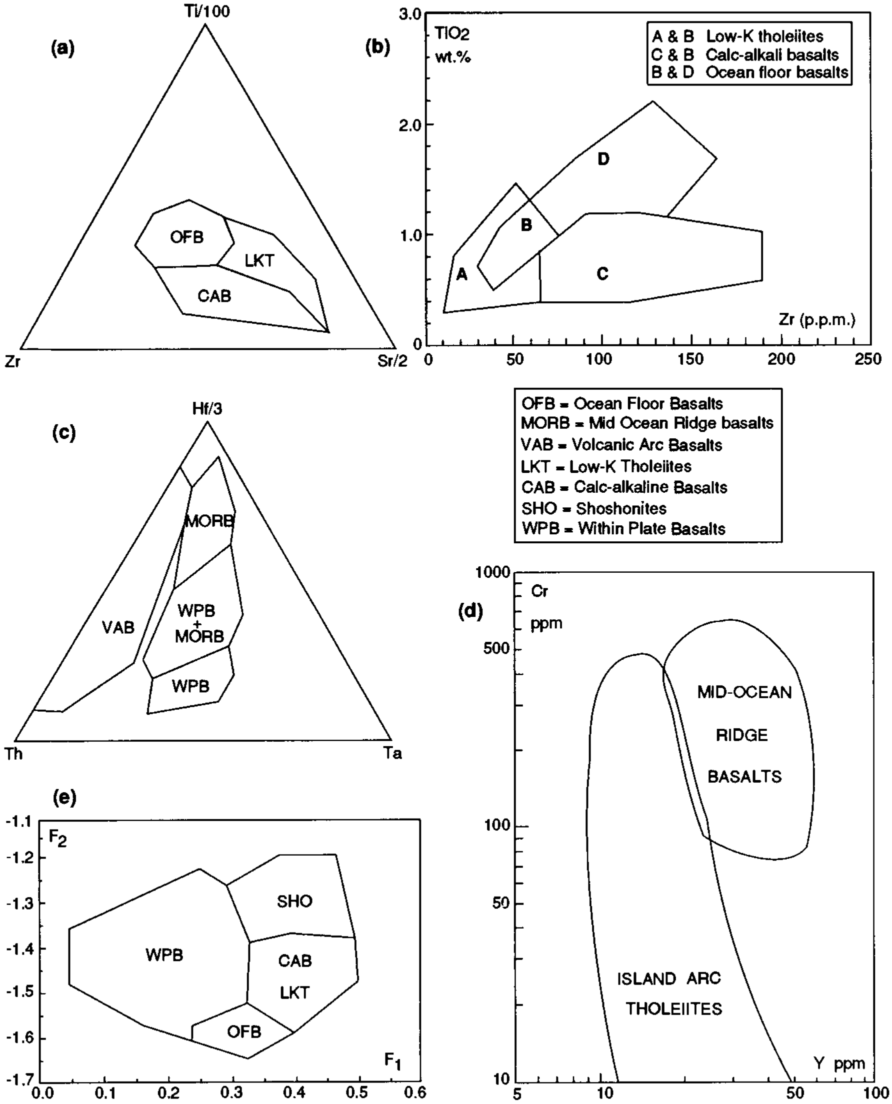


Fig. 2-19. A selection of the more frequently used discrimination diagrams for basaltic rocks. Abbreviations used are shown in inset. (a) Ti–Zr–Sr (all as ppm) and (b) TiO_2 vs. Zr diagrams after Pearce and Cann (1973); (c) Hf–Th–Ta diagram after Wood et al. (1979b); (d) Cr vs. Y diagrams after Pearce (1982); and (e) Major–minor element discrimination factors F1–F2 after Pearce (1976). The original publications should be consulted before using such diagrams.

tectonic environments and these form the basis of bi- or tri-element diagrams (see for instance Pearce and Cann, 1973; Floyd and Winchester, 1978; Wood et al., 1979b; Pearce, 1982). A selection of the more commonly used ones for basaltic rocks is given in Fig. 2-19.

In the discussion that follows the geochemical patterns of basalts and other rock types characteristic of particular tectonic settings are described together with a brief account of the processes which they reflect. The patterns for rocks from settings frequently associated with ore deposits are described as well as those from sequences which are generally barren since it is important that unprospective areas are eliminated from exploration programmes. It is convenient to begin with basalts, as these exhibit a wide range of trace element patterns as a result of variations in the processes of melting of their mantle sources, and in the processes related to their source development.

Ocean floor basalts

Basalts generated at mid-ocean ridge spreading centres are products of melting of peridotite making up the main convecting mantle reservoir (from the base of the lithosphere down to at least the 700 km discontinuity). Typically they show progressive depletion in the light REE (Fig. 2-20a), and the most incompatible trace elements (Fig. 2-20b) and are known as normal or "N-type" MORB. Their depleted geochemistry reflects the progressive extraction of melts from the convecting mantle through geological time, a component of which forms the continental crust. This depleted mantle ("DM") source has low $^{87}Sr/^{86}Sr$ and high $^{143}Nd/^{144}Nd$ isotopic ratios, a consequence of time-integrated low Rb/Sr and Sm/Nd ratios. N-type MORB can be identified using trace elements or isotopic ratios.

Not all mid-ocean ridge basalts are depleted N-type MORB. Basalts erupted in the vicinity of "hot spots" (such as Iceland or the Azores), near major fracture zones, and particularly at slow-spreading ridges (such as the Atlantic or the Southwest Indian Ridge) tend to show a range of light-REE and incompatible element enrichment (Tarney et al., 1979, 1980; Saunders, 1984; Le Roex et al., 1987). Such basalts are considered to be derived from a DM source to which an enriched component with the characteristics of alkalic ocean island basalts (see below) has been added probably in the form of veins or streaks: cf. Tarney et al. (1980). In hot spot regions the mantle may be dominantly of this type: at slow-spreading ridges and near transform faults the lower degree of magma production ensures that this enriched vein component contributes significantly to the available melts. Such basalts also have higher Sr- and lower Nd-isotope ratios than N-type MORB. These enriched ("E-type", also called plume or "P-type": see Fig. 2-20) MORB's show subtle variations in composition from region to region because of the variable composition of the enriched component and the differing proportions of the E- and N-type MORB source components.

Basalts from mid-ocean ridges tend to be dominantly tholeiitic (although some E-type MORB may be mildly alkaline). The products of fast-spreading ridges tend to be more uniform, probably because the presence of a continuous sub-ridge magma chamber buffers variations in magma input resulting from inhomogeneity in the source or variations in the degree of melting. Fast spreading ridges tend to give rise to typical "ophiolite" sections of cumulate

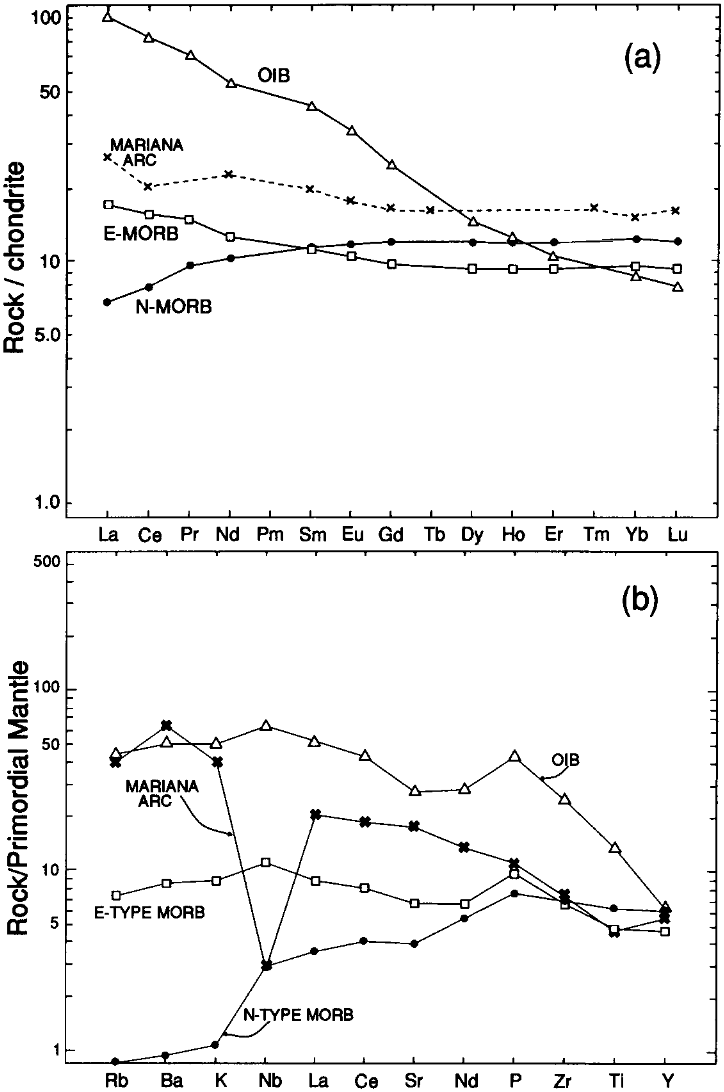


Fig. 2-20. (a) Chondrite-normalised REE patterns of typical basalts from oceanic regions. (b) Mantle-normalised spider-diagram of same rock types. Note distinctive Nb trough for arc rocks.

and homogeneous gabbros, a thick sheeted dyke sequence and a substantial lava pile. Slow-spreading ridges may have only transient magma chambers with attenuated gabbro and sheeted dyke sequences. Moreover the basalts may have more variable trace element compositions inherited from the source, and each magma batch may have undergone more crystal fractionation toward Fe-rich or even silicic differentiates.

Although relatively fresh basalts occur on the seafloor, the vast majority are variably to severely altered as a result of intense hydrothermal activity. Geothermal gradients are high and metamorphic zones compressed (Stern and Elthon, 1979). The chemical changes resulting from interaction with seawater vary with depth, and hence according to the stable mineral assemblages and water/rock ratios. Low-temperature zeolites and clay minerals stable in the uppermost basaltic crust take up Rb, K and U, and to a lesser extent Ba and Sr; conversely at deeper levels, in the amphibole stability field and particularly in the metamorphosed sheeted dykes, these elements are leached out, along with many important metals (Bowers and Taylor, 1985). In the discharge zones of hydrothermal systems, more intense chemical changes take place. Despite intense alteration the original trace element characteristics are generally preserved by the "immobile" elements such as Zr, Nb, Ta, Ti, Y and the REE.

Fast-spreading ridges give rise to a greater number of smaller metalliferous hydrothermal deposits because of the greater thermal input from the continuously refilled magma chambers. Indeed the majority of metalliferous discharge zones located on ocean ridges are situated on the fast spreading East Pacific Rise. More recently discharge zones have been located on the relatively slow-spreading Atlantic Ridge; it is possible that the more fractured nature of slow-spreading ridges enhances and focuses discharge zones leading to fewer, but larger deposits.

Ocean island basalts and submarine plateaus

Although they form only a small proportion of the ocean crust, many thousands of ocean islands and seamounts, mainly consisting of enriched tholeiitic and alkali basalts and their differentiates, are scattered on the abyssal plains. The lavas are characterised by high levels of incompatible elements such as Ba, Sr, Nb, Ta, and the light REE, and strongly fractionated REE patterns (Saunders, 1984) with distinctive small positive anomalies for Nb and Ta, on multi-element spiderdiagrams (Fig. 2-20b). There is a spectrum of ocean island basalt (OIB) isotopic and trace element compositions (Sun, 1980; Weaver et al., 1987; Weaver, 1991), that can generally be resolved into mixtures between three main end-member mantle components. These are HIMU, or St. Helena type, with low $^{87}Sr/^{86}Sr$, anomalously high $^{206}Pb/^{204}Pb$ isotopic ratios and high Nb/La and Ta/K element ratios, and two "enriched" mantle types with low $^{143}Nd/^{144}Nd$ but moderate (EM1) to high (EM2) $^{87}Sr/^{86}Sr$, but lower $^{206}Pb/^{204}Pb$ isotopic ratios, and lower Nb/La and especially Ta/K ratios. Fig. 2-21 summarises the main features in relation to the "depleted" convecting upper mantle (DMM) that is the source for normal MORB. Hart and Zindler (1989) review the available data. The isotopic differences imply that their mantle sources have remained separated for perhaps 2000 Ma, and have developed through progressive differentiation of the original primordial uniform mantle (PUM) that resulted in growth of the continental crust. A consensus of recent models (see Weaver et al., 1986; Saunders et al., 1988; Hart and Zindler,

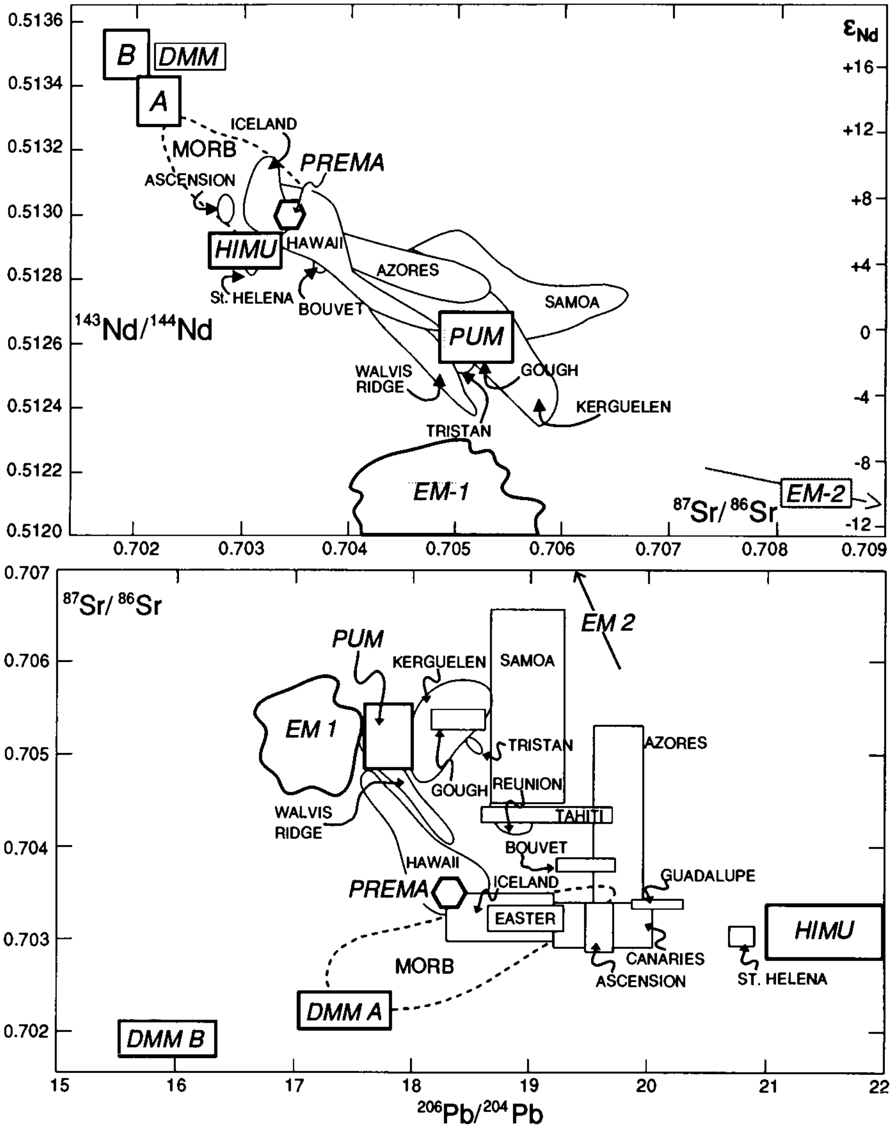


Fig. 2-21. Range of Sr, Nd and Pb isotopic compositions in basaltic rocks from oceanic regions (adapted from Hart and Zindler, 1989). Most basalts have been derived from mantle sources that are mixtures of different end-member components: the depleted MORB mantle (DMM), and three enriched components HIMU, EM1 and EM2 that have evolved over time from the original primordial uniform mantle (PUM). A prevalent mantle component (PREMA) may represent mixtures of all these, but more likely represents material from lower mantle. See text.

1989; Weaver, 1991; Chauvel et al., 1992) suggests that HIMU represents the residues of subducted ocean crust from which continent-forming magmas (with high Pb/U ratios) had been extracted, and is probably located at the 670 km discontinuity. The EM components are similar material that was heavily contaminated with ancient abyssal sediment (EM1) or terrigenous continental-derived sediment (EM2) during Precambrian subduction; these components may be located in the sub-continental lithosphere as well as at the 670 km discontinuity.

Anomalously elevated regions of oceanic crust (such as the huge Ontong Java Plateau) represent massive outpourings of basalt at or near ridge crests, as is presently occurring on Iceland, and giving ocean crust that is 3 or 4 times thicker than normal. It has been suggested that this excess melting corresponds with the periodic release of "superplumes" (Larson, 1991) from the core–mantle boundary (D'' layer). Interestingly, ocean plateau basalts differ from N-type MORB, in that their trace element and REE patterns are either undepleted and like E-type MORB (Fig. 2-20), or only slightly depleted (Saunders, 1986), and their isotopic compositions correspond closely to PREMA on Fig. 2-21. It is possible that there is a major component of lower mantle material in these ocean plateau basalts, as superhot deep mantle plumes are known to entrain into the plume head considerable amounts of the mantle they traverse (see Campbell et al., 1989; Hart et al., 1992). The plume head thus becomes enriched in more fusible mantle components, and it is not surprising that ocean plateau basalts are more Fe-rich and undepleted. However the plume tail retains its high temperature and contains high-Mg komatiitic melts (Campbell et al., 1989). Where active plumes and ridges separate the plume may burn through the oceanic plate to form island chains like the Hawaiian-Emperor chain. Importantly, because plateaus are thick and warm they are resistant to subduction. For instance, extensive plateau crust was obducted onto the continental margin of Colombia and around the Caribbean in the late Mesozoic (Millward et al., 1984). Large volumes of similar material must have been underplated beneath the Andes. Such thick mafic sequences could be a rich source of metals where invaded by later granites. Just as important is the massive thermal energy associated with superplumes, and whether the cyclic distribution of metal deposits through time (Barley and Groves, 1992) can be linked to these superplume events.

Figure 2-22 shows schematically how deep mantle plume heads entrain large amounts of the mantle they pass through. This figure also shows how, if starting plumes cannot penetrate thick lithosphere, they may incubate and interact with the lithosphere. This simple diagram illustrates how mixtures between lower mantle material, upper mantle material, lithosphere mantle and 670 km mantle material may be initiated, thus explaining how the spectrum of basaltic isotopic and trace element compositions may be generated.

Back-arc basalts

In modern oceans there are many examples of seafloor spreading behind intraoceanic island arcs, particularly in the Western Pacific. Typically the arc is split, the two halves eventually being separated by the intervening marginal

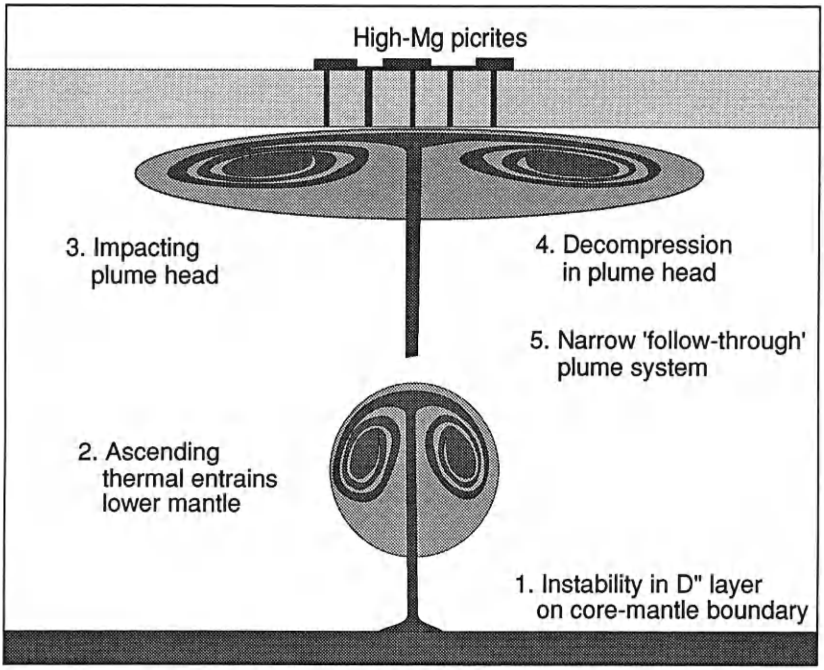


Fig. 2-22. Hot plume initiated at 2900 km depth as a result of instability in D″ layer at core–mantle boundary will entrain significant amounts of lower mantle as it rises. If it penetrates to the surface through a spreading ridge an ocean plateau results. If it rises beneath a plate with a thick mechanical boundary layer (top) there may be extensive interaction with the lithosphere before basalts are extruded. The plume head broadens out to ca. 1000 km diameter, and may be a significant thermal source to drive mineralising hydrothermal systems. After Campbell et al. (1989) and Saunders et al. (1992).

basin (Tarney et al., 1981). The spreading process is similar to that at normal ridge crests, although it lacks the regularity of the latter. There are also many examples of back-arc extension at continental margins (e.g. Saunders et al., 1979; Weaver et al., 1979; Saunders and Tarney, 1984, 1991), but spreading is usually more limited, perhaps because of the greater strength and rigidity of continental lithosphere.

Back-arc or marginal basin basalts (MBB) have many compositional similarities with MORB. However, during the early stages of spreading, the basalts may reflect the trace element characteristics of the sub-arc mantle, exhibiting significant negative anomalies for Nb and Ta on multi-element diagrams, and enhanced levels of the large ion lithophile elements K, Rb, Ba, Th, U and Sr, approaching patterns similar to that of the Mariana Arc patterns (Fig. 2-20). As spreading continues, the sub-arc mantle source is progressively dissipated and the basalts assume MORB characteristics (Saunders and Tarney, 1984, 1991).

Petrographically, and in their major element chemistry, back-arc basalts are similar to MORB but, perhaps because of the entry of water into their

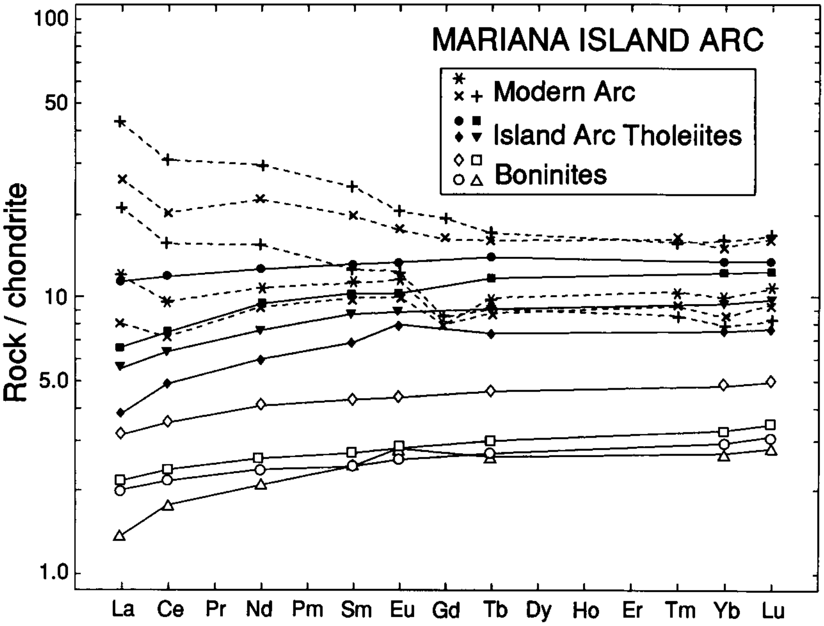


Fig. 2-23. Summary of REE patterns from the Mariana Arc system, after Hickey-Vargas and Reagan (1987) and Hole et al. (1984). The early stage arc tholeiites and boninites have depleted REE patterns, like MORB (Fig. 2-20a), but later stage arc lavas are LREE enriched and with distinct negative Ce anomalies, indicating sediment contamination. All multielement patterns have negative Nb anomalies, like the Mariana Arc pattern in Fig. 2-20b.

source regions, a higher proportion tend to be quartz-normative and there is a tendency to produce more siliceous differentiates (plagiogranites or extrusive dacites). They are affected by seafloor hydrothermal activity, with metalliferous discharge zones, and it is not surprising that classic ophiolite complexes like Troodos, with major copper deposits, have compositions very similar to W. Pacific marginal basins (Tarney and Marsh, 1991), Many massive sulphide deposits are thought to have formed in such an environment in the Archaean (Jensen and Langford, 1983).

Where back-arc extension occurs at continental margins there is an added factor in that sedimentation rates may be high. Hence basalts may be emplaced as sills in the sedimentary succession, hydrothermal activity leaching metals from the sediments. The tectonic environment is similar to that in the Gulf of California and the Salton Sea region where ore deposition is occurring from hydrothermal metal enriched brines (Edmond et al., 1979).

Intra-oceanic island arcs

Primitive island arcs develop where subduction is initiated in oceanic regions, usually following a change in plate motions. The initial arc volcanic pile develops rapidly through the eruption of large volumes of *island arc tholeiites* (IAT). The magma type has similarities to MORB in that they can be depleted in light REE, although they are sometimes moderately enriched (Fig. 2-23). The IAT magmas frequently have higher Fe/Mg ratios than MORB, coupled with consistently low contents of Cr and Ni, which is usually attributed to their prolonged history of crystal fractionation. The fractionation trend is towards Fe-enrichment, with only minor quantities of siliceous differentiates; many lavas are however aphyric, or have only minor olivine and/or pyroxene phenocrysts. Although K contents are usually higher than in N-type MORB, K/Rb ratios are typically high in fresh samples, but low-grade alteration is common and the K/Rb ratio is lowered by the uptake of Rb and K. Multi-element diagrams (e.g. Fig. 2-20b) show these features, together with a negative anomaly for Nb and Ta typical of subduction-related magmas.

High-magnesian andesite, or *boninite*, is also erupted in primitive island arcs, in the fore-arc region, intermixed with arc tholeiites. This magma type is characterised by quite high levels of MgO, Cr and Ni, but at the same time is quite siliceous. There are no known siliceous differentiates however, and it is doubtful that they are consanguineous with the arc tholeiites, despite their common occurrence. Boninites may be aphyric or have olivine or hypersthene phenocrysts; typically they have a groundmass with abundant clinoenstatite. Abundances of elements such as Zr, Ti, Y and the REE are low, and the REE patterns can be LREE-enriched but are mostly depleted (Fig. 2-23). Some boninites are enriched in elements such as K, Rb, Ba, which may reflect alteration. Boninites result from wet melting of refractory sub-arc mantle wedge material during the initial stages of subduction (Crawford et al., 1989).

As primitive island arcs evolve, erupted lavas change towards calc-alkaline compositions. Nevertheless the dominant composition of intra-oceanic arcs is basaltic or basaltic andesite: the proportion of true andesites or dacites remains small. The younger lavas tend however to have higher contents of Ba, K, Rb, Sr and are more light REE-enriched than either N-type MORB or the earlier arc tholeiites (Fig. 2-23). Negative Ce-anomalies imply contamination with subducted sediment, although only a very small proportion of the abyssal sediment subducted beneath the Mariana Arc appears to be involved in magmagenesis (Hole et al., 1984). The multi-element patterns, having negative Nb anomalies, small positive anomalies for Ba, Sr and P and moderately high K/Rb ratios (Fig. 2-20b), reflect fractionation processes in the mantle wedge. Although arcs are relatively easily distinguished in the Phanerozoic their identification in tectonised Precambrian terrains is more difficult. Hence geochemical methods of identifying arc settings are particularly valuable since massive base metal sulphides are common in Archaean terrains.

Ophiolites and orogenic mafic complexes

Ophiolites are obducted fragments of oceanic lithosphere, but there is uncertainty in individual cases whether they represent mid-ocean ridge, back-arc, island arc or fore-arc lithosphere. In fact many ophiolites have a distinct "supra-subduction zone" signature (Saunders et al., 1980a; Saunders and Tarney, 1991) marked by negative anomalies for Nb and Ta and enhanced LIL element abundances. Indeed, the "type" Troodos ophiolite has lavas and sheeted dykes with distinct arc-like trace element patterns, Pb isotopic evidence for subducted sediment contamination of the mantle source, Sr isotopic evidence for seawater–rock interaction, abundant plagiogranites and Cu–Zn–Pb mineralisation linked to tectonically controlled hydrothermal discharge zones. Together with the clear evidence for spreading and fossil transform faults, boninitic Upper Pillow Lavas, and very close chemical comparison with Mariana rocks (Tarney and Marsh, 1991), there is little doubt the complex formed in an extensional fore-arc or back-arc environment. It is tectonically easier to obduct warm buoyant arc or back-arc basin lithosphere than the cool dense ocean basin lithosphere which is subducting. Chromite is an early precipitating phase in the rather siliceous Troodos magmas, but significant chromite precipitation may have occurred before the magmas left the mantle source, leading to the formation of podiform chromite bodies which are relatively common in Tethyan ophiolites.

Other major mafic complexes which tend to be of gabbro-norite composition (i.e. orthopyroxene-rich) and have distinct arc-like trace element signatures occur in orogenic belts. Examples include the Chilas Complex in the western Himalayas (Khan et al., 1989), and the Border Ranges Complex in Alaska (Beard, 1986), and similar bodies in the Ivrea-Sesia root zone in the Alps (Pin and Sills, 1986). They have been interpreted as the roots of island arcs, or as major mafic bodies emplaced during the initial stages of back-arc spreading. Ultramafic rocks at the base of these complexes are not necessarily cumulates. They may have local chromite segregations, but otherwise are relatively unmineralised.

Continental flood basalts and layered mafic intrusions

Continental flood basalts (CFB), the voluminous extrusives most particularly associated with the breakup of the continents during the Mesozoic, are also found throughout geological time. In the Precambrian, for instance, the magma type is represented by the vast dyke swarms that traverse many Precambrian shield areas (Tarney and Weaver, 1987b). A fairly Fe-rich quartz tholeiite is the dominant rock type, although minor noritic and picritic compositions are also found. Silicic differentiates occur locally in thicker sills and intrusive bodies.

Typically, CFB basalt REE patterns are moderately enriched in LREE like E-MORB (Fig. 2-20a), but usually with distinct negative Eu anomalies. Multi-element patterns (Cox, 1983; Weaver and Tarney, 1983) usually (though not exclusively) show marked negative anomalies for Nb (Ta), Sr, P and Ti with distinct LIL element enrichment (Fig. 2-24). Their Sr isotopic ratios are invariably higher than those in MORB, reaching extreme values of over 0.710 in Ferrar and Tasmanian dolerites. The trace element signature of many flood basalts is essentially calc-alkaline, but the petrological characteristics are tholeiitic. It

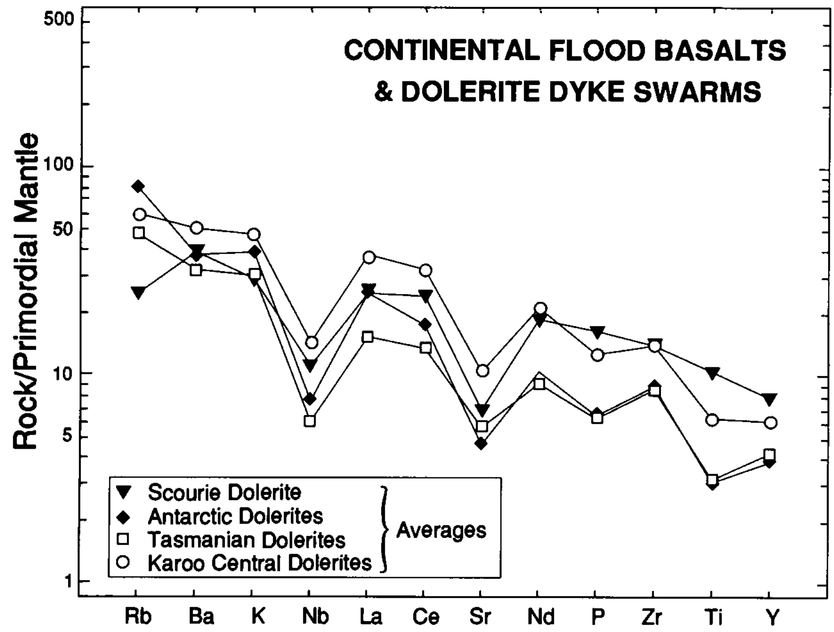


Fig. 2-24. Spidergram patterns for continental flood basalt type magmas covering an age span of some 2000 Ma, illustrating the consistent geochemical character of this magma type (compare with Fig. 2-20). After Ahmed and Tarney (1991). There is dispute as to whether the prominent troughs for Nb, Sr, P and Ti reflect source characteristics or crust assimilation.

was commonly thought that the trace element and isotopic characteristics of flood basalts reflected contamination of the magmas by crustal assimilation, but it now seems more likely that the characteristics are inherited from the sub-continental lithosphere (Weaver and Tarney, 1981b) and a consequence of their mantle source being contaminated by subducted sediment, or being metasomatised by LIL element rich hydrous fluids. No significant mineralisation appears to be associated with CFB, the subaerial extrusion and lack of associated plutons not being conducive to the development of hydrothermal convective systems.

Some large layered mafic intrusions such as Skaergaard, Bushveld and Stillwater, share many of the trace element and isotopic characteristics of CFB, may have been derived from a similar sub-continental mantle source. The simple models of gravitational crystal fractionation and convective overturn initially invoked to explain the mineralogical layering (cf. Wager and Brown, 1968) have been replaced by more complex models invoking concepts of stratified liquid columns, double-diffusive convection, nucleation phenomena, and multiple magma batch injection, as more comprehensive data have been accumulated (cf. McBirney and Noyes, 1979; Irvine, 1980; Huppert and Sparks, 1984; Eales et al., 1986). Multi-element patterns for cumulate-rich layers will in general have low abundance levels for the incompatible elements that are concentrated in the liquid fraction, but may develop prominent peaks for trace elements concentrated in the cumulus phase, such as Sr and Eu in plagioclase, Zr in zircon, P in apatite, V in magnetite and Ti in ilmenite. Conversely the liquid fraction from which these phases have crystallised will develop corresponding negative troughs for these elements. However many classic layered intrusions now seem to be a result of multiple magma injection.

Continental alkaline igneous rocks

Alkaline igneous rocks are rather heterogeneous, varying in both their degree of silica undersaturation, and in their Na/K ratio. Moreover being low viscosity liquids in which crystal separation occurs easily, they show a wide range of fractionation. Extreme volatile-rich alkaline and carbonatitic liquids are also very reactive and in their plutonic form may interact extensively with the crust. Carbonatites and associated highly alkaline intrusions may provide sources for elements such as Nb, Ta and the REE.

Continental alkaline rocks have many chemical similarities with ocean island lavas (though frequently more extreme) in having strongly fractionated REE patterns with marked enrichment in the light REE, and multi-element diagrams that also show high levels of LIL elements such as Ba, Sr, Th, U, Nb, Ta and P, though not always K and Rb. The enrichment in Nb and Ta contrasts markedly with the low abundance of these elements in normal crustal rocks, and alkaline pegmatites are one of the most significant exploitable sources of these elements. There is a tendency for highly alkaline igneous rocks to occur in the older cratons, suggesting that their immediate source lies in the sub-continental lithosphere: chemically enriched material having been continually added from below and later re-mobilised by further hot spot activity. Mafic alkaline lavas frequently carry sub-continental mantle xenoliths, which in the case of kimberlites are garnet-bearing and locally diamondiferous.

Calc-alkaline volcanic rocks

Calc-alkaline lavas are, in volume and extent, the dominant extrusive on the continents, and indeed the composition of the average calc-alkaline andesite approximates to that of the estimated bulk continental crust (Taylor and McLennan, 1985). Andesite is however a much rarer lava type in the Precambrian, and particularly the Archaean. The present day distribution of calc-alkaline volcanoes correlates with active continental margins, and a similar distribution is inferred for most Phanerozoic examples.

The calc-alkaline lava series ranges in composition from basalt (or more rarely picrite) through andesite and dacite to rhyolite. Basic members of the suite are subordinate, except in intra-oceanic island arcs, and andesites and dacites are normally dominant. As an example of a continental margin volcanic suite, data for the Aegean Arc are shown in Fig. 2-25. There is always a distinct enrichment in LIL elements and the LREE, and the prominent negative Nb

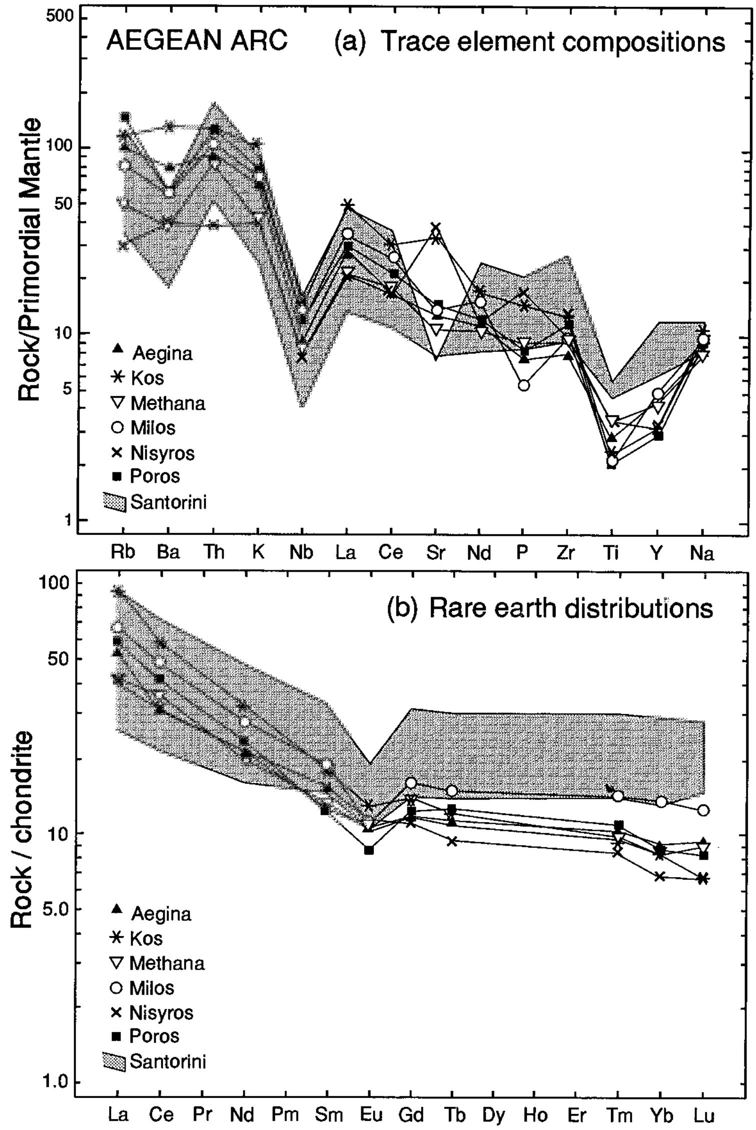


Fig. 2-25. Calc-alkaline lavas typified by the Aegean Island Arc (after Mitropoulos and Tarney, 1992). Multielement patterns (a) always have prominent Nb troughs, Ti troughs, but variable Sr anomalies. REE patterns (b) are always LREE enriched with negative Eu anomalies. The flatter patterns for Santorini reflect greater lithosphere extension and larger asthenosphere input into the Santorini magmas.

anomalies, moderate negative Ti and small negative Eu anomalies are typical of many andesites. The former helps distinguish calc-alkaline from alkaline rocks (which may have positive Nb peak). In practice the degree of light REE enrichment varies from region to region, and there is even more variation in the abundances of LIL elements such as Ba and Sr and in the Ba/Sr ratio, etc. Additionally there is the well known "K–*h*" variation; increase in K_2O (and other LIL elements) at constant SiO_2 levels with increasing distance from the trench (Saunders et al., 1980b). Nonetheless the essential features of calc-alkaline trace element patterns are preserved from region to region.

In the Phanerozoic, the calc-alkaline series is closely linked with subduction, or at least the cessation of subduction. The most satisfactory models (Peacock, 1991; Saunders et al., 1991) envisage that, during dehydration of the subducting slab, LIL-enriched hydrous fluids migrate into the mantle wedge of the overriding plate where hornblende forms. Induced convection in the wedge drags hornblende-bearing mantle down such that the hornblende undergoes pressure-induced breakdown, releasing fluids which migrate up into hotter zones to cause melting. The trace element signature is inherited largely from the mantle wedge (sub-continental mantle), but with replenishment from the sub-continental lithosphere caused by the induced convection, and a smaller but variable component from the dehydrating subducting slab (including subducted sediments), and through interaction with the crust during ascent. The subduction zone is however a dynamic environment which is very susceptible to changes in plate motions. Variations in dip of the slab, a change from compression to extension (permitting uprise of the asthenosphere), or ridge subduction can change the zone or conditions of melting and hence the composition of the volcanics produced.

In some Phanerozoic orogenic belts significant volumes of post-collision andesites may be erupted which are not directly related to subduction. These include andesites which may be potassic (shoshonites) and enriched in LREE, Ba and Sr, and others which are not so potassic. This may reflect different proportions of minerals such as phlogopite and hornblende in the mantle wedge.

Calc-alkaline volcanic provinces are important sites of mineralisation. This is more a consequence of the thermal anomaly of the volcano or of associated plutons, which can drive extensive hydrothermal systems, than of any specific compositional feature of the andesitic lavas. The fragmental and permeable nature of the calc-alkaline volcanics means that they are readily altered and leached. Major coast-parallel fault systems, which promote and focus hydrothermal convective systems, are a regular feature of cordilleran margins.

Komatiitic lavas

Precambrian greenstone belts are very important sites of Ni, Au, U, Fe and volcanic-hosted sulphide mineralisations. The origin of the high-Mg komatiitic lavas which characterise these belts has intrigued geologist for many years, not least because liquids with up to 32% MgO represent very high degrees (ca. 60+%) of mantle melting, and it has not been easy to invoke suitable processes that can focus the thermal energy to achieve this. Nor is it easy to explain why komatiites and greenstone belts occur in relatively narrow time zones in the early Archaean (e.g. Barberton, Pilbara), the late Archaean (e.g. Superior Province, Yilgarn), the early Proterozoic (e.g. Birimian), and the Cretaceous (e.g. Gorgona), but with huge gaps in between. The komatiites are associated with larger volumes of basaltic komatiites and even larger volumes of tholeiites, with more calc-alkaline lavas appearing in the late Archaean. Chert is abundant and banded iron formations and then terrigenous sediments fill the basins, before generally being invaded by granites, the hydrothermal activity associated with which is responsible for some of the mineralisation.

Recently considerable progress has been made in understanding the genesis of greenstone belts. Rare earth data from greenstone belts of different ages are summarised in Fig. 2-26. It can be seen that there is a wide range of patterns, the Mg-rich komatiites having low REE abundances and LREE depletion whereas the tholeiites are more Fe-rich, have much higher REE abundances and are generally LREE enriched. It is not easy to achieve this REE distribution by melting of a single source.

The superplume concept outlined earlier offers a better explanation. It has been suggested (Storey et al., 1991) that oceanic plateaus are the sites of komatiite formation, hence the high-Mg liquids result from hot material rising from the core–mantle boundary. The plume head entrains mantle and

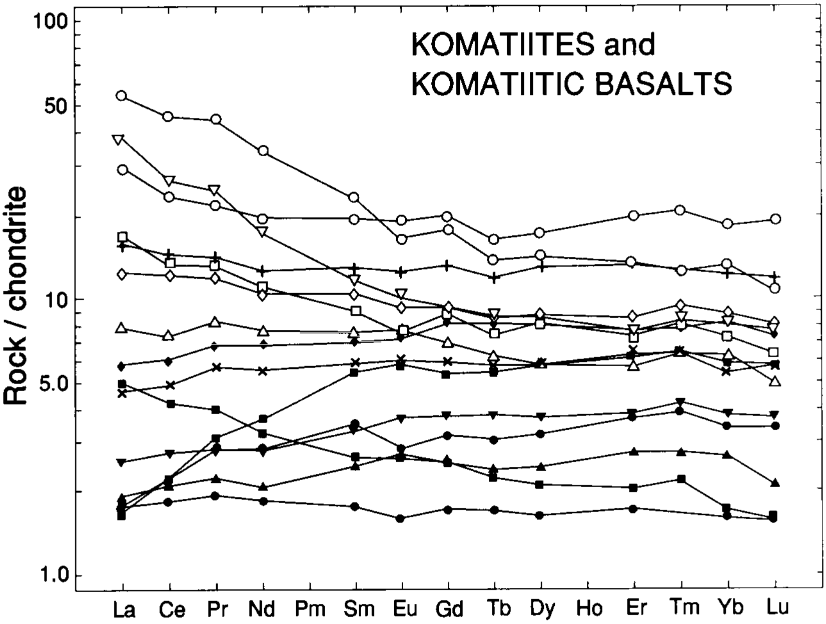


Fig. 2-26. Selection of REE data on komatiites (early Archaean to Cretaceous) — filled circles, and associated komatiitic basalts and tholeiites — crosses and open symbols, respectively. Data compiled by Jochum et al. (1991).

enlarges during uprise, and effectively supplies the basaltic components of the greenstone sequence, whereas the tail of the plume streams with hot komatiite (Campbell et al., 1989). The range of REE patterns simply reflects this mixing process. The chert is a consequence of the excess heat, and hence hydrothermal activity, arising from this enormous heat source. This may have been a very important factor in the metallogeny of greenstone belts, though the later granites may be responsible for the hydrothermal systems which achieve the final metal concentrations.

This leaves us with two possible explanations from the greenstone belt sequences, (a) that they represent obducted ocean plateaus, or (b) that they represent plumes that were able to penetrate thin immature continental lithosphere.

Granites

The Earth's crust is essentially granitic (*sensu lato*), although tonalite (plag + qtz ± biot ± hornb) is the dominant component. The crust is generally regarded as stratified to some extent, with tonalites, diorites and gabbros being more common at depth, and granites (*sensu stricto*) dominating the upper crust. Sediments, primarily derived from the upper crust, have trace element patterns which reflect this dominance of the upper crust by granite. Granites formed by melting of a sedimentary protolith simply reinforce this upper crustal trace element signature. Chappell and White (1974) have classified granites into I-type (of Infrastructural derivation or Igneous precursor) and S-type (of Supracrustal derivation or Sedimentary parentage). Surprisingly, Fig. 2-27 shows that multi-element patterns for the average I- and S-type granites from the Lachlan Foldbelt, Southeast Australia, are not very different, despite their supposedly contrasting origins. Indeed both are close to the post-Archaean average shale (PAAS) composition. This suggests that a trace element pattern once established in the upper crust is not readily altered by melting processes, although major element compositions may be. Figure 2-27 also shows the average A-type (Anorogenic) granite from the same region (Collins et al., 1982), emplaced late in the plutonic cycle, and traditionally proposed to originate as a *remelt* of crust from which the S- and I-type granites had earlier been extracted. This typically has higher concentrations of the more compatible elements, but more pronounced anomalies for Ba, Sr, P, Ti, but usually a smaller anomaly for Nb.

Of course, outside the Lachlan foldbelt the spectrum of granitoid compositions is much wider than these average compositions would suggest. This is leading to a plethora of re- and sub-classifications, with inevitable confusion, particularly regarding the petrogenesis of these granitoids, and especially in terms of the relative upper-crust, lower-crust and mantle contributions. However it is possible to simplify the situation by considering differences in the mantle-normalised spidergrams. Some of these differences can be illustrated by focussing on Scotland where there is a very large database for Archaean and

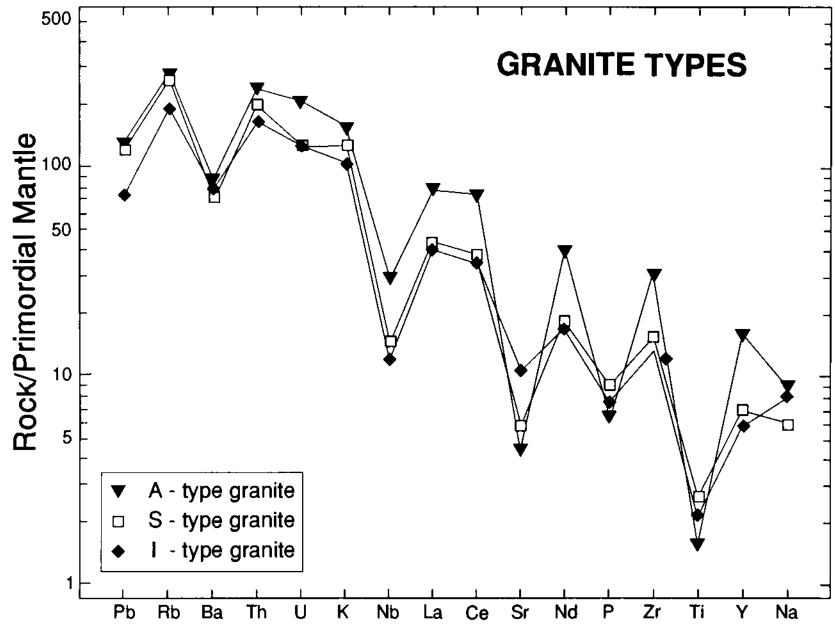


Fig. 2-27. Spidergram patterns of average S-, I- and A-type granites from the Lachlan foldbelt (cf. Chappell and Stephens, 1988 and Collins et al., 1982).

Caledonian granitoids, and some well-known regional differences (Stephens and Halliday, 1984; O'Brien 1985; Plant, 1986; Tarney and Weaver, 1987a). In fact from a petrogenetic viewpoint it is possible to recognise three broad categories of granitoid, exemplified by the Precambrian Lewisian, the Caledonian of Western Scotland and the Caledonian of Eastern Scotland. All these rocks have made a significant contribution to crustal growth, as have similar rock types elsewhere in the world. They have very different mineral potential.

Archaean (Lewisian) granitoids

Like most Archaean granite-gneiss terrains, the Scottish Lewisian is dominated by gneissified tonalite-trondhjemite granitoids ("TTG") with numerous mafic-ultramafic inclusions. The latter are often regarded as relics of the precursor source material from which the TTG suite had been generated by hydrous partial melting. The REE patterns of the suite are illustrated in Fig. 2-28. The mafic gneisses have much flatter REE patterns than the silicic gneisses, and although some are LREE depleted, the majority are LREE enriched, like E-type MORB or ocean plateau material, and are commonly quite Fe-rich. The more silicic granitoids show progressive and severe HREE depletion and the development of a positive Eu anomaly. These features are very different from the I-, S- and A-type granites with their marked negative Eu anomalies and moderate to high HREE levels. The TTG are most readily explained through

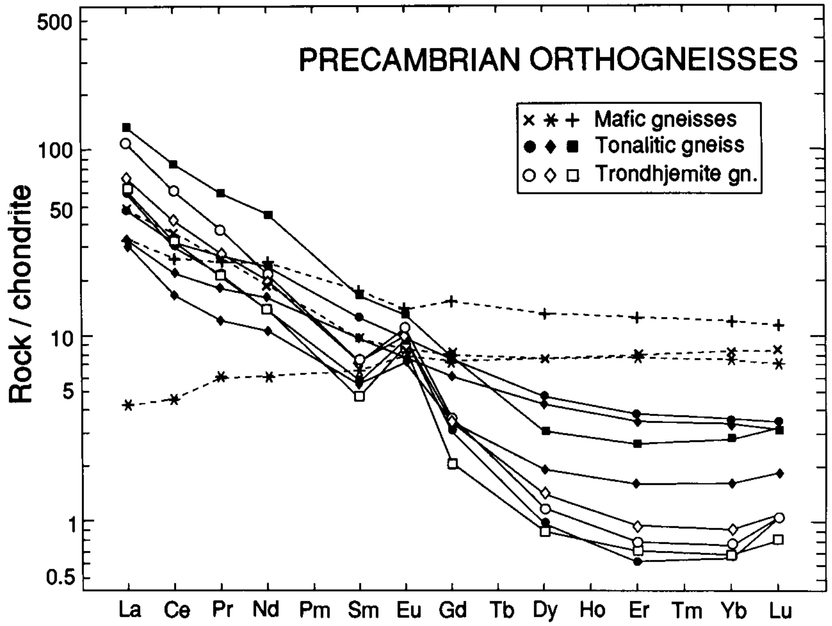


Fig. 2-28. REE patterns of Archaean mafic gneisses and tonalite — trondhjemite gneisses (after Weaver and Tarney, 1980, 1981), showing distinctive positive Eu anomalies and strong heavy REE depletion of the silicic granitoids.

hydrous melting of a mafic source with hornblende or garnet in the residue (Weaver and Tarney, 1980b).

Spidergram patterns of the TTG suite are also quite distinctive (Fig. 2-29) in having marked negative Nb anomalies, Ti, Y and P anomalies, but positive or no Sr anomalies, even in distinctively K-granite compositions. These contrast markedly with those shown in Fig. 2-27, and clearly have been formed in a very different mechanisms.

Many Archaean terranes comprise dry granulite-facies segments, and it interesting to compare the chemistry of the TTG suite at granulite facies with TTG rocks at amphibolite facies (Fig. 2-30). The granulite facies rocks show marked depletion in U, Th and Rb, and to a smaller extent K and Pb, but no significant differences in other element abundances.

Two important implications arise from these data. First is that Archaean rocks of this type are very rarely associated with significant mineralisation. The probable reason for this is that their petrogenesis requires high rates of granitoid production, probably at high pH_2O, and consequent underplating at deep levels in the crust, almost ubiquitously associated with strong deformation that produces the gneissosity; thus such granitoids are unable to develop near-surface hydrothermal systems, and remain barren. Of course they have very little internal heat production. Second is that although models of I-, S- or A-type granite genesis frequently invoke crustal melting, the spidergram

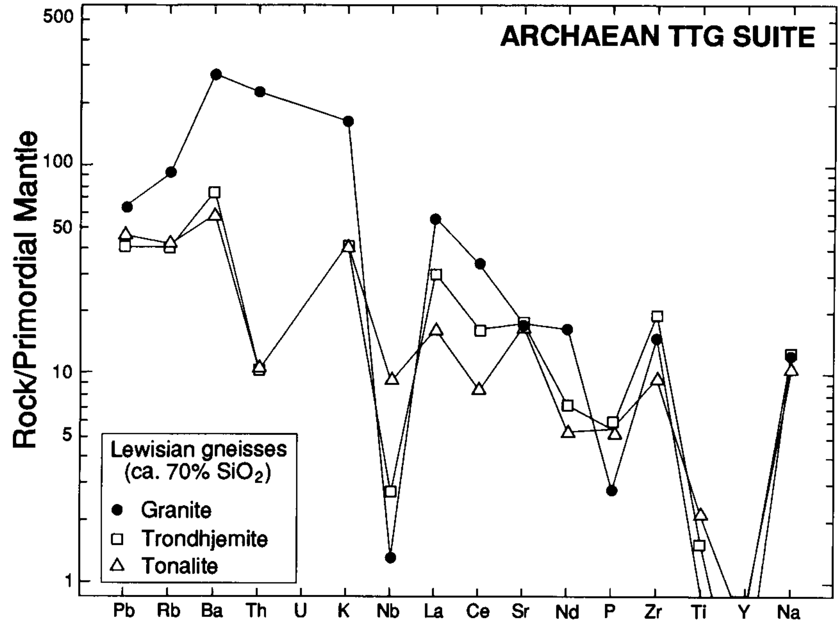


Fig. 2-29. Spidergram patterns of Archaean TTG granitoids (after Weaver and Tarney, 1980; Rollinson and Fowler, 1987), illustrating characteristic Nb, P, Ti and Y troughs.

patterns of Archaean granitoids depicted in Figs. 2-29 and 2-30 are so different from most later Proterozoic or Phanerozoic granitoids (Fig. 2-27) that it is not geochemically possible that they could contribute to these later granites, except in trivial amounts.

West Scotland Caledonian granitoids

The Caledonian granitoids of Western Scotland have long been known as a high Ba and high Sr province (e.g. Stephens and Halliday, 1984). To illustrate their compositional characteristics, a selection, all with about 70% SiO_2, are shown as spidergrams in Fig. 2-31. In many respects such as positive Ba and Sr anomalies, large negative Nb anomaly, high K/Rb ratio, low Th and U, low Y and HREE, and REE patterns with no or positive Eu anomaly, they are similar to the Archaean TTG suite. Indeed there has always been concern that the adjacent Lewisian basement has been mobilised. However, because many tend to have slight positive P anomalies, compared with the negative P of Archaean granitoids, and the rather extreme isotopic compositions of Lewisian gneiss is not apparent in the majority of these granitoids, this seems unlikely. Moreover these very distinctive geochemical features are apparent in basaltic andesites of the Devonian Lorne lavas in the same region (Thirlwall, 1982), which have high Cr and Ni contents implying mantle derivation. High-Mg andesitic magmas with identical characteristics tend to be erupted where there has been

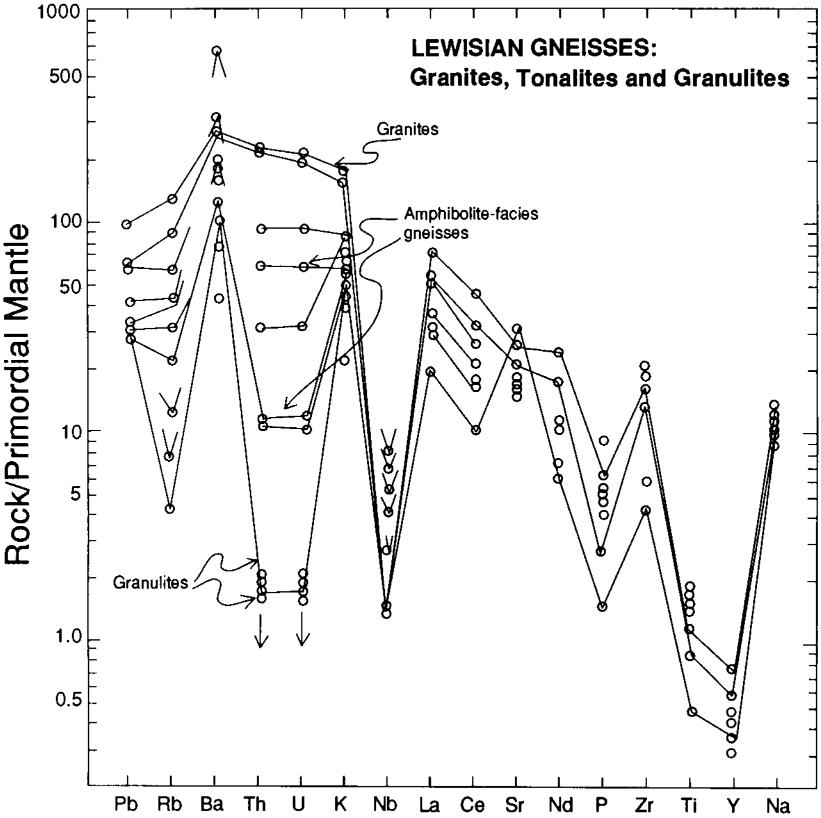


Fig. 2-30. Spidergrams comparing amphibolite facies and granulite facies Archaean granitoids (compiled from Weaver and Tarney, 1980, 1981; Rollinson and Fowler, 1987; assuming $U_N \approx Th_N$), emphasising major differences in Rb, Th and U.

ridge subduction (Rogers and Saunders, 1989), where hot mantle impinges on hornblende-dominated assemblages in the previously-cool mantle wedge. Hornblende typically has a high K/Rb ratio, and on thermal breakdown would produce a garnet-bearing residue which retains the HREE and is responsible for the distinctive HREE depletion in this magma type.

Calc-alkaline magmas of this type are generally emplaced early in the plutonic cycle, and closest to a subduction zone or palaeo-subduction zone, where restoration of normal geothermal gradients, following orogenic collapse (Dewey, 1988) or the onset of extension (Jones et al., 1992), initiates breakdown of hornblende and formation of hydrous magmas (Saunders et al., 1991). The mantle wedge is of course permeated by saline fluids during the subduction episode, and hornblende can hold substantial Cl as well as Na in its structure, that are available to be released during later thermal breakdown of hornblende. Such magmas may gain a little superheat as they traverse the mantle wedge,

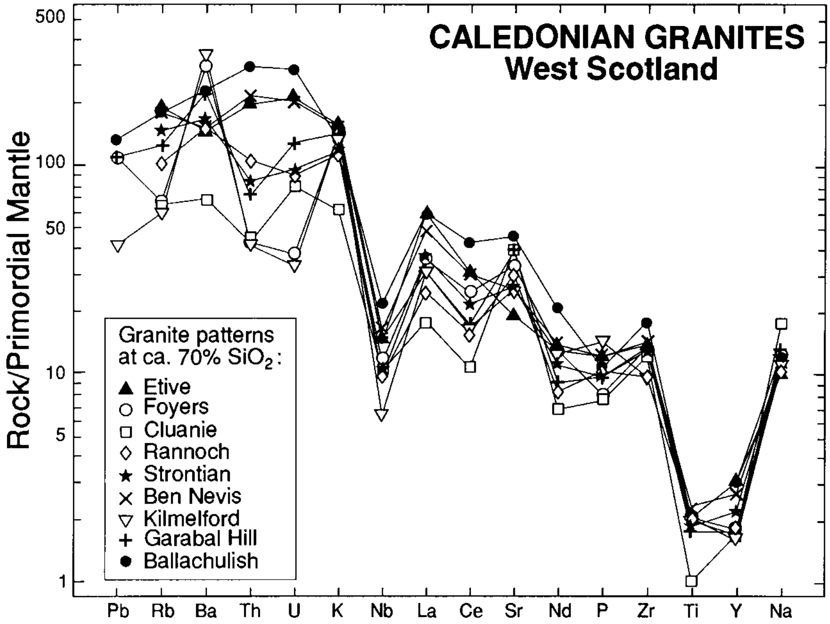


Fig. 2-31. Spidergram patterns of a selection of Caledonian granites from West Scotland (after O'Brien, 1985) showing characteristic high Ba, Sr and K/Rb, low Rb, Th, U, Y, Nb compositions.

but on nearing the surface fluids begin to be expelled as pressure reduces, and more are expelled as crystallisation begins. Repeated fluid expulsion produces the extensive fracture systems characteristic of porphyry copper deposits. Cline and Bodnar (1991) have argued that such magmas contain sufficient Cu, Cl and H_2O to account for major porphyry copper deposits; additionally it should be noted that the mantle wedge closest to the subduction zone could act as an important receptor for Cu and other metals transported by saline fluids from the subducting ocean crust.

Hornblende has a limited range of stability in the mantle wedge and is replaced by phlogopite at greater depths (cf. Wyllie, 1983), and more distal from the subduction zone. However the stabilities of both minerals are substantially enhanced if fluorine replaces hydroxyl in the structures (Foley, 1991), which supports models that require pargasitic hornblende, K-richterite and phlogopite to have a strong controlling influence on the compositions of calc-alkaline magmas (e.g. Sudo and Tatsumi, 1990), so F should increase in hotter, drier magmas.

East Scotland Caledonian granites

The East Scotland granites (Fig. 2-32) have compositions much closer to the classic I- and A-type granites of the Lachlan Foldbelt (compare Fig. 2-27). The contrast with the West Scotland types (Fig. 2-31) is such that their

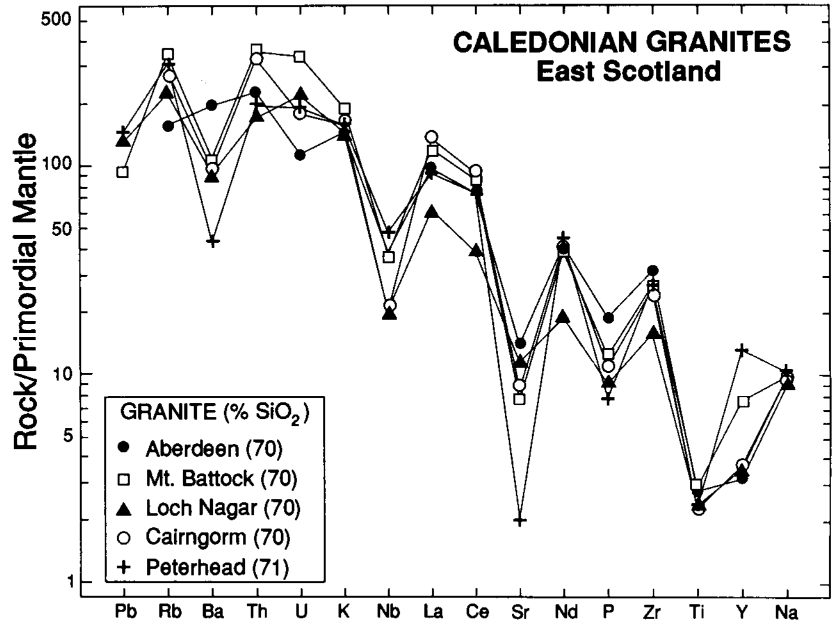


Fig. 2-32. Spidergram patterns of East Scotland granites, on same scale and %SiO_2 as Fig. 2-31 (compiled from O'Brien, 1985), showing characteristic low Ba, Sr, K/Rb coupled with high Rb, Th, U, K, Nb, Y compositions.

spidergram peaks and troughs are almost mirror images of each other. So there are now prominent troughs for Ba, Sr and P, whereas K — and especially Rb, Th and U — are elevated, so the granites have much higher heat production than those in West Scotland. The latest Caledonian granites (e.g. Cairngorm, GlenGairn) have many of the characteristics of A-type granites, having little or no Nb anomaly, high concentrations of Y and the HREE, and higher contents of fluorine and tin than other Caledonian granites. Although the two groups of granite show a range of variation toward each other, there is actually very little overlap between them, even spatially. There must be some fundamental difference in their sources or petrogenesis. For instance whereas many of the West Scotland granites have more dioritic or gabbroic end-members, the East Scotland types are mainly granites s.s., with few basic end-members. This is commonly the case for "evolved" I-type or A-type granites, worldwide.

Interestingly, the chemistry of the large Cairngorm granite is almost identical to the Hercynian Cornubian batholith of Southwest England, but lacks the extensive tin mineralisation associated with the latter. The main difference is that the Cairngorm pluton is intruded into "dry" high grade metamorphic rocks whereas the Cornubian batholith is emplaced into extensive thicknesses of low grade flysch-like pelitic sediments. The latter can supply the fluids necessary for large hydrothermal convective systems, but can they also control the redox state of those fluids, and perhaps supply other components which may control the solubility of Sn? Of course many granites that invade low grade sediments are barren of tin, so the relationship is more complex. The petrogenesis of A-type granites bears on this general problem.

A-type granites

A-type granites are anorogenic, sometimes alkaline and often apparently anhydrous granites that (a) are iron-rich, have higher Fe/Mg, and are generally more reduced (lower f_{O_2}) than associated I-types, (b) have high REE concentrations, but generally flatter REE distributions than associated S- or I-types, and a large negative Eu anomaly, (c) have high F contents, and low H_2O (d) have low CaO, Al_2O_3 and MgO and normally high K_2O/Na_2O, (e) have high Zr, Nb, Ta, Ga, Zn and sometimes Sn, but very low Cr, Ni, Co, Sc, Ba, Sr, and P, and (f) have high Ga/Al ratios and Nb/Zr ratios compared with most other granites. Eby (1990) has constructed numerous discrimination diagrams to separate A-types from other granitoids. Their Sr, Nd or Pb isotopic compositions are not however particularly distinctive, and they have only simple zircon inheritance patterns, possibly a consequence of their high magma temperatures (>900°C).

Most tin granites have A-type characteristics. This poses a problem with the traditional explanation that A-type granites are higher temperature remelts of sources which had earlier yielded I-type granites (Collins et al., 1982) because it has recently been demonstrated experimentally (Taylor and Wall, 1992) that all granite magmas are very undersaturated with respect to Sn, and therefore that the first stage melts would remove all the tin from the source. A preferable explanation, as the more alkaline A-type granitoids can only be mantle-derived (Eby, 1990), is that the parental magmas originate through thermal breakdown of (fluor-)phlogopite-rich assemblages in the upper part of the asthenosphere or lower lithosphere, much as argued earlier for amphibole breakdown. However temperatures would be higher, the magmas generated later, and with phlogopite-dominated assemblages it is easy to convey the high K, Rb, Th, U, Sn and F contents of A-type granites. Other important factors are that dry hot magmas can rise high in the crust, to surface levels, where they can initiate much more extensive hydrothermal convective systems and moreover, because of their own high heat production, maintain them for long periods.

Another important factor is that A-type magmas are invariably anorogenic, and emplacement from such deep levels is only possible under extensional conditions (which promotes uprise of hot asthenosphere). Extension creates the fracture systems in the upper crust that facilitate continued hydrothermal activity (Fehn et al., 1978; Simpson et al., 1979). Breakdown of biotite releases Sn and F and, as Sn has enhanced solubility in a low-f_{O_2} fluid (Taylor and Wall, 1992), sedimentary country rocks will generally help maintain this low redox state. The low-Ca nature of A-type granites will also enhance the activity of fluorine released, which would otherwise be stabilised as fluorite, CaF_2. Because tin has two oxidation states, Sn^{4+} and Sn^{2+}, redox conditions are very important in tin precipitation, particularly as there is a coupled relationship with Fe^{2+} and Fe^{3+}. This model implies that the granite supplies most of the tin, but the ultimate source is in phlogopite-rich assemblages in the upper mantle.

There was a great deal of anorogenic granite magmatism in the mid-Proterozoic (1.7–1.4 Ga), and some of the world's largest mineral deposits, e.g. Mount Isa, Broken Hill and Olympic Dam in Australia, are linked with this activity (Sawkins, 1989). The anorogenic granites appear following assembly of a mid-Proterozoic supercontinent, and uprise of hot mantle beneath that supercontinent (Barley and Groves, 1992). This may well have been a result of superplumes (as in the Cretaceous examples discussed above) impinging on a mature phlogopite-rich sub-continental lithosphere. The HHP granites then acted as a heat engine for a considerable period after their emplacement, but the exact nature of the associated mineralisation was controlled by the rocks, the fluid systems, and environment into which they emplaced. Additionally erosion of these granitoids may provide Au and U for placer or other sedimentary concentrations.

In summary, of three end-member types of "primitive" granitoid, one may result from melting underplated thick warm mafic crust in the Archaean, or very young (<10 Ma) subducted oceanic crust in more recent times. A second may have inherited characteristics resulting from melting of hornblendic mantle wedge, and a third through melting of phlogopitic sub-continental lithosphere under anorogenic conditions. Of course there are many secondary ways of generating granite such as melting thick sedimentary piles to form S-type granites, or mixed sediment–amphibolite sequences in accretionary tectonic environments to form granites with intermediate S- and I-type characteristics.

CONCLUSIONS

The above section we have tried to focus on the geochemical characteristics of igneous rocks that may be useful in identifying tectonic settings favourable for ore deposits, as well as for exploration at the regional and local scale based on an understanding of the way in which ore deposits form. At the same time we have tried to summarise some of the petrogenetic models that have been invoked to account for the petrological and geochemical features. Much more is ascribed to mantle processes than was the case, say, a decade or so ago. Indeed it is now becoming apparent (cf. Barley and Groves, 1992) that styles of mineralisation not only vary throughout geological time, but can be linked, like sedimentation and igneous patterns, to large geological cycles operating within the Earth.

Geochemistry can, in addition to detecting anomalous levels of ore forming and pathfinder elements associated with discrete mineral deposits, be used to prepare lithostratigraphic maps that can help identify large volume crustal source rocks of metals. The following chapter examines the extent to which the trace element pattern and associations characteristic of orebodies and their geologic setting can be used in drainage samples in different surface environments.

Drainage Geochemistry
edited by M. Hale and J.A. Plant
Handbook of Exploration Geochemistry, Vol. 6 (G.J.S. Govett, Editor)

Chapter 3

MODIFICATIONS TO THE GEOCHEMICAL SIGNATURES OF ORE DEPOSITS AND THEIR ASSOCIATED ROCKS IN DIFFERENT SURFACE ENVIRONMENTS

JANE A. PLANT and R.W. RAISWELL

INTRODUCTION

In the surface environment, igneous and metamorphic rocks formed at high temperatures and pressures, in the absence of air and water, are changed into phases that are stable under surface conditions characterized by low temperatures and pressures and the presence of air, water and frequently intense biological activity. Ore deposits, because of their special mineralogy and chemistry, have unusual weathering characteristics, and are commonly the centres of intense alteration. Weathering and intense alteration are particularly associated with deposits such as lode gold, porphyry copper and gold-uraninite placer deposits that contain pyrite. Oxidation of pyrite can cause the pH to fall below 4, mobilizing trace elements which are subsequently enriched on secondary iron and manganese colloids as the pH increases away from the orebody. High concentrations of carbonate and sulphate ions are also liberated during the weathering of some types of ore deposits and precipitation of secondary metal carbonates and sulphates also helps to define geochemical anomalies. Some elements may form negative anomalies directly over ore deposits as a result of the low pH: for example, Zn and Mn have negative anomalies over Mother Lode type Au deposits in central California (Chaffee and Hill, 1989). Weathering of unmineralized rocks normally produces mildly alkaline solutions (see below). The low pH of solutions in and around orebodies is an important factor contributing to their anomalous weathering characteristics. The mineral phases in which ore-forming elements occur in mineralized metamorphic and igneous rocks which give rise to the anomalous weathering characteristics of orebodies are given in Table 3-I).

In the context of exploration geochemistry, reworking of ore deposits in the surface environment has two important consequences. It generally forms or extends halos around ore deposits; and it determines the element associations which can be detected using exploration geochemistry. The elements which are dispersed most widely and which produce the largest halos are frequently different from those comprising the ore. Such "pathfinder" elements are generally relatively mobile. They are closely associated with ore, but form a more

TABLE 3-I

Comparison of host minerals for elements in mineralised and non-mineralised lithologies

Element	Mineralised rocks	Non-mineralised rocks		
		Ultrabasic rocks	Intermediate rocks	Acid rocks
Lithium	Lithium micas (pegmatites), spodumene, amblygonite		Hornblende, biotite, feldspar	Biotite, feldspar
Rubidium	Secondary micas and clays, low *T* potassium feldspar (adularia)		Biotite and other micas feldspars	Micas, K-feldspar
Beryllium	Beryl, bertrandite, phenacite, chrysoberyl		Plagioclase, muscovite	Plagioclase, muscovite
Fluorine	Fluorite, topaz, villiaumite, apatite		Amphiboles, micas	Micas
Manganese	Complex oxides in surface environment	Magnetite, ilmenite, pyroxenes, olivines	Pyroxenes, magnetite, ilmenite	
Copper	Sulphides	Pyroxenes, amphiboles, magnetite	Pyroxenes, amphiboles, biotite magnetite	Biotite in Cu–Mo porphyries
Zinc	Sulphides	Amphiboles, magnetite	Amphiboles, biotite, magnetite	Biotite
Lead	Sulphides		Feldspars, U–Th-rich phases	Feldspars, U–Th-rich phases
Cobalt	Sulphides, arsenides	Amphiboles, magnetite		
Nickel	Sulphides	Olivines, pyroxenes	Pyroxenes, biotite	Biotite
Chromium	Oxides, chromates (crocoite)	Oxides (spinels)	Oxides	

Niobium	Columbite, pyrochlore, niobo-tantalates, loparite	Ilmenite, zircon	Ilmenite, zircon, sphene, biotite	Ilmenite, zircon, sphene, biotite
Tantalum	Tantalite, microlite, niobo-tantalates	Ilmenite, ziron	Ilmenite, zircon, sphene, biotite	Ilmenite, zircon, sphene, biotite
Platinum	Sperrylite	Native metal and alloys		
Molybdenum	Molybdenite, wolfenite		Magnetite, ilmenite, sphene plagioclase	Sphene, K-feldspar, plagioclase
Tin	Cassiterite, tourmaline		Biotite, muscovite	Biotite, muscovite
Cesium	Beryl (pegmatites)		Biotite, muscovite	Biotite, muscovite
Tungsten	Tungstates		Biotite	Biotite
Rare-Earths	Monazite, allanite, xenotime, niobo-tantalates, complex REE silicates	Garnet, amphiboles (LREE)	Monazite, allanite, sphene, plagioclase (Eu), biotite	Apatite, zircon, micas (LREE)
Barium	Baryte, celsian, cymrite	Pyroxenes	Micas, plagioclase	Micas, K-feldspar
Bismuth	Sulphides	Sulphides	Sulphides	Sulphides
Arsenic	Sulphides	Sulphides	Sulphides	Sulphides
Gold	Tellurides, selenides	Native metal and alloys		
Thorium	Monazite, thorite	Zircon, sphene, monazite, apatite, biotite, xenotime, allanite		
Uranium	Uraninite, pitchblende, niobo-tantalates, phosphates, haematite, martite	Zircon, sphene, monazite, apatite, biotite, xenotime, allanite, grain boundaries		

easily detectable halo, either because they are more widely dispersed or because smaller enhancements over background levels are more readily determined analytically.

Halos of both ore and pathfinder elements may be due to either primary dispersion related to high temperature water–rock interaction phenomena associated with ore formation (see previous chapter) or dispersion in the surface environment. The distinction between processes operating in the primary and secondary environments is unclear for several ore deposit types. In the case of Cretaceous to Recent porphyry and epithermal Au deposits formed at low latitudes, for example, the surface environment exerts a direct control on the form of the deposits and their alteration halos as the low permanent water table of many tropical regions and oxidation, particularly of sulphur gases, intensifies near-surface alteration. Moreover, Class 2 ore deposits (see previous chapter) are generally hosted in sedimentary rocks whereas ore deposit types of Class 1, including placer Au and Sn and lateritic Ni and Au deposits, are formed as a direct result of surface processes which in some cases are penecontemporaneous.

The redistribution of elements in the surface environment involves interaction between ore and host rock and water containing dissolved ions and gases and organisms. During weathering bedrock progressively breaks down to produce rock and mineral particles (which are resistant to chemical alteration), solutions, and colloidal products which have physical properties intermediate between solids and dissolved species. Hence chemical elements are variously re-distributed amongst detrital particles of rocks and minerals, solutions and inorganic and organic colloids. Most types of weathering product are represented in tributary drainage systems but their proportions and composition vary in relation to the type of ore deposit and the balance and nature of physical, chemical and biological weathering processes in different surface environments.

In this chapter the processes involved in the redistribution of rock and ore-forming elements are considered and the general effects of surface processes in different surface environments described. The main types of halos developed around orebodies are then briefly discussed, based on the classification of Rose et al. (1979), before considering the modifications to the geochemical signatures of ore deposits in the surface environment. Throughout the discussion particular attention is paid to the behaviour of iron as an example of a major element because of the importance of pyrite in the weathering of orebodies, while arsenic is used to exemplify the behaviour of a pathfinder element.

PROCESSES OF FORMATION OF SECONDARY DISPERSION PATTERNS

Release of elements by weathering

The modification of the primary geochemical signatures of ore deposits and their host rocks involves a combination of physical, chemical and biological processes, although chemical weathering predominates over much of the Earth's surface. Physical and biological processes promote chemical weathering, the former by the breakdown of rock into smaller particles which exposes larger areas to chemical attack, and the latter by the production of acidity and complexation as well as the physical prising action of root systems.

Physical weathering generally predominates only in arid climates, where chemical weathering is inhibited, or in areas of high relief where gravity-driven erosion is important. Processes of physical weathering include glacial plucking, the thermal expansion and contraction of rocks, and expansion due to the crystallization of salts or the freezing of water in fissures. The movement of rock fragments by wind, ice and water also causes abrasion, producing increasingly fine particles. Physical weathering separates chemical elements only where they are concentrated in resistate minerals (e.g., tin in cassiterite) which have a strong density contrast and may be reworked into placer deposits.

Biological weathering is most important in and immediately beneath the soil zone. The physical breakdown of rock is accelerated by the penetration of plant roots into fissures, whereas chemical weathering is accelerated by the increased acidity resulting from CO_2 produced by respiration and the presence of organic acids. Rock surfaces may also be colonised by microorganisms which oxidize iron and sulphur. In the soil zone, organisms disaggregate particles and hence increase permeability and the penetration of air and water.

Chemical weathering includes a range of reactions which occur when primary rock minerals interact with water containing dissolved materials that act to enhance mineral solubility. The principal difference between chemical and other forms of weathering is that it is capable of separating different elements in the surface environment because of their differing reactivities. Thus it is chemical weathering that is mainly responsible for the formation of different types of geochemical anomalies and halos in relation to the type of orebody and surface environment.

Chemical weathering is initiated by interaction between rainwater and rock. Rainwater contains low concentrations of dissolved solids (Fig. 3-1), which are mainly derived from the evaporation of seawater, and small amounts of atmospheric gases. Compared to rainwater, river water contains higher concentrations of dissolved solids and different proportions of the major elements (Fig. 3-1). These changes result from the processes of dissolution, oxidation, hydrolysis and acid hydrolysis acting on rock minerals.

Dissolution

Dissolution is the simplest mineral–water reaction; it mainly affects ionically bonded solids such as NaCl and occurs in pure water (i.e., it does not require the presence of dissolved components).

$$\underset{\text{(Halite)}}{\mathrm{NaCl(s)}} \xrightarrow{H_2O} \mathrm{Na^+(aq) + Cl^-(aq)} \tag{3-1}$$

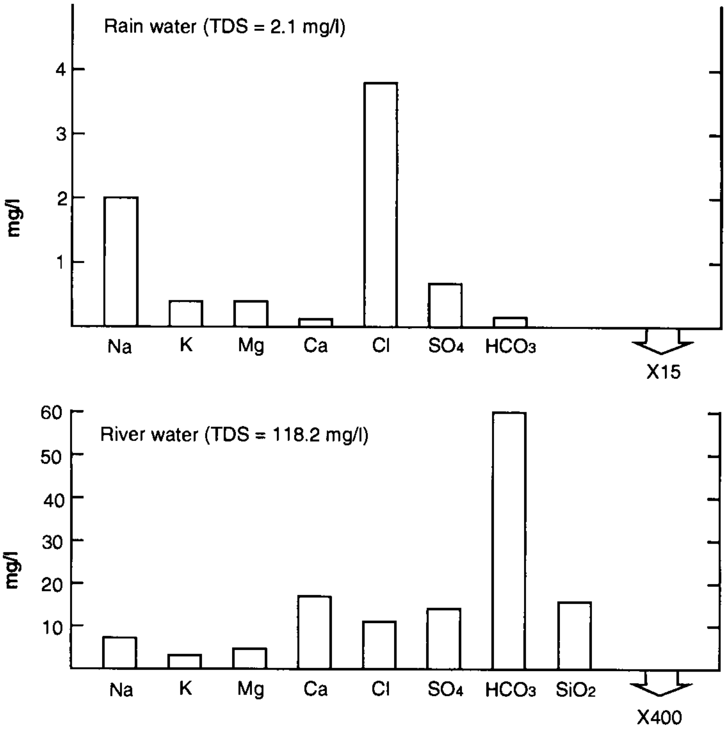


Fig. 3-1. Mean composition of rain water and river water. Note different scales for the two histograms. Derived from Raiswell et al. (1980), redrawn with permission of Hodder Stoughton, Ltd.

The suffixes denote the state of the materials involved, as follows: (s) solid; (aq) aqueous or dissolved; (l) liquid; and (g) gas.

Most mineral phases which are found in rocks or mineral deposits are only poorly susceptible to simple dissolution, with the exception of sulphates such as gypsum, for example:

$$\underset{\text{(Gypsum)}}{CaSO_4 \cdot 2H_2O(s)} \longrightarrow Ca^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O(l) \qquad (3\text{-}2)$$

Some sulphates are only sparingly soluble and Fig. 3-2 shows the concentrations of metal ions in equilibrium with some metal sulphates in typical river water and mine drainage (where sulphate concentrations may be greatly increased by sulphide oxidation). The convention followed here is to regard metal ions as being immobile at concentrations below 10^{-6} M (major elements) or 10^{-8} M (trace elements). Figure 3-2 indicates that the alkaline earth sulphates are soluble even with sulphate concentrations of 10^{-2} M, although Ba^{2+} has only limited solubility. Note the common ion effect, whereby increasing sulphate concentrations decrease the solubility of all alkaline earth metal ions. Hence

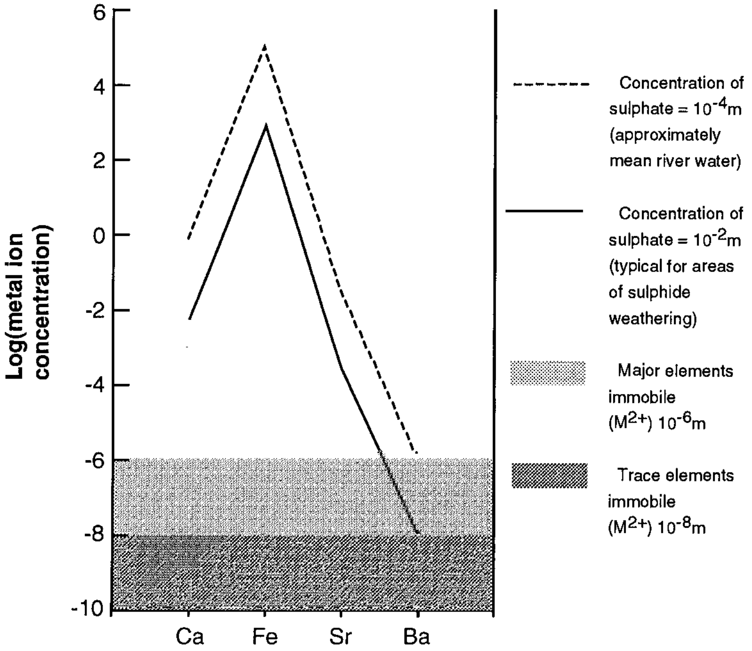


Fig. 3-2. Concentrations of divalent metal ions in equilibrium with their sulphate minerals at different sulphate concentrations representing mean river water and the drainage from weathered ore bodies. Activity assumed equal to concentration. Solubility products derived from thermodynamic data from Wagman et al. (1982) for 25°C, 1 atmosphere.

TABLE 3-II

Selected elements and the percentage ionic character of their bonds with oxygen. (The Al–O and Si–O bonds in the aluminosillicate framework are of roughly equal ionic and covalent character.)

Element	% Ionic character	Element	% Ionic character
Aluminium (Al)	60	Magnesium (Mg)	71
Barium (Ba)	84	Manganese (Mn)	72
Calcium (Ca)	79	Potassium (K)	87
Carbon (C)	23	Silicon (Si)	48
Iron (Fe^{2+})	54	Sodium (Na)	83
Iron (Fe^{3+})	69	Strontium (Sr)	82

simple dissolution will generally remove metal sulphates except in situations where waters have greatly enhanced sulphate concentrations.

In contrast to the ionically-bonded minerals, covalently-bonded minerals are much less readily dissolved in water, because there is little or no charge separation involved in bonding. Hence alumino-silicate minerals, which have bonding properties intermediate between ionic and covalent, are only poorly soluble in pure water (Table 3-II).

Oxidation

Oxidation is important where rocks contain elements such as Fe or S or trace elements of the first row transition series, such as manganese, in their reduced state. Colour frequently provides an indication of oxidation state, for example minerals containing reduced iron are often greenish whereas oxidized forms of iron are usually red-brown. Thus the iron silicate fayalite reacts with oxygen and water to give a red-brown iron hydroxide and silicic acid.

$$\underset{\substack{\text{(Fe(II)}\\ \text{greenish Fayalite)}}}{Fe_2SiO_4(s)} + \tfrac{1}{2}O_2(g) + 5H_2O \longrightarrow \underset{\substack{\text{(Fe(III) red}\\ \text{Iron Hydroxide)}}}{2Fe(OH)_3(s)} + \underset{\text{(Silicic Acid)}}{H_4SiO_4(aq)} \qquad (3\text{-}3)$$

The oxidation of Fe (II) in siderite and biotite proceeds in a similar manner, with the production of iron hydroxides which have a high absorption capacity (see below). The oxidation of iron and sulphur is frequently catalysed by microorganisms and pyrite, which contains both elements, and is particularly rapidly decomposed in most surface environments.

$$\underset{\substack{\text{(Fe(II)}\\ \text{Pyrite)}}}{FeS_2(s)} + \tfrac{15}{4}O_2(g) + \tfrac{7}{2}H_2O \longrightarrow \underset{\substack{\text{(Fe(III)}\\ \text{Iron Hydroxide)}}}{Fe(OH)_3(s)} + 2SO_4^{2-}(aq) + 4H^+(aq) \qquad (3\text{-}4)$$

The reaction proceeds optimally under low pH (<4) conditions, which are commonly found in ore deposit drainage. Oxidation generates further acidity and the high hydrogen ion concentrations enhance the mobility of elements liberated by acid hydrolysis (see below). The oxidation of other sulphide minerals proceeds in a similar fashion.

$$ZnS(s) + 2O_2(g) \longrightarrow Zn^{2+}(aq) + SO_4^{2-}(aq) \qquad (3\text{-}5)$$

$$PbS(s) + 2O_2(g) \longrightarrow Pb^{2+}(aq) + SO_4^{2-}(aq) \qquad (3\text{-}6)$$

The oxidation of these sulphides generates no acidity. The hydrogen ions generated by pyrite oxidation result mainly from the oxidation of Fe (II) to Fe (III), which forms an exceptionally insoluble hydroxide and splits the water molecule to leave residual H^+.

$$Fe^{3+}(aq) + 3H_2O(l) \longrightarrow Fe(OH)_3(s) + 3H^+(l) \qquad (3\text{-}7)$$

Mechanisms of sulphide oxidation are considerably more complicated than suggested by the simple equations presented here (see Stumm and Morgan, 1981) and intermediate oxidation states of sulphur (e.g., thiosulphates, and sulphites) are common. In general, however, acidity in surface drainage over ore deposits reflects pyrite oxidation, because pyrite is relatively abundant and iron hydroxides are readily precipitated. The same conclusion can be reached by considering the ionic potentials of Fe^{3+} compared to other divalent row 4 metals (see Fig. 3.8).

The oxidation pathway described above may not, however, be that followed at higher pH (6 to 9). Experimental work by Goldhaber (1983) shows that the thiosulphate ion is an important intermediate reaction product which, although metastable, can persist in alkaline conditions.

$$FeS_2(s) + \tfrac{7}{4}O_2(g) + \tfrac{5}{2}H_2O(l) \longrightarrow Fe(OH)_3(s) + 2H^+(aq) + S_2O_3^{2-} \qquad (3\text{-}8)$$

The thiosulphate ion has been implicated as an important complex in the dissolution of gold and in the reduction and fixation of uranium in roll-front uranium ores formed where oxygenated uranium-bearing waters invade pyritic sandstone (see below). Oxidation of pyrite under alkaline conditions generates thiosulphate ions, the breakdown of which may be slow if alkaline conditions can be maintained through the consumption of H^+, for example, by carbonate or silicate dissolution. In these circumstances the thiosulphate ion can act to transfer sulphur from the host rock to the ore front, where it is consumed in reducing soluble uranium (VI) and precipitating insoluble uranium (IV), shown below as uraninite (UO_2).

$$4UO_2^{2+} + S_2O_3^{2-} + H_2O \longrightarrow 4UO_2 + 2SO_4^{2-} + 10H^+ \qquad (3\text{-}9)$$

Pyrite is also concentrated at the roll-front, so some thiosulphate must be used to re-sulphidize $Fe(OH)_3$ by reversing the reaction indicated in equation 8 above. The effectiveness of these reactions at Earth surface temperatures has still to be confirmed, but the involvement of thiosulphate provides a mechanism for generating roll-front ores in sandstones that otherwise lack a reducing agent (such as organic carbon) to change U(VI) to U(IV).

Hydrolysis

Hydrolysis, like dissolution, can occur in the absence of solutes, but it differs in that the water reacts chemically with the dissolved ions produced. Examples are the reaction of forsterite (Mg_2SiO_4) and calcite ($CaCO_3$) with water.

$$Mg_2SiO_4(s) + 4H_2O(l) \longrightarrow 2Mg^{2+}(aq) + 4OH^-(aq) + H_4SiO_4(aq) \qquad (3\text{-}10)$$

$$CaCO_3(s) + 2H_2O(l) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq) + H_2CO_3(aq) \qquad (3\text{-}11)$$

Both reactions produce the weak acids H_4SiO_4 (silicic acid) and H_2CO_3 (carbonic acid) which are poorly dissociated in most surface environments. Calcium and magnesium hydroxides are strongly dissociated alkalis, however, and the resulting solutions are therefore alkaline ($pH > 7$). In effect, hydrolysis involves the replacement of mineral cations by H^+ (e.g., Mg_2SiO_4 hydrolyzes to H_4SiO_4, and $CaCO_3$ to H_2CO_3,) leaving residual OH^- in solution. Most silicate, oxide/hydroxide and carbonate minerals yield a weak acid and a strong alkali on hydrolysis and hence, unless hydrogen ions are supplied from an external source, weathering solutions tend to become alkaline.

Acid hydrolysis

Acid hydrolysis is a similar process to hydrolysis, but the waters involved contain hydrogen ions from dissolved acids, which predominate over those derived from the ionization of water. Acid hydrolysis is thus a considerably more effective weathering process than hydrolysis.

The most important sources of acids are from the solution of CO_2, from sulphide oxidation or from the formation of organic acids. Carbon dioxide dissociates in water to produce H^+ ions.

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq) \longrightarrow H^+(aq) + HCO_3^-(aq) \qquad (3\text{-}12)$$

$$HCO_3^- \longrightarrow H^+(aq) + CO_3^{2-}(aq) \qquad (3\text{-}13)$$

The second stage in the dissociation process is significant only at pH 10 or above so that in most surface waters bicarbonate is the principal anion (Fig. 3-1). The CO_2 may be derived from the atmosphere or from the oxidation of soil organic matter. In well-drained agricultural soils, the gases trapped in soil contain CO_2 concentrations one to two orders of magnitude higher than in the atmosphere. In mineralized areas, pyrite oxidation is a major source of H^+ ions (see equation 4), whereas in poorly drained peaty soils organic acids may be of greater significance.

The breakdown of forsterite by acid hydrolysis proceeds as follows.

$$Mg_2SiO_4(s) + 4H^+(aq) \longrightarrow 2Mg^{2+}(aq) + H_4SiO_4(aq) \qquad (3\text{-}14)$$

Writing the equation in this way emphasizes its generality because the source of H^+ is unspecified. However, whatever the source of H^+, there will be an accompanying anion in solution.

$$4H_2CO_3(aq) \longrightarrow 4H^+(aq) + 4HCO_3^-(aq) \qquad (3\text{-}15)$$

$$2H_2SO_4(aq) \longrightarrow 4H^+(aq) + 2SO_4^{2-}(aq) \qquad (3\text{-}16)$$

Acid hydrolysis is the principal weathering mechanism for alumino-silicate minerals (which include most of the primary rock-forming minerals), as illustrated below by the breakdown of the sodium feldspar, albite.

$$\underset{\text{(Albite)}}{2NaAlSi_3O_8(s)} + 9H_2O(l) + 2H^+(aq) \longrightarrow \underset{\text{(Kaolinite)}}{Al_2Si_2O_5(OH)_4} + 2Na^+(aq) + 4H_4SiO_4 \qquad (3\text{-}17)$$

As in the case of forsterite, the alkali metal ions are completely released into solution but aluminium and some silica are left behind and are reconstituted into a clay mineral, in this case kaolinite. The nature of the clay mineral formed depends on how readily silica is removed by weathering solutions. Silica is completely removed when water flow rates are high and the residual aluminium oxides (often accompanied by iron oxides from mafic silicates) form laterites.

$$NaAlSi_3O_8(s) + H^+(aq) + 7H_2O(l) \longrightarrow Al(OH)_3(s) + 3H_4SiO_4(aq) + Na^+(aq) \qquad (3\text{-}18)$$

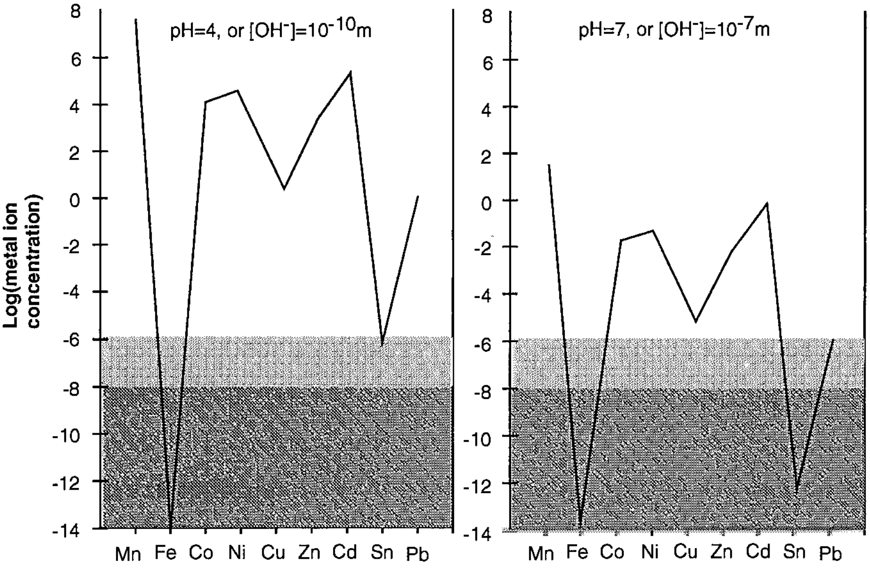


Fig. 3-3. Concentrations of divalent metal ions (except for trivalent Fe) in equilibrium with their hydroxides at pH 4, which is typical of solutions draining from ore bodies, and pH 7 (mean river water). Activity assumed equal to concentration. Solubility products derived from thermodynamic data by Wagman et al. (1982) for 25°C, 1 atmosphere.

Intermediate flow rates, typical of temperate weathering regimes, give rise to kaolinite (as above) while sluggish flow rates in semi-arid environments minimise silica removal and favour the formation of montmorillonite.

$$2NaAlSi_3O_8(s) + 4H_2O(l) + 2H^+(l) \longrightarrow \underset{\text{(Montmorillonite)}}{Al_2Si_4O_{10}(OH)_2(s)} + 2H_4SiO_4(aq) + 2Na^+(aq) \qquad (3\text{-}19)$$

Acid hydrolysis reactions, because they consume protons, also modify dispersion patterns. For example, where acids are generated by pyrite oxidation, ore metals are readily dissolved. Figure 3-3 shows the solubilities of various ore metals in equilibrium with their hydroxides at pH 4 and 7. All of the metals are more soluble in conditions of low pH, typical of solutions draining weathering orebodies. Iron mobility is effectively controlled by the hydroxide phase, which is sufficiently insoluble to retain most iron close to the orebody. Metals such as Pb and Zn, however, which are frequently associated with pyrite, may be mobilized over greater distances. Ultimately, as the hydrogen ions produced by pyrite oxidation are consumed by acid hydrolysis reactions with silicates, the increase in pH tends to favour the formation of hydroxide phases and the retention of metals (e.g., Cu).

Fixation of elements in secondary mineral phases

The weathering reactions described above give rise to a range of dissolved and solid products, and thereby chemically separate the original components of the primary rock and ore-forming minerals. The dissolved products are removed by ground and surface water flow but insoluble and residual solid phases become concentrated over and around the orebody. Secondary insoluble minerals include iron and manganese oxides, clay minerals, sulphates and carbonates, while cassiterite, magnetite, rutile, ilmenite, beryl and zircon are typical residual minerals. The former produce hydromorphic anomalies in drainage systems, the latter clastic dispersion trains.

Newly-formed secondary minerals usually occur as coatings or cements; they often mainly comprise iron oxides/hydroxides, formed by the weathering of pyrite, and are particularly concentrated in gossan (the leached and oxidized part of a sulphide vein). Gossan may be exceptionally enriched in ore-forming elements as a result of their dissolution, rapid precipitation and adsorption. Some of the chemical processes whereby elements are concentrated over orebodies to produce hydromorphic anomalies in drainage sediments are described below.

Precipitation

Mineral precipitation is controlled in the first instance by the solubility product, defined as the product of the activities of the component ions at equilibrium between solid and solution (i.e., when there is no tendency to precipitate or dissolve).

For anglesite ($PbSO_4$),

$$\mathrm{PbSO_4(s)} \underset{\text{Precipitation}}{\overset{\text{Dissolution}}{\rightleftarrows}} \mathrm{Pb^{2+}(aq)} + \mathrm{SO_4^{2-}(aq)} \tag{3-20}$$

The solubility product (K_{sp}) is given by the product of the component ion activities [Pb^{2+}] × [SO4^{2-}] Mol^2 l^{-2} which has the value $10^{-7.8}$ at equilibrium. Measurements of concentration can fairly easily be translated into activities (which are correspondingly lower the more dissolved solids are contained in solution) and the procedure for doing this is described in many geological textbooks (e.g., Garrels and Christ, 1965). The K_{sp} for $PbSO_4$ is exceptionally small and hence anglesite is only poorly soluble in natural waters. The solubility product can be used to assess whether precipitation or dissolution of a particular mineral phase will occur. Thus if a water analysis shows that (Pb^{2+}]aq × [SO_4^{2-}]aq < $10^{-7.8}$, dissolution is favoured, whereas if the ion product exceeds $10^{-7.8}$ precipitation is favoured. In the case of gossan formation, all sulphate ions (derived from whatever source) contribute to [SO_4^{2-}]. Thus the formation of SO_4^{2-} during the weathering of pyrite (equation 4) further reduces the levels of Pb^{2+} which can be held in solution before the solubility product of anglesite is exceeded. Table 3-III shows the solubility products of some common

TABLE 3-III

Solubility products of common gossan minerals compared to alkaline earth carbonates and sulphates

Alkaline earth salts		Gossan minerals	
Sulphates			
$CaSO_4$	$10^{-4.5}$	$PbSO_4$	$10^{-7.8}$
$SrSO_4$	$10^{-6.2}$		
$BaSO_4$	$10^{-10.0}$		
Carbonates			
$CaCO_3$	$10^{-8.4}$	$PbCO_3$	$10^{-13.1}$
$SrCO_3$	$10^{-9.0}$	$ZnCO_3$	$10^{-10.8}$
$BaCO_3$	$10^{-8.8}$	$Cu(OH)_2CO_3$	$10^{-33.8}$
$MgCO_3$	$10^{-5.1}$		

gossan-forming minerals. The values are generally low and solubility is further decreased by the high levels of dissolved carbonate and sulphate ions liberated during the weathering of ore. In contrast, the solubility of alkaline earth carbonates and sulphates are much higher (with the exception of $CaCO_3$ and $MgCO_3$) so that they are more readily removed in solution. This chemical separation greatly modifies the primary geochemical signature, frequently enhancing geochemical anomalies because of the increase in dissolved species from ore-forming elements relative to those from rock-forming elements.

Adsorption

Adsorption also plays an important role in modifying the mobility of ore-forming elements released during chemical weathering. Most adsorption is caused by electrical charges either on the mineral surfaces or arising from lattice substitutions between ions of different charge. Surface charge processes are responsible for the adsorption characteristics of iron and manganese oxides, whereas adsorption on clay minerals arises mainly from lattice substitution. The importance of these processes reflects the large surface area and the small particle size of the phases involved.

The surface charges of oxides, hydroxides and organic matter result from the ionization of surface groups. Consider the surface of a manganese hydroxide mineral and the behaviour of its hydroxide groups in response to variations in the H^+ concentration of the surrounding water.

$$H^+(aq) + Mn - OH(s) \longrightarrow Mn - OH_2^+(s) \quad \text{for high } [H^+] \text{ aq} \qquad (3\text{-}21)$$

$$Mn - OH(s) \longrightarrow Mn - O^-(s) + H^+(aq) \quad \text{for low } [H^+] \text{ aq} \qquad (3\text{-}22)$$

The surface hydroxide groups respond to high concentrations of H^+ by adsorbing H^+ and thus acquiring a positive surface charge. Conversely at low hydrogen ion concentrations, the hydroxide dissociates to lose an H^+ ion and acquire a negative surface charge. At intermediate H^+ concentrations (about pH 3), the

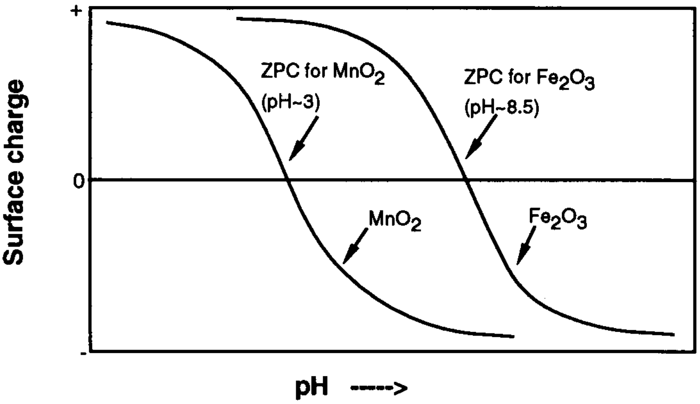


Fig. 3-4. Schematic diagram of surface charge on Mn- and Fe-oxides as a function of pH. ZPC values of both oxides vary greatly depending on the precise nature of the phase concerned.

surface is neutral and the pH of this value is known as the point of zero charge (ZPC). Figure 3-4 shows how the surface charge on iron and manganese oxides varies as a function of pH. In most natural waters, manganese oxides have a negative surface charge, whereas iron oxides are usually positively charged. Because surface charge is controlled by H^+ and OH^- ions, they are termed potential-determining ions.

The extent of adsorption is controlled by the number of charged sites which ions in solution compete to occupy. In general, divalent ions are more strongly adsorbed than univalent ions, and transition metal ions more than ions of non-transition metals. Well-crystallized materials also show different adsorption preferences to amorphous materials. However, most materials which exhibit adsorption show a general order of preference (Table 3-IV), although considerable variations may occur if there are large differences in their dissolved concentrations.

Because of the formation of large amounts of fine-grained iron oxides during the weathering of orebodies containing pyrite, adsorption exerts an important influence on the mobility of many metals and thereby reduces the size and intensifies the magnitude of their dispersion halo. However, large amounts of hydrous iron and manganese oxides that are the products of normal weathering and soil formation over unmineralized rocks can accumulate in soil and drainage sediments in some types of surface environment. The collection of samples with high contents of this material can falsely indicate the presence of an anomaly which reflects only normal adsorption processes.

Adsorption on clay minerals mostly occurs because the unbalanced substitution of Al^{3+} for Si^{4+} in octahedral sites produces negative charge. Clay minerals can adsorb large quantities of metal ions from solution, the quantities of adsorbed ions being a function of their concentrations in solution and their affinity for the adsorber. For ions of equal charge, the affinity for the adsorber increases

TABLE 3-IV

Relative affinity for adsorption of some cations (after Rose et al., 1979)

	Mn-oxides	Amorphous Fe-oxides	Goethite	Amorphous Al-oxides	Humic substances[a]	
					(1)	(2)
Greatest	Cu^{2+}	Pb^{2+}	Cu^{2+}	Cu^{2+}	Ni^{2+}	Cu^{2+}
	Co^{2+}	Cu^{2+}	Pb^{2+}	Pb^{2+}	Co^{2+}	Ni^{2+}
	Mn^{2+}	Zn^{2+}	Zn^{2+}	Zn^{2+}	Pb^{2+}	Co^{2+}
	Zn^{2+}	Ni^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Pb^{2+}
	Ni^{2+}	Cd^{2+}	Cd^{2+}	Co^{2+}	Zn^{2+}	Ca^{2+}
	Ba^{2+}	Co^{2+}		Cd^{2+}	Mn^{2+}	Zn^{2+}
	Sr^{2+}	Sr^{2+}		Mg^{2+}	Ca^{2+}	Mn^{2+}
	Ca^{2+}	Mg^{2+}		Sr^{2+}	Mg^{2+}	Mg^{2+}
Least	Mg^{2+}					

[a] (1) Schnitzer and Hanson (1970); (2) Gamble and Schnitzer (1973).

with decreasing radius of the hydrated ion. Thus the sequence of increasing ease of replacement is:

$$Ba > Sr > Ca > Mg$$

$$Cs > Rb > K > Na > Li$$

In general, the attachment of ions is sufficiently weak to enable them to be replaced easily once ions with a stronger affinity become available. Thus, highly acid solutions which occur in and around orebodies containing pyrite produce mineral adsorption sites which are mainly occupied by H^+. Further from the orebody, as the pH of solutions increases, adsorption sites become increasingly metal-rich. In this situation clay mineral adsorption is frequently less important than that of iron oxides, because the clay mineral products of acid weathering (e.g., kaolinite) have comparatively low adsorption capacities (Table 3-V).

The fixation of elements in biogenic phases

Whereas the incorporation of elements into secondary phases modifies the expression of orebodies in the surface environment, uptake by biogenic materials is more limited and does not modify the dispersion halo so much as reflect it. This is the principle that governs the use of plants in geochemical prospecting. Two forms of biogenic uptake, that by living material (mostly plant) and that by degraded organic matter produced from plant material in the soil system, are described here.

TABLE 3-V

Exchange capacity of some clay minerals and common soils (after Rose et al., 1979)

Minerals and soils	Cation-exchange capacity (meq/100 g)
Kaolinite	3– 15
Halloysite	5– 50
Montmorillonite	80–150
Illite	10– 40
Chlorite	10– 40
Vermiculite	100–150
Organic fraction of soils	150–500
Podzolic soils (USA)	5– 25
Chernozem (USSR)	30– 60
Black cotton soil (India)	50– 80
Latosol (Zambia)	2– 10
Gley soil	15– 25

Plant uptake

Nearly all chemical elements have been found in plant material and for many elements of economic interest there are one or two plant species capable of producing high enrichments. The relative uptake of a given element in a plant species is known as the Biological Adsorption Coefficient (BAC), where

$$\mathrm{BAC} = \frac{\text{Concentration in plant (dry weight)}}{\text{Concentration in substrate}} \tag{3-23}$$

Essential elements such as B, Ca, P, K and S which have BAC values greater than 0.1, are termed biogenic. However, some elements which are essential to plant life (Table 3-VI) (e.g., Fe, Mg, Mo, Na) are relatively weakly taken up by plants whilst others may play a physiological role in some species of plants, but are otherwise unimportant as nutrients (Table 3-VI).

These elements are taken up at the root system or by foliar adsorption. Ions diffuse to the root system from the soil solution or are liberated (usually from clay minerals) by ion exchange. The CO_2 released in respiration dissociates to give H^+ and HCO_3^- (equation 12) and the H^+ ions are extremely effective in displacing nutrient elements from adsorption sites. There are a small number of plants which use these uptake mechanisms so effectively that higher concentrations of some metals can be found in the plant than in the surrounding soil. Such hyperaccumulation is not necessarily favourable for geochemical exploration because small variations in the substrate are poorly reflected by the plant.

Nutrient elements are frequently difficult to prospect for using biogeochemistry because plant BAC values decline with increasing soil concentration (Fig. 3-5), since homeostatic mechanisms regulate uptake to provide the level required by the plant. In contrast BAC values remain constant for non-essential elements (Fig. 3-6) and in such cases plants tend to reflect substrate geochem-

TABLE 3-VI

Mean Biological Adsorption Coefficients (BAC) for vegetation (after Brooks, 1983)

Biogenic elements		Intermediate elements		Nonbiogenic elements	
B *	1.70	Mo *	0.04	Na *	0.01
S *	0.96	Mg *	0.034	Rb	0.007
Zn *	0.90	Ni	0.03	REE	0.003
P *	0.88	Co	0.02	Cr	0.003
Mn *	0.40	U	0.02	Li	0.0015
Ag	0.25	Fe *	0.012	Si	0.0006
Ca *	0.14			V	0.0006
Sr	0.13			Ti	0.0003
Cu *	0.13			Al	0.0003
K *	0.12				
Ba	0.12				
Se	0.10				

* Essential elements.

Note: Concentrations in plant material expressed on a dry weight basis.

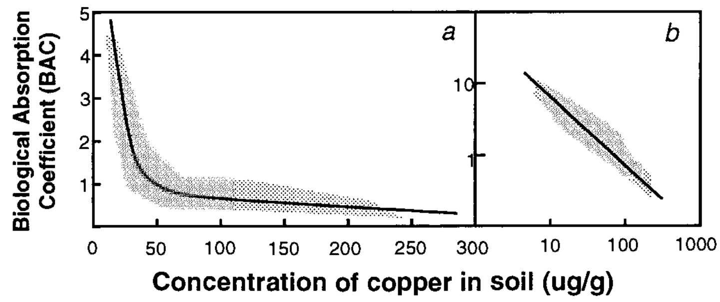


Fig. 3-5. Biological Absorption Coefficients (BAC) for copper in *Quintinia acutifolia* expressed as a function of copper in the soil. Data expressed in both linear and logarithmic units. Derived from Brooks (1983), redrawn with permission of John Wiley and Sons, Inc.

istry and are good prospecting indicators. In the case of drainage sediments the effect of debris from other living plants on trace element concentrations is generally minimal. However, degraded organic material, which is capable of binding vast quantities of trace elements, is important.

Complexation with degraded plant material

Regardless of the initial metal content of plant material, its subsequent breakdown produces humic compounds (fulvic acids, humic acids and humin) which have the capacity to adsorb and complex considerable quantities of metal. The adsorption capacity arises mainly from the presence of various types of OH groups (Table 3-VII), whilst complexation occurs because the elements, C, H, N, O and S also possess unshared pairs of electrons. These pairs can be used to form bonds with metal ions (Fig. 3-7), particularly the divalent and

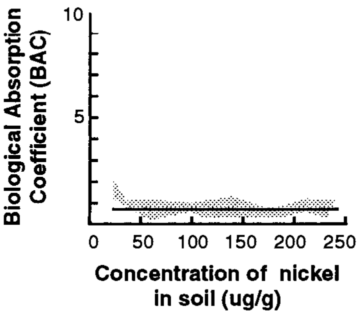


Fig. 3-6. Plot of biological absorption coefficient of nickel in *Northofagus Fusca*. Derived from Brooks (1983), redrawn with permission of John Wiley and Sons, Inc.

TABLE 3-VII

Physical and chemical properties of humic and fulvic acids (from Snoeyink and Jenkins, 1980)

Property	Humic Acids	Fulvic Acids
Elemental composition	*Weight (%)*	*Weight (%)*
C	50–60	40–50
H	4– 6	4– 6
O	30–35	44–50
N	2– 4	<1– 3
S	1– 2	0– 2
Functional groups	*Oxygen distribution (%)*	*Oxygen distribution (%)*
Carboxyl COOH	14–45	58–65
Phenol OH	10–38	9–19
Alcohol C–OH	13–15	11–16
Carbonyl C–O	4–23	4–11
Methoxyl O–CH_3	1– 5	1–25
Solubility in strong acid (pH 1)	Not soluble	Soluble
Molecular weight range	Few hundred–several million	180–10,000

trivalent transition metal ions. Humic acids are also fine-grained and possess a large surface area, thus exposing a high proportion of their electron donor elements to surrounding solutions. The adsorption and complexation properties of humic compounds are considerable, for example, some metals such as U are enriched in peat to a concentration of 10,000 times that in surrounding water. Clearly the accumulation of high concentrations of humic compounds, as in peat bogs, can constitute a significant sink for many ore-forming elements. By contrast, the large alkali metal ions (e.g., K) are poorly complexed and hence the combined influence of weathering and interactions with soil organic compounds can constitute an efficient separation mechanism and an important modification of the primary geochemical signature.

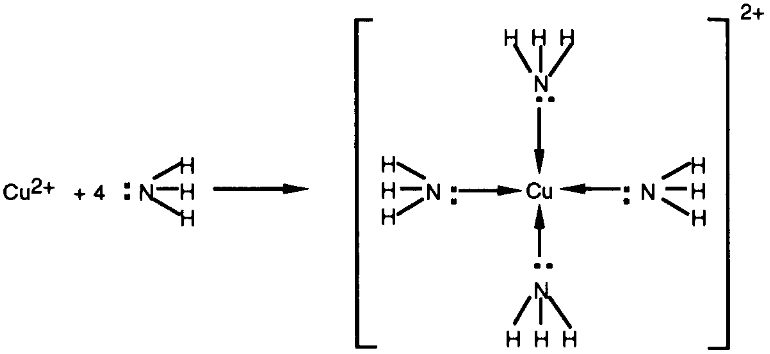


Fig. 3-7. The formation of co-ordinate bonds in the complex $[Cu[NH_3]_4]^{2+}$ by the sharing of lone pairs of electrons between the nitrogen atom of the NH_3 molecule and the Cu^{2+} ion.

ELEMENT AFFINITIES AND ASSOCIATIONS

Having considered element release and re-incorporation the factors that determine element associations are now discussed and two indices are described which are of use in grouping elements of similar behaviour.

Ionic potential

An approximate guide to the mobility of elements in the surface environment is given by the parameter Z/r (where Z is the electronic charge and r is the ionic radius), which is known as the ionic potential. This parameter provides an estimate of the ion-water attractive forces, which determine whether ions remain in solution or are precipitated as hydroxides.

In aqueous solution, ions become surrounded by an envelope of water molecules attracted by the dipole charge on either the hydrogen atoms (positive) or the oxygen atom (negative). These charges arise because the bonding electrons between the O and H atoms are unequally shared, favouring the oxygen atom. Ions with a low ionic potential (<3) simply remain surrounded by the water molecules and exist as hydrated ions in solution. Where ion-water forces are stronger (ionic potential between 3 and 12) a single H^+ ion is expelled from each water molecule and the element is precipitated as a hydroxide. In contrast when ion-water forces are strongest (ionic potential more than 12), both H^+ ions are expelled from a single water molecule to form a soluble complex oxyanion.

The three types of behavior can be distinguished in Fig. 3-8. Much of the weathering chemistry explained previously can be summarised using this diagram, for example, the precipitation of iron hydroxides during the breakdown of iron silicates and the incorporation of the aluminium into clay minerals in preference to its removal as a dissolved phase. Furthermore the elements most commonly found in river water (Fig. 3-1) are those of high or low ionic

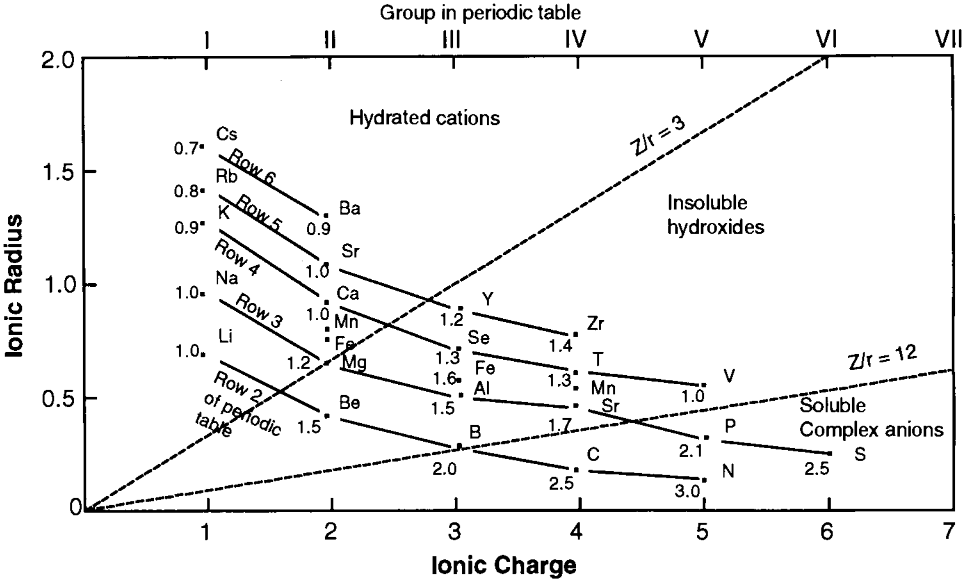


Fig. 3-8. Relationship between ionic charge and ionic radius. Lines connect elements in the same row of the periodic table. Values of the ionic potential Z/r distinguish elements that behave as hydrated cations, insoluble hydroxides and soluble complex ions. Derived from Raiswell et al. (1980), redrawn with permission of Hodder Stoughton, Ltd.

potential. The ionic potential plot provides a simple explanation for the separation of elements between dissolved and solid phases which is important in the modification of primary geochemical signatures.

Redox potential (Eh) and hydrogen ion activity (pH)

A more comprehensive description of element behaviour needs to account for other factors. For example, even metal hydroxides show significant solubility in highly acid solutions which result from sulphide weathering. Thus the pH of a solution is important in controlling whether elements are dissolved or precipitated.

In addition to pH, the oxidizing capacity (ability to accept electrons) or reducing capacity (ability to donate electrons) is important. Many transition elements are poorly soluble in their oxidized form and are more readily mobilized in a reduced state. This effect can be seen in the ionic potential plot (Fig. 3-8) where, for example, Fe^{2+} appears amongst the hydrated ions while Fe^{3+} gives an insoluble hydroxide. The redox potential of an environment is mainly a function of the relative rates of supply of oxidizing agents (mostly dissolved oxygen) in relation to reducing agents (mostly organic matter). If the supply of organic matter exceeds that of oxygen then reducing conditions occur, as in the case of poorly-drained peat bogs. Conversely, in porous sediments the

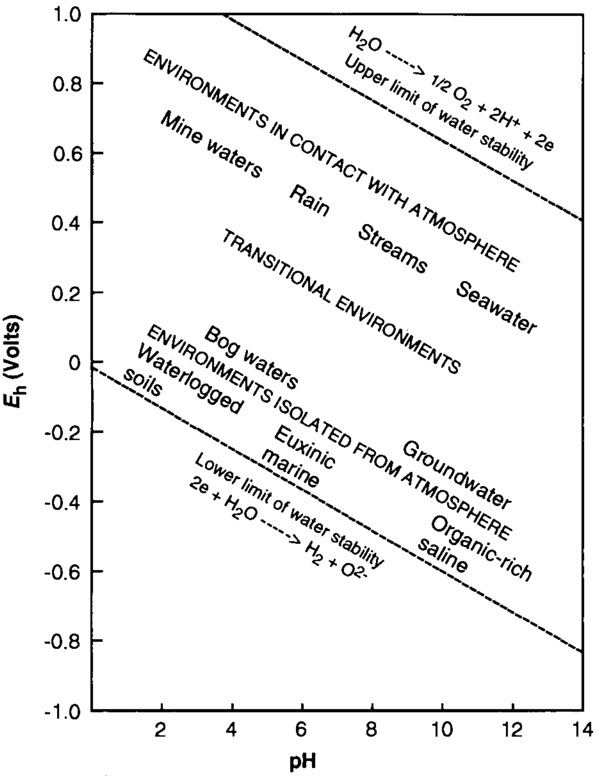


Fig. 3-9. Eh/pH fields for some common natural environments. Derived from Garrels and Christ (1965), redrawn with permission of Harper Collins.

penetration of water (containing dissolved oxygen) is facilitated and oxidizing conditions prevail. The redox potential of a solution is measured by reference to an arbitrary standard, such that positive values indicate oxidizing conditions and negative values indicate reducing conditions.

These two variables, redox potential (Eh) and hydrogen ion activity (pH) are commonly plotted together. Typical ranges of Eh and pH in some natural environments are shown in Fig. 3-9. Detailed Eh–pH diagrams can be constructed for most elements, using the techniques described in Garrels and Christ (1965), and these provide a useful summary of dissolution and precipitation behaviour. For example, under acid conditions iron is stable as Fe^{2+} and Fe^{3+} (Fig. 3-10), with the latter favoured by more oxidizing conditions. Precipitation of iron occurs mainly by increasing the pH to give Fe_2O_3, although the boundary between Fe^{2+} and Fe_2O_3 can be crossed by changes in Eh at constant pH. The minerals containing reduced iron (pyrite, siderite, magnetite) are stable only at low Eh values, but their range of stability is increased by an increased concentration of dissolved sulphide (for pyrite) and dissolved carbonate (for siderite). Note that pyrite has a similar-sized stability field to that of siderite, although the

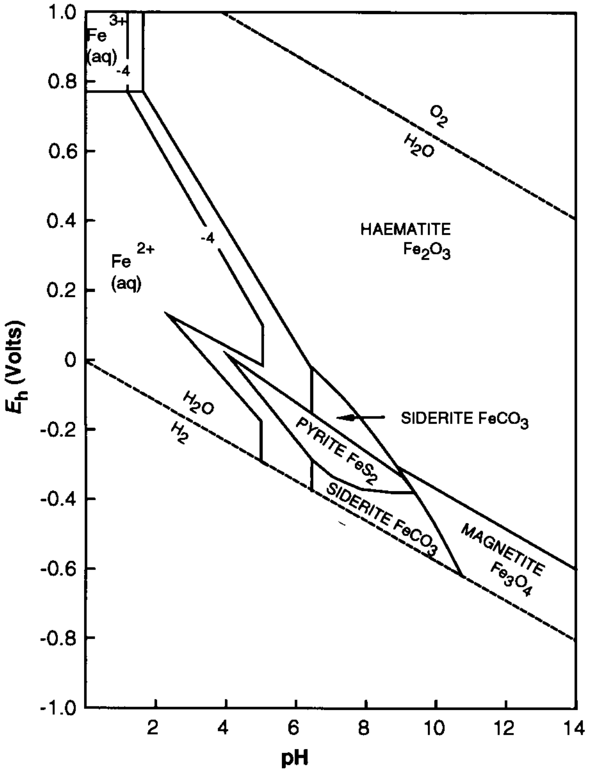


Fig. 3-10. Eh/pH stability relationships between iron oxides, sulphides and carbonates in water at 25°C and 1 atmosphere total pressure. Total dissolved sulphur = 10^{-6} mol l^{-1}, total dissolved carbonate = 10^{0} mol l^{-1}. Solid lines show boundaries plotted for concentrations (strictly activities) of dissolved species at 10^{-6} mol l^{-1}; also shown are boundaries 10^{-4} mol l^{-1}. Derived from Garrels and Christ (1965), redrawn with permission of Harper Collins.

concentration of dissolved sulphide is six orders of magnitude smaller than that of dissolved carbonate. This reflects the much lower solubility product of pyrite (approx. 10^{-28}) compared to siderite (approx. $10^{-10.5}$). The sensitivity of Eh–pH diagrams to variations in anion concentrations can be demonstrated by decreasing the total dissolved carbonate to 10^{-2} M which results in the elimination of the stability field for $FeCO_3$ and FeS_2 is then the only stable solid reduced iron phase.

Similar diagrams can be constructed for most trace elements, although reliable and consistent redox or thermodynamic data are not always available. Values reported for some species may vary significantly between authors (see Wood and Garrels, 1987), even though the net value for a reaction may be the same for each of the different data sets. Clearly errors can arise in using data from different sources, unless all the data are internally consistent. Despite this, trace element diagrams can be of great value particularly in emphasising

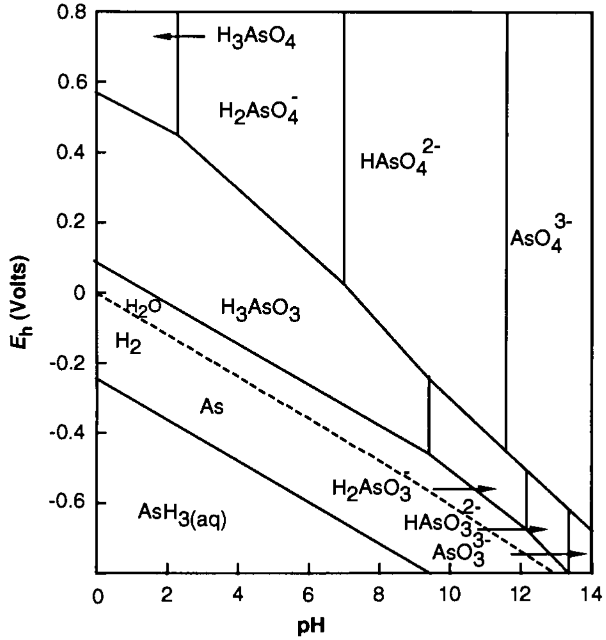


Fig. 3-11. Eh/pH relations amongst arsenic species at 25°C and 1 atmosphere pressure, for total dissolved arsenic exceeding 10^{-6} M. Derived from thermodynamic data from Sergeyeva and Khodakovskiy (1969).

the conditions under which one trace element may be associated with, or separated from another. Thus the pathfinder properties of As for Au arise from their different Eh/pH characteristics. In oxygenated water, containing only low concentrations of Cl^-, native gold is the only stable phase of gold. In contrast, Fig. 3-11 shows that As is completely mobile either as arsenic acid (V) species and its dissociation products (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}) or under mildly reducing conditions as arsenious acid (III) species and its dissociation products (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$). Neither of the oxides As_2O_5 or As_2O_3 are insoluble enough to appear on the diagram, but the stability field of As metal extends slightly above that of H_2O. The high mobility of As under oxygenated conditions makes it a useful pathfinder for elements with which it has a primary association and which are either immobile (e.g., Au) or which have more limited mobility (e.g., Pb) under oxygenated conditions.

Eh/pH diagrams are of great value in summarising the environmental conditions which cause the dissolution and precipitation of elements with different valence states. However, care is needed in their use because of kinetic effects. Thus solid Fe_2O_3 may persist indefinitely in the stability field of Fe^{2+} if it is well crystallized and its dissolution rate is slow. Furthermore, the thermodynamic data from which the boundary conditions are derived often refer strictly to pure phases, whereas many minerals have non-stoichiometric and/or variable compositions. Finally, the diagrams are valid only for the chosen conditions of temperature and pressure (usually 25°C and 1 atmosphere) at specified anion concentrations. The latter in particular exert an important influence on predicted stability relations. The relative mobilities of chemical elements in the surface environment are presented in Table 3-VIII and discussed further below.

Coefficient of aqueous migration

Ionic potential and Eh/pH relations are based, to some extent, on theoretical models of element behaviour, and their success in explaining secondary dispersion patterns indicates that simple mineral–water equilibria are an important control on major element geochemistry. The behaviour of trace elements is more complex, however, because of the role of adsorption and complexing. Hence empirical estimates of element behaviour can be of considerable value. One such index of element mobility, a coefficient of Aqueous Migration (K), has been constructed by Perel'man (1977) based on comparisons of the composition of natural waters with the rocks or soils with which they are associated.

$$K = \text{Coefficient of aqueous migration} = \frac{100M}{aN} \qquad (3\text{-}24)$$

where M is the concentration of the element in water (mg l^{-1}); a is the total mineral residue in the water (%); and N is the concentration of the element in the solid phase (%).

Values of K represent the integral effects of all the processes which determine element behaviour, and measurements of K in a variety of environments with different Eh and pH characteristics reveal the pattern of element mobility and association shown in Table 3-IX. Such a classification is more useful than the one based simply on Eh and pH conditions in surface environments since the activity of major anionic species and particular combinations of surface environments are considered. These data provide a useful summary of how the processes outlined in the previous section chemically separate and disperse the elements originally concentrated in an orebody. The extent of the separation determines how far the primary geochemical signature can be modified in different surface environments.

DIFFERENT SURFACE ENVIRONMENTS

Conditions in the surface environment represent a complex interplay of climatic, physiographic, biological, anthropogenic and geological factors and hence are highly variable from the local to the continental scale. Moreover, climates have changed frequently and often profoundly since the mid-Tertiary (Butt and Zeegers, 1992). Whereas temperate and higher latitudes are dominated by the effects of Pleistocene glaciation, the warmer lower latitudes have regoliths and associated landforms related to past (or continuing) periods of deep weather-

TABLE 3-VIII

Relative mobility of elements in different surface environments (after Andrews-Jones, 1968)

Relative mobilities	Environmental conditions			
	Oxidizing	Acid	Neutral to Alkaline	Reducing
Very high	Cl,I,Br	Cl,I,Br	Cl,I,Br	Cl,I,Br
	S,B	S,B	S,B	
			Mo,V,U,Se,Re	
High	Mo,V,U,Se,Re	Mo,V,U,Se,Re		
	Ca,Na,Mg,F,Sr,Ra	Ca,Na,Mg,F,Sr,Ra	Ca,Na,Mg,F,Sr,Ra	Ca,Na,Mg,F,Sr,Ra
	Zn	Zn		
		Cu,Co,Ni,Hg,Ag,Au		
Medium	Cu,Co,Ni,Hg,Ag,Au			
	As,Cd	As,Cd	As,Cd	
Low	Si,P,K	Si,P,K	Si,P,K	Si,P,K
	Pb,Li,Rb,Ba,Be Bi,Sb,Ge,Cs,Tl	Pb,Li,Rb,Ba,Be Bi,Sb,Ge,Cs,Tl	Pb,Li,Rb,Ba,Be Bi,Sb,Ge,Cs,Tl	
		Fe,Mn	Fe,Mn	Fe,Mn
Very low to immobile	Fe,Mn			
	Al,Ti,Sn,Te,W Nb,Ta,Pt,Cr,Zr Th,Rare Earths	Al,Ti,Sn,Te,W Nb,Ta,Pt,Cr,Zr Th,Rare Earths	Al,Ti,Sn,Te,W Nb,Ta,Pt,Cr,Zr Th,Rare Earths	Al,Ti,Sn,Te,W Nb,Ta,Pt,Cr,Zr Th,Rare Earths
			Zn	Zn
			Cu,Co,Ni,Hg,Ag,Au	Co,Cu,Ni,Hg,Ag,Au
				S,B
				Mo,V,U,Se,Re
				As,Cd
				Pb,Li,Rb,Ba,Be Bi,Sb,Ge,Cs,Tl

ing and lateritization under seasonal tropical conditions. Such conditions were probably widespread from the Cretaceous or earlier until the mid-Tertiary and subsequently contracted to the present near equatorial latitude. Some regions of the Earth's crust, such as parts of Russia, have remained stable for a relatively long period of time and have been subjected to many different types of climate. Such changes have traditionally been studied by landscape geochemists such as Polynov (1937) and Perel'man (1977).

Despite considerable local complexity, dispersion characteristics may be suf-

TABLE IX

Geochemical classification of elements based on characteristic features of supergene migration (after Perel'man, 1977)

AERIAL MIGRANTS

Active (forming chemical compounds)	Passive (not forming chemical compounds)
O,H,C,N,I	Ar,He,Ne,Kr,Xe,Rn

AQUEOUS MIGRANTS

Mobility	Cations	Anions
Very mobile ($K = 10n - 100n$)		
Constant valence	–	**Cl,Br**
Variable valence	–	**S**
Mobile ($K = n - 10n$)		
Constant valence	**Ca,Na,Mg,Sr,Ra**	**F,B**
Slightly mobile ($K = 0.n - n$)		
Constant valence	**K,Ba,Rb,Li,Be,Cs**	**Si,P**
Variable valence	Tl	Ge,Sn,Sb,As
Mobile and slightly mobile in oxidizing and gley environments ($K = 0.n - n$), *immobile in reducing sulphidic environments*		
Mobile in acid (oxidizing or reducing) conditions. Precipitated by alkaline conditions	**Zn,Cu**,Ni,Pb,Cd	–
Mobile in acid (oxidizing and reducing) conditions	Hg,Ag	–
Mobile or slightly mobile in oxidizing conditions ($K = 0.n - n$), *immobile under reducing (sulphidic and gley) conditions*	–	V,**Mo**,**Se**,U,Re
Mobile and slightly mobile in reducing gley environments ($K = 0.n - n$), *immobile in oxidizing and reducing, sulphidic environments*	**Fe**,**Mn**,Co	–
Slightly mobile in most environments ($K = 0.n - n$, *or less*). *Slight migration with organic complexes*		
Some migration in acidic environments	Al,Ti,Cr,Ce,Nd,Y,La,Ga Th,Sc,Sm,Gd,Dy,Tb,Er Tm,Ho,Eu,Lu,Yb,In,Bi	–
Some migration in alkaline environments	–	Zr,Nb,Ta,W,Hf,Te
Form few chemical compounds (if at all). Characteristically occur in the native state	Os,Pd,Ru,Pt,Au,Rh,Ir	

Bold letters indicate those elements in which biogenic accumulation is important.

TABLE 3-X

Classification of geochemical environments in the supergene zone based on composition (after Perel'man, 1977)

Aqueous composition	Nature of redox environment			
	Oxidizing environment		Reducing environment	
	In rocks containing reducing agents	In rocks containing no reducing agents	Without hydrogen sulphide (gley)	With hydrogen sulphide (sulphidic)
H^+, SO_4^{2-}, Fe^{2+}, Zn^{2+}, Cu^{2+}	Sulphuric acid	–	Sulphuric acid gley	Sulphuric acid sulphidic
H^+, HCO_3^-, Mg^{2+} organic acids	Acid oxidizing	Acid	Carbonate-free gley	Acid sulphidic
Ca^{2+}, HCO_3^-, Mg^{2+}	Neutral oxidizing with slightly mineralized waters	Neutral calcium carbonate	Carbonate gley	Neutral carbonate sulphidic
Cl^-, SO_4^{2-}, Na^+	Oxidizing with strongly mineralized waters	Salt-bearing (chloride sulphate)	Salt-bearing gley	Salt-bearing sulphidic
Ca^{2+}, SO_4^{2-}	–	Gypsum	Gypsum gley	Salt-bearing sulphidic
SiO_2, Na^+, HCO_3^-, OH^-	Oxidizing sodium carbonate	Sodium carbonate	Sodium carbonate gley	Sodium carbonate sulphidic

ficiently similar over extensive regions to develop some general models and exploration methods for drainage samples. Some of the characteristics of different surface environments are shown in Table 3-X in relation to the major dissolved ion composition and are discussed here as a basis for considering alternative sampling procedures.

In cool temperate regions such as those of northwest Europe, which are characterised by relatively high rainfall and high levels of organic activity, two main types of surface environment can be distinguished. First, areas of comparatively impervious crystalline rocks, where water contact times are low, and low concentrations of major cations and anions in surface water, are reflected by exceptionally low conductivity values (Plant and Moore, 1979; Plant and Raiswell, 1983; Steenfelt, 1987). Concentrations of H^+ ions generally exceed those of Ca^{2+} ions, and surface conditions are predominantly acid (partly as a result of organic activity) with large areas of peat bogs and/or acid soils. Oxidation of organic detritus in cool wet climates is generally slow and accumulations of peat and poorly drained acid soils give rise to reducing conditions. The acidity may be further increased by precipitation from air masses containing acid gases, such as SO_2 from industrial sources. In such acid reducing conditions Fe and Mn are soluble but precipitate near to the surface in iron pans and in streams in equilibrium with atmospheric oxygen, resulting in the formation of hydrous Fe and Mn oxides. The ability of these oxides and organic material to absorb large quantities of trace elements, especially the first row transition elements and Ba, is an important control on trace element concentrations in stream channels. In areas of strongly acid surface conditions aluminium may also be mobilized in soil profiles and reprecipitated in stream channels. Younger or uplifted mountain fold belts represent an extreme variant of this type of regime, although the organic component may decrease at high altitude.

The second important type of surface environment in cool temperate regions is represented by lowland areas consisting of agricultural soils underlain by generally more permeable sedimentary rocks, which have surface waters predominantly of the Ca^{2+}–HCO_3^- type (Plant and Raiswell, 1983). The pH varies between 6.5 and 8.5 and both the Eh and the levels of the major cations Ca^{2+}, Na^{2+}, Mg^{2+}, and K^+ and anions are generally higher than in areas of crystalline rocks. Hence there is an increase in water hardness, while the content of organic acids is low since they are precipitated under such conditions. Mobilization of heavy metals by complexation and adsorption on colloidal organic matter, Fe and Mn oxides is also correspondingly reduced.

At higher latitudes, particularly in areas of poorly drained permafrost, the accumulation of organic matter may increase further, giving rise to extensive areas of muskeg swamp, as in parts of northern Scandinavia, Canada and Russia. Finally in arctic/sub-arctic areas such as north Greenland, which have a dry climate and where vegetation is sparse or almost totally lacking, weathering and transport are almost totally mechanical (Steenfelt and Kunzendorf, 1979), and the effects of organic matter and of Fe and Mn oxide scavenging of trace elements in stream channels is correspondingly minor. The chemical dispersion of elements is generally assumed to decrease in cold climates, particularly in areas where a thick permafrost boundary exists, but the detection of halos in snow around silver–arsenide veins (Jonasson, 1976b) suggests that some form of chemical dispersion may be important. One of the most significant problems of high latitudes is the presence of thick glacial and fluvioglacial deposits, which can effectively mask any geochemical response from bedrock. This is particularly important where the material represents exotic tills. Detailed studies in Scotland (Plant et al., 1984), Canada (Shilts, 1984) and Finland (Björklund et al., 1976) suggest, however, that in some areas of extensive exotic till sheets, geochemical anomalies may be displaced by less than 2–3 kilometres, which is relatively insignificant at reconnaissance or regional geochemical mapping scales. This partly reflects the re-incision of stream networks during post-glacial uplift as a result of isostatic readjustment, and partly the local derivation of a significant proportion of till detritus.

In contrast to cold and temperate climates, tropically weathered terrains commonly comprise thick (up to 100 m) sections of local, but deeply leached, overburden. The problem may be compounded where a fully preserved "fossil" lateritic weathering profile has been affected by further deep weathering under a very humid climatic regime, for example in parts of Western Australia. In such a situation many chemical elements, including ore-forming and pathfinder elements, can be strongly depleted in all of the different horizons of the current profile (Butt and Zeegers, 1992). Oxidation of organic matter may be intense with pH varying from acid values in areas of heavy rainfall/dense rainforest to slightly acid to alkaline in more arid terrains. The former type of terrain is characteristic of parts of Central Africa and Brazil, where extensive plateaux of low relief are characterised by deeply leached soils in which aluminosilicates are broken down to give a dissolved phase, mainly cations and silicic acid, and a residue consisting of clay minerals with high Al/Si ratios, secondary iron oxides and resistate minerals. These areas generally grade into seasonally wet/dry regions characterised by lateritic soils elsewhere in Africa and South America. In both the permanently humid and seasonally wet/dry tropics there may be pronounced short and long term climatic fluctuations (e.g., cyclones, droughts) superimposed on the normal pattern of seasonal variation. Finally, in semi-arid to arid regions, such as much of central Australia and north and southwest Africa, there is a more variable surface cover, sometimes with extensive areas of aeolian sands. Surface conditions are strongly oxidizing and the pH is generally high with chloride and/or sulphate species dominant in surface–near surface waters. Here, and in the seasonally wet/dry terrains, intermittent, but frequently turbulent, water flow along the drainage network promotes dispersion and abrasion, so that the coarse sediment fraction is representative of the immediate surroundings while progressively finer material has a more distal provenance. The finest fractions in the more arid regions may contain a windborne component which dilutes the geochemical signature from waterborne sediments (Zeegers et al., 1985).

Types of halos

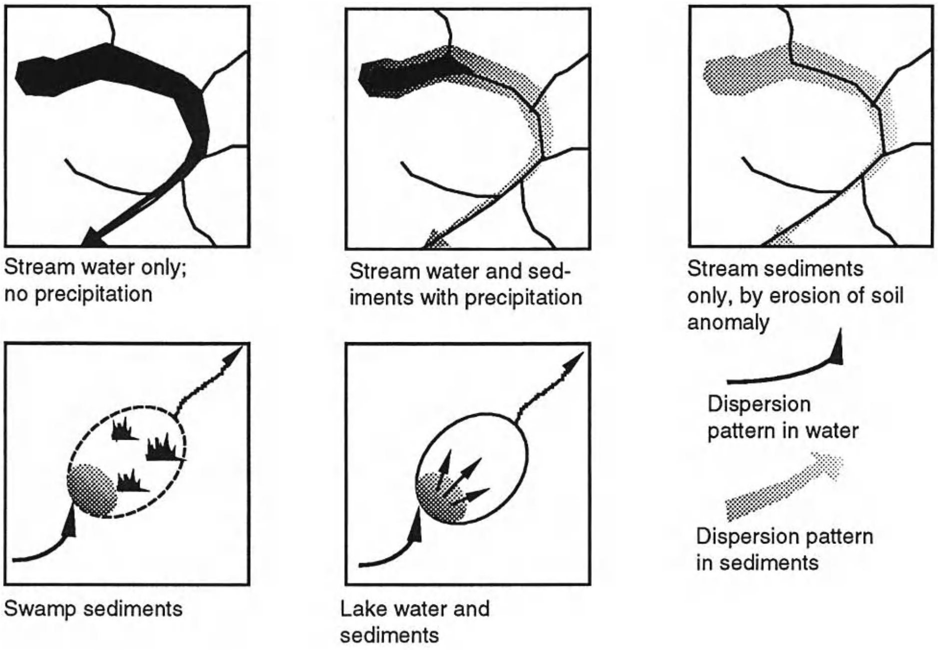
The types of halos developed over orebodies have been classified by Rose et al. (1979) on the basis of their time of formation relative to the host matrix (e.g., syngenetic or epigenetic) and their mode of formation (e.g., clastic, hydromorphic or biogenic). The principal characteristics of the various types of dispersion are summarised in Table 3-XI. Halos are often formed as the result of several different processes and climates (Fig. 3-12). The classification nevertheless provides a relatively simple summary which can be used to develop alternative sampling strategies.

The classification emphasises the importance of clastic syngenetic dispersions particularly in areas not subjected to deep chemical leaching, such as mountainous regions and cold and hot arid environments. In contrast, clays, secondary Fe and other sesquioxides and precipitated salts are likely to be of greater importance at lower latitudes; organic matter is generally rapidly oxidized in such environments. Organic precipitates are generally most important in stream sediments in cool temperate areas particularly in areas of peat bog or muskeg typical of northern Scandinavia, Canada and Russia. Iron oxides generally reflect acid surface conditions typical of leached tropically

TABLE 3-XI

Surficial dispersion patterns and their characteristics (after Rose et al., 1979)

Genetic classification		Dispersion process	Principal transporting agent	Matrix	Mode of occurrence of dispersed elements	Form of dispersion pattern
SYNGENETIC PATTERNS	Clastic	Weathering in situ		Weathered rock Residual overburden Gossan	Resistant primary and secondary minerals; minor constituents of clay minerals and secondary hydrous oxides	Superjacent patterns
		Movement of solid particles by	Gravity	Residual overburden Gossan Colluvium		Fans and asymmetrical superjacent patterns
			Ice	Moraine		Fans
				Glaciofluvial deposits		Trains and irregular patterns
			Water	Sheetwash deposits		Fans
				Stream sediment		Trains
				Lake sediment		Delta fans
			Wind	Aeolian deposits		Fans
	Hydromorphic	Movement of solutions	Groundwater	Groundwater solution	Soluble salt complexes and sols	Fans
			Surface water	Surface-water solution		Trains
				Precipitates and evaporite deposits	Precipitated salts	Lateral patterns
	Biogenic	Plant metabolism	Uptake by living plants	Living-plant tissue	Metallo-organic components	Superjacent and lateral patterns
				Organic debris		
EPIGENETIC PATTERNS	Hydromorphic	Movement of solutions followed by precipitation	Ground water	Any classic overburden	Ions sorbed on clay minerals; hydrous oxides and organic matter; ions co-precipitated and occluded in hydrous oxides; metallo-organic compounds; precipitated salts	Superjacent patterns; fans
				Soils of seepage area		Lateral patterns
			Surface water	Stream sediments		Trains
	Biogenic	Plant metabolism followed by redistribution of organic decomposition products	Nutrient solutions; soil moisture	Any classic overburden		Superjacent and lateral patterns



Stream water only; no precipitation

Stream water and sediments with precipitation

Stream sediments only, by erosion of soil anomaly

Swamp sediments

Lake water and sediments

Fig. 3-12. Principal types of dispersion patterns in surface drainage. Derived from Rose et al. (1979), redrawn with permission of Academic Press, Inc.

weathered profiles, or occur as surface precipitates in organic-rich temperate environments.

The composition of surface waters also varies from dilute acid solutions in areas of high precipitation at high latitudes/altitudes to Ca^{2+}–HCO_3^- solutions in areas underlain by porous sediments. Highly saline Cl^- dominated brines characterise hot desert conditions, whereas SO_4^{2-} enriched waters reflect the oxidation of sulphide, industrial contamination or the presence of red-bed sandstones containing such phases as gypsum. Traditionally groundwaters have been used mainly for exploration in arid terrains lacking well developed surface drainage systems but they are becoming increasingly important in exploration for buried ore deposits including deposits covered beneath thick glacial-fluvioglacial deposits (Chapter 8, this volume). Surface water sampling is also becoming important generally as analytical detection limits are lowered by new techniques such as ICP-MS.

Element associations

The relative mobility of elements in different Eh/pH conditions, and the elements forming stable soluble Cl^-, CO_3^{2-} and SO_4^{2-} species, are given in Tables 3-VIII and 3-IX. In humid oxidizing environments such as tropical terrains many ore forming and pathfinder elements may have been leached and are represented in stream sediments only where they have been reprecipitated as secondary phases or where they occur as detrital grains. Gold is a special case which, until recently, was considered to be resistant to alteration in the surface environment. Detailed studies of the dispersion of gold in tropical terrains, (e.g., Lecomte and Colin, 1989) suggest that gold is present as fine (<500 μm) particles formed by the dissolution of gold grains and reprecipitation and adsorption/complexation of secondary Au. This is consistent with the findings of Butt and Zeegers (1992) who have shown that gold may be remobilized as chloride, thiocyanite or thiosulphate complexes in certain types of oxidizing surface environments. The platinum group elements (PGE) are generally relatively immobile, Ir being the least mobile of all. Iridium can be used to determine the extent of mobilization of the other PGEs and of Ni, Co and Cu during the weathering of basic lithologies (Taufen and Marchetto, 1987). Of the suite of elements associated with sulphide deposits in ultrabasic-rocks Ni, Co and Cu are the most mobile particularly in acid oxidizing conditions. Uranium, Mo, V, Se and Zn are also easily leached in oxidizing conditions, U, Mo, V and Se being particularly mobile in alkaline conditions. Of the ore-forming elements only Sn, W and the PGE have low mobility in all types of surface environments. Most ore forming and pathfinder elements are least mobile in reducing conditions typical of acid soil profiles, peat bog, muskeg and stream sediments which are generally found at high latitudes. Manganese and Fe are unusual in being relatively more mobile in reducing conditions, and this behaviour can give rise to false anomalies where reducing soil solutions or groundwater enters streams which are relatively oxidizing. Other situations which can give rise to false anomalies for other elements are shown in Table 3-XII. The ability of organic matter to act as an electron donor and hence as a powerful reducing agent combined with its ability to sorb and complex trace elements is the basis of methods of organic stream sediment sampling applied in northern Scandinavia (Brundin and Nairis, 1972) and Canada (Jackson et al., 1978).

Considering the elements used to indicate the tectonic setting of rock assemblages and water/rock interaction around orebodies (Chapter 2, this volume) the high field strength elements such as the REEs, Al, Y, Th, Nb, Ti, Ta, Cr, Zr and Hf are likely to be useful in most terrains since they are relatively resistant to alteration by chemical or biological processes. Titanium, Y and Zr are particularly important since, as noted in Chapter 2, they are widely used in classifying basalt and other igneous rock types. Other elements such as B, which may be incorporated in tourmaline as a result of mineralization processes, and which can indicate the presence of Sn, base metal deposits and some types of epithermal Au deposits, may also survive deep leaching. The alkali and alkaline earth elements such as Na, K, Mg, Ca, Li, Rb are likely to be deeply leached in regimes dominated by chemical weathering and their ratios disturbed, although they can provide useful information in terrains where dispersion is predominantly detrital. Hence although these elements may be of value in exploration for volcanic exhalative, granite and porphyry style mineral deposits using rock samples (Govett and Atherden, 1988), they are unlikely to be useful in stream sediment or lake samples in areas of present or past deep leaching and the REEs and other poorly mobile elements are likely to be of greater value. The REE patterns of the Pikes Peak granite of the southwest USA have been shown to be preserved in stream sediment samples (Howarth et al., 1981) and would be predicted to be stable in most surface environments (Taylor and McLennan, 1985). Element ratios such as Ga/Al, Sn/Zr, and PGE and REE patterns (Chapter 2, this volume) are likely to be useful in most environments except those of intense chemical leaching, whereas ratios such as Mg/Li, K/Rb and Ba/Sr are likely to be of value only where samples contain a high proportion of clastic rock fragments and primary minerals. B/Ga ratios may be useful in determining sediment–magma interaction, including in deeply weathered tropical terrain, if the B occurs in tourmaline (Taylor et al., 1987). Evidence of disequilibrium between U and its daughter products, which can be calculated by measuring the difference between U determined by total methods such as the delayed neutron method and equivalent U determined by gamma spectrometer, may provide particularly useful information on recent weathering processes (<ca. 1 million years). Lead isotopic data may also be useful in detecting buried U, base metal and some types of Au deposits (Gulson et al., 1987).

GENERAL IMPLICATIONS FOR SAMPLING

Detailed descriptions of alternative sampling media in different surface environments are discussed by specialists in succeeding chapters but some general recommendations about the selection of alternative sampling methods for different types of surveys in different surface environments are made here. Two main types of samples can be distinguished according to the objectives of particular surveys (Plant et al., 1988a):

(1) Representative sampling designed for the preparation of high precision multi-element geochemical surveys.

(2) Samples designed to enhance anomalies.

Representative (stream-sediment) samples — Type (1)

Active stream sediments, which comprise composite samples of weathering products and have a limited Eh range because they are in contact with atmospheric oxygen, are the most representative sample type. They have been used as a basis for geochemical mapping in areas ranging from tropical rain forest, through savannah and desert, to high mountain ranges and arctic regions. This type of sample is particularly important in geochemical mapping where petrogenetic elements are included in the programme, as in the case of the NURE, CUSMAP and other resource analysis programmes in the U.S.A., the regional geochemical programmes conducted by the BGS in Britain, the BRGM in France and north Africa and the Nordkalott project in the Scandinavian countries (Plant et al., 1988a).

TABLE 3-XII

Major geochemical barriers of the supergene zone

Class of the barrier	Geochemical environment		Concentrations of elements	Examples of concentrations
	Before the barrier	Beyond the barrier		
Physiochemical barriers				
Oxidizing iron or manganese	Gley	Oxidizing	Fe, Mn	Bog and lake ores
Oxidizing sulphur	Hydrogen sulphide	Oxidizing	S	Sulphur deposits of the Sernye Bugry Gaurdak and Shorsu types (in Kazakhstan)
Reducing hydrogen sulphide	Oxidizing or gley	Reducing hydrogen sulphide	Fe, V, Zn, Ni, Co, Cu, Pb, U, As, Cd, Hg, Ag, Se	Epigenetic uranium deposits, cupriferrous sandstones
Reducing gley	Oxidizing	Gley	U, Se, Cu?	Epigenetic uranium deposits, native copper in bogs
Pyrite	Oxidizing or gley	Gley or hydrogen sulphide	Chalcophile elements	Cementation zone of sulphide deposits
Sulphate	Carbonate or chloride	Sulphate	Ba, Sr, Ca	Barite and celestine
Carbonate	Chloride, sulphate, bicarbonate with slightly mineralized waters	Hard waters saturated with CO_3^{2-}	Ca, Fe, Ba, Sr	Calcite, witherite, strontianite, siderite, and others

Basic	Neutral, acid, basic	More basic	Fe, Ca, Mg, Mn, Sr, V, Cr, Zn, Cu, Ni, Co, Pb, Cd	Secondary aureoles in carbonate rocks on sections of oxidizing sulphide ores
Acid	Neutral acid, basic	More acid	SiO_2, Mo, Se, U	Uranium-selenium-molybdenum ores of epigenetic deposits, secondary aureoles, silicified wood
Evaporating	Strongly mineralized waters	Waters with higher mineralization or evaporated	R^+, R^{2+}, U, Mo, Cl, S, F, Zn, N, I, Br	Frequently anomalous evaporites without ore
Adsorption	Waters of low activity	Waters of low activity	R^+, R^{2+}, P, S, V, Cr, Zn, Ni, Co, Cu, U, As, Mo, Hg, Ra	Secondary aureoles of many metals in peats and clays, uranium ore concentrations in peat bogs and clays (supposedly)
Mechanical barriers				
Aqueous-Air	Strong mechanical migration	Less vigorous migration	Fe, Ti, Zr, C, Cr, Nb, Th, Ta, Sn, Pd, Au, Ru, Ir, W, Hf, Os, Pt, Rh and others	Diamond, gold, platinum, thorium, zirconium, titanium, and other alluvial deposits
Biochemical barriers				
Class not identified	Diverse	Diverse	O, C, H, Ca, K, N, Si, Mg, P, S, Na, Cl, Fe, Ba, Sr, Mn, B F, Zn, Rb, Cu, V, Ge, Ni, As, Co, Li, Mo, I, Se, Ra	Secondary aureoles and non-mineralized anomalies in the humus horizon, accumulation of guano (N and P) and possibly less common elements in the bones

Where stream sediments contain a significant detrital component field sieving should be employed to ensure that adequate quantities of the fine size fractions are collected. Slurry screening (wet sieving with the minimum of water; Plant and Moore, 1979) ensures that the fine and colloidal fractions are recovered while achieving more quantitative separation of the fine fraction than is the case when sieving is carried out on previously dried samples.

The optimum size fraction of stream sediments varies in different environments. A generally coarse upper screen is required at high latitudes and altitudes, while organic stream samples have been widely employed in northern Scandinavia, where normal sedimentary material may be lacking for long distances in the stream channels. Centre lake samples also comprising predominantly organic material have also been collected for geochemical mapping over large areas of Canada. In arid and semi-arid terrains an ultrafine or coarse fraction may be most suitable since intermediate fractions may comprise mainly barren siliceous material.

Stream sediment sampling is generally precluded where the surface drainage is dominated by lakes and in karst areas, and it is generally replaced in such areas by lake sediment and soil sampling, respectively. In areas of heavy metal contamination, stream sediments can yield ambiguous data (Chapter 13, this volume), and overbank sediments or deep soils may be used instead.

In some cases it is desirable to supplement stream sediment sampling with water sampling, particularly in arid terrains where buried ore deposits are sought and for U exploration generally in areas where the levels of dissolved carbonate are high. In low-lying arid terrain the long residence time, the high salinity and low organic content of surface water and the relatively stable flow regime mean that the trace-element contents may be well above the analytical limit of detection of several multi-element methods. However, a sound knowledge of mineral equilibria in aqueous systems in required for data interpretation (Chapter 8, this volume).

The systematic determination of U and Zn in surface waters to identify uranium and base-metal deposits, and of pH, total dissolved carbonate and total conductivity for interpretative purposes, has been shown to be useful in Greenland and in Britain. Where levels of total dissolved carbonate or P are high, U determinations in water are preferred to those made on stream sediment samples, which may fail to show anomalies even if they have been collected directly over uranium mineralization (Institute of Geological Sciences, 1978).

Samples designed to enhance anomalies — Type (2)

As discussed earlier, ore deposits are generally also associated with increased quantities of secondary minerals such as oxides, carbonates and sulphates and sometimes metals bound to organic matter in the surface environment. Special sampling media can be used to take advantage of the physical or chemical properties of such phases which distinguish them from common, predominantly silicate, rock-forming minerals. Heavy-mineral concentrates, aimed at improving contrast for elements held in resistate mineral phases, are particularly useful in exploration for elements that are of high value and low average concentration and which occur in discrete heavy-mineral grains, including the PGE, and sometimes, Au. They may also be useful in concentrating material from iron pans and ironstones that are enriched in trace elements and they have been found to be effective in laterite and arid terrains.

Precision and sensitivity are less important in sampling and analysis that is based on Type (2) samples. Moreover, Type (2) samples are generally less suitable for multipurpose geochemical mapping because petrogenetic elements are not included. In the case of colloids large numbers of false anomalies can be generated that reflect complexation and adsorption in the surface environment rather than the concentration of elements in bedrock. This is particularly the case where organic matter may sorb aerial contaminants or where secondary Mn and Fe oxides are enriched in trace elements. On the other hand, mineral exploration, particularly for certain elements, such as Au and its pathfinders, may be performed more profitably with the use of Type (2) samples since the average level of Au in stream sediments is commonly below the detection limit of most of the analytical techniques used for geochemical mapping. Heavy-mineral concentrates are of value in detecting Au where it occurs in +80 mesh (180 μm) particles, whereas epithermal Au deposits and mineralization at low latitudes may be better detected by the use of colloids or ultrafine stream sediment samples. Further details of sampling methods and their advantages and disadvantages in different types of surface environment are discussed by specialists in the following chapters.

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Chapter 4

STRATEGIC CHOICES IN DRAINAGE GEOCHEMISTRY

MARTIN HALE

INTRODUCTION

A bewildering array of procedural options faces the explorationist embarking on a drainage geochemistry survey. They can be classified into three groups, although their inter-relations have to be considered in making strategic decisions. The first group of options is concerned with the scientific and commercial objectives of the survey, and is strongly influenced by the state of knowledge about geochemical dispersion and its utilization to maximum exploration advantage. The second group comprises factors of logistics and technical feasibility. Finally, the budget for the survey prompts certain choices that help contain costs whilst still fulfilling survey objectives.

SURVEY OBJECTIVES

Whatever the specific objectives of a drainage geochemistry survey, they are met through the considered application of sampling, analysis and data reduction and presentation. Decisions about which methods to adopt at each of these stages cannot be taken in isolation; rather the last stages are best decided first, and the sampling and analysis are then programmed to provide the necessary data input. Nevertheless, these three stages, along with the role of the orientation survey, provide a basis for discussing the strategic choices that are relevant to achieving the objectives of different drainage geochemistry surveys.

Sample media

The choice of sample medium for tracing dispersion patterns in drainage systems is firstly between waters and sediments. At depth, water alone is usually the only available sample medium, but in surface drainage channels there is a choice between water and sediments experiencing various forms of transport (Fig. 4-1).

The solubility — or aqueous mobility — of the element(s) of interest determines the more suitable medium. For elements that are highly soluble, or

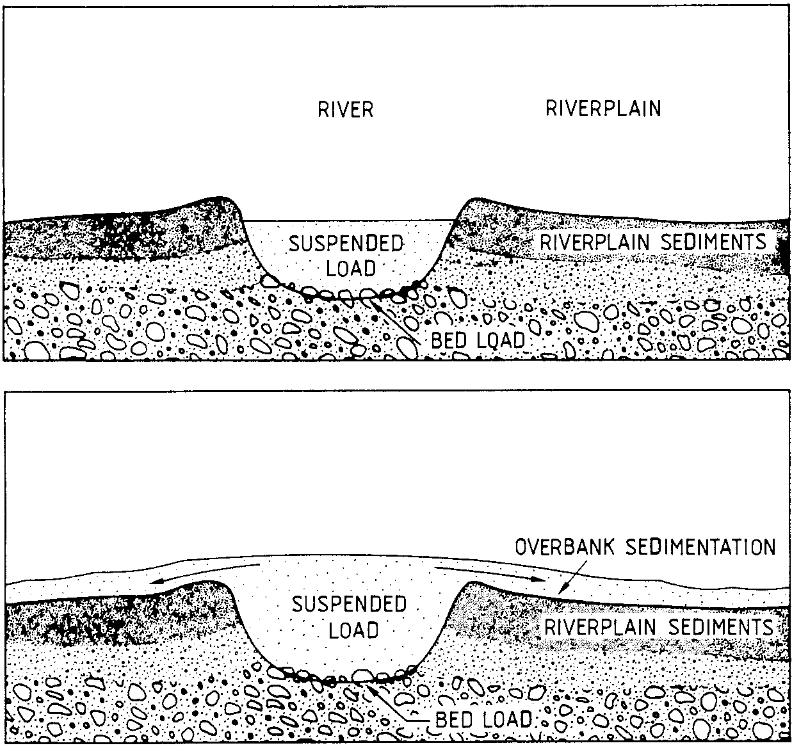


Fig. 4-1. Stream discharge under normal conditions (top) and during flood (bottom) showing bed load, suspended load and overbank sediments (from Ottesen et al., 1989).

highly mobile, such as U, Mo, F and Zn, water is often the medium preferred, although consideration of the overall chemistry of the waters to be sampled and its influence on the solubility of target element(s) is essential (Chapter 8, this volume). When the element of interest occurs within the lattice of a resistate mineral, the element is regarded as relatively immobile and sediment is usually the obvious sample medium. Examples include Cr present as chromite, Sn as cassiterite, Nb as pyrochlore, W as scheelite or wolframite, and Au, although traces of these elements can also be found in solution. Elements of intermediate mobility are those which are substantially soluble in the vicinity of oxidizing sulphide mineralization, but whose solubility is highly sensitive to changes in redox potential (Eh) and pH, leading to the formation of allochthonous or hydromorphic patterns in the sediments at some distance from their initial dissolution. Elements of intermediate mobility include Cu, Ni, Co, Ag and As.

Waters (hydrogeochemical dispersion patterns)

Waters have the advantage of furnishing a highly homogeneous sample compared to sediments, but in general have found no particular favour by virtue of this attribute. This may be due to their several disadvantages. First, their concentrations of ore elements and pathfinders are usually low and hence analysis is often difficult or inconvenient, compared to that of sediments. An analytical technique with a suitably low detection limit obviates this problem, and such techniques for U and F contribute to making waters the preferred sample medium for tracing drainage dispersion patterns of these elements. Second, variations in water flow rate due, for example, to heavy rainfall, can either flush out additional soluble constituents or simply dilute the established soluble load. Either effect renders interpretation of data acquired in a fluctuating hydrologic regime more difficult. This problem can sometimes be alleviated by ratioing the element(s) of interest to total dissolved solids (TDS) or conductivity (which is proportional to TDS), but sampling during a period of stable flow is to be preferred. Perhaps the greatest disadvantage of waters is their fragile chemical stability, which in turn calls for attention to scrupulous cleanliness of water containers and exercising filtration and/or acidification options on samples immediately after their collection. Wenrich-Verbeek (1977a) found that in general field-filtration of stream water circumvents the leaching of elements from the suspended fraction during storage, and subsequent acidification minimizes adsorption of dissolved species onto sample container walls.

Groundwaters have the advantage of offering a direct guide to subsurface geochemistry. As such they are a valuable sample medium in exploration for ore deposits that have no surface expression, and have probably been most widely used in the search for uranium mineralization (Chapter 15, this volume). Decisions are required on what parameters must be determined, in addition to the concentrations of ore elements and pathfinders, in order to characterize groundwater chemistry. The redox state of the water tends to be particularly important: oxidizing groundwaters can carry much higher concentrations of dissolved U than reducing groundwaters, and the transition to reducing conditions can indicate ore accumulation; conversely, reducing groundwaters can carry relatively high concentrations of base metals, which precipitate in various ways as Eh rises. The pH of the water also influences the solubility of trace elements, as do the concentrations of certain other anions, cations and soluble organic complexes, which can form insoluble compounds with trace elements if the solubility products of the compounds are exceeded. Measurements of Eh, pH and the appropriate complexing anions and cations (and possibly soluble organic matter) may be vital if the concentrations of a trace element are to be interpreted in their full thermodynamic context. The age of groundwaters can also be important and may be determined by isotopic methods. Old waters may have acquired relatively high trace element concentrations by virtue of nothing more than their long residence times and protracted opportunity to leach their host rock, and such enrichments have to be distinguished from significant anomalies.

Stream waters, especially those which are to some degree turbulent, are oxidizing and very young, and so measurements of Eh and age are rarely, if ever, relevant. Measurement of pH, however, can provide vital supplementary data for most stream water trace element geochemistry surveys, as most trace element cations show an increasing predisposition to precipitation in some way as their pH of hydrolysis is exceeded (Tables 3-VIII and 3-IX). For many anionic complexes, however, such as the molybdate and uranyl anions, solubility is dictated as much by the presence of other ions as by pH and the determination of other soluble species in stream water may be as important an aid to data interpretation in stream water as in groundwater.

Fine sediments (hydromorphic dispersion patterns)

Stream (and lake) sediments have the advantages of incorporating clastic and hydromorphic dispersion patterns into a medium which constitutes a highly robust geochemical sample. But sediments are a far more diverse and inhomogeneous medium than water, and choices must be made about the fraction of the sediment that is to be recovered.

The sediment transported in stream channels comprises the bedload and the suspended load. The latter represents the finest, lightest, most physically mobile and probably the most chemically active (adsorptive) part of the sediment. Perhac and Whelan (1972) showed that the suspended colloids downstream from zinc mineralization in Tennessee were more anomalous in lead and zinc than the coarser suspended particulates and bedload sediments. However, the existence of a suspended load is solely a function of stream flow rate and turbidity, so that the same material reports in the bedload when flow rate and turbidity fall. Sampling the suspended sediment is often more difficult than sampling the bedload, and additional problems can arise from the varying availability of suspended material, both in geographical and temporal terms. A closely related sample medium which overcomes some of these limitations is the overbank sediment (see below).

Fine clay minerals, colloidal Fe and Mn oxides and some insoluble organic compounds have large, electrically-charged surface areas, and in streams these constituents adsorb and co-precipitate soluble trace elements. There is a strong tendency for the resulting hydromorphic dispersion patterns to be best developed in the fine fraction of stream sediments. The <80 mesh (<177 μm) fraction is often collected for its high clay mineral content, but this fraction also includes much silt and coarser material, and in some surveys a finer mesh size yielding a higher proportion of clays may be appropriate. In Surinam, for example, Zeegers and Pollack (1980) found the <37 μm fraction to be more useful. Slurry screening with the minimum amount of water tends to lead to better recovery of the fine and colloidal fractions and a more quantitative separation of the fine fraction compared to dry sieving. In arid climates the finest material my be windborne, and a slightly coarser fraction, such as the 250 μm to 1 mm fraction, may avoid anomaly dilution (Bugrov, 1974). In stream sediment surveys generally, either slurry screening or dry sieving at the sample site ensures that sufficient material of the desired fraction is acquired.

Colloidal iron and manganese oxides exhibit a tendency to precipitate as coatings on pebbles in streams. Such coatings, usually black in colour, are common on stream-bed pebbles in temperate regions where the bedrock provides an adequate supply of soluble iron and manganese. As these elements precipitate from stream water, they co-precipitate (or adsorb) other trace elements. The resulting hydromorphic dispersion patterns can be traced in these coatings by first collecting coated pebbles at the sample sites and subsequently selectively analyzing their coatings (Carpenter et al., 1975, 1978; Whitney, 1975, 1981; Nowlan, 1976).

Similarly, organic matter in streams in temperate and glaciated regions adsorbs trace elements (Table 3-IV) and reflects their hydromorphic dispersion patterns. Brundin and Nairis (1972) compared mineral stream sediments, organic matter in streams and stream water as drainage reconnaissance sample media in northern Sweden, and found that organic matter was equally or more suitable than the other sample media in prospecting for Cu, Pb, Zn, Mo and U.

Coarse sediments (mechanical dispersion patterns)

The bulk of the sediment in most streams is mineral and rock fragments derived from the mechanical dispersion of outcropping rocks, ores and their weathering products. The detection of anomalies in this dispersion medium is often optimized by the selection of a coarser fraction than that suitable for detecting hydromorphic patterns. For example, Davis et al. (1990) found Ba anomalies to be most pronounced in the relatively coarse 600–250 μm fraction of the sediments of wadis draining baryte mineralization in Saudi Arabia and in the 600–150 μm fraction of streams draining baryte mineralization in Scotland; anomalous concentrations of Ba appear in finer fractions further down-stream as baryte breaks into cleavage fragments.

Indurated ferruginous weathering products also tend to maintain a relatively coarse grain-size when they are carried into and along surface drainage channels, and where they have formed near mineralization these particles often carry an anomalous trace element signature. Dunlop et al. (1983) compared Pb in the <63 μm and the 2.12–1.18 mm fractions of material in drainage channels draining the Elura polymetallic deposit in New South Wales, Australia, and found that the coarser fraction, which contained abundant ferricrete fragments, yielded better contrast anomalies and longer dispersion trains related to mineralization, especially after correcting the Pb values for the Fe content of samples (Fig. 4-2). Similarly, Martin et al. (1984) enhanced anomalies of several elements in the sediments of streams draining mineral deposits in the Ardennes of Belgium and the Massif Central of France by analyzing paramagnetic separates of the 250–63 μm fraction of samples, which they found to contain relatively coarse-grained ferriferous materials, including clastic oxidation products (gossan).

As the medium in which anomalies are sought becomes coarser, its homogeneity tends to decrease, introducing possible representativity problems in sampling. When only a very few mineral grains can constitute an anomaly, it is necessary to take comparatively large samples in order to ensure that each sample contains the appropriate number of particles of the target mineral that

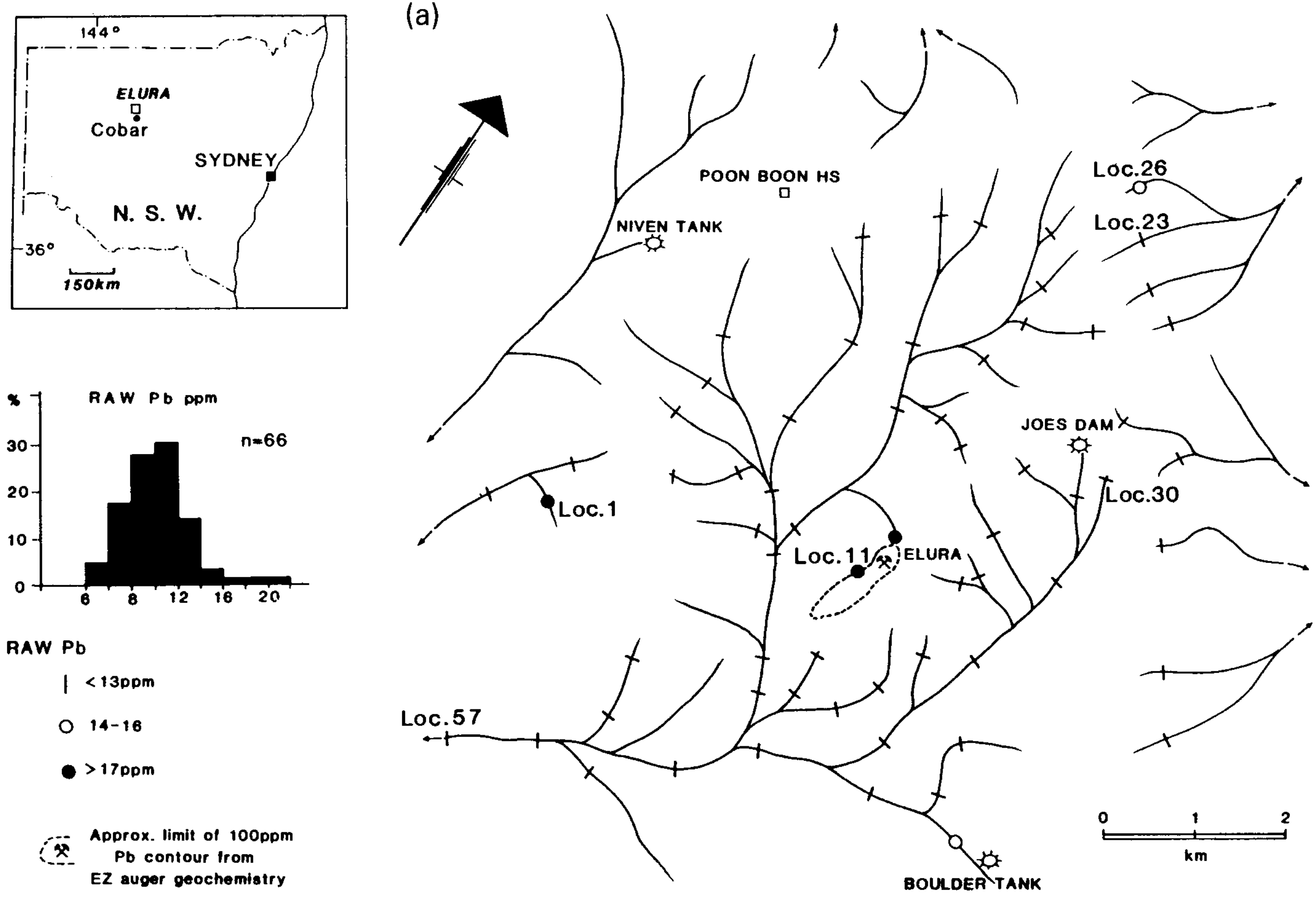


Fig. 4-2. (a) Importance of size fraction of samples from drainage channels at Elura, New South Wales, Australia: <63 μm fraction shows restricted dispersion of Pb (from Dunlop et al., 1983).

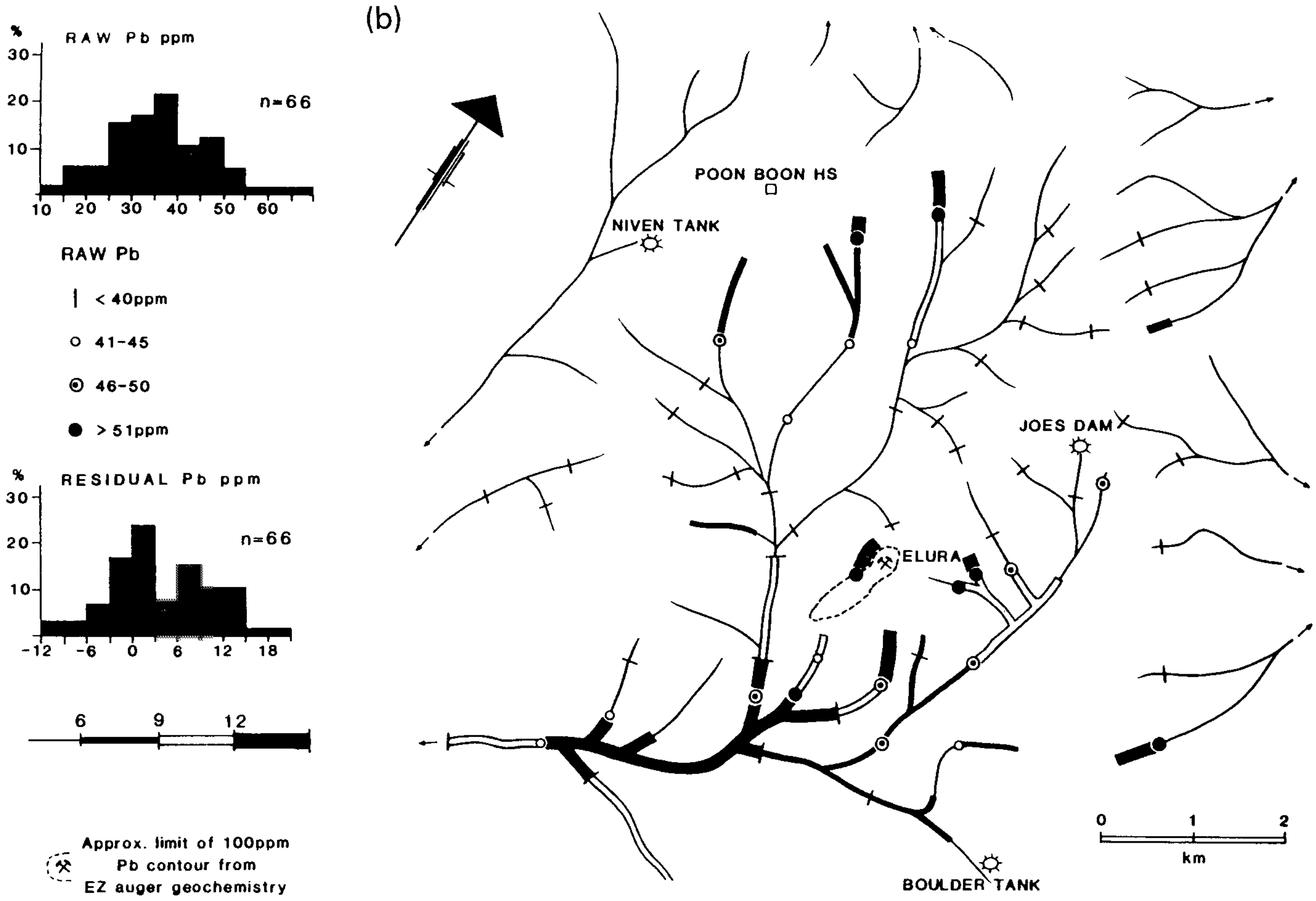


Fig. 4-2. (b) Importance of size fraction of samples from drainage channels at Elura, New South Wales, Australia: 2.12–1.18 mm fraction shows longer dispersion trains and higher contrast anomalies for Pb (dot symbols), which are further enhanced as residual Pb after correction for Fe content of samples (worm lines) (from Dunlop et al., 1983).

unambiguously reflects the anomaly status of each sample site. Many of the target minerals that experience predominantly clastic dispersion in drainage systems also have a high specific gravity, and so offer the option of on-site (or subsequent) sample volume reduction through selective concentration of denser minerals. There are numerous examples. Nuchanong and Nichol (1992), for example, panned 30 litres of stream sediment at each sample site during investigations into gold dispersion in Thailand. Salpeteur and Jezequel (1992) found that Pt and Pd concentrations downstream from PGE-bearing ultramafics in Madagascar were much higher in concentrates panned from 40 kg of sediment than in various sieved fractions of non-panned sediment. Tompkins (1987) obtained ilmenites and garnets as pathfinders for kimberlites in Brazil by panning 200 litres of stream sediment at each sample site.

In the case of surveys for sparse heavy minerals, a more careful selection of sample site within the stream channel than simply choosing active (transported) sediment is important. Minerals of high specific gravity preferentially accumulate in high-energy environments where stream flow is sufficient either to winnow away or limit deposition of lighter minerals (Fletcher and Day, 1989; Chapter 14, this volume).

Analysis

There is still more choice in geochemical analysis of drainage samples than there is of sample media, and extensive reviews of procedures have been made by Fletcher (1981), Potts (1987), Van Loon and Barefoot (1989) and Hall (1992a). However, options in analysis are narrowed by the nature of the sample material, by the need for data of adequate sensitivity for the element(s) of interest and, in many cases, the desirability of maximizing anomaly contrast. In practice there are often two component parts to this choice: selecting the analytical instrumentation most appropriate for making the element determinations; and selecting an appropriate method to prepare samples for presentation to the instrument. These two components of choice are rarely independent, but rather inter-related, certain instruments demanding the analyte to be introduced in a particular form (e.g., solid, acid solution, organic solvent or vapour).

Sample preparation

Filtered natural waters may require no further preparation if the instrument to which they are to be presented for analysis has sufficiently low limits of detection for the elements of interest. If not, a pre-concentration step is required. For major elements and the more abundant trace elements, a ten or one hundred fold concentration by evaporation of much of the original sample usually yields concentrations in the remaining solution above instrumental detection limits. Evaporation to dryness may be still more effective if the solid residue can be analyzed without re-dissolution or can be taken up in a small volume of dilute acid. Where the trace element concentrations are extremely low (for example, dissolved gold) extraction from a large aqueous sample into a small volume of organic solvent (such as methyl isobutyl ketone, MIBK) is the preferred concentration method. This can also be used for the determination of trace quantities of volatile elements, which may be lost if the sample is heated to effect evaporation.

Sediments may be dry when they are collected, but if they are not the first decisions to be made concern the method of drying. Ambient air-temperature drying is slow but ensures retention of volatiles; freeze-drying offers the same advantage, is much quicker and produces a friable powder that is more convenient to sub-sample. Oven-drying at 80°–100°C is efficient when volatile elements, some of which may be partially lost, are not to be determined. Some types of sediments have to be ashed at 450°C to drive off the organic matter which could otherwise prove dangerous during acid dissolution of the sample or cause spectral interferences during instrumental determination; a wide range of volatile elements is likely to be completely or partially lost during ashing.

Drying may be a prerequisite to simply weighing a sub-sample for analysis, or to sieving the desired fraction of the sample for analysis. When this fraction is relatively coarse (above, say, 200 μm) or its grain-size distribution is heterogeneous, it is desirable to pulverize the material prior to analysis. During pulverization one must again be conscious of the possible loss of volatiles and select the pulverizing equipment accordingly. Loss of gold grains by smearing onto the walls of a mill is also a potential problem during pulverization.

Element determinations in solution

A choice which has occupied exploration geochemists for several decades is that of the reagent(s) to be employed for taking a sub-sample of sediment into solution for analysis. When mixtures of strong acids are used on sediments, their attack is often regarded as "total" in order to distinguish their effect from that of selective leaches. In practice most minerals dissolve in one or more strong acids but some resistate oxides (e.g., cassiterite, chromite, beryl, ilmenite, rutile, spinel) are incompletely dissolved. Truly total dissolution is achieved by first fusing the sediment sub-sample with a flux, such as lithium metaborate, to give a bead which is subsequently taken up in acid; but a high dilution factor is unavoidable, and this restricts the number of trace elements that can be detected with this procedure. Chao and Sanzolone (1992) review the applications in geochemical analysis of hydrofluoric, hydrochloric, hydrobromic, nitric, perchloric, sulphuric and phosphoric acids in open and closed systems, and the applications of sodium carbonate, sodium hydroxide, lithium metaborate, lithium tetraborate, sodium peroxide, ammonium iodide, potassium pyrosulphate and sodium pyrosulphate fusions.

From the earliest days of exploration geochemistry it was recognized that a partial leach, termed "cold-extraction" because of the use of hydrochloric acid or citrate solution at room temperature, selectively takes into solution only the loosely-bound metals; and as these are particularly abundant where metals experience hydromorphic dispersion around oxidizing sulphide mineral deposits, the resulting dispersion patterns include high contrast anomalies. Subsequently many partial, or selective, leaches have been advocated (Chao, 1984). Although the selectivity of most leaches is far from perfect, their use does produce trace element dispersion patterns in which the geochemical response from detrital oxides and silicates is substantially suppressed.

Schemes employing the sequential application of different selective leaches have been devised, and that used by Sandström (1984) is typical: first ammonium acetate selectively leaches trace elements adsorbed onto clay minerals; then cold hydroxylamine hydrochloride removes those associated with manganese oxides; next hydrogen peroxide releases those complexed by organic matter; hot hydroxylamine hydrochloride (alternatively ammonium oxalate) leaches elements associated with iron oxides; and the residue is dissolved in a mixture of strong acids. Data from such schemes can be used to glean information about dispersion pathways. In the vicinity of polymetallic sulphide mineralization in Finland, much of the zinc is leached from the clay fraction of stream sediments by ammonium acetate, suggesting that zinc is highly mobile; a high proportion of the copper, however, is leached by hydrogen peroxide, indicating that copper is strongly complexed by organic matter (Fig. 4-3).

Natural waters, concentrates from the evaporation of natural waters, selective leaching of sediments and total dissolution of sediments all provide essentially aqueous analytes which lend themselves to determination of their dissolved constituent elements by any one of several analytical instruments. Most of these instruments can also accommodate organic solvents and so can be used where a solvent extraction of the element(s) of interest has been used.

Of the instrumental methods suitable for the analysis of aqueous solutions, atomic absorption spectrophotometry (AAS) has been widely used in exploration geochemistry since it was first introduced in the early 1960's. Viets and O'Leary (1992) have reviewed its current role (Fig. 4-4). It is particularly well-suited to the determination of the transition metals, alkalis and alkali earths by nebulization of the analyte into an air-acetylene flame. Elements with volatile hydrides, including arsenic and antimony, can be determined by generating the hydride from an aqueous solution and sweeping this vapour into the spectrophotometer, and in a similar fashion mercury can be determined with great sensitivity as the elemental vapour. Several precious metals, including gold, can be determined by introducing organic solvents, into which the metal has been extracted, into a spectrophotometer equipped with a graphite furnace. Still more elements can be determined by using a nitrous oxide and acetylene flame. Though versatile, AAS is limited to the determination of one element at a time, so that several elements may be determined in the same analyte only by presenting the analyte to the instrument on several separate occasions, on each of which the instrument set-up has been adjusted to be appropriate for the element sought.

When the survey objectives include information on a wide range of elements, two modes of inductively coupled plasma spectrometry offer convenient multi-element capabilities and other attractive attributes, especially long linear

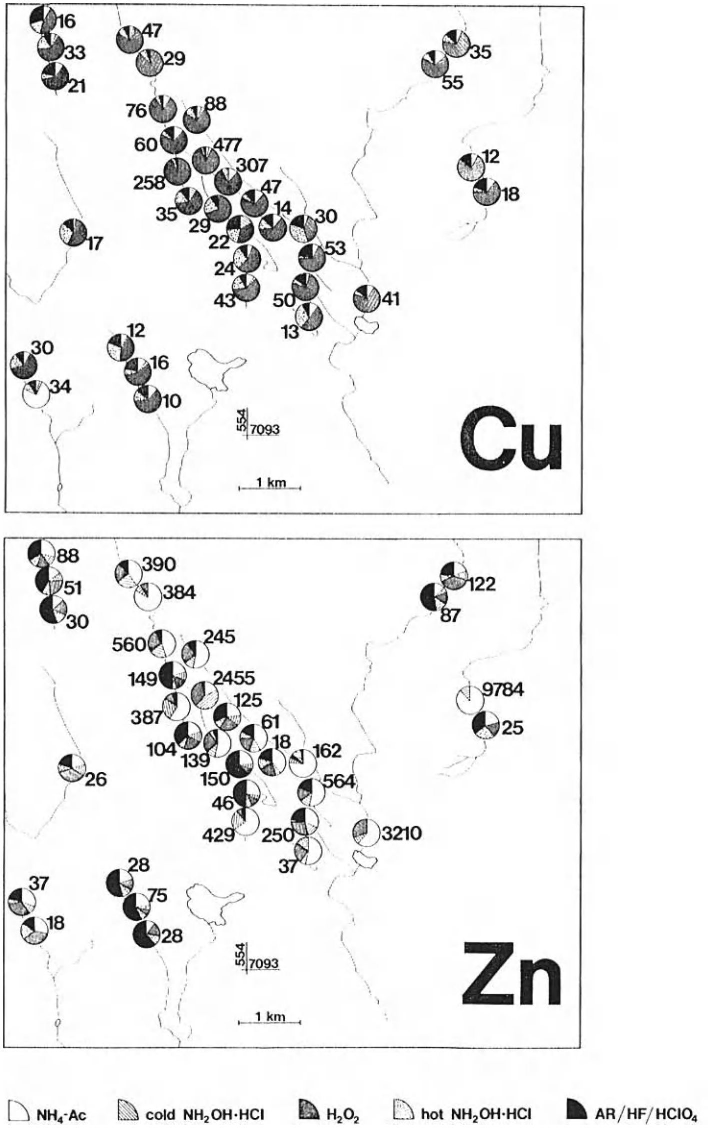


Fig. 4-3. Sequential extractions of Cu (top) and Zn (below) from stream sediments draining polymetallic sulphide mineralization (in centre of map area) at Talvivaara, Finland; cumulative proportions of metal extracted in five stages are shown as pie diagrams at each sample site and total metal content is shown in ppm (from Sandström, 1984).

dynamic calibration ranges. Jarvis and Jarvis (1992) point out that inductively coupled-plasma atomic emission spectrometry (ICP-AES) has excellent sensitivity for elements of low atomic number, alkali earths, refractory elements, rare earth elements (REE) and the transition metals. The range of elements

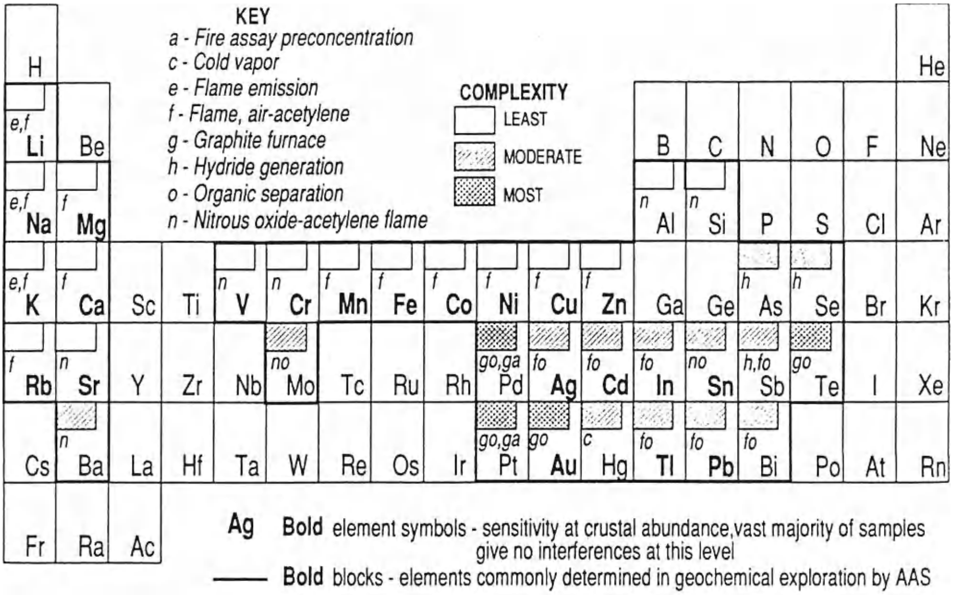


Fig. 4-4. Suitability of elements to determination by AAS methods (using acid solution, except as noted) (from Viets and O'Leary, 1992).

available from ICP-AES can be extended still further by hydride generation and solvent extraction techniques. A rival to ICP-AES, inductively coupled plasma mass spectrometry (ICP-MS) became available in the mid-1980's. According to Hall (1992b), its advantages are superior sensitivity (generally by several orders of magnitude), simpler spectra (only a few lines per element) and hence less spectral interference, and isotope capability. As a result, it is possible to determine many elements, including precious metals and rare earths, at their natural abundance levels using ICP-MS. Hall (1992b) considers these two ICP instruments as complementary (Fig. 4-5) and Jarvis and Jarvis (1992) note that sample solutions prepared for ICP-AES can also be used directly for the determination of ultra-trace levels of heavier elements by ICP-MS.

Element determinations on solids

There are three methods in general use for the determination of the total concentration of elements by the direct analysis of powdered sub-samples: dc-arc source atomic emission spectroscopy (ES); wavelength dispersive X-ray fluorescence (XRF); and instrumental neutron activation analysis (INAA). Each has the advantage of considerable simultaneously multi-element determination capability but, as Plant et al. (1988a) mention, each is best suited to a particular range of elements (Table 4-I) and so there is a choice to be made according to survey objectives.

The longest-established of the methods is ES, which is most suitable for

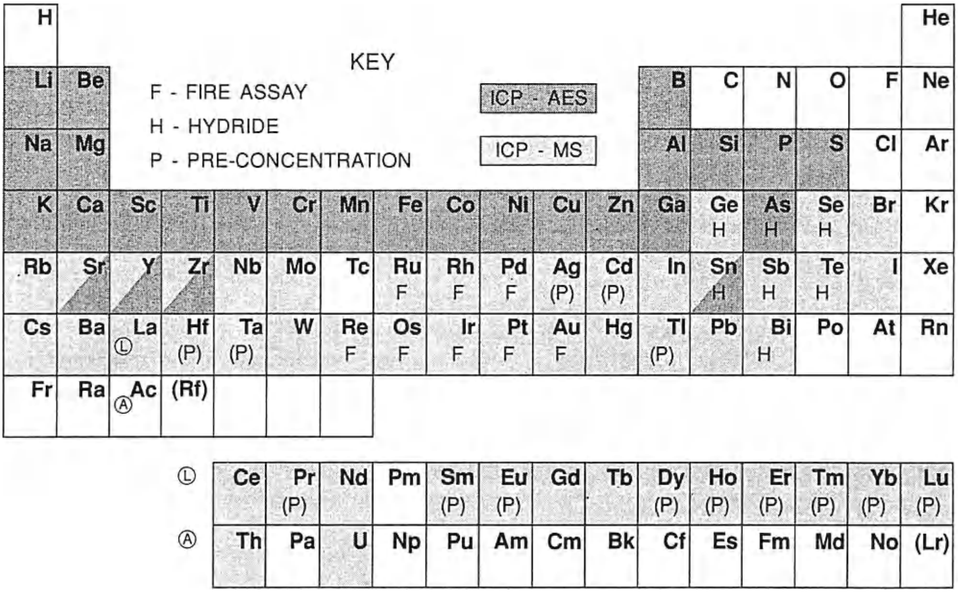


Fig. 4-5. Suitability of elements to determination by ICP methods (using acid solution, except as noted) (from Hall, 1992b).

the light and transition elements and some major rock-forming elements. The instrument is sensitive, but has marked detection ceilings, variable from element to element, which make it better suited to broad scale mapping than quantifying anomaly magnitude. The increasing importance of boron and the light elements as pathfinders for gold and base metals has given ES a role in providing analytical data that complement those obtained for mineral exploration by other analytical techniques. Former difficulties inherent in ES, such as long-term drift and the maintenance of precision, have been overcome through the inclusion of computer control systems in the latest generation of instruments. Fine grinding of samples, elimination of volatiles by ignition at 450°C and long burn times in the arc eliminate interferences and improve precision. It is essential, however, that ES is adequately calibrated with materials properly representative of the matrix encountered in the samples; for example, stream sediments may contain much higher levels of iron and manganese than calibrators made from rocks, and interferences unrecognised from the calibrators may seriously affect results from the samples (Plant and Moore, 1979).

Potts and Webb (1992) have reviewed the use of XRF in mineral exploration. With limits of detection down to a few parts per million for most elements with atomic weights greater than that of sodium, XRF is particularly suited to the determination of the first- and second-row transition elements. Trace elements are normally determined in pressed pellets, but major elements can also be

TABLE 4-I

Comparative attributes of instrumental methods routinely used for multi-element analysis of stream and lake sediment samples without sample dissolution (modified after Plant et al., 1988a)

Element group	ES	XRF	INAA
Li, Be, B	***		
Na, Mg, Al, Si, K, Ca	***	***	
Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn	***	***	
Sn	#	***	
Pb	#	#	
Y, Zr, Nb	#	***	#
Rb, Sr, Ba, La	***	***	#
Ga, Ge, As, Se, Th, U, REE		#	***
Ta, Hf, Au, Ag, In, Sb, Te, W, PGE			***

*** Suitable for most elements listed.

Acceptable but with poor limits of detection for many elements listed.

determined accurately and precisely in samples fused into a borate glass. The routine use of large samples weights for XRF analysis compared with those used for ES reduces sub-sampling error and improves precision. The large dynamic range of XRF makes it especially suitable for mineral exploration programmes which require the multi-element analysis of heavy mineral concentrates.

Most suitable for the determination of elements of intermediate to high atomic number is INAA. According to Hoffman (1992) as many as 50 elements can be determined routinely by INAA. In particular it is useful for the determination of gold, its pathfinders such as arsenic and antimony, the platinum group elements, tungsten, uranium, thorium and the rare earths (Fig. 4-6). The advantages claimed for INAA include the ability to analyze samples ranging in size from very small up to 1 kg, the non-destructive nature of the method and the matrix independence of the determinations. Samples of heavy mineral concentrates can be subjected to mineralogical analysis following cooling after irradiation. However, INAA exhibits relatively poor sensitivity for many transition metals and rock-forming elements.

The convenience of omitting sample dissolution is one of the attractions of all methods of element determinations on solids, and innovative ways of achieving this convenience are always sought. For example, a combination of sensitivity and versatility has led to experiments on the introduction of solids into ICP instruments by laser ablation. Hall (1992b) summarizes the advantages and difficulties compared with introducing aqueous solutions into the instruments. Hale et al. (1984) show how laser ablation ICP-AES of iron-manganese oxide coatings on stream sediment pebbles produces trace metal anomaly definition as good as or better than either selective leaching of the coatings or acid dissolution of the fine fraction of steam sediment from the same sample sites (Fig. 4-7).

RELATIVE SENSITIVITIES FOR ROCK MATRICES BY INAA

HIGH - H
MEDIUM - M
LOW - L

H																	He
Li	Be											B H	C	N	O	F L	Ne L
Na H	Mg L											Al H	Si L	P	S L	Cl M	Ar M
K L	Ca L	Sc H	Ti M	V H	Cr H	Mn H	Fe M	Co H	Ni L	Cu L	Zn L	Ga M	Ge L	As H	Se M	Br H	Kr L
Rb M	Sr L	Y L	Zr L	Nb L	Mo M	Tc	Ru H	Rh H	Pd H	Ag L	Cd L	In H	Sn L	Sb H	Te L	I H	Xe L
Cs H	Ba M	La H	Hf H	Ta H	W H	Re H	Os H	Ir H	Pt H	Au H	Hg L	Ti	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	(Rf)	(Ha)													
				Ce H	Pr L	Nd M	Pm	Sm H	Eu H	Gd H	Tb M	Dy H	Ho L	Er L	Tm L	Yb H	Lu H
				Th H	Pa	U H	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	(Lr)

Fig. 4-6. Suitability of elements to determination by INAA (from Hoffman, 1992).

Analytical data quality

Whatever the analytical procedures and instrumentation adopted, a series of important decisions have to be made on laboratory error control. One option is to ignore this matter. This substantially raises the risks of truly anomalous samples being missed because their analytical results fall into the background range due to laboratory error, and of expending effort in following-up false anomalies from samples which should have reported background values. A system of error control can be chosen which simply ensures that samples reporting as anomalous are reanalyzed as a check on anomaly validity. This avoids the latter of the two problems cited above, but not the former. More rigorous schemes of error control involve the routine analysis of some samples in duplicate, the inclusion of one or more reference materials in each analytical batch, and randomizing the sequence in which samples and reference materials are analyzed.

The analysis of a percentage of samples from a survey (typically about 10%) in duplicate provides the basis for a rapid graphical estimation of the acceptability of the precision of the entire analytical procedure from the means and differences of the duplicate pairs (Thompson and Howarth, 1978). An alternative is to use the standard deviation obtained by replicate analyses of a reference material; but duplicate samples have the advantages of comprising the same matrix as the survey samples and providing an estimate of the variation of precision with concentration. It may be appropriate to consider extending the scheme to include sampling errors. Garrett (1969) has shown that a properly constituted suite of sampling and analytical duplicates can be decomposed by

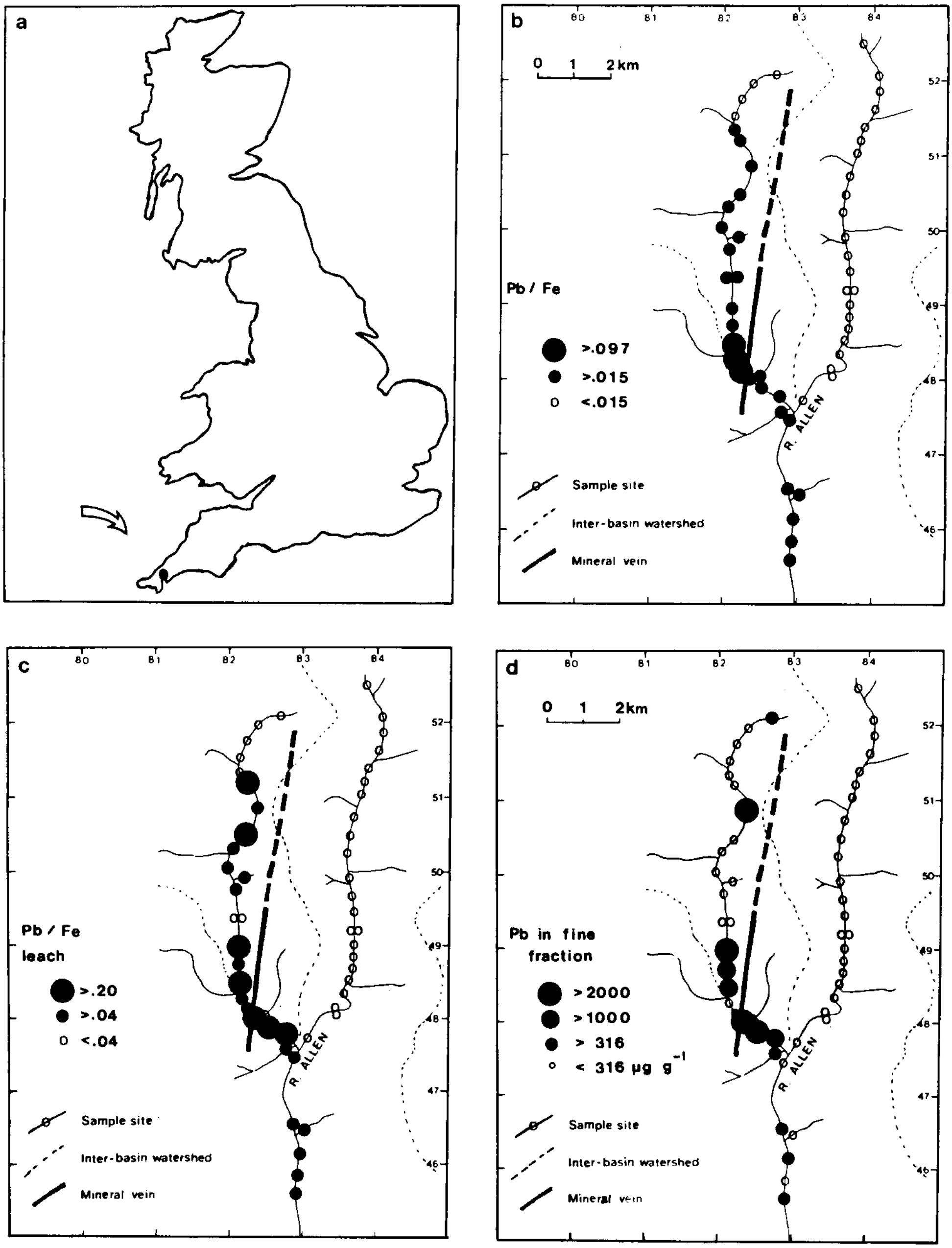


Fig. 4-7. Choices of stream-sediment sample media and analytical method: (a) location of drainage basin in southwest England; (b) Pb content of stream-sediment pebble coatings determined by laser ablation ICP-AES (arbitrary units corrected for Fe content); (c) Pb content of stream sediment pebble coatings determined by selective leaching (arbitrary units corrected for Fe content); and (d) Pb content of <200 μm fraction of stream sediment (from Hale et al., 1984).

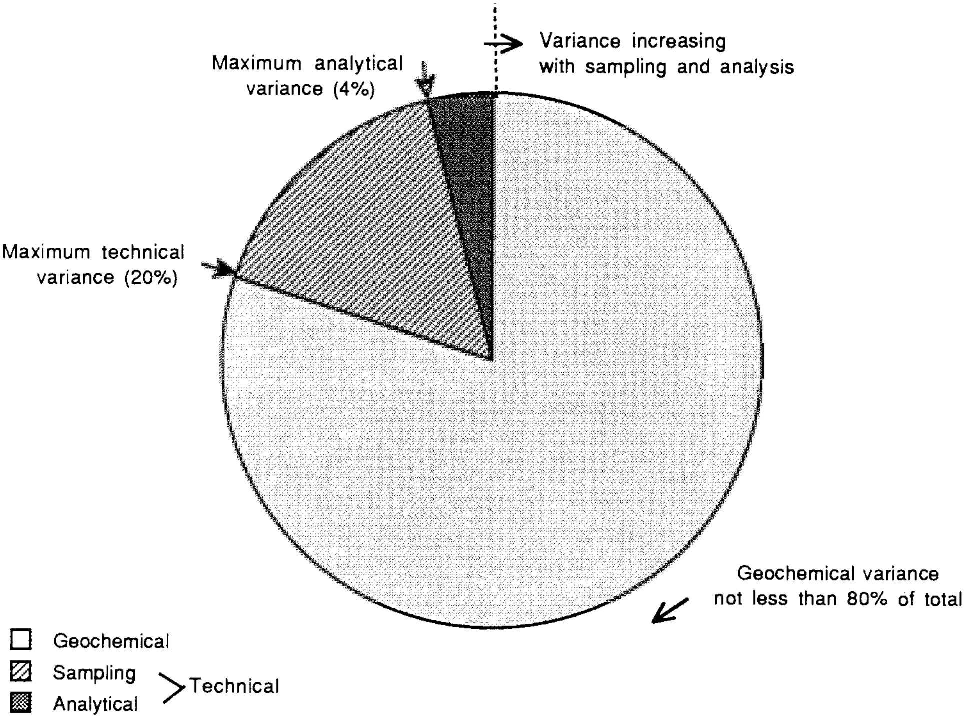


Fig. 4-8. Target variances in geochemical data (from Ramsey et al., 1992).

analysis of variance into its sampling, analytical and geochemical components as a means of ensuring that each of the first two are sufficiently low to accept the geochemical patterns as being effectively error-free. Ramsey et al. (1992) demonstrate the partitioning of sampling, analytical and geochemical variances in stream sediment data using robust analysis of variance. They suggest that the decision to improve sample reproducibility, analytical precision, or both, should be based on a model in which analytical variance lies between 1 and 4% of total variance, and combined sampling and analytical variance does not exceed 20% (Fig. 4-8).

The inclusion in each analytical batch of one or more reference materials with widely accepted values affords monitoring of analytical accuracy and bias. Achieving good analytical accuracy is not necessarily an important consideration in exploration geochemistry, but is closely allied to consistency of analytical data, which is vital when numerous separate analytical batches, different types of analytical procedures, or different laboratories are providing data for a single large survey. It is worth noting that, in principle, reference materials should allow the transfer of accuracy between different analytical procedures or different laboratories, but as Kane (1992) emphasizes, this is not always accomplished. Reference materials should have a matrix composition similar to that of the survey samples, and homogenized composites from several sites in the survey area best meet this criterion. This material then has to be analyzed by different methods and different laboratories to establish accepted values. Alternatively or additionally, reference materials unrelated to the survey area, but for which accepted values are well known, may be imported; however, the limited availability and expense of these favours their selective rather than routine use. Xie et al. (1989) describe how 12 primary reference stream sediments have been used to bring the data quality of more than 10 laboratories to the same level in China's Regional Geochemistry National Reconnaissance, while secondary reference materials have been used locally to monitor between-batch bias. Xie (1990) uses maps from the analysis of the same samples by different methods and in different laboratories to illustrate the success of this data quality monitoring scheme (Fig. 4-9).

Plant et al. (1975) stress the importance of randomization of samples so that their spatial relations in the field are quite dissimilar from their proximity in the sample preparation and analysis scheme. This ensures that contamination during preparation or analysis, or changes in instrument operating conditions, are not misconstrued as spatial clustering of anomalous values. Thompson (1992) additionally advocates the inclusion of duplicates and reference materials at random within each analytical batch in order to ensure properly representative data quality control, and points out that pre-analysis randomization and post-analysis re-ordering of data can be achieved with a simple computer program.

It should be assumed that the measurement and control of procedural error is ultimately the responsibility of the geologist in charge of the geochemical survey and not of the analyst. In terms of meeting that responsibility, the geologist has the choice of liaising with the analyst to ensure a scheme of error control is operated and reported by the laboratory, or of including anonymous duplicates and reference materials among the powders submitted to the laboratory, or a combination of the two. Reimann (1989) cites sample mix-ups, higher-than-quoted detection limits, changes in precision between batches, analytical variance approaching total variance, and lack of reproducibility of reference materials as just some of the problems identified through the use of anonymous quality controls during a stream sediment, soil and rock geochemistry programme in Austria.

Orientation

Having considered the sampling and analytical choices in relation to the objectives of a drainage geochemistry survey, options should be finalized by orientation prior to the main survey. In the ideal situation, which unfortunately may not always present itself, orientation for a mineral exploration survey is carried out within the main survey region, in the vicinity of a known example of undisturbed mineralization of the type which is the exploration target. Where an example is not available within the main survey area, orientation around mineralization located elsewhere, but in similar geologic, topographic

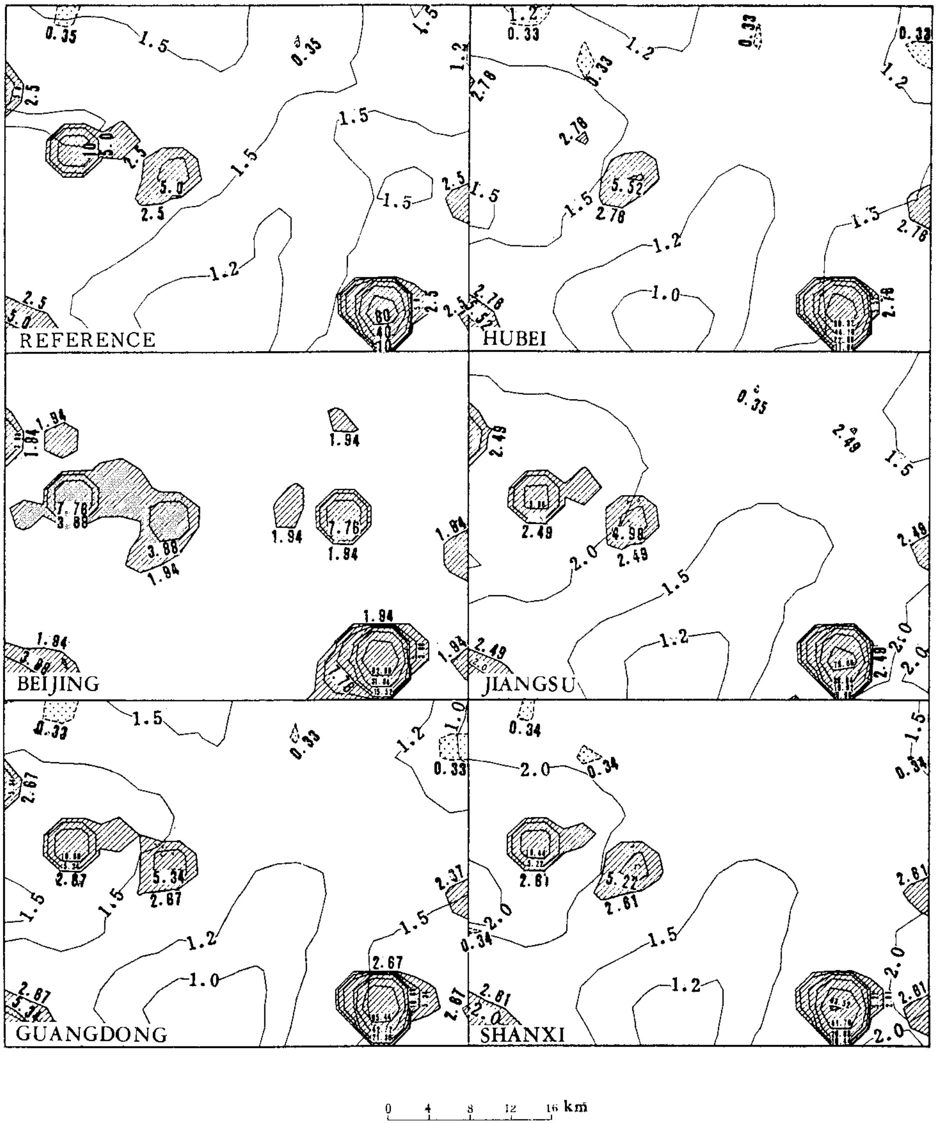


Fig. 4-9. Contour maps of Mo distribution in stream sediments from a part of China, produced by analysis of sub-samples of the same parent samples in five different laboratories and using three different analytical methods: Hubei — polarography; Beijing — ICP-AES; Jiangsu — ES; Guangdong — polarography; Shanxi — polarography (reference map is based on the mean of all five data sets) (from Xie, 1990).

and climatic settings, is an acceptable alternative. When several types of mineralization are sought, several orientation studies may be required, with their findings carefully balanced to provide optimum procedures for the main survey.

During orientation, samples of the available media which host geochemical dispersion patterns of potential interest might be collected in order to assess not only the value of dispersion patterns in different drainage media, but also the value of drainage dispersion patterns compared to those in rocks, soils and vegetation. Samples should be taken at a relatively high density and relatively large samples should be taken at each site. Different components of samples (such as different size or paramagnetic fractions of sediments) should be separated prior to analysis. The analytical stage of orientation should attempt different methods of leaching sediments, include the determination of all elements thought likely to help meet survey objectives (for example, not only ore elements but also pathfinders and in some cases petrogenetic elements), perhaps evaluate alternative instrumental methods, and may be extended to assess the performance of different laboratories. Sampling and analytical variability should be determined, for example, by duplicating some sampling and some analyses, in order to ensure that routine procedural errors do not mask geochemical patterns and anomalies. The results of orientation should reveal which combination of sample medium and analytical procedure yields the best anomaly contrast at the lowest sampling density; data on element ratios and other derivative data should also be evaluated. Rose et al. (1979) provide a checklist of factors to be considered in orientation for drainage surveys (Table 4-II), and Simpson et al. (1991) describe orientation in Jamaica in which the multi-element geochemistry of rocks, waters, heavy mineral concentrates and various size fractions of soils and stream sediments was examined.

Although orientation should identify a procedure by which the main survey can be carried out with the confidence that its objectives will be fulfilled, one option open to the explorationist is to forego orientation and rely solely on prior experience. The norm is probably a compromise in which personal experience and published information are used to narrow the scope of orientation and focus on key alternatives. For example, Garrett and Geddes (1991), on the basis of their review of published geochemical research in the Caribbean and elsewhere, confined their orientation to stream sediment size fraction optimization prior to a drainage geochemistry reconnaissance covering 18% of Jamaica.

Data reduction and presentation

Howarth (1983) gives an extensive account of methods in geochemical data reduction and presentation. The main choices are how to allocate uni-element data to appropriate classes, how to use additional elements to advantage in data reduction, and how to map data according to the application of the data.

Single-element data reduction

In mineral exploration, drainage geochemistry data are most usually reduced and then presented on maps by methods which are intended to enhance anomalies of one or more elements associated with the target mineralization(s). In the case of the simplest uni-element data, the reduction step involves setting a threshold and allocating data to background and anomalous classes. There are

TABLE 4-II

Factors to be evaluated in an orientation survey preparatory to a drainage geochemistry survey (modified after Rose et al., 1979)

General	Sediment	Water
Availability of sample sites.	Choice of: seepages, stream channels, flood plain, centre-lake, near-shore lake	Choice of: groundwater, stream water, lake water.
Best indicator elements, including both major and minor constituents or ore.	Optimum material: grain-size range, paramagnetic material heavy minerals, coated pebbles, organic matter.	Relation to recharge areas, difference between aquifers, controls on flow of groundwaters; possible variations with type and depth of lakes.
Length of and controls on downstream decay patterns.	Magnitude of contrast of anomaly at source; metal content of bank material.	pH, Eh, precipitants, adsorbents.
Background range of indicator elements, relation to rock types.	Correlation with Fe–Mn oxides and/or organic matter.	Relation to total dissolved solids and major elements.
Timing of sampling campaign.	Seasonal and other temporal variations.	Seasonal and other flow-rate variations.
Analytical methods: detection limits, precision, accuracy, form of elements.	Most effective extractant or method of anomaly enhancement.	
Cost of sampling and analytical procedures; elapsed time for reporting results.		

a number of means of setting such a threshold. It can be based upon published information about typical background levels in the region from which the survey data are derived, or a region of essentially similar geology, physiography and climate. Alternatively, the results of prior orientation in the region may provide the necessary information. Equally, threshold may be set from the drainage geochemistry survey data themselves; in this case there is a choice between experimental and model-based methods of setting threshold (Sinclair, 1991). The former includes visual inspection of the data, selecting a percentile level in the data or, when the data (before or after transformation) conform to a normal distribution, setting threshold at the mean plus two (or more) standard deviations. Model-based methods make use of the fact the anomalous and background samples are members of statistically different populations (Fig. 4-10), the separation of which can be optimized by statistical and graphical methods such as the gap statistic (Miesch, 1981) and probability plots (Sinclair, 1974, 1991).

Multi-element data reduction

When several ore element and pathfinder data sets are generated in a mineral exploration drainage geochemistry survey, the data may be treated separately

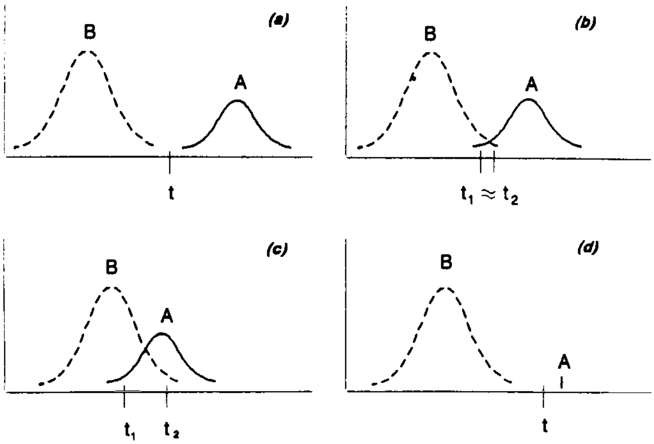


Fig. 4-10. Models for setting threshold (t, t_1, t_2) to separate anomalous (A) and background (B) populations: (a) populations with no overlap; (b) populations with minimal overlap, with almost identical thresholds from the upper limit of the background population and the lower limit of the anomalous population; (c) populations with extensive overlap, with significantly different thresholds from the upper limit of the background population and the lower limit of the anomalous population; and (d) anomalous outliers constituting members of a poorly represented anomalous population with no apparent overlap with the background population (from Sinclair, 1991).

for each element, with supplementary information on inter-element behaviour derived from correlation matrices and bivariate scatter plots. Data for some elements may be needed to aid the interpretation of ore elements or pathfinders. For example, variations in the Fe-oxide, Mn-oxide and organic contents of stream or lake sediments can cause corresponding fluctuations in adsorbed and co-precipitated trace elements, sometimes raising natural background concentrations to levels that appear to be anomalous. Butt and Nichol (1979) illustrate a graphical method of distinguishing true zinc anomalies from false anomalies caused by manganese oxides in stream sediment samples in Northern Ireland (Fig. 4-11). Where data for many variables are available, interpretation may be aided by factor analysis, cluster analysis and, perhaps most widely used, principal components analysis. In this last method, data are reorganized into a number of factors, each with loadings on some or all of the constituent elements of the data set; these factors can then be interpreted in terms of lithological variation, dispersion processes, associations of elements related to mineralization, and so on. For example, in multi-element lake sediment data from Nova Scotia, Canada, Wright et al. (1989) found four principal components reflecting mechanical dispersion, base metal mineralization, gold-tungsten mineralization and granites. Similarly Thompson et al. (1992) show how the Dolgellau gold belt of northwest Wales is easily recognized in stream sediment pebble coatings data that did not include gold by a principal component with high loadings on As, Cd, Co and Zn.

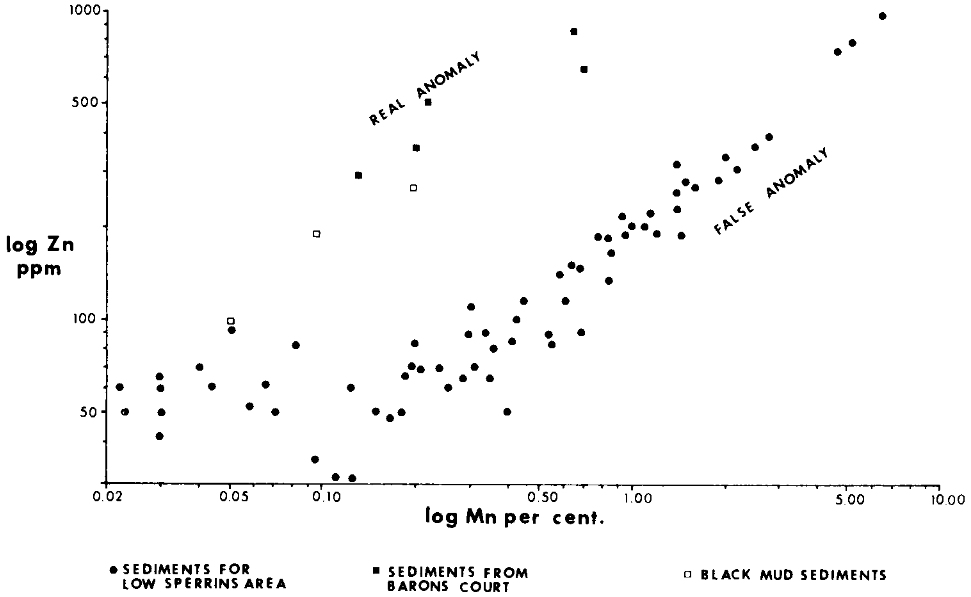


Fig. 4-11. Use of scatterplot of stream-sediment data from Co. Tyrone, Northern Ireland, to distinguish real Zn anomalies (>230 ppm) associated with mineralization at Barons Court from many equally high false anomalies related to Zn adsorption by Mn oxides in the unmineralized Low Sperrins area (from Butt and Nichol, 1979).

Drainage data mapping

At the data presentation step it is usual to ensure that anomalies are enhanced through their portrayal as bold and/or large symbols, whilst background data are shown in relatively unobtrusive symbols. Sub-division of the anomalous class according to anomaly intensity, but with no corresponding sub-division of background, can be advantageous. Separate classification of the near-threshold high-background data, however, can minimize the consequences of mis-classifying subtle anomalies. Figure 4-7 provides examples of the use of symbols of different size and density to map stream sediment data, and Fig. 4-2 additionally shows how representing the width of the drainage channel upstream from a sample site as a function of element concentration at that site produces a worm map. Figure 4-3 illustrates how several variables can be presented on the same map by shading segments of a pie diagram at each sample site.

When drainage data are to presented as regional maps emphasizing broad-scale geochemical features, methods of data reduction that suppress anomalies but perhaps reflect lithologies are adopted, such as subjective selection of data classes by concentration ranges or percentiles. Each element concentration at each sample site is attributed to an arbitrary surrounding area or, preferably, to the catchment basin upstream (Bonham-Carter et al., 1987) and contouring

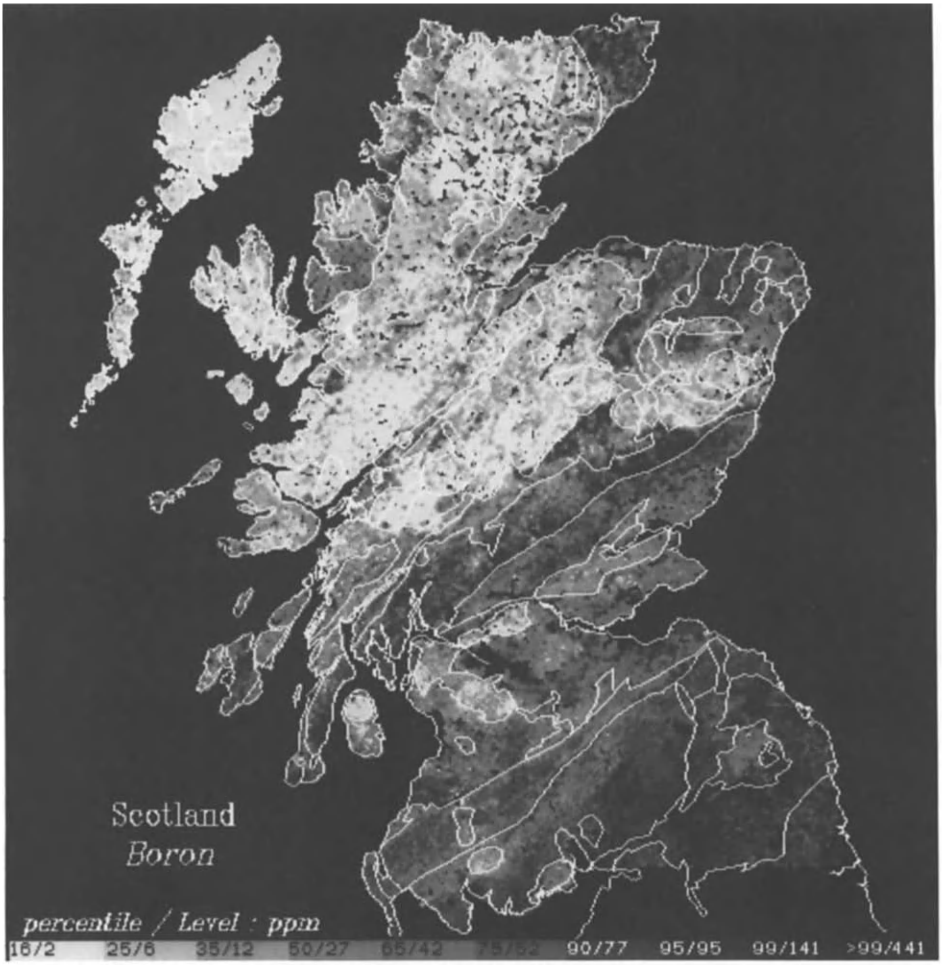


Fig. 4-12. Grey-tone geochemical map of boron in stream sediments in Scotland, with principal geological boundaries in white (courtesy of J.A. Plant).

or shading is applied so that the resulting map represents an apparently continuous geochemical picture of the region (Fig. 4-12). The final appearance of regional maps is often improved by geostatistical data smoothing or filtering techniques, such as trend surface fitting and kriging (Howarth, 1983).

Computerized mapping has facilitated the presentation of the same geochemical data to emphasize either broad-scale geochemical features or point source anomalies. Björklund and Gustavsson (1987) show how this can be achieved by expanding and attenuating the range of element values represented by symbols of different diameter on geochemical maps of Finland (Fig. 4-13); their example is based on till geochemistry, but the mapping technique is equally applicable to drainage data. Koljonen et al. (1989) combine two styles of presentation into

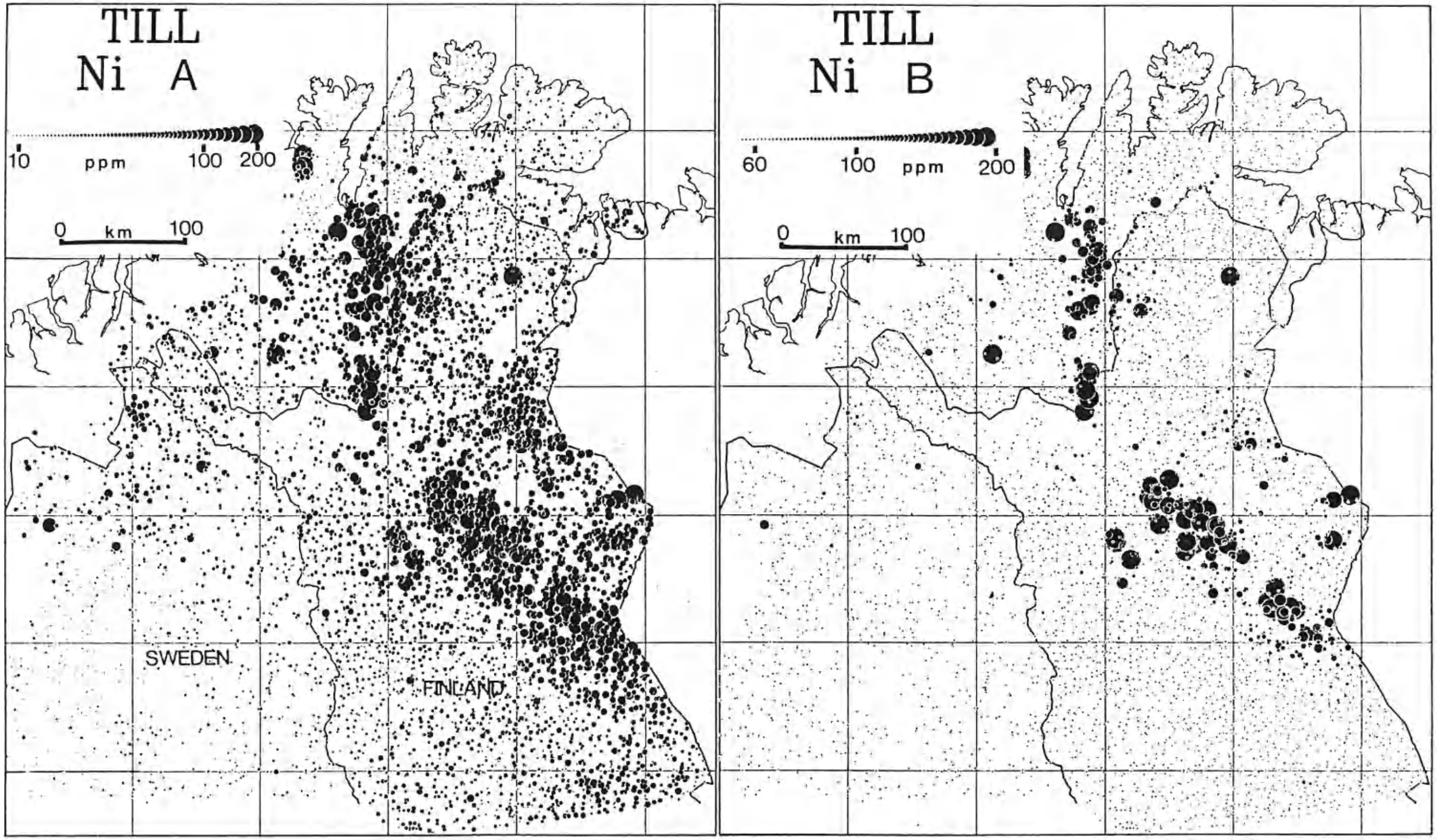


Fig. 4-13. Choice of range of Ni contents of till represented by dot symbols: (a) to show patterns over the entire concentration range; and (b) to emphasize high concentrations (from Björklund and Gustavsson, 1987).

each single-element map, depicting broad-scale features by continuous colour tones and superimposing anomalies as black symbols.

SURVEY LOGISTICS

Having examined the choices dictated by the scientific objectives of a drainage survey, constraints may yet be imposed — and further informed choices may be required — when the logistics of the survey are considered. Most of these choices are related either to sampling or analysis.

Sample constraints

Geology and climate

Geology, sometimes in combination with climate, can impose various logistical limitations on sampling. In granitic and crystalline terrains generally, an absence of sub-surface aquifers restricts drainage geochemistry to run-off water and drainage sediments. This applies to considerable parts of the surface of the Earth, including highly prospective regions such as granite-greenstone belts. Conversely, where surface drainage is poorly developed, but groundwater flows in sub-surface aquifers or circulates in fracture systems in crystalline terrains, wells may offer the best opportunity for obtaining drainage samples. Groundwaters are the medium most usually sampled from wells, although Vriend et al. (1991) have demonstrated the efficacy of sampling well sediments. In limestone terrains surface drainage may be sparse or absent, but springs usually occur where there are outcrops of limestone overlying less permeable rocks, and Pirc et al. (1991) found that the fine fraction of sediment at karst springs was a suitable medium for geochemical mapping throughout the entire Yugoslav karst belt.

In high latitudes recent glaciations have produced partially-impeded surface drainage systems in lowland areas, which are often characterized by bogs or lakes. The widespread absence of conventional stream sediment (composed mainly of rock fragments and mineral grains) in northern Sweden led Brundin and Nairis (1972) and Larsson (1976) to choose organic matter in drainage channels as an alternative sample medium.

Where lakes are present, as in northern Canada, their waters are often in continuity with the surrounding groundwaters, and so constitute convenient sites for acquiring water samples that have a groundwater component as well as sediments that have hydromorphic and clastic components (Chapter 7, this volume).

Temporal factors

Where surface drainage is sufficiently abundant for the survey objectives, seasonal factors may greatly influence the geochemical response in both waters and sediments. High flow regimes tend to reflect rapid run-off rates and low residence times, and the concentration of dissolved solids in the waters is correspondingly low. On the other hand, water flow may cease during a protracted dry season, rendering surface water samples unavailable. Periods of steady flow are the most desirable for stream water surveys conducted over a wide region. In the groundwater regime, a dry period tends to cause a fall in the level of the water table to a level at which no oxidation of minerals occurs, and around the unoxidized zones of mineral deposits concentrations of dissolved metals may not be conspicuously anomalous. The onset of flow after a dry season often has the effect of flushing into the drainage system the accumulated soluble products of mineral weathering, producing striking but transient anomalies in waters (Chapter 15, this volume). In stream sediments anomalies can be sharply diluted by heavy rainfall following a sustained dry period (Ridgway and Dunkley, 1989). Furthermore, stream sediment samples collected during one dry season may not contain the same trace element levels as those taken from the same sites during a subsequent dry season. Ridgway and Dunkley (1989) therefore recommend confining stream-sediment sampling in seasonal climates to the true dry season, and treating with caution data sets produced by merging sampling over two or more dry seasons. Regular sampling of a reference site may need to be considered if data from samples acquired in different seasons or years are to be normalized.

In high latitudes sampling during the summer is usually favoured because working conditions in winter are too harsh. During the early summer thaw, streams experience high flow rates, which can flush away anomalous material. As summer progresses, lakes may become stratified due to surface warming, with deeper water depleted in oxygen and dissolution of trace elements previously adsorbed on lake-bottom sediments (Levinson, 1980). Trace element partitioning between lake waters and sediments can reverse later in the summer as surface warming diminishes and the water returns to isothermal conditions and more uniform oxygenation. Allan et al. (1973a) mitigated these problems by sampling near-surface lake waters and lake-bottom sediments more than 2 cm below the water-sediment interface.

Field measurements

While collection of water or sediment samples in the field followed by their analysis in the laboratory is generally acknowledged as the most efficient data acquisition method in drainage surveys, the merit of measuring certain parameters at the sample site deserves consideration. The pH of natural waters is prone to shift in a sample held in a container for any length of time, due to chemical reactions and microbial activity. Similarly the redox potential (Eh) of water and sediment samples changes as soon as they are removed from their original environment. Radioactivity measurements rely on the gamma-ray flux provided by the measurement site and its immediate surroundings, so that a small sample in the laboratory gives a far weaker signal.

At surface drainage sites, field measurements of pH and Eh can be made with probes linked to a visual display, and gamma-ray measurements can be made with a hand-held geiger counter; measurements on groundwater in wells and boreholes are possible, but more elaborate equipment is needed. Measurements of pH and Eh can be extremely useful in aiding the interpretation of hydrogeochemical data, in particular, and can contribute directly to exploration for redox-controlled roll-front uranium deposits (Chapter 8, this volume). On the other hand, many drainage sediment surveys have been entirely successful without the inclusion of pH or Eh measurements.

Instruments, however, may experience faults or calibration errors which render measurements impossible or suspect, and revisiting sites to fill gaps in the data set is often prohibitively expensive. Thus, due thought must be given to which field measurements, if any, are truly essential.

Laboratory logistics

The principal logistical choices in the analysis of samples is who should perform the analyses and where. The matter of who should perform the analyses is governed by resources, confidence and perhaps the perception of data confidentially. An established exploration organization with its own laboratory would probably consider this to be the obvious facility for its samples. Others might acquire suitable, relatively low-cost, equipment to analyze their samples, or send them to an independent service laboratory, ideally after consultations and tests to ensure that the laboratory uses procedures and instrumental methods appropriate to the survey objectives.

Where the laboratory is sited depends upon communications and the management structure of the exploration programme. Airline transportation of sieved or pulverized sediments and fax or E-mail transmission of analytical results mean that it can be efficient to send samples halfway around the world for analysis if the appropriate analytical facilities happen to be so distant; in many cases the slowest step is bringing the samples from a field camp to an international airport. For instance, samples from an exploration programme in Saudi Arabia have been analyzed in a service laboratory in the United Kingdom and samples from a programme in Turkey have been analyzed in the parent company's laboratory in Vancouver.

Nevertheless, there is a tendency for local laboratories to be established where the sample flow justifies the capital expenditure. When an exploration organization chooses to equip its own laboratory, logistical considerations may influence the choice of instrument. Macalalad et al. (1988) recognized the many advantages of ICP spectrometry, but preferred to determine 16 elements in stream sediments, soils and rock chips in the Philippines by AAS because its productivity was less seriously affected by power failures and electronic component failures. When several organizations are actively exploring in one region, one or more service laboratories is likely to spring up, as in Western Australia during the nickel exploration boom of the late 1960's. Local laboratories obviate any customs difficulties that might arise with international sample shipment, though in practice these are rare.

The field laboratory, built at the field camp to which samples are brought daily from the sample sites, did much to promote the use of exploration geochemistry in the 1950's. In its original form or more modern guise, the caravan or other vehicle fitted out as a complete transportable laboratory, the field laboratory continues to be an attractive choice when a large programme produces a steady flow of samples for the determination of a limited range of elements and consumables and spares can be brought in efficiently and, if necessary, quickly. In practice these criteria are often too demanding, and transporting the samples to an established laboratory is the preferred choice. But in very isolated regions the field laboratory is particularly advantageous when overall programme management rests with a geologist in the field, who can have analytical data within two or three days of sample collection and, if appropriate, put follow-up work in hand.

Even if the very rapid turnaround available from a field laboratory is not paramount, it is usually important to the survey logistics for laboratory turnaround times to be clearly defined and closely adhered to. In regional geochemical mapping programmes or where exploration fieldwork is restricted to a short season each year, the receipt of results may not be urgent, but in exploration programmes with continuous fieldwork, it is desirable to strive to receive analytical results within a few weeks of submitting samples to the laboratory.

SURVEY BUDGET

Each of the stages in a drainage geochemical survey has an attendant cost, and so choices made solely on the grounds of survey objectives or logistical feasibility ultimately dictate the cost of the survey. But programmes almost always have budgetary constraints, and therefore some decisions have to made on the grounds of containing costs.

Sampling

Usually the largest cost in regional geochemical reconnaissance is obtaining samples. In general, sampling costs are closely dependent upon the sampling rate, which is in turn dependent upon the mode of transport for travelling between sample sites, the sampling density and the amount of work performed at each site.

Transport

For transportation to sample sites, the choice is between renting a helicopter and crew, costing from US $200 per hour, and overland by road or on foot, for which the cost might be less than $20 per day for the salary of a competent sampler. Of course, several teams of samplers may have to be deployed to achieve the same sample collection rate as that possible from a helicopter, and the cost of operating vehicles and even opening roads has also to be taken into account. In practice, where surface transport is convenient, helicopter services may be unavailable or expensive, but where surface transport is difficult there is likely to be competition to provide helicopter services, and hence more reasonable costs. Consequently, local circumstances often guide the geochemical survey programme organizer to the most cost-effective means of reaching sample sites.

Sampling density

In some cases the availability of sample sites (such as wells) dictates a maximum sampling density which is judged to be consistent with survey objectives. In other cases the sampling density has to be chosen to meet survey objectives at an acceptable·(if not minimal) cost.

For the detection of stream sediment anomalies from individual mineral deposits, it is usual to sample first or perhaps second order drainage channels immediately upstream of their confluences. This strategy ensures that anomalies are not missed as a result of catastrophic dilution below confluences, but usually leads to a high sampling density, typically of the order of one sample per 1–2 km^2. Hawkes (1976a), however, proposed and successfully tested an idealized formula that quantifies the persistence of anomalous trains from mineralization; its application allows selection of sample sites on higher order drainage channels and hence lower sampling densities without the loss of significant anomalies.

In stream sediment surveys, little time is spent at the sample site so costs are mainly a function of sampling density and mode of travel. For typical sampling density surveys, sample collection rates range from 40 sampling sites per day in a region with good helicopter access to as few as five sites per day where access is only possible on foot (Chapter 6, this volume).

Lake sediment and lake water surveys can be carried out even more economically than stream sediment surveys because helicopter access is easy and the time at the site is short. Unit costs in northern Canada are of the order of \$30 per km^2 for high density surveys falling to \$10 per km^2 for low density surveys (Chapter 7, this volume; Fig. 7-26). Cameron and Ballantyne (1977) estimated that lake-sediment sampling for uranium at a sampling density of one site per 13 km^2 incurred approximately the same costs as an airborne radiometric survey at 5 km line spacing.

Large-scale regional geochemical mapping strives to reveal broad scale geochemical patterns. This can be achieved economically if representative samples can be acquired at very low sampling densities. Ottesen et al. (1989) point out this is possible using overbank sediments. These are deposited in periods of spate, when rivers attain sufficient energy to carry in suspension not only more fine sediment than usual, but also larger particles and some of high specific gravity normally confined to the bedload; transport distances are also greater during these periods. In more mature lowland regions, streams and rivers in spate are prone to breach their banks and, in the low energy environment beyond, to deposit their suspended load (Fig. 4-1). Such overbank sediments are thus largely fine grained, but may include heavy minerals and are a composite of an exceptionally large upstream area. The use of overbank sediments in regional geochemical mapping has been demonstrated in Norway, where geochemical maps covering 320,000 km^2 have been produced from 690 overbank sediment sample sites representing drainage basins of 60 to 300 km^2 (Ottesen et al., 1989).

Minimizing sampling densities for regional geochemical mapping using sediments from active stream channels has also been investigated. Using data sets from regional geochemical surveys in a variety of geologic, physiographic and climatic regimes with different but relatively high sampling densities, Ridgway et al. (1991) found that selecting data from samples representing densities as low as one sample per 500 km^2 could yield meaningful results in some areas.

Sitework

The length of time spent collecting sample material at drainage sediment sites naturally influences the overall rate (and therefore cost) of sample collection. Thus, for example, panning a heavy mineral concentrate at a sample site requires far more time than the collection of a stream sediment sample. However, the reduction in the overall sampling rate is not as great as might be expected, because the cost of moving between sites remains the same. Indeed, panned concentrates can be collected at much the same overall rate as stream sediments in regions where reaching the site is the main time-consuming activity. However, where moving between sample sites is accomplished quickly, the overall rate at which concentrates are collected is only about half of the rate at which stream sediments can be obtained (Chapter 6, this volume).

Site observations are often recorded in a notebook or on a pre-printed from. Factors such as estimates of water flow rates, turbidity, the width and depth of streams, the texture and colour of sediments and so on, can be recorded systematically. This information acquisition takes time and, if the information cannot subsequently be put to good use, that time represents an unnecessary expense. Roquin and Zeegers (1987) point out that in stream sediment surveys in various parts of France, the nature of the sub-stratum, overburden and sample material and the importance of Fe-Mn oxides are better characterized by multi-element analytical data than by coded field observations.

The distinction that Plant et al. (1988a) make between representative drainage samples and those designed to enhance anomalies needs to be considered. In the case of a small organization undertaking a geochemical survey with clearly-defined exploration objectives — perhaps the identification of base metal anomalies — and in which sample site access is obtained by helicopter, time spent at the sample site tends to be regarded as costly, and work is kept to a minimum, such as obtaining a few hundred grams of heterogeneous sediment. On the other hand, the argument applicable to large regional reconnaissance or geochemical mapping programmes is that, having made the expenditure to reach the sample site, economies should not be made that restrict the amount of geochemical data that can be obtained from the visit. A range of representative samples should be taken at the site, which might include field sieving or slurry screening to obtain sufficient fine fraction material, panning to recover a heavy mineral concentrate, collection of a filtered water sample and on-site measurement of pH and Eh.

Sample material acquired and analyzed in an exploration or mapping programme may be stored in a sample library for possible subsequent retrieval and analysis. The availability of such a library may eliminate a costly field campaign when new exploration targets come under consideration. The preparation of regional geochemical maps of the distribution of arsenic, antimony and bismuth in stream sediments of the southwest Highlands of Scotland (Plant et al., 1989a) and the Lake District of northwest England (Plant et al., 1991) was undertaken to assess the applications of these elements as pathfinders for gold deposits in these terrains by analyzing samples from the sample library of the British Geological Survey (J.A. Plant, pers. commun., 1993). As part of its National Geochemical Reconnaissance Programme, the Geological Survey of Canada has catalogued and stored 140,000 stream and lake sediment samples, and is finding that re-analysis of this material by more advanced analytical methods than were available when some of the samples were collected is proving increasingly important (Friske and Hornbrook, 1991). Of course, the cost of land and buildings for long-term sample storage, the compilation of a sample catalogue and the maintenance of samples in good condition all have costs which have to be set against what is essentially a contingent cost that sample sites may have to be re-visited.

Analysis

The costs of analysis can be limited to a simple recurrent cost by the use of a service laboratory, or can involve a combination of building acquisition and/or refurbishment, capital equipment, payroll and consumables costs for the establishment and operation of an in-house laboratory. If cost is the only consideration, the foreseeable magnitude and duration of the need for analytical facilities determines whether the capital investment in an in-house laboratory will be recouped and whether it is appropriate for the organization to appoint laboratory staff onto its payroll. Large organizations that calculate that an in-house laboratory is the most cost-effective option can reasonably equip themselves with any or all analytical instrumentation except a nuclear reactor. Various types of ICP and XRF instruments cost several hundred thousand dollars while an AAS instrument can be purchased for as little as $10,000. Safety regulations must be adhered to and often give rise to considerable expense. Equipping a laboratory for sample preparation soon becomes expensive if strong acid fumes have to be vented, the installation of one hydrofluoric-acid tolerant fume cupboard costing about $40,000.

Service laboratories publish brochures which describe the analytical procedures that they offer along with their specifications (such as limits of detection and precision) and current unit prices. The determination of trace elements by AAS is usually broken down into the price of sample dissolution alone or dissolution plus the determination of one element (typically up to $4.00), and the additional price of determining each subsequent element (typically up to $0.50) that can be chosen from the published list. The determination of perhaps thirty major and trace elements usually of interest in exploration by an ICP method is often a competitively priced alternative at about $10.00. Gold and platinum group elements are offered on a choice of sample weights and procedures, according to the limit of detection and accuracy required, for prices between $10 and $150. For many other elements, analysis is available for between $5 and $10 per element. The analytical results are now often available on disk as well as on paper, and some laboratories offer to quote for — or even provide free of charge — computerized data processing and/or map-making.

There are costs associated with error control, which must be set against the problems risked by its omission. The analysis during a survey programme of 10% of samples in duplicate and the inclusion of a reference material for every twenty samples or so means a 15% increase in the analytical costs compared to that for the single analysis of each sample. Even small quantities of international standard rocks command a high price; and the work and expense involved in preparing one or more in-house bulk reference materials and establishing accepted values for them is considerable. If overall procedural error is to be monitored using analysis of variance, a still more elaborate scheme of sample duplication at both the sample site and the laboratory has to be devised, organized and funded.

Data reduction and presentation

The long-established method of hand plotting drainage geochemistry data on maps as concentration values or symbols representing data classified by simple graphical methods is effective and is a relatively inexpensive component part of the overall cost of a drainage geochemistry survey. But the advent of computers in the 1960's offered a new, convenient and — in particular — versatile method of managing large sets of drainage geochemistry data. Dramatic reductions in both the physical size and price of computers have greatly encouraged their widespread use, initially as tools for the statistical manipulation of data and subsequently for map-making. Today a personal or laptop microcomputer costing less than $2,000 can perform virtually any statistical treatment of all but the largest multi-element data sets. Furthermore, programs to perform these tasks — some written especially for the exploration market — can be purchased for no more than a few hundred dollars; and some are in the "public domain" category and are virtually free. Thus for a few thousand dollars (perhaps the equivalent of a few hundred multi-element analyses and certainly less than the cost of an atomic absorption spectrophotometer) the geologist can have at his fingertips a powerful, sophisticated and portable microcomputer and software that quickly perform the full spectrum of potentially useful statistical analyses on uni-element and multi-element drainage geochemistry data sets. The low costs of computing have meant that modern laboratory instruments write directly to disk, and the geologist can receive his analytical results in this form, ready for investigation and manipulation on a personal computer.

Computerized map-making has followed close behind data manipulation. In general it demands larger amounts of computer memory, more sophisticated software and higher resolution output devices, but these are now widely available, although rather more expensive, than what is required for statistical analysis of data. Flat-bed and drum plotters, often using pens of different colours, have been used for making paper copies of scaled geochemical maps for over two decades, but they are large, slow and expensive. The latest output device for map-making is the colour laser printer, which is desktop size, prints a map in a minute or so, and costs from $20,000.

In terms of the value of computerized cartography, however, the hard copy is simply an end-product for inclusion in a report or publication. The true value of the technology to the geologist lies in the opportunities it provides to view spatially registered drainage geochemistry data as many different screen images, of which only those reflecting patterns judged to be of exploration interest are printed for further study. Uni-element data can be mapped using a variety of alternative class boundaries. Multi-element data can be mapped as a series of colour-mixed single element overlays or principal components, and geochemical data can be co-registered with geophysical, remotely-sensed and other data in order to recognize and enhance coincident features that may represent exploration targets. The huge array of combinations that is possible on a computer would be quite unthinkable by any other means. So rapidly is the power of computers rising, and the cost of computers and high quality printers falling, that it cannot be many years before sophisticated computerized cartography of drainage geochemical data is as inexpensive as statistical analysis of data.

CONCLUSIONS

Strategic choices abound in drainage geochemistry; simply being fully informed of the options available is vital. Thereafter the first consideration should be a careful assessment of the objectives of the survey. With these clearly defined, options in sampling and analysis can be evaluated, preferably with the aid of orientation studies. Constraints imposed by logistics and budgets are likely to narrow the choices.

Wise choices pave the way to technically competent surveys. Indeed the success of drainage geochemistry over almost half a century owes much to the fact that explorationists and other have repeatedly recognized that different survey objectives in varying geologic and climatic environments can be met by innovation, by exploiting new developments and by employing appropriate strategic combinations of sampling, analysis and data treatment.

Drainage Geochemistry
edited by M. Hale and J.A. Plant
Handbook of Exploration Geochemistry, Vol. 6 (G.J.S. Govett, Editor)

Chapter 5

STREAM SEDIMENTS IN MINERAL EXPLORATION

R.T. OTTESEN and P.K. THEOBALD

INTRODUCTION

Stream sediment as an exploration tool

Alluvial dispersion trains of valuable minerals and metals have provided exploration guides for thousands of years. Theophrastus (Hill, 1746), for example, documented the tracing of detrital anomalies in the search for lode deposits in 300 B.C., and it is likely that sources of copper for pre-Bronze Age cultures were also located by the use of alluvial dispersion trains (Wertime, 1973). Early explorers depended on the identification in alluvial materials of native metals such as copper or gold, ore minerals such as cinnabar, or precious stones such as ruby or sapphire.

The advent of rapid, sensitive methods for the determination of a wide variety of trace elements in geologic materials in the period 1930 to 1960 led to the use of chemical analysis of stream sediments in exploration (for example: Lovering et al., 1950, in North America; Fersman, 1930b, in the USSR). The ease with which high metal contents could be detected in fine-grained stream sediment in the vicinity of ore deposits led to the widespread adoption of rapid methods of analysis (Hawkes, 1957). There can be difficulties with simple approaches, however. In some environments, false anomalies (anomalies not related to ore deposits, nonsignificant anomalies) as high as those near some ore deposits may be reported (Canney, 1966). Sizing the sediment sample by sieving out coarse, resistant, ore minerals can reduce or eliminate chemical anomalies downstream from some types of ore deposits (for example, Sainsbury et al., 1970).

The need to recognize subtle anomalies, and to distinguish those most likely to be related to mineral deposits, has led to the widespread use of particular fractions of stream sediments, for example heavy-mineral concentrates (Chapter 6, this volume). Organic matter (Brundin and Nairis, 1972) or secondary iron and manganese oxide fractions (Chao and Theobald, 1976; Ottesen et al., 1994) may be used for the enhancement of hydromorphic anomalies. The variety of alternative sample types from stream sediment that has been found useful for exploration ranges from the collection of mineralized pebbles (Erickson et al., 1966) or pebbles coated with Fe and Mn oxides (Carpenter et al., 1975; Hale et al., 1984) to the isolation and analysis of a single mineral phase such as magnetite (Theobald et al., 1967; Granath, 1983) or cassiterite (Haapala, 1983). The choice among the numerous sample types is largely based on practical considerations such as experience, resources, and expected deposit types.

The application of stream-sediment geochemistry in exploration is based upon the premise that stream sediments represent a composite sample of rock and overburden in the drainage basin upstream of the sample site. Hence, an unusual chemical situation in the drainage basin, such as the presence of a mineral deposit, should be reflected by anomalous chemical characteristics in the sample. The assumption that the stream sediments are a composite sample has been accepted to be true. However, studies of fluvial erosion in Scandinavia have shown that erosion takes place in the Quaternary glacial overburden at a restricted number of small source areas along individual drainage channels. As a consequence, a sample of active stream sediment is representative of only a very limited portion of the drainage area (Ottesen et al., 1989).

Emperically, stream sediments have been successful as a sample medium for mineral exploration. They are also the most widely used medium for regional geochemical reconnaissance; being used in programmes such as the Nordkalott Project in Scandinavia (Bölviken et al., 1986), and the National Geochemical Mapping Programmes of Great Britain (Webb et al., 1973; Plant and Moore, 1979), France (Guigues and Devismes, 1969), Canada (Darnley et al., 1975), the United States of America (Dahlem, 1975; Foster et al., 1976, 1979), Germany (Fauth et al., 1985) and Austria. At the relatively small scale of these mapping programmes, generally 1:100,000 to 1:250,000 and low sampling densities, on the order of one sample per 10 to 100 km^2, stream sediments provide information on geochemical provinces and areas within which more detailed investigations have the greatest likelihood of discovering mineral deposits. Overbank sediment (floodplain sediment) appears to be a promising alternate sample medium for regional scales (Ottesen et al., 1989; Bölviken et al., 1990b, 1993; Demetriades et al., 1990; and Bogen et al., 1992).

Stream sediments at intermediate scales of 1:20,000 to 1:50,000 are most often used to define targets for detailed exploration. With sample densities of one to several samples per km^2, specific target areas of one to several square kilometers can be defined.

At large scales, $\geq$1:10,000, detailed traverses along individual stream segments can be used to identify the point of entry of metal into the stream system. Generally, however, the drainage net is too coarse to provide adequate sample coverage, and it is likely that soil or rock geochemistry will be needed to find the metal source. Thus, stream-sediment geochemistry provides a screening technique capable of delineating areas meriting further detailed examination (Levinson, 1980, pp. 792–799).

Applications of stream-sediment geochemistry

The information contained in stream-sediment data sets accumulated for exploration purposes, particularly the large regional surveys incorporating multi-element data, has been applied to a variety of problems (Webb et al., 1968; Bölviken et al., 1986). Stream sediments are a composite of the lighologies of the drainage basin, thus they provide a mechanism for mapping regional geochemical characteristics of the terrain. Under ideal conditions, the details of a geologic map may be reproduced from the chemistry of the stream sediments (Theobald and Allcott, 1973). Thus regional geochemical surveys using stream sediments are now reasonably well established as a means for characterizing the geochemical environment of large tracts of land (Wallis et al., 1978; Plant and Moore, 1979; Bölviken et al., 1986).

Expansion of the applications of regional stream-sediment data to include the fields of agriculture, health, and the environment is usually indirect. Water, soils, air, vegetation, lake and overbank sediment are usually more directly applicable in these fields, although regional patterns do provide useful information on the location and extent of areas within which more detailed surveys using the other media will be most fruitful (Webb and Howarth, 1979a, b).

The basic data produced from regional stream-sediment reconnaissance may be used for both exploration and the elucidation of regional geochemical patterns; however, the methods of interpretation differ markedly as emphasized by Webb and Howarth (1979a, b). The explorationist seeks to amplify the contrast between anomalies and the regional patterns, the regional interpreter will seek to minimize the anomalies so that more subtle differences of pattern are apparent. In addition, the monitoring of the more subtle, country rock related patterns often requires more careful control of sampling and analytical procedures than are necessary for the identification of anomalies. The explorationist will seek to avoid areas of artificial contamination and accentuate the natural anomalies attributable to a mineral deposit, whereas the environmental geochemist's objectives are the reverse. Thus, a broad based programme of stream-sediment geochemistry designed to meet all of these objectives will be considerably more complex and costly than a programme designed to address a single objective. For the explorationist, it may well be prudent to ignore possible additional uses of the data and concentrate on the design and implementation of a programme tailored to his own objectives.

THEORETICAL CONSIDERATIONS

Definition of stream sediments

Stream sediments, as used here, include all of the material transported by, and deposited from stream water during the present geomorphological cycle. Hence, active stream sediments, those being reworked during periods of high stream flow, and inactive stream sediments (the alluvial deposits of the modern flood plain lateral to the active stream channel) are included (Rose et al., 1979, pp. 416–418). The sediment may represent the deposits of the active stream channel, of the bank adjacent to the active channel, or of the

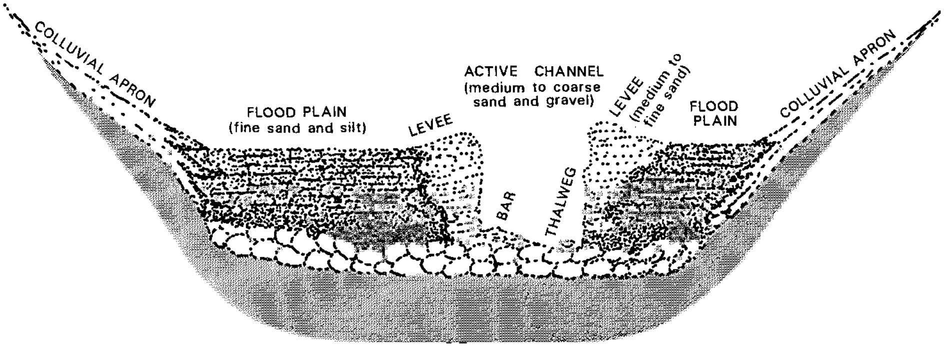


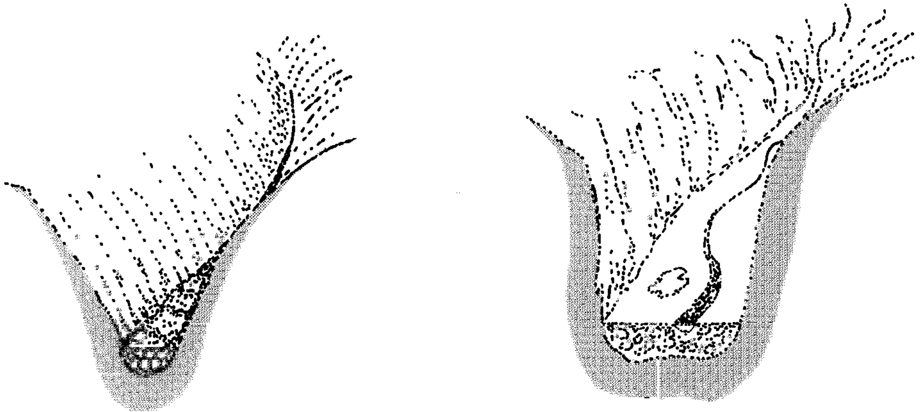
Fig. 5-1. Schematic cross section of an alluvial valley in a mature, temperate physiographic setting.

overbank deposits of the flood plain (Fig. 5-1). All three comprise mixtures of inorganic, detrital mineral matter with varying proportions of organic matter and chemical precipitates.

Climatic and geomorphic controls

A variety of climatic and geomorphic attributes of drainage basins can affect the stream sediment composition. For example, an intense, localized storm such as that which occurred in Big Thompson Canyon, Colorado (McCain et al., 1979), can, in a matter of a few hours, completely rearrange the sedimentary sequence (Shroba et al., 1979). Sampling before and after the Big Thompson flood, M.E. Allan (pers. commun., 1980) found that the sediments of the active channel had reequilibrated within a few years after the flood, in terms of the proportion of heavy minerals.

Geomorphological provinces also have their own stream regimen (Fig. 5-2). This is rarely a problem in detailed geochemical surveys because the survey area is usually within a single province, but regional surveys may span several geomorphological provinces. This Big Thompson River, for example, crosses three geomorphological provinces from the crest of the mountains with alpine glacial valleys, across a mature landscape with open valleys, and then through a youthful canyon to the mountain front. The proportion of detrital heavy minerals increases upstream in each of the provinces, but this increase is more than offset by the order of magnitude decrease in the proportion of heavy minerals that occurs between the canyon and mature valley provinces and again between the mature valley and the glacial valley provinces (M.E. Allan, pers. commun., 1975). The Tanacross quadrange (a 1° × 3° quadrangle in Alaska), although largely in the mature topography of the Yukon-Tanana upland, also includes a part of the youthful Alaska Range. Curtin et al. (1976) found secondary oxides of Fe and Mn to be the best sample media in the upland were hydromorphic dispersion was predominant, whereas the heavy-mineral concentrate was best in the Alaska Range where mechanical dispersion was predominant.



Immature Valley
Gravel floored canyon with little or no floodplain.

Immature Alpine Glacial Valley
An underfit stream flows on a broad valley floor filled by glacial debris rather than alluvium.

Mature, Temperate Valley
Stream channel cut into its own floodplain.

Mature Arid Topography
Wind erosion and deposition predominates. Isolated Inselbergs rise through the desert pediment. Drainage channels are poorly developed and choked with silt and fine-grained aeolian sand.

Fig. 5-2. Examples of four physiographic settings in which stream sediments have markedly different character. Each setting will require a different approach to sampling and to interpretation of geochemical data.

Raeburn and Milner (1927, pp. 90–119) review many of the geomorphologic conditions that affect placer formation and heavy-mineral accumulation. For example, lakes serve as traps for all types of suspended sediment, often, where organics are abundant, providing the nucleus for peat bogs and behaving as settling ponds for the production and entrapment of the secondary oxides and heavy minerals. They form a barrier to dispersion in streams by chemical or mechanical processes.

Waterfalls occur at constrictions in a valley, preceded by a pool where sedimentation is dominant (a trap) and followed by a fall pool where scour is dominant. The most useful samples for geochemical exploration purposes are from above the upper pool or well below the lower pool. Even in arid environments where the falls are usually dry, the sediment accumulating in the fall pools consists of relatively sterile and sand skimmed from the top of the sediment in the pool above.

Minor variations in stream-channel gradient can also have a marked effect on the accumulation of stream sediments, particularly of heavy minerals as described in natural and artificial streams (flume experiments) by Lidstone (1981). A slight increase or decrease in the gradient leads to pronounced enrichment in detrital heavy minerals above, in, or below the inflection, greatly enhancing lag enrichment of minerals of high specific gravity (sp. gr. >7) (Theobald, 1981, fig. 10). In one example, the bedrock source contained approximately 0.5% Pb whereas lag enrichment in soils contains about 1% Pb and placer accumulations in stream sediments below the source contained as much as 20% Pb. Such variations are not usually important in district-wide or regional surveys but they do present a serious problem in detailed follow-up surveys. Where such problems occur, alternative methods of exploration should be used. The extremely rich stream sediments can foster misleading optimism about the richness of the source, and their richness limits the range of values within an anomaly so that definition of sources is difficult.

Sources and composition of stream sediment

The ultimate source of the stream sediment is the rocks exposed in the drainage basin and cover materials such as glacial till or loess. The composition of stream sediment at a give site is the product of weathering, erosion, transport, and deposition.

Weathering is generally selective. At most latitudes, altered rocks associated with mineral deposits are usually more readily weathered than the unaltered country rocks. In the humid tropis the extreme chemical weathering accompanying the formation of lateritic soils may selectively leach the metals associated with mineral deposits to the extent that the surface environment may appear depleted. In higher latitudes the surface of a drainage basin may be blanketed with soils, in various stages of maturity, resulting from the chemical and mechanical disintegration of subjacent strata and from addition of material from the biosphere.

Erosion is also a selective process, taking place in two ways. Groundwater draining overbodies, enriched in metals, may produce hydromorphic anomalies. This process depends on factors such as the porosity, permeability, chemical susceptibility of the source terrain, and the chemistry of groundwaters. In general, ore minerals are preferentially leached. Where chemical weathering is intense and circulation is deep, groundwater may strip metal from the surface environment and from the stream sediments. In extreme cases this may produce supergene enrichment ores; for example, the copper ores at La Caridad, Mexico (Coolbaugh, 1979).

Surface water also causes erosion and contributes to the detrital train. Sheet flow, during which thin layers of surface material are gradually removed more or less evenly from the whole drainage basin, would provide representative sediments. Unfortunately, this type of erosion is largely confined to the immediate vicinity of a storm cell and to interfluvial areas. Most often runoff is rapidly channeled and the channeled water gains volume, velocity and erosive power. This channel erosion provides the major input of detrital sediment to a stream system, and once the initial rills have coalesced to form a stream, it becomes the dominant erosive mechanism. Both sheet and channel erosion operate on the loose debris of the drainage basin (Colby, 1963). Therefore the detrital component of stream sediment is selectively enriched in material derived from the least consolidated and most thoroughly weathered rocks of the drainage basin. This aggravates sampling problems in areas blanketed by till, loess, or lateritic weathering profiles where these source materials provide a disproportionate share of the sediment.

Channel erosion, in particular, can provide an extremely uneven sample of the drainage basin because sediment is entrained from the bed or banks of the channel (Colby, 1963). The channels are scoured in areas of least resistance, and lateral feed of material to the channel banks is often by mass movement of unstable materials from valley walls (Bogen, 1980). Thus, stream sediments, although providing a composite sample of the drainage basin, will only rarely be representative (Ottesen et al., 1989).

The detrital material, both inorganic and organic, entrained during erosion, moves along the stream bed, in suspension and in the bed load at rates dependent upon the state of flow of the stream and on the nature of the entrained material. During overbank flooding, for example, fine sediment is deposited on the flood plain surface while only the largest and heaviest particles lag behind in the scouring channel. At low water, deposition of all but the finest components of the sediment takes place in the channel until, in semi-arid and arid environments, flow ceases and deposition is complete. Within the stream system, the interrelation of deposition and channel erosion is cyclic, leading in general to a long range sorting of the sediment. The finest particles, traveling in suspension, are transported a greater distance downstream than coarser, sand-sized material which moves by saltation, slipping and rolling in the bed load (Kukal, 1971). The transition from suspended to load has been estimated to range from particle sizes of 0.15 mm in lowland streams (Sundborg, 1956) to about 0.5 mm in faster flowing mountain glacial streams (Ziegler, 1974). Thus, only the largest and heaviest particles resist transport and are deposited in the upper reaches of a stream, whereas progressively finer, lighter particles are deposited in quieter and flatter reaches downstream (Rose et al., 1979).

The grain sizes most often used for exploration are in the range deposited from the suspended load, which is estimated to be 80 to 90% of the total sediment load of streams (Sundborg, 1967; Nordseth, 1976). A sample passing

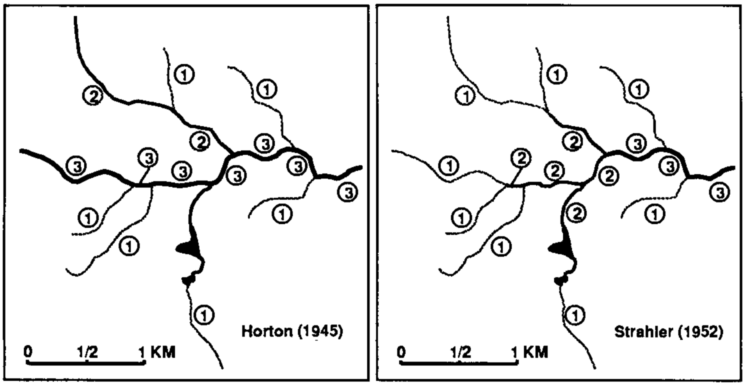


Fig. 5-3. Stream order as used herein, and as generally preferred, is designated after the pattern of Horton (1945, pp. 281–283, the figure on the left) as modified by Strahler (1952, footnote on p. 1120, the figure on the right). The modified scheme yields streams of similar size for a given stream order in a given environment and at a given scale. The smallest, normally ephemeral channels, constitute the first-order segments. A second-order segment is formed by the junction of any two first-order streams. A third-order segment is formed by the joining of any two second-order streams; et seq.

a 100-mesh sieve is composed of particles less than 0.15 mm whereas a sample passing 30-mesh is of particles less than 0.5 mm. However, the mesh size used generally reflects the bulk composition of the sediment; this mainly comprises rock-forming minerals such as quartz and feldspar, which are of little importance to the exploration geochemist. The primary and secondary minerals of the detrital train from a mineral deposit are frequently of higher specific gravity than the bulk sediment; hence hydrologically equivalent particles of ore minerals are generally finer than the average grain size of the sample. In first- and second-order streams (Fig. 5-3) erosion predominates over deposition. Fine detrital material has generally been transported out, leaving a lag enrichment of coarser and heavier particles. Samples from such sites should, therefore, be more sensitive for the detection of mineral deposits.

Deposition takes place (1) along the thalweg (the deep part of the main channel), where coarse and heavy particles of the bedload lag, (2) adjacent to the thalweg, where reduced flow allows the accumulation of bars, and (3) on the flood plain surface where overbank deposits at high water are deposited from the suspended load. Within the channel, erosion and deposition vary with the stream flow. “A rising river erodes from its deeps and deposits on its shoals, while a falling river scours from the deposit in its deeps” (Twenhofel, 1926, p. 29). In semi-arid and arid environments, culmination from the depositional cycle often yields nearly featureless, sand-floored dry washes.

Pebbles and cobbles of water transported rock fragments are confined to the channel deposits, where they are most abundant and coarsest in the deepest part of the channel. Bank deposits and bars grade rapidly into well sorted sand composed largely of discrete grains of quartz, feldspar, or other major mineral components of the bedrock terrain. The overbank deposits consist of fine sand, silt, and clay (Kukal, 1971). Detrital heavy minerals are most abundant in the main channel and deeps, where they may comprise the major part of the sand-sized fraction of the sediment. Although secondary accumulations of heavy minerals occur at the upstream point of a bar and along the transition from bar to deeper channel deposits, there is a rapid diminution in the quantity of heavy minerals from the channel deposits to the well sorted bar deposits. Overbank deposits contain few heavy minerals, and these may reflect only the very-fine-grained minerals of the suite characteristic of the drainage basin (Overstreet et al., 1953).

The detrital component

The minor and trace element composition of the detrital component of the sediments reflects the composition of resistant minerals from the parent rocks and of secondary minerals produced by weathering. The elements commonly associated with mafic rocks and with iron and magnesium minerals, including Co, Ni, V, Cr, Sc, Ti, Mn and Cu (Goldschmidt, 1929; Landergren, 1943), generally occur in minerals which have high specific gravity and concentrate along the thalweg of the stream channel. However, most of these minerals are susceptible to both abrasion and chemical weathering, particularly in tropical terrains, yielding fine-grained secondary products that move into the suspended sediment load of the stream and are deposited in quiet water of with the overbank sediments. Thus, the concentrations of these elements is generally highest in heavy-mineral-rich sediments or concentrates and in fine-grained sediments, whereas the bulk of the remainder of the channel and bank deposits may contain low concentrations.

The incompatible elements which are concentrated in felsic rocks, for example, Zr, Nb, Th, U, the rare-earth elements and Be, are generally concentrated in accessory minerals such as in zircon (zirconium), thorite, or monazite (thorium and the rare-earth elements), or occur as a minor component of common resistant minerals, for example, the rare-earth elements in sphene, apatite, or garnet and Nb in rutile. Most of these minerals are heavy and resistant to weathering and abrasion so they are concentrated in the heavy-mineral-rich stream sediments along the thalweg. Some of these minerals, particularly zircon and rutile may be present as extremely fine-grained particles and are deposited with fine-grained sediments in the channel, bank or overbank deposits. In general, the more complex detrital assemblage of the active thalweg is preferred to the more selective assemblage of the finer-grained sediments. Again, the highest concentration of these elements is usually along the thalweg with intermediate values in overbank sediments and lowest values in the other channel and bank deposits.

Other sediments associated with felsic rocks, such as Ba, Pb, Sr and Rb occur as minor components in rock-forming minerals such as feldspars which tend to concentrate in the coarser sands of the bar and bank deposits. These elements are also enriched in micas, and may therefore accumulate in overbank deposits, and in insoluble carbonates and sulphates that accumulate in heavy mineral-rich deposits of the thalweg.

Two types of sedimentary rocks in the drainage basin produce additional problems. Where streams drain limestones or dolomites, heavy-mineral concentrates may be so rich in barite, celestite and apatite that other heavy minerals are diluted to the point of being of little use. Shales, particularly the organic-rich black shales, shed fine rock chips that can be extremely rich in V, As, Zn and Cu, producing a high geochemical background against which only extremely high geochemical anomalies can be detected.

Clays and colloids

Clay is defined in two distinct ways. In physical sedimentology, clay is material finer than 2 μm, the finest size class of sediments. In mineralogy, clay includes a group of phyllosillicate minerals that are most commonly ver-fine-grained, hydrous aluminium silicates. The two definitions are not mutually exclusive: clay-sized sediment contains a high proportion of clay minerals.

Colloids are similarly defined as very-fine-grained particles, although the upper size limit of colloids is not consistently stated in standard references, ranging from 0.1 to 10 μm. The larger of these limits (McCarthy and Zachara, 1989) includes clay-sized particles and silt, and is probably too high. As these authors state, most colloids are less than 1 μm. Colloids are also defined functionally as particles transported in stable suspensions. Following this latter definition, a chemical change is necessary to break the suspension and allow sedimentation by flocculation, sorbtion or precipitation.

Active stream sediments contain little clay and only the relics of reconstituted colloidal material. The clays are transported in sufficiently stable suspension to resist sedimentation in all but the most isolated, ponded areas of the stream system. Ponded water relict from overbank flooding and stagnant water in bogs are favoured sites for the accumulation of clays, although even these deposits are predominantly silt. Organic material provides favoured sites for the trapping and preservation of clay-sized material along the channel banks (for example, mosses) (D.C. Smith, 1976; R.W. Boyle, 1979a; Matysek et al., 1988) and on the flood plain (for example, peat bogs and thickets). Colloids may be present in interstitial water in a stream sediment. They are incorporated in the solid phase of the sediments only by agglomeration or sorbtion on other particles, in which form they loose their colloidal characteristics.

Both the clays and colloids may contribute significantly to the chemical characteristics of stream sediments. Many of the metals sought in exploration are transported as colloidal complexes in the aqueous phase, and when incorporated in the sediments will be indistinguishable from metals transported in true solutions. McCarthy and Zachara (1989) emphasize the potential for long distance transport of metals and radionuclides by colloidal suspension not only in surface waters, but also in groundwater. In addition, many of the traps for sorbed metals in stream sediments, such as the organics and hydrous oxides, may form a major part of the colloids in the aqueous phase. Thus, the role of colloids in stream sediment is a source of both sorbants and metals that, in appropriate settings, will be incorporated in the sediments. When incorporated in the sediments, however, they lose their colloidal character.

Detrital particles of ore minerals in the clay-sized fraction of sediments are probably rare. Crushing or grinding to clay-sized particles of originally coarser particles is difficult to achieve within a stream (cf. Russell and Taylor, 1937). Thus, an initial very-fine-grain size is required. This condition is met in relatively few ores: fine-grained gold, some molybdenite, and perhaps disaggregated secondary uranium minerals.

The clay minerals, particularly the expanding clays or smectites, are ion exchangers. However in the stream environment this capacity is rendered relatively ineffective because metal ion uptake on the prominent basal planes of these micaceous minerals is weak (Luoma and Davis, 1983). The major coordination sites are on the edges and these sites are often occupied by a coating of organic matter in the natural environment (Davis, 1982). The major contribution of the clay-sized particles and the clay minerals is to provide a large surface area to serve as the substrate on which secondary oxides and organic compounds are precipitated (Jenne and Zachara, 1987). The metal ions coprecipitated with, or sorbed by the oxides and organic compounds, usually dominate the chemical contribution of the clays.

In the practical world of mineral exploration, clay or colloidal relics incorporated in stream sediment are rarely if ever used. Where collected, they are usually lumped with the silt in a −230 mesh (−62 μm) fraction, but even this fraction is difficult to isolate in most stream sediments. Where successfully employed, the clays and colloids are usually strained from the water column rather than from the stream sediment (cf. Siegel, 1985).

The chemical component

The term secondary oxides as used here denotes a variety of minerals and precipitates from ground and surface waters in the oxygenated surface or near-surface environment. They are primarily iron and manganese oxides, but a variety of oxides of other elements, as well as carbonates, phosphates, and sulphates, can occur and are often physically indistinguishable from the principal Fe and Mn oxides. Secondary oxides form as a result of Eh and pH changes accompanying the mixing of ground and surface waters and atmospheric oxygen (Whitney, 1975). These processes take place within the stream sediments (Carpenter and Hayes, 1980), soils (Chao and Theobald, 1976) and weathered rocks from which the sediments are derived. Hence, the oxides occur both as in situ precipitates reflecting local water chemistry and as detrital particles reflecting the water chemistry of some other parts of the drainage system.

Secondary oxides are generally considered to be ubiquitous in stream sediments (Rose et al., 1979); however, the quantities vary greatly in response to bedrock type (Ottesen et al., 1994), water temperature (Ljunggren, 1953) and sediment load (Carlson, 1982). Within a given environment, secondary oxides may be particularly abundant, as in bog areas (Nichol et al., 1967; Nowlan, 1982) in response to Eh changes or near places where groundwater enters the stream sediments (Whitney, 1981) in response to either Eh or pH changes. Spectacular development of secondary iron oxides often occurs around oxidizing sulphide deposits. The Red Dog deposit in Arctic Alaska is so called because of the brilliant red iron oxide coatings in stream sediment for many kilometres below the exposed massive sulphide deposit (Tailleur, 1970). In the montane and alpine zones of the Montezuma mining district in Colorado, the bog iron ores, derived from oxidation of disseminated pyrite, have been mined for their iron content (Lovering, 1935) and in the first major stream junction below the bogs, manganese, iron and aluminium selectively precipitate in response to pH changes (Theobald et al., 1963). In the less humid, lower montane zone of the West Shasta mining district, California, accelerated weathering of massive sulphides produces a train of highly coloured efflorescences, mostly sulphates, for 6 km downstream (Filipek et al., 1987). In the arid environment of Arizona, the Red Mountain porphyry copper deposit (Corn, 1975) gives rise to iron ozide deposits cementing Quaternary and Tertiary gravels flanking the deposit, and stream deposits around the mountain are often coated with alum.

Secondary oxides are usually a complex, multiphase assemblage of iron and manganese oxides and hydroxides, in various stages of hydration and crystallinity, admixed with other coprecipitated oxides, organic compounds, and fine detrital material (Vogt, 1915; Ljunggren, 1953; Greenland, 1965a, b; Varentsov, 1972; Vasari et al., 1972; Halbach, 1975; Gjessing, 1976; Potter and Rossman, 1979; Carpenter and Hayes, 1980; Filipek et al., 1981; Carlson, 1982; Robinson, 1982; Filipek et al., 1987; Kjeldsen et al., 1994). The mineraloids ferrihydrite, birnessite and vernadite, of variable composition and poor crystallinity, are those most often identified (Chukhrov et al., 1973; Schwertmann and Fischer, 1973; Carlson, 1982; Kjeldsen et al., 1994). Time and dehydration, particularly in arid environments, leads eventually to more stable, crystalline minerals such as goethite, manganite, and hematite. In the vicinity of oxidizing sulphide deposits, the mineralogy of the oxides may be much more complex. Lead-rich jarosite, molybdenum-rich lepidocrocite or ferrimolybdate, chrysocolla or malachite may be major constituents of the secondary oxides, and a variety of metal phosphates, sulphates, arsenates, and vanadates may be present.

These secondary oxides may be present as detrital particles, as nodules or concretions, as coatings or crusts on other detrital particles, or as cement consolidating the entire detrital sequence. Detrital particles of secondary iron and manganese oxides are almost ubiquitous, appearing in nearly all heavy-mineral concentrates from stream sediments. They are a mixture of material derived from soils and weathered rocks of the drainage basin with material abraded from the other forms of the secondary oxides in the stream system. Coatings and crusts, like the detrital particles, are nearly always present. Only in situations where solution or abrasion exceed precipitation are they completely absent. In humid environments the secondary oxide coating begins at the sediment-water interface and covers the exposed surfaces (Carpenter and Hayes, 1980). Thicknesses of as much as 5 mm have been reported for some Swedish streams (Ljunggren, 1953). Similar conditions in arid environments lead to the formation of "desert varnish", the geochemistry of which has been used to date sediment surfaces (cf. Harrington and Whitney, 1987). In situations where they may be scraped or leached from the surface of larger, inert fragments such as quartz pebbles or cobbles, the coatings can be isolated from other forms of the secondary oxides (Carpenter et al., 1975).

Nodules and concretions are another form of secondary oxides but have a more restricted range than coatings or detrital secondary oxides (Callender and Bowser, 1976). They have been described in Fennoscandia by Bölviken et al., 1994, Kjeldsen et al., 1994 and Ottesen et al., 1994, and from Maine by Nowlan et al. (1983). Nodules range in size from less than 1 mm to several centimetres. In areas of abundant secondary oxides, the coatings, nodules and detrital particles merge to fill all available pore space in the sediments. The result of this cementation process is most often seen in the vicinity of ore deposits and in the semi-arid environment where periodic wetting by metal-rich solutions allows the build up of successive layers of secondary oxides in the wet cycle and dehydration of these layers during the dry cycle. In extreme cases, the oxide-cemented gravels become sufficiently indurated to break across grains rather than along grain boundaries.

Secondary oxides as metal scavengers

The high surface charge, small volume, and the large surface area of precipitates of secondary iron and manganese oxides make them efficient collectors of anions and cations (Chao, 1984). In general, the secondary oxides have higher concentrations of minor and trace elements than associated stream sediments (Calvert and Price, 1977; Kjeldsen et al., 1994). This scavenging of metals by secondary oxides takes place by one or a combination of the following mechanisms: (1) coprecipitation, (2) adsorption, (3) surface complex formation, (4) ion exchange and (5) penetration of the crystal lattice (Chao and Theobald, 1976). The composition of the secondary oxides depends upon the composition of the water from which they precipitate, on the mineralogy of the precipitate, and on the environment of the secondary oxide after precipitation (Koljonen et al., 1976; Carlson et al., 1977; Vuorinen et al., 1983).

Secondary iron and manganese oxides can have markedly different minor and trace element compositions by virtue of their surface charge. This elemental partitioning is usually controlled by the pH of precipitation. Secondary manganese oxides are electronegative at the pH of most natural waters (Healy et al., 1966; and Murray, 1974, give values for the isoelectric point in the pH range of 1.5 to 7.3 for well-characterized synthetic manganese oxides). By contrast, iron oxides in alkaline waters may be electropositive whereas those in neutral to alkaline waters may be electronegative (Parks, 1965; Schwertmann and Taylor, 1977; and Schwertmann and Fechter, 1982, give isoelectric points in the pH range of 5.3 to 9 for natural and synthetic iron oxides). Metals occurring in anionic complexes, such as molybdates and arsenates, may be more attracted to iron oxides, particularly at low pH, whereas metals traveling in cationic form (normally ionized atoms) may be selectively attracted to the manganese oxides. Thus, the manganese oxides often appear to have a stronger affinity for the chalcophile elements when compared to the more lithophile character of the iron oxide (Roy, 1981).

With time, particularly in the drier climates, crystallinity of the secondary oxides increases and they become dehydrated. This process is accompanied by an increase in the stability of the secondary oxides (a decrease in solubility) and a decrease in the amount of adsorbed elements (Vuorinen et al., 1983). In general, the more complex crystal structures of the manganese oxides, accompanying the greater variety of oxidation states for manganese allows greater accommodation of ions than in the crystallographically simpler iron oxides.

The high background levels of metals in secondary oxides can overwhelm the generally lower metal content of normal detrital stream sediments if secondary oxides are abundant. In exploration practice, the use of bulk stream sediments in such an environment can yield large variation in the amounts of the minor and trace elements that reflects only the variation in the amount of the secondary oxides (Canney, 1966; Brotzen, 1967; Nichol et al., 1967). Isolation of the secondary oxide fraction is necessary in such circumstances. Once isolated, secondary oxides provide a mechanism for enhancing chemical variation due to hydromorphic dispersion from the surrounding bedrock (Carpenter et al., 1975; Chao and Theobald, 1976; Nowlan, 1976, 1982; Carpenter and Hayes, 1979a, b; Filipek et al., 1981; Whitney, 1981). Where used as a direct exploration sample medium secondary oxides are best obtained from the active stream channel. Secondary oxides in the main stream channel are precipitated from the continuous flow of the stream, while those in the overbank sediments may be derived from more local or ephemeral sources of water.

The organic component

Organic matter forms a significant component of stream sediments in some environments. In general, the effects of this organic matter on exploration geochemistry are most pronounced in forested areas, particularly in the deciduous forests of the northern and southern temperate zones and in the humid tropics. Organic accumulations are also conspicuous in many tundra areas of the far north. The influence of organics in further compounded in areas of low relief where the stream valley may be choked by accumulations of peat and the organic component may be the dominant material in the stream sediment.

Organics are contributed to the stream sediments by three processes: detrital fragments and sedimentation, solution transport and trapping, and in situ biological activity. Detrital fragments are swept from the slopes and floors of the stream valley during rain storms and are transported into the stream system. The vast majority of this detritus at high elevations consists of plant remains, and is more than 90% of the organics in streams in southern Norway (Larsson and Tangen, 1975). The detrital organics, due to their low specific gravity, tend to travel in the suspended load, which may comprise 15 to 20% of organics in a stream (Bulguru, 1977; Bogen, 1979a, b; Brandt, 1982a, b). Deposition is primarily in isolated, quiet pools adjacent to the stream channel, by entrapment in channel deposits, or with the overbank sediments.

Decomposition of the detrital organic debris in the alluvial cycle leads to the production of humic and fulvic acids which are transported in solution and deposited in sediments largely by adsorption to mineral surfaces (Schnitzer and Kodama, 1977; Yariv and Cross, 1979; Hunter, 1980; Tipping, 1981; and Davis, 1982). Drying and probably ageing of the adsorbed organic material leads to organic films highly resistant to chemical attack (Greenland, 1965b).

A variety of aquatic bryohpytes, along with other higher plants, grow in sediments (Allen, 1965; Greenland, 1965a, b) and have long been recognized to be active in the geochemical cycle (Brooks, 1972; Erdman and Modreski, 1984). In addition, algae, fungi and bacteria also take part in the cycling of the elements in stream sediments (for example, Filipek et al., 1981; Watterson, 1985).

Organics as metal scavengers

The detrital organic material in the stream system is derived almost entirely from plant remains and, to some extent, may be expected to reflect the minor and trace element content of the original plants. However, direct comparisons with biochemistry are not possible because the detrital material is a mixture of plant parts from a variety of plant species that have been modified by chemical degradation (see Brooks, 1972, or Kovalevskii, 1979, for a description of chemical variations in plants). The products of chemical degradation are abundant in some northern and tropical waters where the water-soluble humic acids, particularly the fulvic acids, are efficient scavengers of metals (Schnitzer and Skinner, 1965; Manskaya and Drozdova, 1968; Gamble and Schnitzer, 1973; Jackson et al., 1978). These acids serve a dual role in metal dispersion. Humic complexation or ion exchange can yield waters many orders of magnitude richer in metal than predicted by norma solubility constants (Gjessing, 1981a, b), thus allowing metal to be flushed through the fluvial system. On the other hand, humus readily adsorbs to mineral surfaces, both in parent soils and in the sediments, where it becomes an efficient sink for soluble metals within the sediments (Greenland, 1965a, 1971; Schnitzer and Kodama, 1966; Kodama and Schnitzer, 1968; Mortland, 1970; Rashid et al., 1972; Jackson, 1975; Jenne, 1977; Schnitzer and Kodama, 1977; Yariv and Cross, 1979; Hunter, 1980; Tipping, 1981; Davis, 1982). The organic component of stream sediments contains higher mean concentrations of many metals than are present in the inorganic fraction (Brundin and Nairis, 1972; Tanskanen, 1980) and, in areas where organic matter is abundant, their role in concentrating metals must be considered in exploration geochemistry.

The quantities of metals incorporated in organics in the stream system can vary dramatically. Stable accumulations of humic matter, such as peat bogs, act as efficient traps for soluble metals in the hydromorphic dispersion trains. Accumulations of copper in excess of 1% are not uncommon, and the bogs themselves may constitute ore (Boyle, 1977). Although many of the richest bogs are near ore deposits, some evidently owe their existence solely to the efficiency of the organic material to extract and hold metal brought to the bogs in solution from small, low-grade, or dispersed sources. As noted by Boyle (1977), the bogs retain the metal so that dispersion in the stream sediments downstream from the bogs is extremely limited. Uranium is similarly concentrated to extreme values in bogs downstream from rocks with only slightly elevated background levels; these bogs constitute a class of ore deposits referred to as the "surficial uranium deposits" (Toens, 1984). Spectacular levels of zinc and elevated levels of lead are also reported from bogs (Cannon, 1955; Jonasson et al., 1983). It is likely, as pointed out by Boyle (1977), that most of the elements of the Periodic Table can be scavenged and held in bogs.

Organic material in the drainage train thus has both positive and negative effects on stream sediments when used for exploration purposes. As a collector of metals, the organics may be isolated from the stream sediments and provide an enhanced sample medium in themselves. However, where organics are present, they can be responsible for the major part of the elemental content of the bulk sediment and apparent variation in the elemental content may simply reflect variation in the quantity of the organics. Where organics are abundant and the detrital dispersion train is to be tested, it is prudent to sample minor drainages upstream from the highest bogs and to select an active sediment as poor in organic matter as possible.

Interrelations among the components of stream sediments

The major components of stream sediments (detrital particles, secondary oxides and organic matter) interact to form a composite environment for the transport or retention of the minor and trace elements. The detrital particles form the substrate for both the secondary oxides and the organics.

The complex of interrelations among these components of the stream sediment are poorly understood and vary markedly from one environment to another on both local and regional scales. In general, the metal concentration in organic matter and secondary oxides is greater than that of the inorganic detrital fraction. On a volume for volume basis: Guy and Chakrabarti (1975) considered the absorption capacity for the metals to decrease in the sequence manganese oxides, humic substance, hydrous iron oxides and clay minerals. Jenne (1977) gives a similar sequence. Filipek et al. (1981) found the organics to be the most efficient scavengers in sediments whereas in the oxide coatings, the relative efficiency of the manganese oxides, iron oxides and organics varied from element to element and site to site. Rose et al. (1977) consider that the organic fraction of stream sediment is the main concentrator of uranium. These studies assume hydromorphic dispersion to predominate. In many areas, away from mineralization, metals occur in chemically resistant minerals in the detrital fraction (Earhart et al., 1977; Rose et al., 1977; Filipek and Theobald, 1981). In many environments, samples collected from the active channel of the stream are dominated by the inorganic detrital fraction, which contributes the greatest proportion of metals. The detrital fraction of the sediments is most widely used in exploration. Secondary oxides or organics constitute a significant fraction of the sediments in some environments, primarily the northern deciduous forests and the humid tropical environments. Here two options are available: (1) select detrital samples to minimize the influence of the other components (a mathematical manipulation [Howarth and Sinding-Larsen, 1983] will sometimes accomplish the same goal), or (2) isolate oxide and/or organic fractions and take advantage of the enhanced metal contents of these fractions. There is, however, a growing tendency in complex environments to opt for a multiple media approach (Curtin et al., 1976; Bölviken et al., 1986). The practical limitations of this trend must be carefully weighted against the objectives of a given project.

Despite these complexities and uncertainties for exploration geochemistry, stream sediments are still the most used sample medium in mineral exploration.

Incorporation of ore-related elements in stream sediments

Ore-forming and associated pathfinder elements move into the stream sediments by detrital and hydromorphic dispersion processes, and in the vicinity of exposed sulphide deposits, the stream regimen may be considerably different from that over unmineralized country rocks. Waters are commonly acid and metal enriched with an increased variety and quantity of secondary oxides (Chapter 3, this volume). The normal biologic community can be disrupted, and streams may appear sterile. In extreme cases, for example near large, high-grade massive sulphide deposits, metals may be dissolved out of the stream sediments which may then appear to have less than normal, producing "negative anomalies". In such extreme conditions even relatively immobile elements such as Au, Sn and Rb form hydromorphic anomalies.

The detrital train from an ore deposit can include primary ore minerals, accessory and gangue minerals of the deposit, secondary minerals of the ore and associated elements, and detrital fragments of secondary oxides and possibly organics. For primary ore minerals to occur in sediment, the deposit or material derived from it must be exposed to erosion (mass movement may feed material into the fluvial system even though the deposit is not visually exposed). It also requires that the ore minerals are resistant to chemical and mechanical disintegration or that they have not been exposed to these processes of decay for long. Thus, in the detrital dispersion train below the wolframite deposits of Baid al Jimalah, Saudi Arabia, wolframite survives only a short distance, whereas the minor scheelite of the deposits has a long dispersion train (R.V. Sale, pers. commun., 1982). In the same environment, coarse-grained zoned scheelite and powellite crystals in the primary deposit yield a detrital dispersion train of nearly pure, more resistant, scheelite (Theobald and Allcott, 1973).

Less resistant minerals, when present in the detrital train, may be taken as an indication of proximity to the source. Less resistant minerals like galena, sphalerite and chalcopyrite are occasionally encountered near a source in environments with a high rate of mechanical erosion.

Secondary minerals produced by near surface oxidation of ore minerals are more common in stream sediments than primary minerals. Although chemically more stable in the surface environment, many secondary minerals are soft and/or brittle, and hence from relatively short dispersion trains. Where secondary ore minerals precipitate in the sediment, the length of the dispersion train may be increased. The variety of secondary minerals encountered in stream sediments is great, particularly in semi-arid regions where frequent wetting and drying of the sediments causes chemical recycling. Rozelle (1978, as reported in Theobald, 1981) documented four secondary minerals of lead in a drainage in northern Sonora, Mexico. The most resistant of these (wulfenite and vanadinite) could be recognized in heavy-mineral concentrates for more than 5 km downstream. In Arizona, eight secondary minerals of lead have been described from stream sediments, including secondary oxides, carbonates, molybdates, arsenates, vanadates and chromates. Secondary ore minerals are tabulated in Dana and Ford (1948).

Detrital secondary iron and manganese oxides that are fragments of precipitate formed upstream from their present residence in the alluvium or soils of the drainage basin may contain large quantities of ore elements in the vicinity of deposits. In the vicinity of the major and minor porphyry copper deposits of northern Sonora, Mexico, Chao's (1972) hydroxylamine leach, intended to be specific for manganese oxides, yields copper contents of 10 to 85% (Theobald, 1981). Although the oxides have the black, opaque, amorphous character typical of manganese oxides, they would be better described as manganiferous secondary oxides of copper. In southwestern New Mexico, detrital Mn and Fe oxides in stream sediments in the vicinity of mineral deposits contain 1% or more of zinc, lead and copper and more than 5,000 ppm molybdenum (Alminas et al., 1975a, b; Watts et al., 1978b). Hence, in some environments, Mn and Fe oxides may contain the majority of the anomalous metals in the streams detritus (Ottesen and Volden, 1983; Ottesen et al., 1985).

Comparison of dispersion trains of secondary oxides with those of ore minerals can be used to derive an equation relating the partitioning of elements between the secondary oxides and ore minerals to depth of burial of the metal source (Alminas and Watts, 1978). This assumes that a fully exposed deposit will shed only ore minerals into the drainage system whereas a deeply buried deposit can shed only metals that have migrated upward by hydromorphic dispersion to be trapped in the secondary oxides. Although empirical, and restricted to similar deposits in similar topographic and climatic environments, the formula has been used successfully to estimate target depths in adjacent parts of Arizona and Mexico.

The main source of organic detritus in stream sediments in the vegetation growing in the drainage basin. This is often sparse, stunted, or absent, and the dry weight metal content of plants often low (Kovalevskii, 1979). Thus, high levels of metal in organic matter in stream sediments usually result from absorption by decaying organic debris.

Accumulations of organic debris along the alluvial train, particularly in the high latitudes, operate as metal sinks. The amount of metal that can be extracted by the organic debris can be spectacular, as demonstrated by Lovering (1928); Boyle (1977); and Jonasson et al. (1983), and it seems likely that microorganisms increase metal fixation (Filipek et al., 1981). Molybdenum derived from primary molybdenite provides an example of variation in mobility with environment. In the forested, montane environment of Colorado, where groundwaters tend to be acid, molybdenite is either stable or, when it weathers to release molybdenum, converts to stable ferrimolybdate or molybdenum-rich lepidocrocite. On entering the alluvial train, these minerals degrade to fine-particle sizes and are rapidly dispersed in the suspended load. Anomalies in stream sediments are barely detectable even in the immediate vicinity of the molybdenum ore deposits. In this case the molybdenum is considered immobile because the anomaly is confined to the exposed ore deposit. By contrast, in the southwestern U.S., where the waters are neutral to basic, small amounts of molybdenite associated with porphyry copper deposits are readily weathered to stable, secondary detrital minerals and to solution. Molybdenum anomalies are readily recognizable in stream sediments for tens of kilometres downstream from the deposits (Lee-Moreno et al., 1976). In the arid environment molybdenum is mobile.

Understanding the variation in mobility among the elements is a prerequisite for the design of effective geochemical exploration programmes. The more mobile elements are those best suited to regional reconnaissance programmes, whereas the less mobile elements are suited to more detailed target definition. Thus, in the western Brooks Range, Alaska, large quantities of barite in stream sediments define regions to explore for massive sulphides. Hydromorphically transported zinc in the secondary oxide fraction of the stream sediments defines more restricted targets for massive sulphides (Churkin et al., 1978). Within the zinc anomalies, lead, presumably as insoluble secondary minerals in the detrital train, even more closely defines the exploration targets.

Dispersion of elements in the surface environment separates and regroups elements (Chapter 3, this volume). The effect can be particularly pronounced where primary zoning occurs. Studies of molybdenum distribution at district scale, in northern Sonora, Mexico, provide an example (Theobald, 1981). Molybdenum is mobile in this environment, and the central, hypogene copper-molybdenum-rich part of the system has lost molybdenum in the supergene environment. A hypogene lead-zinc-silver-rich zone well outside of the central system has lost mobile zinc and silver in the supergene environment, whereas the immobile lead has stripped hydromorphically transported molybdenum from groundwaters and fixed it in the immobile lead molybdate mineral, wulfenite, which has accumulated in surficial placers. As a result, the primary lead zone is well represented by a prominent supergene molybdenum anomaly of higher magnitude than that of the hypogene molybdenum zone. Thus, extrapolation from stream-sediment geochemistry to primary dispersion patterns must be carefully tempered by consideration of supergene processes and products.

Exotic cover materials

There are five types of material that can contribute readily eroded products to the sediment load of a stream: (1) glacial till, (2) loess, (3) alluvial plains, (4) lateritic soils and (5) man-made contaminants. The effects of these may be to subdue or dilute geochemical anomalies associated with deposits, or, conversely, to produce exotic false anomalies.

Glacial flour from continental ice sheets is more readily eroded from glacial till than is local bedrock. This material usually dilutes the stream sediments, masking local anomalies. In instances where the glacier has eroded large, exposed deposits, metal-rich detritus may be transported across drainage divides. Erosion of this detritus can yield anomalous stream sediments for many kilometres in the direction of ice flow (Nowlan et al., 1987).

Till from valley glaciation is less of a problem; it is of more local origin. Nevertheless, ice produces less sorting than water. Stream sediments in glacial valleys are less well sorted then those outside of the glacial limit. Moreover, while stream sediments in the main stream of a glacial valley normally represent a composite of the drainage basin, those from lateral tributaries will contain material derived from higher up in the main valley. Hence, tributaries should be sampled above the top of the lateral moraines of the main valley or interpretation should attempt to account for the mixed sources of sediment.

Loess is the fine-grained material transported by wind. Although usually identified with the arid environment, wind transport is global. Perhaps the greatest accumulations of loess are in the temperate environment of the steppes of Asia. As an agent of transport, wind is relatively inefficient for coarser-grained material but provides a powerful means of transporting material fine enough to be suspended in turbulent air (Bagnold, 1941). Coherent clouds of distinctive composition have been traced for 1500 km in the Near East (Dickson, 1949, pp. 258–262). Loess has a modal grain size in the very fine-grained sand range. The size distribution of the wind transported material is rather sharply peaked, with few coarse sand or larger particles and little material finer than silt. The coarser material is transported only short distances in the "bed load" and rarely surmounts topographic obstacles, whereas the finer material is widely dispersed. The composition of loess is extremely uniform: an extremely well-mixed composite of material from a variety of distant sources. Thus, silt from the central Arabian Shield (Theobald and Allcott, 1973) is chemically indistinguishable from silt in the Yemen more than 700 distant (W.C. Overstreet, written commun., 1985). Loess readily enters the fluvial train and, where abundant, it may totally obliterate local geochemical signatures. The presence of a prominent, or dominant, aeolian component in stream sediments can usually be recognized by the abundance of drab-coloured silt. Size analysis of stream sediment rich in aeolian debris also indicates a distinctive mode in the very fine sand to silt range, unlike normal active stream sediments from which these sizes have been flushed. Rigorous mechanical analysis is rarely needed, however, because the abundance of the fine material is easily recognized when sieving samples for analysis. Where dilution by aeolian debris is expected, a coarse-grained fraction of the stream sediments may be used to overcome the problem (Theobald and Allcott, 1973; Ren et al., 1984; Carver et al., 1985). Heavy-mineral concentrates are little affected by the aeolian dilution (Theobald and Allcott, 1973; Overstreet and Day, 1985).

Broad alluvial gravel plains in the semi-arid environment often cover bedrock over large areas. Where the alluvium is of local derivation, these are of little problem to exploration geochemistry. In tectonically active areas, such as the Basin and Range Province of southwestern North America, the flood of gravel is extensive and sources may be distant. Entire ranges may be overridden and buried. The problem then is to sort locally derived material from exotic material. The ratio of metals in secondary oxides, reflecting both local and exotic sources, to that of the detrital fraction, reflecting the exotic sources, has had limited success in stream sediments (for example, Erickson and Marranzino, 1960). More commonly this problem is avoided by abandoning stream sediments in favour of biogeochemistry (for example, Horsnail and Lovstrom, 1974) or more recently soil gas (Hinkle, 1986). This topic is explored by Lovering and McCarthy (1978).

Lateritic weathering yields surface material that, by virtue of extreme chemical redistribution, may appear to be exotic with respect to underlying materials. Unlike the laterally transported exotic cover materials discussed above, chemical transport in a lateritic soil is largely downwards, leaving a trace-element depleted residue. Stream sediments in tectonically stable parts of the humid tropics are derived from lateritic soils. In the Piedmont Province of the southeastern U.S., for example, 10 to 50 m of relict saprolite, the deeper and thoroughly leached part of the lateritic soil profile, effectively insulates unweathered bedrock from erosion. Because of the residual nature of the lateritic soils, and despite the extreme chemical redistribution, stream sediments have been extensively used for regional exploration in this environment. Many heavy minerals resist chemical attack and remain in the detrital train. When these are ore minerals, such as cassiterite, scheelite or gold, the direct approach using heavy-mineral concentrates is applicable (Overstreet et al., 1968). Alternatively, the composition of a resistant accessory mineral in a host rock associated with a mineral deposit may survive the weathering and carry the host rock characteristics into the alluvial train (Theobald et al., 1967). Secondary oxides, both from detrital grains and in situ precipitation, have also been used (Carpenter et al., 1975; Smith et al., 1980).

PRACTICAL CONSIDERATIONS

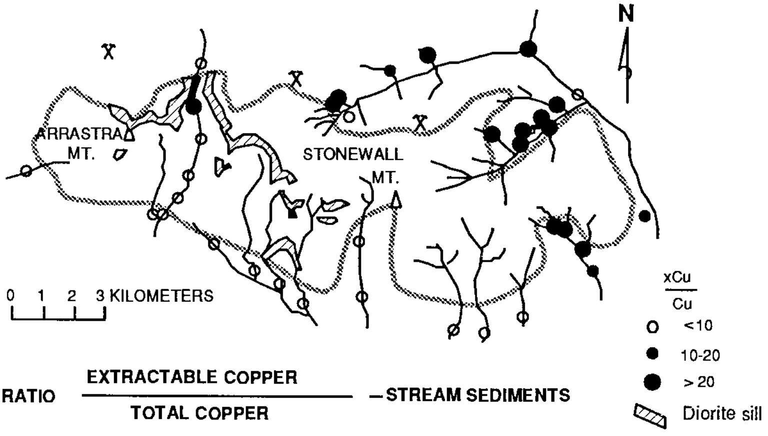
Contrast

Contrast is defined as the ratio of an element in an anomalous situation to that in a background situation. It is a measure of the reliability of anomaly recognition. Numerically, this ratio may vary from less than one to several orders of magnitude, though in practice the "negative anomalies" (those with a ratio of less than one) are rarely employed. Contrast is partly a function of the overall abundance of the element. Gold in heavy-mineral concentrates may exhibit a contrast of six orders of magnitude or more, whereas a contrast of two is rarely possible for abundant elements such as aluminium or silicon in bulk stream sediments. As it is maximum contrast that is desired for easy and reliable anomaly recognition, exploration geochemists constantly strive to use the rarer elements and specialized sample media.

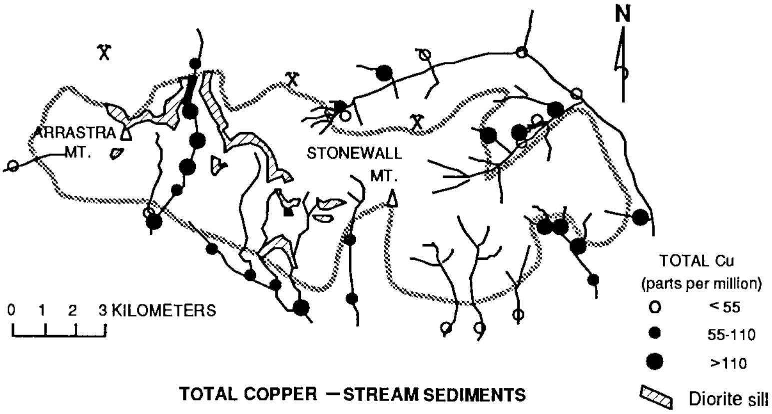
Where an anomaly with large contrast is present, the source must be near the sample site, of large surface area, or of high grade. The general formula for the downstream dilution is given by Hawkes (1976a). Commonly, contrast using stream sediments is small, and resource to statistical techniques can be helpful in establishing the presence of anomalies.

Contrast is usually expressed as a simple ratio. However, both the numerator and denominator may represent ranges that may be large when compared to the contrast. In regional studies, background may vary by an order of magnitude or more while in more detailed studies, usually within anomalous areas previously defined, a true background population may not be present at all and the range of values arbitrarily used for background is likely to be the lower part of a continuum of anomalous values. In these detailed studies, the range of anomalous values often encountered is extreme, may overlap or be continuous with the background population, or may even be within the back-ground population. The problem of anomaly recognition and establishing contrast is one of sorting among two noisy populations. Two approaches can be used: (1) more complex statistical procedures, often involving multi-element data (see Howarth and Sinding-Larsen, 1983), or (2) more careful selection of sample media to increase the contrast, often involving more complex sample preparation and analysis. In the opinion of these authors, the second alternative is preferable.

An excellent example of the problem is provided in the data of Grimes and Leinz (Earhart et al., 1977; Fig. 5-4) in Montana. Geologically the area consists of variety of Precambrian sedimentary rocks interlayered with mafic sills. Background copper concentrations in the sedimentary rocks are normally less than 10 ppm, whereas those in the mafic sills range up to 500 ppm. Stream sediments normally contain 50 ppm or less of copper but range up to several hundred ppm, clearly reflecting mixing of the sedimentary and igneous rocks. Stream sediments from below known copper-bearing vein deposits adjacent to the study area contain no copper than stream sediments taken from drainage



RATIO $\frac{\text{EXTRACTABLE COPPER}}{\text{TOTAL COPPER}}$ —STREAM SEDIMENTS



TOTAL COPPER —STREAM SEDIMENTS

Fig. 5-4. Enhancement of contrast using a partial dissolution technique in terrane where mafic sills contribute as much or more copper to stream sediments than stratabound copper occurrences (compiled from data from Earhart et al., 1977). The partial dissolution is by 0.8 N HNO_3. A fraction of the sill-hosted copper, extracted by the dilute solvent, is eliminated by using the ratio of extractable to total copper.

basins with abundant mafic igneous rocks. Grimes and Leinz were able to sort the truly anomalous copper population from the high-background population by recourse to a specially tailored partial dissolution technique, isolating and distinguishing the hydromorphically transported metal (only about 20 ppm) derived from the veins from that due to detritally transported metal (several hundred ppm) in the igneous rocks. Using the copper to vanadium ratio give a similar result. Vanadium is uniformly low in the sedimentary rocks and high in the mafic rocks. (Other transition elements vary dramatically within the sedimentary rocks, hence are not as useful). The simple ratio of copper to vanadium in the stream sediments identifies those streams which are copper-rich but do not contain mafic sills. However, this statistical approach may produce a misleading result where both vein copper and mafic-rock copper are present.

Sample media

The selection of the sample media, the appropriate fraction of the stream sediment to be analyzed, is critical to the problem of optimizing contrast. The object is to maximize contrast and to minimize natural variation within the background and anomalous populations, keeping costs and expected benefits in mind. However, specialized media used to enhance anomalies generally have greater natural variation than stream-sediment samples. Moreover, although anomalous values may be greatly enhanced in the special sample media, background is also usually higher.

Size fractions of stream sediment

The conventional stream-sediment sample is usually taken as a sieved fraction of the fine sand from the active stream channel. It allows ease of collection and preparation while optimizing the probability of obtaining anomalous metal contents from either the hydromorphic or detrital dispersion. Material passing an 80-mesh sieve is most commonly used (Hawkes, 1957, p. 325). Sieves are identified by the number of wires per inch, in a square mesh. The actual sieve opening depends upon the uniformity and thickness of the wires and the uniformity of the weave. The maximum particle size that will pass through a sieve depends upon the sieve opening and the particle shape. Thus only a nominal particle size can be given for a particular sieve, 80 mesh corresponding to a maximum particle size of about 0.18 mm.

Both coarser and finer fractions of the active stream sediment have proved useful for certain applications. Fractions finer than 100 mesh (0.15 mm) are recommended for elements which are contained in detrital minerals of fine grain size or which are easily ground to fine grain size. Fine fractions of sediments also have higher adsorption capacity for elements transported in solution. Under normal stream conditions, the fine fraction constitutes only a small part of the stream sediment, so that their influence in samples sieved at coarser grades is small. Further, losses of fines during sieving of a coarser sample, particularly wet sieving, further diminishes their influence. The principal limitations of the fine fraction are the difficulties of sampling and sieving and the higher background for many elements. In some areas, dilution by loess limits the value of the fine fractions. Uranium, molybdenum (D.F. Siems, pers. commun., 1985), and fine-grained gold can give improved contrast in the fine-grained fraction of stream sediments when little or no response is obtained using coarser fractions, because these are present in fine-grained particles. Beeson (1984) recommends the use of the fine fraction for a wide range of elements in semi-arid and arid environments, in contradiction to the findings of Theobald and Allcott (1973); Ren et al. (1984); and Carver et al. (1985).

Fractions in the size range of 5 or 6 mm to 0.18 mm (80 mesh) have been used to simplify sample collection and to minimize aeolian dilution (Theobald and Allcott, 1973; Ren et al., 1984; Carver et al., 1985) and in situations where the detrital train includes coarse-grained primary or secondary ore minerals (Theobald and Thompson, 1959; Rozelle, 1978). Coarser particles may also have oxide coatings. Coarser fragments of organic debris may be present although these may be easily washed from the sample. The major disadvantages of the coarse fractions of the stream sediment are that the sample must be ground for analysis, a larger sample is necessary to ensure representativity and the presence of a few large fragments of unusual composition may cause unacceptable large sampling error (the nugget effect). Moreover, selective weathering near quartz-rich mineral deposits often yields a lag of coarse-grained, barren-quartz so that coarse particle sizes can contain less metal in mineralized than background areas (Theobald and Allcott, 1973). Contrast in the coarse fraction of the stream sediments may be similar to or larger than that of finer fractions of the sediment, because the background levels are usually lower in the coarse-grained sediments. Where aeolian dilution disguises contrast in the fine fractions or the ore metals are selectively present as coarse grains, there is no alternative but to use the coarse fraction.

Pebble- to cobble-sized detritus has been used in exploration in two contrasting ways. Erickson and Marranzino (1960) used the coarse fraction of stream sediment to identify altered or mineralized fragments. The technique is similar to that of boulder tracing in glacial terrain. In a similar manner, the quartz porphyry pebbles characteristic of the Climax-type molybdenum deposits can be traced up to the Colorado River to an undeveloped deposit in Rocky Mountain National Park (R.G. Blair, pers. commun., 1975). Pebbles and cobbles are also used when hydromorphic manganese and iron oxide coatings are being sought because the finer fractions of the sediment contain detrital oxides in addition to the hydromorphic oxides (Carpenter et al., 1975; Whitney, 1975; Hale et al., 1984).

Physical and chemical subsamples of stream sediment

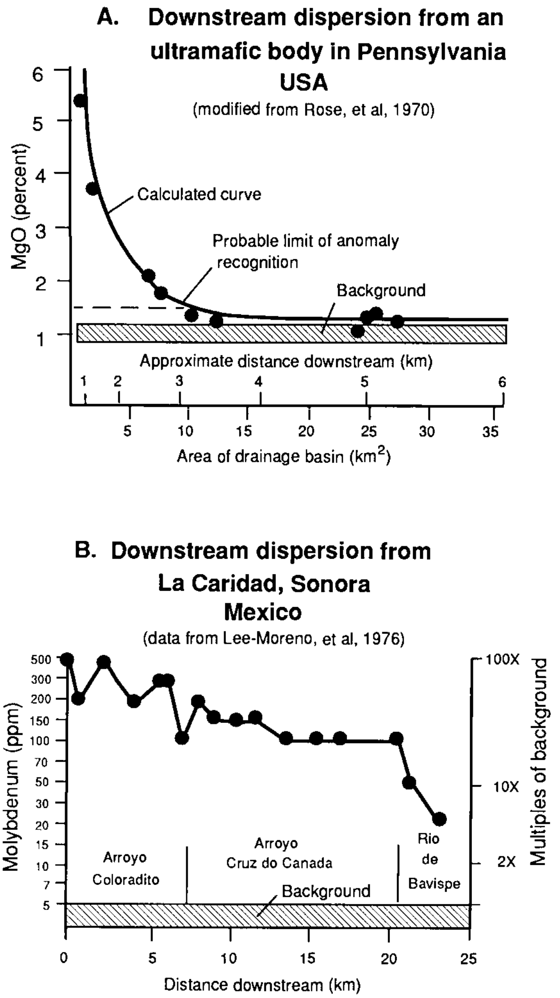
Gravity, magnetic and partial chemical dissolution techniques are all effective in isolating particular fractions of stream sediments to reduce the affects of dilution from barren material and to reduce background. However, although contrast is increased, interpretation of the resulting data is often more complex, and extrapolation of values from the subsamples of stream sediment to a bedrock source can be misleading. For this reason, it is usually advisable to also have data on a conventional stream-sediment sample.

Care must also be exercised in selecting appropriate subsamples. In a deeply weathered, humid environment where hydromorphic dispersion predominate, the heavy-mineral concentrate may not be an effective sample medium. Moreover, selection of particular subsamples requires that other subsamples are discarded, or are included at additional cost. While one particular type of subsample may be best for some elements, contrast for associated elements may be reduced or destroyed.

The high-contrast subsamples of stream sediments have maximum value in regional programmes where more widely spaced samples are collected, and the more subtle, low-contrast anomalies in the outer fringe of a dispersion pattern need to be recognized. At more detailed scales, the enhancement may be desirable when the surface expression of the mineral deposit is weak. On the other hand, the enhancement may be a hindrance where the surface expression of the mineral deposit is strong. For example, a few samples in a regional data set containing 1% or more of metal in an enhanced sample will clearly identify a target area. Follow-up within that target area, however, will have a local background in the enhanced sample of 1% or more, and contrast within the target will be constrained by the shear intensity of the anomaly. Thus, follow-up investigations may require sample media with less enhancement of metal values.

The most commonly used subsamples of the stream sediments are those produced by gravity and/or magnetic separation of a particular group of minerals. Elements such as gold, tin and tungsten are usually sought in heavy-mineral concentrates produced by one or another of the gravity separation techniques because their primary minerals are chemically and mechanically stable in the surface environment and are of high specific gravity. Another group of elements, notably those associated in sulphide deposits, from heavy, stable secondary minerals that may be isolated in heavy-mineral concentrates. These include a variety of molybdates, vanadates and arsenates of lead (for example, Theobald, 1981, fig. 11). A third group of elements which includes Ba and Sr are relatively abundant in the common rock-forming minerals, but have ore or ore-related minerals of high specific gravity. Gravity separation may be used to isolate Ba in barite from that occurring in rock-forming minerals (Overstreet and Marsh, 1981, fig. 4). Likewise, separation of the magnetic fraction can be used to distinguish Cu and Zn-rich provinces (Theobald et al., 1967; Granath, 1983).

Partial chemical dissolution techniques which are designed to determine the amount of hydromorphically transported metal in samples, are reviewed by Fletcher (1981) and by Chao (1984). These techniques fall into two categories: selective and nonselective methods (Fletcher, 1981). Several of the nonselective methods have been routinely employed in regional exploration programmes (for example, Hawkes et al., 1960; Curtin et al., 1976). Some, like the Bloom test (Bloom, 1955), used by Hawkes et al. (1960), extract only the readily exchangeable metals of the sample; while others, like the method of Alminas and Mosier (1976), used by Curtin et al. (1976), dissolve a substantial part of the oxide and/or organic fraction of the samples. In contrast, selective techniques are designed specifically to extract the oxide, organic or sulphide fraction, and are most commonly used in more detailed studies on selected samples. As emphasized by Sandström (1984), selective extractions are considerably more expensive and are therefore inappropriate for routine analysis of large numbers of samples. For reconnaissance studies, Sandström recommends an indirect attack for organic samples utilizing an ashing technique (Gustavsson et al., 1979) similar to that described by Brundin and Nairis (1972). Selective extractions are mostly used for interpretation, after an anomaly has been identified.


A. Downstream dispersion from an ultramafic body in Pennsylvania USA

(modified from Rose, et al, 1970)

B. Downstream dispersion from La Caridad, Sonora Mexico

(data from Lee-Moreno, et al, 1976)

Fig. 5-5. Comparison of the downstream dispersion from a small deposit (A) with that from a large deposit (B). The influence of background on contrast is also evident. The MgO content of stream sediment (background 1%) cannot exhibit a contrast of two orders of magnitude as is shown by the molybdenum (background 5 ppm).

Dispersion

Dispersion is the distance downstream from a metal source that significant contrast can be recognized. Loss of contrast with distance downstream is predicted by the equation of Hawkes (1976a) and graphically illustrated by Rose et al. (1970). In Rose's example (Fig. 5-5), the chemical composition of the stream sediment cannot be distinguished from background by the time the drainage area is 10 km^2 equivalent to a linear dispersion train of less than 3 km. In conventional stream sediments, maximum dispersion trains of the order of 1 km have been recorded frequently. Woolf (1983) gives a figure of 0.5 km for the arid environment of Saudi Arabia, Hale et al. (1984) a figure of 1 to 2 km in southwest England, and Ren et al. (1984) a figure of 1 to 2 km in Inner Mongolia. These figures are somewhat misleading, however, because all of these examples are based on relatively small (both in size and grade) metal sources. Large metal sources yield longer dispersion trains than smaller sources. Lee-Moreno et al. (1976) document dispersion trains of 10 to 20 km below La Caridad in Sonora, Mexico (Fig. 5-5), and Hawkes (1976a) used examples more than 10 km below the source in testing his general formula.

Dispersion is also larger when appropriate subsamples of the stream sediment are used. Theobald and Thompson (1959), for example, documented a dispersion train of more than 70 km for tungsten in heavy-mineral concentrates even though the host mineral, huebnerite, is among those considered highly susceptible to loss through abrasion (Raeburn and Milner, 1927). Below smaller deposits, Carpenter et al. (1975) and Hale et al. (1984) describe increases in the dispersion train by a factor of three when the secondary oxides are used as the sample media rather than the conventional stream sediments. In contrast, Boyle (1977) describes the abrupt termination of hydromorphic dispersion trains where streams cross organic-rich sediments or bogs.

The length of a dispersion train effectively controls the size of stream that must be sampled. Deposits with large exposed areas have detectable anomalies tens of kilometres downstream even using conventional stream sediments. Where deposits have small surface exposure, dispersion trains of the order of one to a few km are most likely, depending upon the sample type and the nature of the dispersion process. For most practical applications samples should be taken from small first- or second-order tributaries.

Target size

The target size provides a second constraint on the sample design. If the target is small enough to be entirely within a single drainage basin, then all drainage basins need to be sampled to ensure its discovery. Fortunately, a variety of primary and secondary characteristics of ore deposits reduces the need for such high-density sampling programmes. Mineral deposits often occur in clusters, frequently in geologic terrains that are metal-rich (metallogenic provinces). Moreover, processes of primary zoning and dispersion, coupled with supergene dispersion during weathering, effectively increases the size of the chemical target around both individual deposits and deposit clusters. Thus, most of the deposits worthy of extensive follow-up will be within geochemically anomalous target areas of 10 or more km^2. In the Saudi Arabian examples summarized by Woolf (1983), where dispersion "seldom exceeds 0.5 km", almost all of the target areas exceed 10 km^2 (R.V. Sale, pers. commun., 1982). In this circumstance, sampling streams of 0.5 km length, or less, at a frequency of two samples per 10 km^2 would have a high probability of two adjacent samples being within a given anomalous target area. Indeed, these concepts provide the basis for regional geochemical surveys using stream sediments (the "point source" concept of Plant and Moore, 1979). Saturation sampling is economically impractical at regional scales, and is not necessary. Follow-up studies within anomalies defined in regional studies may well require saturation sampling. Thus at regional reconnaissance scales, the dispersion determines the size of stream to be sampled and the target size determines the frequency of samples; whereas, at more detailed follow-up scales both the size of the stream and the frequency of samples are determined by dispersion.

Orientation

Orientation studies are surveys of restricted in the vicinity of known, preferably little disturbed, mineral occurrences and in background areas. They are used to assess the variety of available exploration methods and decide which will be most efficient for use in a larger exploration programme. Such studies must be made in an environment geologically, geomorphologically and culturally similar to the larger area to be explored, preferably within the larger area. Factors to be considered are the suitability of geochemical exploration to the problem, which of the numerous geochemical methods is most applicable (in the case of stream sediments this selection usually includes surface and subsurface waters and soils as a minimum (Rose et al., 1979, pp. 431–435)), what type of sampling within the chosen method is most appropriate, what type of preparation and analytical scheme is most appropriate, and how well the resulting data can be interpreted. The decisions resulting from the orientation must be couched in terms of the cost of a particular scheme and the value of the possible conclusion.

There are many ways to accomplish the objectives of an orientation survey. The cheapest, and most effective, is to exploit experience already at hand. During the early years of exploration geochemistry, the physical conduct of orientation surveys in the field was considered mandatory. Over the last few decades, however, a large amount of the necessary data has been accumulated and resides either in the minds of experienced individuals or in the literature. Particularly valuable are the conceptual models volumes of the Journal of Geochemical Exploration, and the symposium volumes of the Association of Exploration Geochemists, while specific major environments have been covered in international symposia on glaciated terrain, arid terrain and tropical forest areas (Table 5-I). Numerous regional symposia on exploration technology provide more provincial information on most parts of the world. These sources should be carefully searched to determine what combination of techniques is most likely to succeed in finding a deposit of a type appropriate to the area of interest. It is no longer necessary, or feasible, to physically test all possible combinations of methods in all projects.

A number of constraints should be designed into an orientation survey before it is begun. Almost all projects operate under restrictions of time and cost. An expensive, multi-element analytical scheme, for example, is not appropriate

TABLE 5-I

Thematic publications containing reports of stream sediment geochemistry orientation studies, showing editors, year of publication and individual journal and book titles

Special Volumes on Conceptual Models in Exploration Geochemistry		
Australia	Butt, C.R.M. and Smith, R.E., 1980	J. Geochem. Explor., 12: 89–365
Basin & Range	Lovering, T.G. and McCarthy, J.H., 1978	J. Geochem. Explor., 9: 113–276
Canada	Bradshaw, P.M.D., 1975	J. Geochem. Explor., 4, 213 pp.
Norden	Kauranne, L.K., 1976	J. Geochem. Explor., 5: 173–420.
Proceedings of International Geochemical Exploration Symposia		
1st	Cameron, E.M., 1967	Geol. Surv. Can, Paper 66-54, 282 pp.
2nd	Canney, F.C., Bloom, H. and Hansuld, J.A., 1969	Colo. Sch. Mines Quart., 64, 530 pp.
3rd	Boyle, R.W., 1971	Can. Inst. Min. Metall., Spec. Vol. 11, 594 pp.
4th	Jones, M.J., 1973	Geochemical Exploration 1972. Inst. Min. Metall., London, 458 pp.
5th	Elliott, I.L. and Fletcher, W.K., 1975	Geochemical Exploration 1974. Elsevier, Amsterdam, 720 pp.
6th	Butt, C.R.M. and Wilding, I.G.P., 1977	J. Geochem. Explor., 8, 494 pp.
7th	Watterson, J.R. and Theobald, P.K., 1979	Geochemical Exploration 1978. Assoc. Explor. Geochem., Rexdale, Ont., 504 pp.
8th	Rose, A.W. and Gundlach, H., 1981	J. Geochem. Explor., 15, 698 pp.
9th	Parslow, G.R., 1983	J. Geochem. Explor., 19, 243 pp.
10th	Björklund, A.J., 1984	J. Geochem. Explor., 21, 501 pp.
11th	Garrett, R.G., 1987	J. Geochem. Explor., 28, 494 pp. and 29, 440 pp.
12th	Jenness, S.E., 1989	J. Geochem. Explor., 32, 491 pp.
13th	Rose, A.W. and Taufen, P.M., 1991	J. Geochem. Explor., 40, 451 pp. and 41: 1–252.
14th	Dickson, F.W. and Hsu, L.C., 1993	J. Geochem. Explor., 47, 390 pp.
Proceedings of Conferences on Prospecting in Areas of Glaciated Terrain		
1st	Jones, M.J., 1973	Inst. Min. Metall., London, 138 pp.
2nd	Jones, M.J., 1975	Inst. Min. Metall., London, 140 pp.
3rd	Jones, M.J., 1975	Inst. Min. Metall., London, 140 pp.
4th	Anon., 1979	Inst. Min. Metall., London, 110 pp.
5th	Davenport, P.H., 1982	Can. Inst. Min. Metall., 339 pp.
6th	Gallagher, M.J., 1984	Inst. Min. Metall., London, 232 pp.
7th	Anon., 1986	Inst. Min. Metall., London, 269 pp.
8th	Rogers, P.J., 1988	Can. Inst. Min. Metall., 644 pp.
Proceedings of Conferences on Prospecting in Areas of Desert Terrain		
1st	Jones, M.J., 1985	Inst. Min. Metall., London, 283 pp.
2nd	Zimmerman, D.O., 1988	Aust. Inst. Min. Metall., 154 pp.
Proceedings of Conferences on Prospecting in Tropical Rain Forest		
1st	Laming, D.S.C. and Gibbs, A., 1982	AGID Rept. 7, 221 pp.

where either the time factor or the budget cannot accommodate it. In addition, the availability of expertise and the physical plant necessary to accomplish a task often limit the options. Where, for example, the available field personnel are limited to talented and experienced, but scientifically illiterate, prospectors equipped with a shovel and a gold pan, it would be wise to limit the options to those within the competence of the prospectors. The stage of the orientation process provides the first decision point. If the available expertise and facilities cannot provide the desired product within the budget and time allocated, the project should be aborted. If however, several techniques offer promise for defining exploration targets within the area of interest, a physical test of these should be undertaken.

The design of a scheme for orientation in a field setting is covered by Garrett (1983) and by Miesch (1976a, b). The object is to compare the selected, most promising techniques to determine which provides the most efficient solution to the overall problem. The object of this is to optimize, not to maximize or minimize. The use of an analysis of variance (ANOVA) design is appropriate so that the variance within and between samples may be objectively quantified and reliability monitored. Where options are available, each of the various components of the overall method need to be tested. The reliability of identification of an anomalous population, in contrast with background, is evaluated for each option. Where several options meet the required reliability, recourse to the various "cost" factors allows optimization of the choice. Where two options meet requirements for anomaly recognition, for example, and option A is twice as reliable, twice as expensive, and takes twice as long, opt for option B.

The most difficult decisions to make are those relating to sample type. For stream sediments, dispersion, contrast and anomaly size should all be known or determined by orientation. It is these criteria that determine the maximum size of stream that may be sampled, the reliability or utility of the sample, and sample spacing. The decision among options at the sampling level must consider the impact of these criteria in consort on the overall programme. Again, where two sampling schemes meet the reliability criteria, option A costs five times more than option B on a per sample basis, but option B requires one sample per km^2, whereas option A allows one sample per 10 km^2, opt for option A because the overall cost will be halved.

Programme design

Careful consideration of geologic environments, geomorphological history, and climate are required for the appropriate choice of sample media, sample spacing and analytical scheme. These are considered in relation to the size and scale of the study, acceptable types and sizes of deposits, and the economic constraints on the programme. Where economic constraints preclude a reasonable chance of reaching the objectives, the programme should be aborted. There are all too many, rarely publicized, examples of programmes that exhausted the resources of the mission only to prove the obvious or nothing. Finding known mines is not, of itself, a valid objective of stream-sediment geochemistry.

The conventional, sieved, largely inorganic fraction of active stream sediment is still the most universally accepted sample medium by virtue of its ease of collection, preparation and analysis. Contrast in this medium is less than in the more selective media and dispersion trains are usually short. For regional surveys, it is most useful as an indicator of the major chemical characteristics of a terrain and will highlight conspicuous anomalies. At intermediate scales, within an anomaly, stream sediment may be preferred over more selective media, wherein the local background may be raised to the point where contrast is obscured. The conventional stream-sediment sample is probably not appropriate in environments where there are abundant, and variable quantities of organics and secondary oxides in the stream sediments. These are primarily in the high latitudes and humid tropics, particularly in continentally glaciated terrain of low relief.

The choice of grain sizes within the conventional stream sediment depends upon climate, topography and the elements sought. Fractions coarser than 80 mesh are preferred in areas of loess, in semi-arid environments and in youthful montane and alpine environments where finer fractions of the sediment are difficult or impossible to find because stream gradients are steep and flow torrential. Fractions finer than 100 mesh are preferred for elements where primary and secondary minerals are in, or rapidly degrade to, very fine particles (notably U, Mo and sometimes Au), and in some situations where the sorption capacity of the very fine sediment is advantageous. These fine fractions have somewhat higher background levels for a variety of elements and are more difficult to collect, although easier to prepare for analysis. The 80-mesh sample is a compromise between these two, and has many of the advantages and disadvantages of both. In general, it is the most broadly applicable sample medium.

Heavy-mineral concentrates are the most commonly used of the more selective samples. Contrast in the concentrates often exceeds that in equivalent conventional stream sediments by several orders of magnitude and dispersion trains are much extended. Concentrates have been used successfully in practically all climatic zones. They are considerably more expensive to prepare and are more difficult to analyze because of the unusual and extremely variable matrix. The ferromagnetic fraction of concentrates yields regional patterns related to metallogenic provinces, or less commonly, direct information on the potential location of mineral deposits. It is usually removed from the concentrates before analysis because: (1) it often constitutes the bulk of the concentrate, and (2) it is composed almost entirely of iron, which interferes with many analytical methods. A greater degree of magnetic separation is often employed to remove the common, rock-forming mafic minerals, leaving a nonmagnetic fraction enriched in many of the important ore minerals. Contrast in this nonmagnetic fraction may be misleading, with values of 10^3 to 10^6 produced for such elements as lead, zinc, copper, gold, silver, arsenic, antimony, bismuth, tin and tungsten.

The intermediate magnetic fraction, comprising the paramagnetic minerals, is most suitable for elements in minerals with intermediate magnetic properties (the columbite-tantalite series, the wolframite series, many of the thorium and rare-earth minerals) and for detrital particles of mature, secondary iron and manganese oxides with their contained metals. The intermediate fraction is difficult to analyze and has higher background levels for many elements, hence lower contrast, than other sample types. A common compromise is to combine the nonmagnetic and paramagnetic fractions, thus avoiding a second magnetic separation and the necessity to decide which group of elements is most important. The major disadvantage of the concentrates, other than cost, is the exclusion of organics, fine-grained or porous secondary oxides (and coated grains), and ore minerals of low specific gravity such as beryl. An advantage of concentrates which is often overlooked is that they provide a mineralogical sample which can be used to gain an understanding of the genesis of the anomaly.

The use of nonselective chemical subsamples of the stream sediment is restricted to situations where the elements of interest are (1) transported hydromorphically, at least in some parts of the dispersion train, and (2) are trapped in the sediment in a form susceptible to dissolution by the chosen solvent. Nonselective chemical subsamples are most often applicable in organic- or oxide-rich environments, and in extreme situations may be the only useful alternative. Their use requires some prior knowledge of the residence and the nature of dispersion of the elements of interest and by analytical facilities capable of the chemical extraction. Where applicable, the techniques can significantly increase contrast and, for some of the more mobile elements, greatly increase dispersion. They are more expensive to use than the conventional stream sediments, but generally less expensive than heavy-mineral concentrates. As with the concentrates, some compromises are involved; information, which is gained for the chemically mobile elements must be balanced against that which is lost for the chemically immobile elements in each programme and environment.

The selective sequential dissolution techniques are generally too expensive for routine application for large numbers of samples. Their primary use is with selected anomalous samples where knowledge of the partitioning of elements among the several phases dissolved is needed, as in orientation surveys and during follow-up studies. Although primarily of value where hydromorphic transport and trapping in secondary oxides or organics are significant, extended sequential dissolution techniques can include a final "total" digestion that attacks the residual silicates and primary oxides. These extended techniques have provided valuable information in environments ranging from arctic to tropical and from arid to rain forest.

Regional reconnaissance surveys, particularly those designed to seek a wide variety of deposit types, often opt for two or more media. In many instances this approach yield valuable information on the nature of the anomaly source. For example, an anomaly readily detected in nonmagnetic heavy-mineral concentrates, but not distinguishable in the secondary oxides, is most probably derived from an exposed source. Knowledge gained in the reconnaissance surveys should allow for more streamlined follow-up studies wherein fewer, more selective media, or fewer elemental determinations are utilized.

Sample spacing is largely a function of scale, the size of the area to be covered. The problem is most difficult at small scales, where large areas are to be covered. Arguments based on dispersion require the sampling of relatively small streams. Arguments based on target size require sample densities of the order of one sample per 10 km^2 to have a reasonable probability of collecting from at least one anomalous site in each target area. Collecting one small stream in each 10 km^2 area leaves a lot of unsampled terrain. Where the resources are adequate, the risk of missing something significant may be reduced by higher density sampling, as high as one sample per 2 km^2 as adopted by the British Geological Survey (Plant and Moore, 1979). However, where the object of a survey is solely the detection of mineral deposits, saturation sampling should be avoided because of the high cost and the vast quantity of redundant data that is generated. Experience in North America, South America, Scandinavia and Asia indicates that much lower sample densities, as low as one sample per 30 km^2 in the Nordkalott project (Bölviken et al., 1986, 1990a), one sample per 500 km^2 in the geochemical mapping of Norway (Ottesen et al., 1989), effectively define the most promising target areas.

Two approaches have been widely used to select sample sites for regional studies. The more rigorous approach involves subdivision of the area into cells and the random selection of sample sites on streams within cells (the stratified random sampling design of Garrett, 1983). This approach validates mathematical tests of the sources of variation and is most frequently used in environmental geochemistry where overall variation is not great. (Indeed, the anomalous samples are usually discarded in analyses of this sort.) In the second approach, practical consideration of access, geomorphology and geology often dictate a simple scheme of arbitrary selection of sample sites to provide as uniform coverage as possible of the most favourable parts of the area. This approach leads to a non-uniform, non-random, hopefully haphazard distribution of sites that, in the long run, is probably more efficient for exploration purposes. A large plateau basalt field might well be left totally unsampled because it was inaccessible, had no surface drainage, and a negligible potential for mineral deposits. Similarly, the large gravel-filled basins of the western U.S. are often left unsampled because the surface drainage is poorly developed, and it is unlikely that deposits below the gravel would be detected in stream sediments.

Detailed sampling for follow-up or orientation surveys usually aims at saturation sampling. For orientation, some form of rigorous nested sample design as described by Garrett (1983) under the heading of "Analysis of Variance" is appropriate so that the validity of decisions on the sources of variation, expected target sizes and recommended sample spacing can be tested. The object of follow-up studies is to locate the point or points of entry of anomalous metal into the drainage system. A non-uniform, biased spacing of samples, often developed in an iterative manner, is appropriate. Rapid availability of analytical results, such as on-site analysis, can greatly improve efficiency at this stage of the programme by allowing choices of sampling spacing to be made at the site.

Much has been made of the detail that should be recorded at each sample site; such observations as stream width, velocity, vegetation, nature of the sediment and gradient. Standardized forms for encoding such data have been developed for several of the large regional reconnaissance programmes (for example, Garrett, 1974; Plant and Moore, 1979). There have been arguments that the cost of recording and interpreting this data exceeds its value (for example, Meyer et al., 1979) and that this qualitative information is poorly reproducible (Plant and Moore, 1979). To the contrary, Matysek et al. (1983) argue for the value of the detailed descriptive information and present a mathematical analysis of the interrelations among the descriptive parameters and the geochemical data from the Canadian Uranium Reconnaissance Programme. It should be noted, however, that Matysek at al. had to discard anomalous sites from the analysis; thus, though of value in relating the various components of the background population, the techniques are not yet of direct value in exploration. There is no question, however, that field notes of some sort are requisite to sorting among anomalous areas once they have been identified. Questions about the environment of anomalous sites (unusual characteristics rather than the usual characteristics) can often be answered by reference to the field note — such comments as "mine dump on slope above", "collected just above a peat bog" or "stream sand was black" can be extremely useful to the interpreter who needs to decide where to go or what to do next.

Data interpretation

Data interpretation is basically a matter of anomaly recognition and of the convincing display of the data. The spectrum of anomaly-recognition techniques is reviewed in the companion volume edited by Howarth (1983), which includes a wide range of techniques from simple to complex. Of particular value is Chapter 5, Mapping, which reviews the wide variety of display techniques currently in use.

Stream sediments represent point data that are only a crude composite sample of the drainage basin above the sample site. For this reason, interpretation techniques that extrapolate data from a single site to the drainage basin, though often of value, should be used with caution. A particular element concentration at a specified sample site may only reflect a single point source in the drainage basin. Fortunately for the explorationist, it is usually the highest concentrations that are recognized and these often obscure less-rich point sources. It is for this reason that mineral-resource-oriented programmes usually display data in a point source plot, accentuating individual high values of groups of high values, whereas those interested in regional patterns more commonly plot smoothed data, subduing the influence of individual high values.

Multi-element data, commonly available in regional programmes, should be treated in a similar manner. Multi-element data consist of data for several individual elements, but very high values for one of these elements, perhaps of great significance for exploration, can easily be lost when interelement relations are used as the basis for interpretation. In this situation, a staged interpretation is recommended. First, consider the implications of the elements of interest separately. If the desired objectives are met at this stage, there may be no need to go further. In some instances, particularly when working with conventional stream-sediment samples, anomalies may be subdued in the single-element data and may be enhanced when proper combinations of elements are considered. A second stage of interpretation that considers the interelement relations is then appropriate. A common failing of multi-element interpretations, when blindly applied using the more complex mathematical manipulations, is the loss of much of the most valuable information for exploration. All analytical techniques have a lower limit of sensitivity. Where that limit for one or several elements is above the background level, the majority of the data for those elements (perhaps all but a few) will be recorded as not detected. The few positive values may be of critical importance in exploration, but they must be interpreted by non-parametric methods.

Scale is also critical in interpretation. Simple coherent anomalies in regional data sets often turn out to be complex anomalies reflecting several metal sources of different character at more detailed scales. Conversely an assemblage of elements interpreted as a single complex deposit at the regional scale may comprise several simpler anomalies when examined in detail. Overstreet and Marsh (1981) describe linear regional anomalies related to regional structure. At intermediate scale, these resolve into circular anomalies reflecting centres of mineralization along the regional structure, and in detail the circular anomalies resolve into linear segments reflecting local sites of mineral accumulation. In general, it is not prudent to interpret geochemical data beyond the scale at which it is collected.

The nature of both the interpretation and the display of the data depends upon the problem, the sample design and sample media, the internal structure of the data and the scale of the problem. For exploration purposes, the internal structure of the data may yield to direct interpretation with little data manipulation. A cluster of uniquely anomalous samples, clearly outliers from the rest of the data, may constitute the major anomaly and may well be recognized before analyses are even competed. In such a situation, all that need be done is to locate the samples on a map and begin follow-up (for example, Theobald, 1970). At the opposite extreme would be the search for significant anomalies in a regional data set using conventional stream sediments where there are known deposits yielding the uniquely anomalous values and a variety of geologic units yielding an extremely wide range of background values. In such a situation, it may be necessary to unravel the internal structure of the data using one of the complex mathematical techniques, such as factor analysis, present this interpretation in terms of a smoothed map of regional trends, such as a contoured map of gridded data from a particular factor score, and then seek outliers from expected values of a given element, "residuals", to plot against the regional patterns (De Vivo et al., 1984). Where the secondary oxides and organic material are the major metal traps, a minimum interpretation will often involve regression analysis and/or ratios of the elements to compensate for variation in the abundance of the oxides or organics (Selinus, 1983; Hale et al., 1984).

Both interpretation and presentation are usually simpler at detailed scales than they are at regional scales. Smoothed data are rarely necessary, and the need for multi-element combinations is less frequent, in part because more information about the anomaly is available beforehand and fewer elements need be determined. Smoothed data and contour maps are less frequently used. The most common forms of presentation are point plots or "worm diagrams". The "worm diagrams", in which the apparent width of the stream above a sample site is scaled to the metal content of the sample, is most useful where hydromorphic dispersion is prominent and the dispersion train need not follow the stream channel. Bulges along the "worm" identify reaches of the stream where metal adsorption is greatest, for instance where lateral influx of metal-rich groundwater occurs. Point plots have the distinct advantage of specifying the location of the sample points, and the reaches that have not been sampled. For presentation of detailed information, it is often desirable to annotate plots with the actual values measured, either for the entire sample net or for selected anomalous points. Such annotation is best associated with points.

The method of interpretation and presentation will be most convincing if it is simple. Although large data sets with many variables are often most efficiently handled by automated data processing systems, the urge to proceed automatically into complex interpretation and presentation should be resisted. Not only is information blurred by the complex approaches, but the audience will be less convinced. The use of complex approaches should be reserved for situations of low contrast and where interelement relations are required to obtain the objective. A complex interpretation of the interrelations of arsenic, mercury and thallium will have much less impact than a simple presentation of a gold anomaly.

SUMMARY

Stream sediments are the most widely used media for geochemical exploration at intermediate to regional scales. Overbank sediment (floodplain sediment) appears to be a promising alternate sample medium for regional scales.

Sieved fractions of stream sediments analyzed for the suite of elements of interest for a particular exploration strategy provide the simplest, most efficient and cheapest approach. This is traditionally the most commonly used method, and it should remain so where the desired end can be achieved with this approach. Decades of experience has shown, however, that this simple approach primarily yields information on major lithologic units rather than

specific information on the location of targets for mineral exploration. This particularly true of regional exploration programmes. The problem stems from the fact that dilution in the raw stream sediments reduced contrast so that only the largest and richest exposed deposits can be readily recognized.

A variety of techniques using selected fractions of stream sediment has been devised to increase the contrast. These include subsamples of the sediment produced by both mechanical and chemical means that isolate the element enrichment of interest. Preparation of these subsamples is more costly, often complex, and often yield data that are more difficult to interpret. Nevertheless, as exploration increases for deposits not discovered by the simple methods, it is likely that use of these more complex methods will increase. Further, there is a growing use of multiple media which, though still more expensive, help to resolve some of the uncertainties.

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Chapter 6

HEAVY-MINERAL CONCENTRATES IN GEOCHEMICAL EXPLORATION

H. STENDAL and P.K. THEOBALD

INTRODUCTION

Many primary and secondary ore minerals and some gangue minerals are resistant to chemical weathering and have high densities which facilitates concentration by gravity separation techniques. The concentration of heavy minerals from alluvial sediments is one of the oldest methods of prospecting for ore. Hill (1746) refers to Theophrastus, who described circa 300 B.C. the concentration of cinnabar from alluvial sand using a vessel like a gold pan, and of the application of the method to the search for lode mercury deposits. The technique was traditionally used in exploration for gold and the platinum-group metals, gems, and the tin and tungsten minerals, all of which can be identified visually. More recently, heavy-mineral concentrates have been analysed chemically. During the last 40 years, exploration based on heavy minerals has been used systematically in the Soviet Union, and in many other parts of the world. Mineralogical studies of heavy minerals have also been applied as a tool for geological mapping (Mertie, 1954), while analyses of heavy-mineral concentrates by multi-element chemical techniques have been processed by multivariant statistical methods for both exploration and other geological applications (e.g., Leake and Aucott, 1973).

Sediment deposited by water is sorted according to the size and shape of particles and the specific gravity of the minerals. The majority of the particles present are common rock-forming minerals, such as quartz and feldspar, which are of low specific gravity and can be removed by gravity separation, thereby concentrating the more dense ore minerals. The common enrichment is three to four orders of magnitude, which increases the probability of recognizing ore minerals proportionately.

A high proportion of many trace elements in stream sediments may be incorporated in iron oxide, manganese oxide and mafic silicate minerals, which have a high specific gravity and are also concentrated with the other heavy minerals. In some instances the concentration of common rock forming minerals and their products of oxidation can mask anomalous values related to the presence of ore minerals. Mafic minerals are usually magnetic to some degree and can be removed by magnetic separation. Over the last two decades, it has become common practice to use a combination of gravity and magnetic separation to prepare nonmagnetic heavy-mineral concentrates for use in exploration.

The heavy-mineral methods facilitate the detection of many elements such as gold, silver and antimony, the concentration of which would otherwise be too low to be detected in stream sediments, as well as identifying situations where elements such as barium and strontium, occur in gangue minerals such as barite and celestite, rather than common rock-forming minerals.

Heavy-mineral concentrates generally enhance the contrast between ore-related, anomalous values and background values. However, the use of heavy-mineral concentrates increases the cost of sample collection and preparation and sample reproducibility can be poor. Moreover, elements associated with ore bodies which are held in materials of low specific gravity, such as beryl or oxide coatings on the common rock-forming minerals, or which occur in magnetic minerals such as the wolframite and columbite groups of minerals, or the anhydrous iron oxides (hematite and magnetite), may be lost. In some environments, particularly the tropics, elements dispersed hydromorphically may be better sought using stream sediments or water samples.

In this chapter, minerals with a density of 2.9 g/cm^3, or more, are termed heavy minerals. This definition is based on the specific gravity of the heavy liquids most commonly used in mineral separation, which range from 2.89–2.96 g/cm^3. Mertie (1954) further distinguishes between "heavy-accessory minerals, such as iron ores, zircon and monazite... (and) semi-heavy minerals, exemplified by garnet, biotite, or sillimanite". In the German literature, heavy minerals are those with densities greater than 4.2 g/cm^3 and minerals with densities from 2.9 to 4.2 g/cm^3 are designated "heavy sands" (semi-heavy minerals). Another commonly used subdivision of heavy minerals is at specific gravity of 3.3 g/cm^3, corresponding to the heavy liquid methylene iodide (for example, Brundin and Bergström, 1977).

The definition of magnetic splits of the heavy-mineral concentrates is commonly imprecise. Although precise measures of magnetic fields are available, they are impractical for routine use, and magnetic properties are measured in relation to the equipment used for the separation and adjusted according to individual projects. Three magnetic splits may be defined on the basis of their predominant mineralogy: (1) the strongly magnetic fraction (ferromagnetic), which is easily separated with a hand magnet and is composed primarily of magnetite, and sometimes ilmenite; (2) the intermediate paramagnetic fraction, which is separated in stronger electromagnetic fields and includes most of the mafic, rock-forming minerals such as pyroxene, amphibole and biotite; and (3) the nonmagnetic fraction, which is the residue from the separation in strong electromagnetic fields and includes the common accessory minerals such as apatite and zircon. The ore minerals are distributed among these magnetic splits, so care must be exercised in their selection. For example, pyrrhotite and some of the platinum alloys may appear in the strongly magnetic fraction, the niobates, tantalates, and most of the rare-earth minerals in the intermediate fraction, whereas most of the common sulphides and their immediate oxidation products, pyrite, sphalerite, galena, goethite, and jarosite, will appear in the nonmagnetic fraction.

Heavy minerals from media other than drainage sediments

Almost all of the solid, inorganic sample media available to the exploration geochemist have been evaluated for heavy-mineral separation. Successful enhancement and enlargement of anomalies have been demonstrated in glacial till, surficial soils, talus, deep lateritic weathering profiles (saprolite), bedrock, and even in lacustrine and marine sediments.

Separation of heavy minerals from glacial till is described by Brundin (1969); Gleeson (1970); Brundin and Bergström (1977); Toverud (1977); and Peuraniemi and Heinanen (1985). Heavy-mineral concentrates from surficial soils have been used in Saudi Arabia (Theobald and Allcott, 1973) and in Colorado (Barton, 1985a, b).

The transition from alluvial sampling to soil sampling is often accomplished by “base of slope” sampling. The sample medium is colluvium, scree, or talus. Theobald and Thompson (1959) used heavy-mineral concentrates from avalanche debris in Colorado to locate the source of tungsten being fed into the alluvial train. Hallenstein et al. (1981) and Stendal (1982) successfully located the points of lateral input of tungsten, arsenopyrite, and galena into alluvial trains in East Greenland using heavy-mineral concentrates from scree. Raeburn and Milner (1927, pp. 53–54) give an excellent description of the change in proportions of cassiterite and wolframite in the transition from hill-slope soils to alluvium.

In saprolite, the soft clay-rich product of thorough chemical weathering of rocks, the chemically resistant heavy-accessory minerals are often the only original minerals to survive. Derby (1889, 1891) and Mertie (1954) advocated the use of heavy-mineral concentrates in the study of saprolite derived from crystalline rocks. Mertie (1953, 1979) and Overstreet et al. (1963) successfully applied these techniques to the classification of rocks in the southeastern US. Unweathered bedrock does not yield heavy-mineral concentrates as readily as its easily disaggregated weathered products. Nevertheless, Allen and Nichol (1984) successfully applied heavy-mineral techniques to rocks in the search for massive sulphide deposits in Canada. Dissolution techniques closely allied to heavy-mineral separation and analyses have been used by Neuerburg (1961, 1971) for silicate rocks and by Erickson et al. (1981) for carbonate rocks in the US.

Characterization of lithologies with heavy-mineral concentrates

The mineralogical and chemical data derived from heavy-mineral concentrates reflect in large part the mix of country-rock lithologies in the drainage basin above the sample site. These data may be used to derive the patterns of distribution of the major lithologic units, particularly in regional surveys, thereby creating a geological map. For example, Leake and Aucott (1973) found the composition of concentrates from England and Scotland to be useful in mapping major rock types that otherwise showed little contrast. They use a variety of individual elements and element ratios to distinguish several phases of granite as well as the Old Red Sandstone, lavas and a variety other sedimentary rocks in the Cheviot area of north England, and to distinguish rocks of Moinian and Lewisian age from the Old Red Sandstone, Caledonian granites, and siliceous gneissess in the Scottish Highlands. The regional distribution of major lithologies and metamorphic facies was unraveled in a large segment of North and South Carolina using the abundance of key minerals (Overstreet et al., 1968) and trace element abundances in magnetite (Theobald et al., 1967). Catchings (1978) used the distribution of garnet, staurolite and kyanite in concentrates to define the metamorphic isograds in the Barnardsville quadrangle, western North Carolina. Stendal (1978) used the abundance of hornblende and hypersthene in heavy-mineral concentrates to define metamorphic facies in southwestern Norway.

THEORETICAL CONSIDERATIONS

The major part of the concentrates normally comprises the common minor rock-forming and accessory minerals and their alteration products. For exploration purposes, the minerals sought are the primary and secondary minerals associated with ore deposits and the gangue or alteration minerals that can serve as indirect indicators of mineral potential.

The variety of heavy minerals in the alluvial dispersion train depends on the nature of the country rocks in the drainage basin, on the nature of any mineral deposits present, on the climatic and weathering processes that have modified the source rocks, and on the transportation and depositional history of the stream system. Thus, in a terrain of crystalline rocks, the heavy minerals tend to be coarser in grain size, angular to euhedral, and more abundant and varied than in a terrain of mature, clastic sedimentary rocks, where they are fine grained, well rounded and consist only of the most resistant minerals. Erosion of some deposits causes resistant ore minerals, such as cassiterite or scheelite, to enter the fluvial dispersion train, whereas other types of ore deposits will be reflected in the concentrates only by the presence of secondary minerals or resistance gangue minerals such as barite or fluorite. The preservation of minerals in alluvium depends greatly on climate and weathering. Thus, the heavy-mineral suite of the humid arctic differs from that of the arid arctic, while both are quite different from the humid tropics. Mechanisms of transport and deposition within the drainage system generally yield coarser grained accumulations of minerals with the highest specific gravity near the mineral source and progressive enrichment downstream of minerals of smaller grain size and lower specific gravity. Geomorphic irregularities, constrictions, or changes in gradient, can

TABLE 6-I

Minerals identified in 1300 heavy-mineral concentrates from 8000 km^2 in the semiarid environment of the southwestern United States

Varietal and accessory minerals	Primary ore minerals	Secondary ore minerals	Alteration and gangue minerals	Contamination
Amphibole	Acanthite	Bismutite	Barite	Aluminum
Anatase	Arsenopyrite	Carnotite	Chlorite	Brass
Andalusite	Cassiterite	Cerargyrite	Fluorite	Lead shot
Apatite	Celestite	Conichalcite	Sericite	Plastic
Aragonite	Chalcopyrite	Crocoite	Rutile	Tin
Biotite	Galena	Chrysocolla	Tourmaline	
Brookite	Gold	Copper		
Clinohumite	Isostannite	Descloizite		
Corundum	Molybdenite	Malachite		
Epidote	Powellite	Mimetite		
Garnet	Pyrite	Minimum		
Hematite	Scheelite	Silver		
Ilmenite	Sphalerite	Vanadinite		
Kyanite	Thorite	Willemite		
Leucoxene		Wulfenite		
Limonite				
Muscovite				
Moissanite				
Olivine				
Perovskite				
Prehnite				
Pyroxene				
Rutile				
Sillimanite				
Sphene				
Spinel				
Staurolite				
Talc				
Topaz				
Tourmaline				
Xenotime				
Zircon				

produce local traps for heavy minerals at intervals along the stream channel.

Two lists of minerals encountered in heavy-mineral concentrates (Tables 6-I and 6-II) illustrate the variety and the marked differences between regions. The first was prepared from one suite of 1300 nonmagnetic heavy-mineral concentrates from the southwestern US, collected from active alluvium in first- and second-order streams. The long list of rock-forming and accessory minerals reflects the geologic heterogeneity of the area, the lack of intense weathering, and the immaturity of the alluvial train in the semiarid environment. The list of primary ore minerals and of secondary ore minerals includes a surprising

TABLE 6-II

Minerals identified in heavy-mineral concentrates from the gold-bearing conglomerates of the Witwatersrand and the diamond-bearing conglomerates of Brazil (after Von Putzer, 1968)

Varietal and accessory minerals	Primary ore minerals	Secondary ore minerals	Alteration and gangue minerals
Amphibole	Arsenopyrite	Autunite	Barite
Andalusite	Cassiterite	Braunite	Fluorite
Apatite	Chalcopyrite	Cerussite	Rhodonite
Baddeleyite	Cinnabar	Hydrozincite	
Celsian	Columbite	Malachite	
Chromite	Copper	Psilomelane	
Corundum	Diamond		
Epidote	Galena		
Garnet	Gold		
Hematite	Molybdenite		
Ilmenite	Niccolite		
Kyanite	Osmiridium		
Magnetite	Palladium		
Monazite	Platinum		
Pyroxene	Pyrite		
Rutile	Pyrochlore		
Sillimanite	Pyrrhotite		
Sphene	Scheelite		
Topaz	Sphalerite		
Tourmaline	Stibnite		
Wollastonite	Tetrahedrite		
Xenotime	Thorianite		
Zircon	Thorite		
	Torbernite		
	Uraninite		
	Wolframite		

number of chemically or mechanically weak minerals. Although the numbers of primary and secondary mineral species are about equal, the secondary minerals are frequently more abundant. There are relatively few alteration and gangue minerals, or contaminants in this remote area, although recognition of the latter are essential.

The second list, based on Von Putzer (1968, p. 29), is from Precambrian, fossil placers of the Witwatersrand and the diamond gravels of Brazil. The abbreviated list of minerals reflects the maturity of weathering in the source area and of the sediments. The large number of primary ore minerals, and the relatively few secondary minerals, reflects the exotic nature of the source terrain, the depositional environment, and diagenetic processes in ancient placers. Both suites of minerals contrast markedly with the lists of Raeburn and Milner (1927, pp. 71–79) which suggest the modification of heavy-mineral assemblage downstream as a result of the chemical and mechanical disintegration of less resistant minerals.

Climate and weathering

A combination of climate, relief and maturity of landscape controls the weathering of parent materials, and hence the composition and physical characteristics of heavy minerals entering drainage systems. Where chemical weathering predominates, minerals such as the amphiboles and most of the sulphides will be broken down, whereas chemically resistant species such as zircon, rutile, and tourmaline may become the dominant mineral phases. In contrast, where mechanical erosion exceeds weathering, a wide variety of minerals will be present.

The interrelation of climate (and latitude) with chemical weathering to modify the heavy-mineral suite is well displayed in Greenland (Ghisler and Stendal, 1980; Stendal, 1980). Arsenopyrite, bornite, chalcocite, covellite, galena, pyrite, pyrrhotite, sphalerite, tetrahedrite, and native copper have been observed in heavy-mineral concentrates from North Greenland (80–83°N). In East Greenland (72–74°N) the less resistant copper minerals such as bornite, chalcocite, and covellite are absent despite their presence in mineral deposits in the region. Under more temperate climatic conditions, sulphides are found in panned concentrates from drainage sediments and glacial till in northern Sweden (Toverud, 1977; Nikkarinen et al., 1984). Pyrite, chalcopyrite, pyrrhotite, sphalerite, molybdenite, native copper, native silver, and native bismuth persist in concentrates from southwest Norway (Stendal, 1978). Sphalerite is occasionally seen in concentrates from Scotland (Stone and Gallagher, 1984), although lead anomalies are due to the secondary phosphate, plumbogummite. Zantop and Nespereira (1979) report sphalerite, stibnite, molybdenite, pyrite and arsenopyrite in heavy-mineral concentrates as far south as northern Spain.

In subtropical climates sulphides are replaced by secondary minerals such as malachite, chrysocolla (Newberg, 1967), hydrozincite, smithsonite, anglesite, and cerussite.

In tropical areas, the heavy-mineral suite is much reduced by weathering, although concentrates can assist in the search for deposits of U, Sn, and Au (Watters and Sagala, 1979; Watters, 1983), where these elements are incorporated in detrital iron and manganese oxides. Tungsten minerals in the equatorial and tropical conditions of central Africa are comminuted, partly dissolved, partly mixed wit fine alluvium, and are transported "for distances that may be expressed in kilometres and tens of kilometres" (Varlamoff, 1971; see also Raeburn and Milner, 1927).

Minerals such as barite, gold, platinum, cassiterite, magnetite, chromite, ilmenite, rutile, tourmaline, zircon, monazite, and phosphate minerals are stable over most of the climatic zones, although some solution and redistribution may occur, particularly in tropical terrains. More than two-thirds of the literature on heavy-mineral exploration describes the search for gold, scheelite, and cassiterite (in decreasing order of frequency).

The stability of heavy minerals during weathering has been studied by several authors (Dryden and Dryden, 1946; Grimm, 1973; Nickel, 1973). The sequence reported by Nickel (1973) on the basis of experimental observations is similar to that observed from natural weathering. This is, in order of decreasing stability, zircon > rutile > kyanite > tourmaline > epidote > hornblende > almandine > apatite. Grimm (1973) obtained a similar sequence in the residual quartz gravel of the Bavarian Molasse: zircon > rutile > tourmaline > kyanite > andalusite > staurolite > zoisite > epidote > garnet > apatite > hornblende.

Transportation and deposition

Subaerial erosion, transportation, and deposition of material from the weathered land surface leads to progressive sorting of the rock and mineral fragments by particle size and specific gravity. Under favourable conditions these processes lead to economic concentration of valuable heavy minerals in placer deposits. These conditions are reviewed in thematic papers on placer deposits prepared for the Geological Society of London (1985). The same processes control the transport and deposition of heavy minerals that are used for geochemical exploration, although the combination of conditions necessary for their economic concentration is unimportant. Diffuse concentrations of heavy minerals in the "cover rocks" often indicate the presence of placer deposits.

The processes controlling the segregation and concentration of heavy minerals are poorly understood, but in general, heavy minerals are enriched near the source and also toward the base of the surficial cover. Lag enrichment yields the familiar eluvial placers in the soil and colluvium on interfluvial slopes between the bedrock source and the valley alluvium. Vertical migration through the surficial cover can also begin in the soil and colluvial phases of the dispersion train, at least in the humid tropics. The diamond-bearing, "stoneline gravels" described by Thomas et al. (1985) in Sierra Leone provide an example.

Within the drainage system, processes of erosion, transport, and deposition all operate to produce segregation of heavy minerals. Lag enrichment is fostered by the inertia of heavy particles resting on the stream bed and by the combination of factors involved in entrainment equivalence (Slingerland, 1977). Vertical, downward concentration of heavy-mineral particles is aided by dispersive equivalence (Sallenger, 1979) and by hydraulic equivalence (Rubey, 1933). Once segregated, the heavy minerals are protected by infiltration into the interstices of coarser sediment of the stream bed (Reid and Frostick, 1985) and by entrapment in irregularities of the bedrock floor of the valley. Turbulent flow around obstacles and at stream junctions further segregates heavy minerals at certain sites in the stream bed (Best and Brayshaw, 1985). In addition to size and specific gravity, shape and surface roughness are also factors in the segregation of heavy minerals. Micaceous minerals lying flat in the stream bed offer little resistance to the stream flow, hence are not lifted into saltation or suspension as easily as minerals with more blocky shapes. Once in suspension, micas settle more slowly than would be predicted by their density and size. Thus, flaky specularite and molybdenite are rarely concentrated in placers despite their high specific gravity (Jensen and Bateman, 1979). Within the

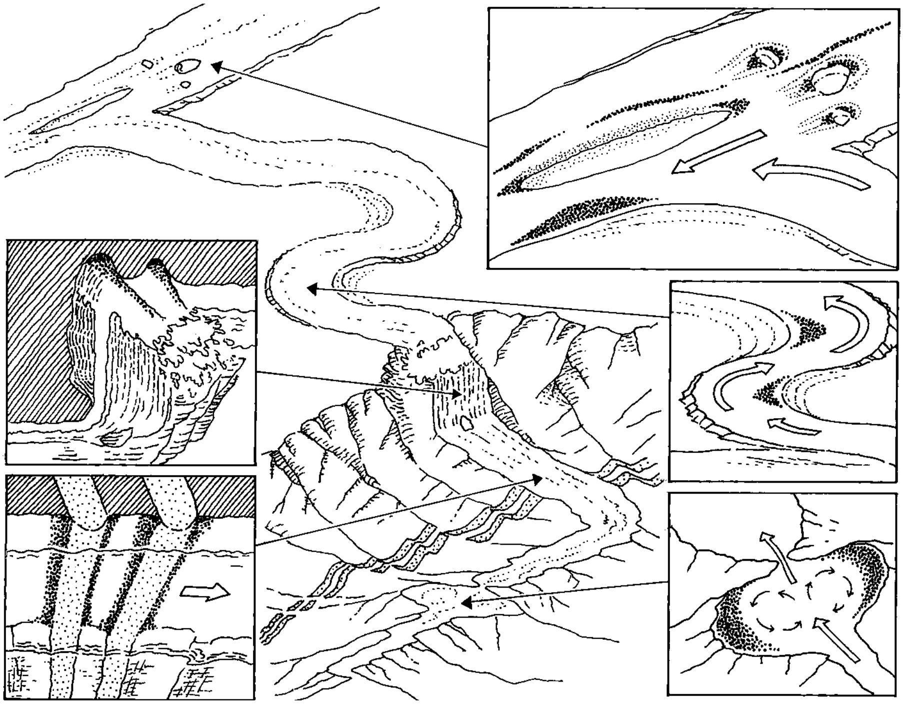

Fig. 6-1. Favourable sites for the accumulation of heavy minerals (stippled) in a drainage system.

fluvial train, repeated cycles of erosion, transport, and deposition modify both the shape and size of the heavy-mineral particles (Dietz, 1973). Although the distances required for significant abrasion of durable minerals are large — 1000 to 4500 km (Dietz, 1973) — less durable minerals abrade more rapidly. Native gold or silver is rapidly shaped into smooth flakes, and the secondary minerals after sulphides are often powdered within hundreds of metres.

The overall effect of these interacting processes is to segregate the heavy minerals in particular regions of alluvial channels (Fig. 6-1). An excellent tabulation of such sites (Table 6-III) has been compiled by Slingerland (1984).

Dispersion

The maximum distance downstream that an unusual heavy-mineral source can be detected (the dispersion) is a function of the composition and size of the exposed source, the nature of chemical changes in the source area and within the fluvial train, and the mechanical changes inherent in fluvial erosion, transport, and deposition. Most of these factors are dependent on climate and geomorphology (Sutherland, 1985). In the fluvial train, mechanical processes of sorting by grain size, specific gravity, and abrasion operate.

Minerals resistant to chemical and mechanical disintegration can survive for

TABLE 6-III

Observed sites of heavy-mineral placers in the fluvial system (after Slingerland, 1984)

System scale (10^4 m)	
Bands parallel to depositional strike	McGowen and Groat (1971); Smith and Minter (1980).
Heads of wet alluvial fans	Schumm (1977).
Points of abrupt valley widening	Crampton (1937); Kuzvart and Bohmer (1978).
Points of exit of highland rivers onto a plain	Toh (1978).
Regional angular unconformities	Minter (1978).
Bar scale (10^2 m)	
Concave sides of sharp bends	Kuzvart and Bohmer (1978).
Convex banks of meanders	Kuzvart and Bohmer (1978).
Heads of mid-channel bars	Kartashov (1971); Toh (1978); Smith and Minter (1980).
Points bars with suction eddies	Bateman (1950); Toh (1978).
Scour holes, esp. at tributary confluences	Kuzvart and Bohmer (1978); Mosley and Schumm (1977).
Inner bedrock channels and false bedrock	Schumm (1977); Adams et al. (1978); Kuzvart and Bohmer (1978).
Bedrock riffles	Cheney and Patton (1967); Toh (1978).
Bed scale (10^0 m)	
Scoured bases of trough cross-strata sets	McGowen and Groat (1971); Toh (1978).
Winnowed tops of gravel bars	McGowen and Groat (1971); Toh (1978).
Tangential toes of foresets	McGowen and Groat (1971); Toh (1978); Smith and Minter (1980).
Thin ripple-form accumulations on dune stoss slopes	Brady and Jobson (1973).
Dune crests	Brady and Jobson (1973).
Dune foreset beds	McGowen and Groat (1971); Brady and Jobson (1973).
Plane parallel laminae	Slingerland (1977).
Leeward side of obstacles	Lindgren (1911).

remarkable distances downstream. Zeschke (1959, 1961) tabulates distances of tens, hundreds, and even more than thousands of km for minerals such as hydrozincite, stibnite, uraninite, chromite, monazite, gold, zircon, wolframite, and scheelite. These appear to be extremes and perhaps represent additional sources along the drainage as suggested by Zeschke (1961). Distances of tens of kilometres have been reported by others for gold (Boyle and Gleeson, 1972) and for wolframite (Theobald and Thompson, 1959). These relatively great distances reflect the limit of detection of an anomaly rather than extreme values of distance. Aleva (1985) showed, however, that economic concentrations of cassiterite in Indonesian placers have maximum transport distance of the order of 500 m. It is thus necessary to distinguish between economic placers and alluvial heavy-mineral accumulations used for exploration purposes. R.G. Taylor (1979, p. 222), for example, documents workable tin placers 16 km

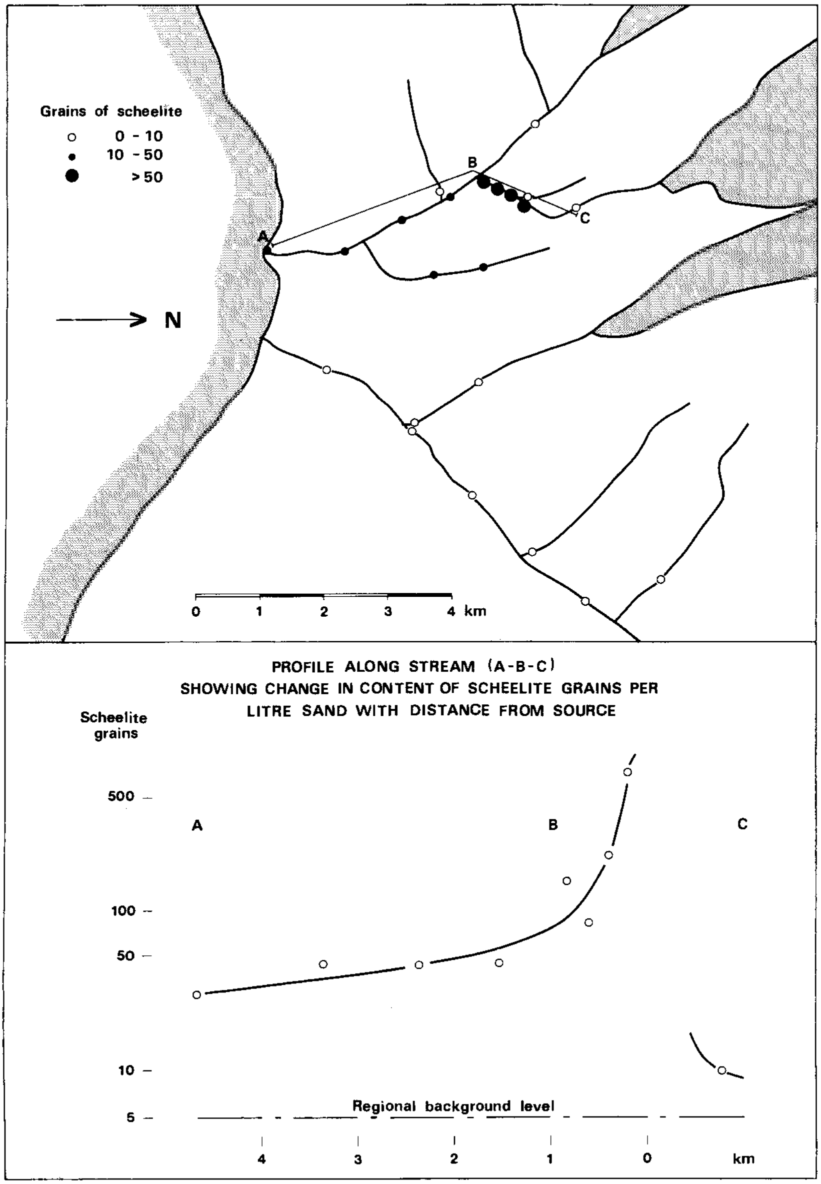

Fig. 6-2. Exponential decline in the scheelite content of heavy-mineral concentrates downstream from a scheelite occurrence (from Hallenstein et al., 1981).

below the source in Western Australia and anomalous dispersion for 50 km or more.

Much shorter dispersion trains are encountered downstream from less well exposed deposits. Hallenstein et al. (1981 and Fig. 6-2) were able to detect anomalous scheelite for more than 5 km below massive veins in East Greenland (Hallenstein and Pedersen, 1983; Pedersen and Stendal, 1987). The amount of scheelite, however, declines by 90% within the first kilometre. Stendal (1978) describes dispersion trains of less than 400 m below both large and small scheelite sources in southwestern Norway. Concentrates rich in cassiterite are found near deposits in Cornwall (Stendal, unpublished data), Australia (Rossiter, 1976), and Spain (Zantop and Nespereira, 1979). The dispersion exceeds 5 km and is probably of the order of tens of kilometres, although the amount of cassiterite decreases drastically in the first kilometre. The pyrochlore content of concentrates is several percent over the Sokli carbonatite complex, Finland, and it can be detected for several kilometres downstream (Vartiainen, 1976).

Less durable minerals will have shorter dispersion trains. Sulphides are particularly susceptible to removal within a short distance of the source. In East Greenland, the transport for As, Cu, Pb and Sb is less than one kilometre. Coats et al. (1984b) recognize dispersion of less than 0.5 km for zinc in Scotland. The secondary minerals derived by oxidation of sulphides in the near-surface environment can extend these dispersion trains for some elements. In Sonora, Mexico, Rozelle (1978) documented a dispersion train for pyromorphite (the lead phosphate) of less than 1 km, whereas wulfenite (the lead molybdate) and vanadinite (the lead vanadate) could be traced for more than 3 km downstream. Many of the secondary minerals, however, are less durable than the parent mineral. Soft and brittle minerals such as cerussite and anglesite rarely survive as recognizable fragments in heavy-mineral concentrates, and lead arsenates such as mimetite seldom travel more than a few hundred metres. Similarly, the secondary silver minerals, both native silver and the silver halides, are usually seen only in heavy-mineral concentrates from streams within a few hundred metres of the source.

Grain size of heavy minerals

Three factors control the grain size of the heavy minerals in the fluvial dispersion train: (1) the grain size of the source material; (2) the durability of the minerals; and (3) the sorting that accompanies transport and deposition downstream from the source. The grain size of heavy minerals affects the nature of the appropriate sample and the apparent limit of downstream dispersion. Very fine grained sand or silt-sized heavy mineral particles travel with the suspended load of the stream and may not be concentrated in the usual heavy-mineral traps in the stream. Stendal (1979, 1982) describes a situation in East Greenland where anomalies related to As, Pb, and Cu sulphides are seen in stream sediments rather than in heavy-mineral concentrates (Fig. 6-3). Berger et al. (1979) make a case for the use of very fine grained stream sediments for molybdenum, and Shelp and Nichol (1985), and Day and Fletcher (1986) make a similar case for gold. Gladwell and Lett (1985) even include cassiterite among the minerals that can be dispersed in the suspended load of streams.

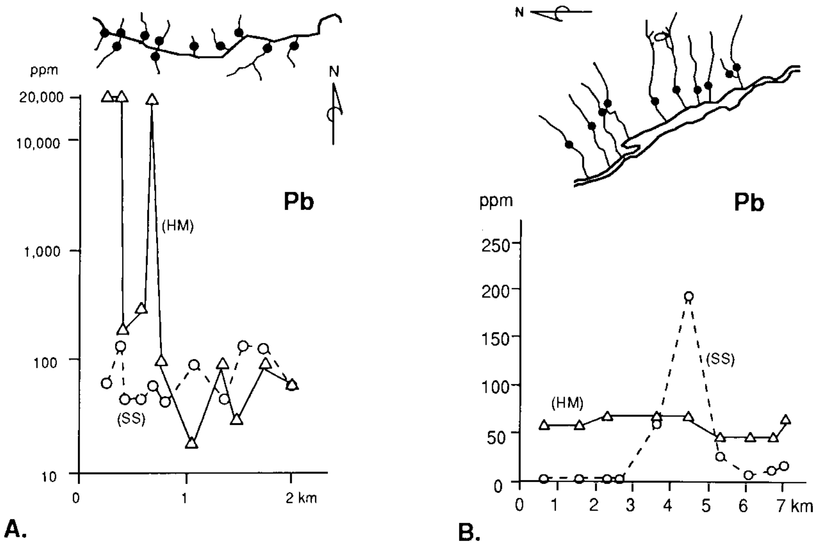

Fig. 6-3. Comparison of Pb content of fine fraction stream sediments (open circles) and heavy-mineral concentrates (open triangles) in contrasting situations: (A) predominantly detrital dispersion typically produces an anomaly of higher contrast in heavy-mineral concentrates than in the fine fraction stream sediments, as in New Mexico, USA (compiled from data from Griffitts and Alminas, 1968); (B) higher contrast in fine fraction stream sediments downstream from unusually fine-grained lead–zinc mineralization in East Greenland (compiled from data from Stendal, 1982).

The grain size of the source material is the primary control on the grain size of minerals in the fluvial train. In the examples given above, the primary grain size is small, hence downstream accumulation of coarser particles is unlikely. On the other hand, Theobald and Thompson (unpublished data, 1985) were unable to detect tungsten in near-source stream sediments from the Boulder County Tungsten District, Colorado, because the ferberite grains were nearly all coarser than 0.2 mm. These were readily detected, both visually and chemically, in heavy-mineral concentrates.

Theobald and Allcott (1973) describe an example where the grain size of scheelite is of the order of centimetres. Tungsten is rarely detected in unconcentrated stream sediments, and without care may be lost by sieving before heavy-mineral concentration. Rozelle (1978) describes near-source stream sediments in Mexico with more than 50% of the lead, predominantly as wulfenite, in grains coarser than 0.7 mm. B.L. Reed (written commun., 1973) also noted the absence of detectable tin in fine-grained stream sediments from Alaska that contain abundant pebble-sized wood tin.

The exponential decrease in the average grain size of heavy-mineral particles downstream has been described by Zeschke (1961) in the case of scheelite, hydrozincite, and uraninite (Fig. 6-4), and by Rozelle (1978) for pyromorphite, wulfenite and vanadinite. Most explanations of this phenomenon follow Ritten-

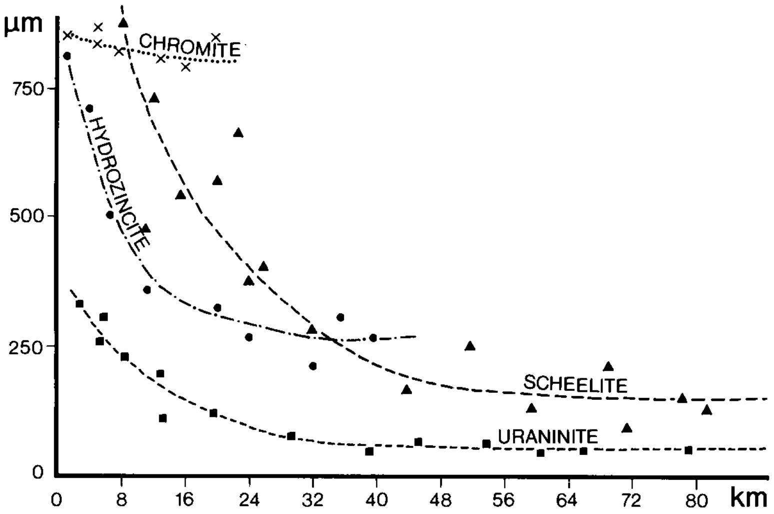

Fig. 6-4. Decrease in grain size of heavy minerals with increasing distance of transport: chromite in the Hindubagh River, scheelite in the Siran River, and uraninite in the Judus River, Pakistan; and hydrozincite in the Rio Ter, Spain (reproduced with permission from Zeschke, 1961, Economic Geology, 1961, Vol. 56, p. 1252).

house (1943) in attributing the decrease in grain size to weathering, abrasion and sorting. Weathering has little effect in normal active stream channels, although, in some cases (perhaps most commonly in the vicinity of oxidizing sulphide deposits), highly corrosive stream water may greatly accelerate "weathering". The reduction of grain size of the minerals of most interest in exploration is likely due to dissolution rather than corrosion. Mechanical abrasion was documented by Thiel (1940) in experimental studies, but distances of the order of thousands of kilometres were required to significantly reduce the grain size of heavy minerals. In natural streams, relatively soft minerals such as apatite and the amphiboles persist for tens to hundred of kilometres downstream as angular to pristine euhedral fragments (Russell and Taylor, 1937; Rittenhouse, 1943). Hence, pure abrasion is insignificant for exploration geochemistry. Crushing may reduce the grain size of extremely soft, brittle, or readily cleavable minerals in some high-gradient streams. Sorting is the dominant process causing grain size to decrease downstream.

The practical effect of grain size of the heavy minerals on exploration practice can be dramatic where the initial grain size of the minerals is coarse. The anomalies determined in a fixed grain size from alluvium would be misleading, if an arbitrary, fine-grain size were chosen for analysis (Theobald and Allcott, 1973; Rozelle, 1978). In one example, cyclically zoned crystals of scheelite and powellite, often 1 cm or more in diameter, near the source are succeeded within tens of metres by fine-grained, nearly pure scheelite. Molybdenum is lost from the detrital train. In a second example, coarse-grained pyromorphite and wulfenite near the source is succeeded in the alluvial train by finer grained wulfenite and then by fine-grained vanadinite. Thus, a pronounced downstream change in the chemical composition of the concentrate accompanies the change in grain size. Tracing this anomalies upstream using material finer than 0.18 mm would yield a maximum anomaly for lead, molybdenum and vanadium 800 m below the source. Using material finer than 0.6 mm, the maximum anomaly for lead and molybdenum would be 400 m below the source. Only in material coarser than 0.6 mm would the anomaly for lead, phosphorus, and molybdenum peak at the source.

Sampling density, spacing and target size

Sampling density is dictated by the size of the area to be evaluated and the time, money, and manpower available in the survey. Regional studies, generally involving thousands of square kilometres, are usually not restricted to the search for a single commodity, and may be undertaken with minimal knowledge of the types of orebodies in the region. In the follow-up studies, on the other hand, the type of deposit or its geochemical characteristics are known in a general way. Several successively more detailed stages are involved, and each type of survey requires a different sampling density.

The technical constraints on sampling density are the length of dispersion trains and the size of the expected target. For heavy-mineral prospecting, the size of the target is that of the supergene dispersion halo. The length of the fluvial dispersion train dictates the maximum size of stream that can be sampled, whereas the target size dictates the minimum frequency with which streams of the selected size must be sampled to allow a reasonable probability of discovery.

Regional reconnaissance surveys provide the greatest dilemma in selecting an appropriate sampling density; for follow-up studies the sampling density is largely predetermined by the preceding work. Maximum dispersion for most heavy ore minerals is usually of the order of 5 km. Thus, first-, second-, or third-order streams are preferred. Drainage areas of one to a few square kilometres will be reflected in the sample. In most terrains, secondary dispersion halos around significant ore deposits or districts are of the order of tens of square kilometres. In these situations, one first- or second-order stream sampled for each 10 to 20 km^2 has a high probability of two or more anomalous samples in each significant target area.

Follow-up of anomalies identified from reconnaissance surveys usually requires a systematic survey of the smaller, anomalous area at densities of one or more samples per square kilometre. Commonly, what appear to be simple anomalies at the small scale turn out to be complex anomalies reflecting several types of mineralization at larger scales (for example, Overstreet and Marsh, 1981, p. 782). Hence, a second stage of systematic sampling is required. Where follow-up is at scales larger than about 1 : 25,000, saturation sampling of small areas within the anomalous area may be appropriate, with many samples

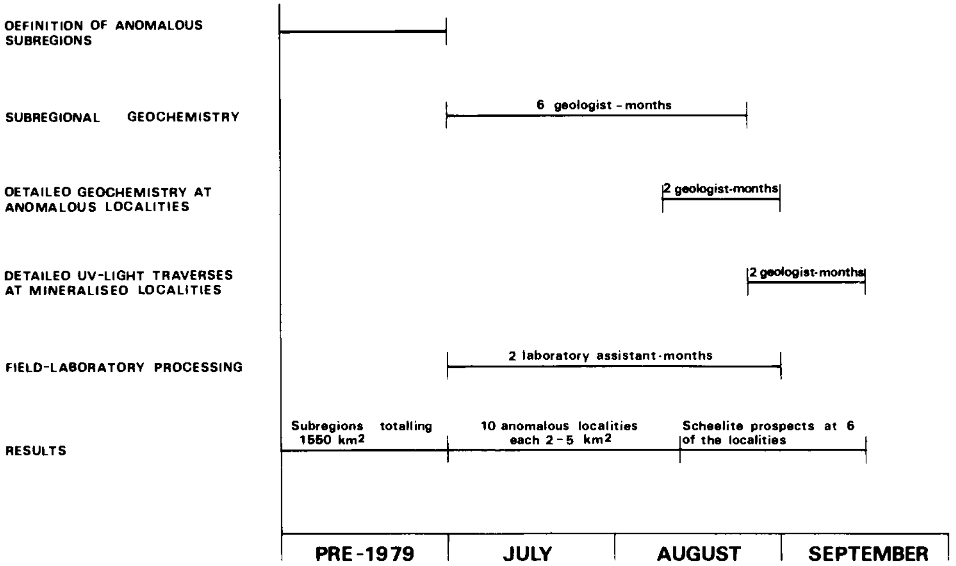

Fig. 6-5. Summary of exploration progress during 2.5 months of fieldwork in East Greenland (from Hallenstein et al., 1981).

collected along drainage systems to establish the point(s) of entry of the ore minerals.

The sequence from regional to detailed sampling is well illustrated by Hallenstein et al. (1981) in their work in East Greenland, where 2100 samples were collected from an area of 100,000 km^2 (Fig. 6-5). This was reduced to 1550 km^2 on the basis of anomalous levels of scheelite. In the second phase, heavy-mineral concentrates collected at a density of one sample per 1 to 3 km^2 on first- and second-order streams with drainage basins of 2 to 5 km^2 were used to assign priorities. The most promising areas within the subregions were then sampled in detail using heavy-mineral concentrates collected from stream sediments and scree on the valley sides at 200- to 300-m intervals.

Element assemblages in heavy-mineral concentrates

The strongly magnetic fraction of heavy-mineral concentrates consists principally of magnetite with included, intergrown, or absorbed metals and can be enriched in Zn, Ti, Sn, W, Cr, Co and Ni. Examples of the use of detrital magnetite in geochemical exploration are given in Theobald and Thompson (1962), where zinc in magnetite was related to zinc-rich deposits, and by De-Grys (1970), who used copper and zinc in alluvial magnetite for exploration in central Ecuador. A general investigation of minor elements in alluvial magnetite from the inner Piedmont Belt, North and South Carolina, demonstrated regional patterns of distribution (Theobald et al., 1967). In the Yukon Territory

(Gleeson and Boyle, 1980), anomalous values for Cu, Zn, Ni, Co, As and Sb in the magnetic fraction reflect areas containing lead–zinc–silver lodes. The same elements are anomalous in the nonmagnetic fraction. Overstreet and Day (1985), in a comprehensive review of the magnetic fraction, conclude that ferromagnetic concentrates may be the most suitable geochemical sample medium for the Pt-group metals, and for titanium and vanadium deposits.

Elemental assemblage in the nonmagnetic fraction of heavy-mineral concentrates are more erratic and have a much greater range of values than those of conventional stream-sediment samples. The contrast between anomaly and background is usually greatly enhanced over that in stream sediments.

The assemblages also vary according to the method of isolation of the nonmagnetic fraction. Where only the ferromagnetic minerals are removed, the remaining concentrate will usually be dominated by the paramagnetic such as amphiboles, pyroxenes, and garnet. These minerals host many trace elements, thus background levels may be higher than in stream sediments. "False" anomalies may be created where yttrium garnet, niobian rutile, or tin-rich sphene are abundant. Thus, many of the anomalies being sought in nonmagnetic minerals can be diluted and obscured by paramagnetic minerals. However, tungsten in the wolframite group of minerals, niobium and tantalum in the columbite-tantalite series, and hydromorphically transported metals incorporated in mature iron and manganese oxides are found in the paramagnetic fraction.

The nonmagnetic fraction of the concentrates, which is usually prepared to include the least magnetic of the paramagnetic minerals such as monazite and many of the secondary copper minerals, provides the most diagnostic mineral and elemental suites. Deposits associated with granites and the skarn and hornfels of contact-metamorphic aureoles give rise to anomalous Sn, W, Mo, Bi, As, REE, and Nb. Scheelite and arsenopyrite mineralization in East Greenland is characterized by Ti, Zr, and W in heavy-mineral concentrates (Stendal, 1980). The fluorine-rich porphyry molybdenum deposits of Colorado give heavy-mineral concentrates rich in Mn, Sn, and W (Theobald and Thompson, 1959). In the Brooks Range, Alaska, Marsh and Cathrall (1981) use the assemblage Mo–Sn–W and Mo–Cu–Te–Au to define mineral potential related to porphyritic igneous rocks. Granites in the southeastern part of the Keno Hill District, Yukon Territory, give rise to concentrates enriched in Zr, Th, U, Y, Ce, La and Yb (Gleeson and Boyle, 1980). Concentrates near lode deposits containing W, Sn, As, and Au in the same area yield anomalous Au, Ba, Pb, Sn, W, Zn, Th and REE. Veins containing Pb, arsenopyrite, and sulphosalt minerals are associated with concentrates anomalous in Pb and As.

Strata-bound sulphide deposits in the Appalachian-Caledonian Orogen are less frequently sought using the nonmagnetic fraction of the heavy-mineral concentrates. In East Greenland, Stendal (1979, 1982) and Stendal and Hock (1981) traced copper mineralization in quartzite using the association of Cu, Ba, Ni and Sr. In the Bathhurst-Jacquet River district of New Brunswick, Boyle (1967b) found anomalous Cu, Pb, Zn, Ag and Ba in the vicinity of sulphide deposits. In the Dalradian schists north of Aberfeldy, Scotland, Coats et al. (1980) successfully used the assemblage of Ba and Pb in concentrates to define strata-bound Ba–Zn mineralization.

Isolation and characterization of the suites of associated elements is often facilitated by recourse to multivariate statistical techniques, as described in the companion volume edited by Howarth (1983). Examples of the application of these techniques to data for heavy-mineral concentrates can be found in Clausen and Harpoth (1983) (discriminant analysis), Bell (1976) and Petersen and Stendal (1987) (Q- and R-mode cluster analysis), Granath (1978) (principal components analysis), Schock and Steidmann (1976) (Q-mode factor analysis with Varimax Rotation), and Rossiter (1976) and Bolivar et al. (1983) (R-mode factor analysis). When applying these mathematical methods of grouping the elements, it is common to find dominant suites of elements that relate to gross variations in the chemistry of the country rocks. Element suites related to mineralization may be subdued or even lost in situations where the anomalous samples are a small proportion of the total. Suites commonly encountered include: the elements normally associated with basic igneous rocks such as Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Sc (Landergren, 1943); the felsic igneous rocks, including the REE, Zr, Nb, Be, Sn, Mo and sometimes Ti; and in carbonate terrain, various combinations of Ca, Mg, Sr and Ba. In order to isolate an assemblage related to mineralization, it is often necessary to normalize data against the various country-rock units. This may be done either by direct isolation of the samples from major lithologic units where the geology is sufficiently simple and well known, or by normalization of individual elements against the broader chemical characteristics of the terrain (for example, residuals to a factor score).

Pathfinder minerals

In general, the secondary minerals are used in similar way to the primary minerals, although there are situations in which the secondary minerals reflect hydromorphic dispersion over considerable distances, and the anomalies generated may be displaced from the metal source. Molybdenum in wulfenite is an example (Johnson, 1982; Theobald, 1982).

The pathfinder minerals provide less direct indications of mineralization since they are often accessory minerals that can occur in unmineralized rocks. They may be used to indicate either the presence of favorable rocks or the presence of a mineralizing event. The presence of suites of minerals is usually more diagnostic than the presence of individual minerals. The best known example is the assemblage of chromian pyrope, chromian spinel, chromian diopside, magnesian ilmenite, perovskite, and niobian rutile that, in one combination or another, is characteristic of kimberlites and is used in diamond exploration (Boyd and Meyer, 1979). The pyrope garnet usually has a distinctive deep purple colour and the chromian diopside a similarly distinctive bright green colour.

A characteristic suite of minerals can also be identified from the basalt hosts of peridot and sapphire. In this case, the presence of zircon with chrome diopside is distinctive. The zircon in this assemblage is usually of large size (1–2 mm), with a subhedral, rounded, and highly polished appearance, in contrast with the normally small, prismatic crystals derived from most crystalline rock terrains or the small spherical grains derived from mature sedimentary rocks.

The presence of gold is easily detected in concentrates, but sampling problems related to the low concentration of gold and its occurrence in discrete grains can lead to erratic results. The association of gold with arsenopyrite and several of the sulphosalt minerals can help to define favourable terrains. Boyle and Gleeson (1972) suggest that jamesonite, for example, would be an excellent pathfinder mineral in the Keno Hill District of the Yukon. In the fine-grained, epithermal deposits, where gold is rarely found in conventional heavy-mineral concentrates, the association with minerals such as cinnabar and stibnite can improve the definition of anomalous areas.

Fluorine is rarely determined chemically in concentrates, but the two principal fluorine minerals, fluorite and topaz, are easily identified and are excellent indicators of a mineralizing event. Fluorite, in association with pyrite, pyrrhotite, arsenopyrite, and sometimes molybdenite or tourmaline, is indicative of tungsten mineralization, and it is also diagnostic of skarn-type mineralization. The association of fluorite, topaz, and tourmaline with wolframite, cassiterite, and molybdenite is characteristic of strongly differentiated granites and rhyolites and of the vein, stockwork, and greisen deposits associated with them. In these instances, the dispersion of fluorite is normally greater than that of topaz. Topaz is typical of greisens, of the alteration zone immediately above stockwork molybdenum deposits, and it is also associated with cassiterite in tin rhyolites. Fluorite is more broadly dispersed through the host rocks and the altered rocks surrounding the deposits. It is also a constituent of some precious-metal deposits, can itself form ores, and can be associated with some uranium ores.

Barite is a common gangue mineral in base-metal deposits, and its presence in heavy-mineral concentrates with other minerals characteristic of such deposits provides a useful pathfinder that often enlarges the target area. Barite is also a common mineral in chemical sedimentary rocks and occurs as concretions in shaly rocks. Massive bedded barite ore occurs in some sedimentary sequences. In the vicinity of such deposits the quantity of barite may be so great that heavy-mineral concentrates become diluted beyond utility for other purposes. A special case of the super-abundance of barite is the shale-hosted massive sulphides that commonly occur in close stratigraphic proximity to bedded barite (Churkin et al., 1978; Carne and Cathro, 1982; Lange et al., 1985). Todorov (1983) has suggested that the gold content of barite can be used to distinguish barite from gold deposits.

Tourmaline can be derived from primary magmatic rocks, from metamorphic rocks, from detrital sediments, from hydrothermal alteration zones, or from ore deposits. The presence of tourmaline with an appropriate suite of elements and minerals can add confidence to the interpretation of an anomaly, as noted above for the tungsten mineralization in East Greenland. More discrimination may be gained when the composition of the tourmaline is considered. Taylor and Slack (1984) note the value of both the major and minor components of Mg-rich tourmaline as a guide to massive sulphide deposits. S.M. Smith et al. (1987) describe minor element variations in Fe-rich tourmalines from Sonora, Mexico. These variations display zoning of the elements attributed to zoning of the hypogene mineralization.

Cassiterite is the best diagnostic mineral for tin deposits, but is often difficult to recognize in heavy-mineral concentrates. Associated minerals, such as tourmaline, wolframite, columbite/tantalite, monazite, xenotime, topaz and fluorite, can help to identify concentrates in which cassiterite is most likely to occur. The composition of cassiterite may provide valuable information on the nature of the source. Haapala (1983) showed that the Nb, Ta, and Fe content can be used to distinguish among granite-, pegmatite-, and greisen-derived cassiterite associated with the rapakivi granites of southwestern Finland.

Gahnite, the zinc spinel, is easily recognized by its colour, lustre, and morphology. It is durable, unlike the principal zinc ore, sphalerite. In metamorphosed massive-sulphide deposits, some of the zinc is usually present as gahnite, and this mineral has been suggested as a pathfinder for metamorphosed zinc-enriched massive sulphides (Sheridan and Raymond, 1977). Similar associations of exotic minerals with specific deposit types are probably more common than generally recognized. Petersen (1986), for example, notes the association of nigerite and hogbomite with the massive sulphides of the Manitouwadge District, Ontario, and suggests that these minerals, like gahnite, may serve as pathfinders in heavy-mineral concentrates.

PRACTICAL CONSIDERATIONS

Gravity separation techniques

A variety of gravity separation techniques is employed in the preparation of heavy-mineral concentrates. All are based on the simple principle that the heavier the particle, the faster it will fall through a liquid (Stokes' law). Two physical properties are dominant in controlling the rate of fall of most minerals: the size of the particle, and its specific gravity. Thus, for optimum separation by specific gravity, the particles should be of uniform size. Particle shape has a subsidiary influence on the rate of fall; a streamlined particle encounters less resistance than a sphere, cube, or foil.

Gravity separations may be performed in the field or in the laboratory. Where awkward equipment or toxic liquids are used, a laboratory is required. Readily transported devices using water as the separation medium are the best used in the field. The desirability of collecting large samples for exploration favours initial concentration in the field.

TABLE 6-IV

Heavy liquids used to separate minerals for exploration

Heavy liquid	Density (g/cm^3)	Dilution medium	Composition
Tribromomethane	2.89	Methanol Acetone	$CHBr_3$
Zinc chloride	2.91	Water	$ZnCl_2$
Tetrabromoethane (acetylene tetrabromide)	2.96	Methanol Acetone	$C_2H_2Br_4$
Thoulets solution (highly toxic)	3.20	Water	$KI + HgI_2$
Dicodomethane (methylene iodide)	3.32	Ether Acetone	CH_2I_2
Kleins solution (reactive with carbonates)	3.36	Water	Cadmiumboron-wolframate
Rohrbach solution (unstable)	3.59	Water	$BaI_2 + HgI_2$
Clerici solution (highly toxic)	4.03	Water	Thallium (1) formate and thallium malonate (1 : 1)

Heavy liquids

The standards for heavy-mineral separation are based upon heavy liquids. The most commonly used are bromoform (sp. gr. 2.89), tetrabromoethane (sp. gr. 2.96), and methylene iodide (sp. gr. 3.32), although a variety of other liquids are available (Table 6-IV). A simple sink-float method of separation is used (Fig. 6-6). The sample is added to the liquid in a suitable container, usually a separator funnel, and particles with a specific gravity than that of the liquid are allowed to settle to the bottom of the container where they can be tapped off and washed. These liquids are both toxic and expensive. The techniques are not easily adapted to the processing of large samples — a few hundred grams are usually used rather than the several kilograms commonly employed for exploration. For these reasons, heavy-liquid separations are most often used in the laboratory to clean rough concentrates prepared in other ways (Brundin and Bergström, 1977; Meyer et al., 1979).

Alminas et al. (1984) have designed a laboratory-scale magnetohydrostatic separator that eliminates many of the problems inherent in heavy-liquid separation. The technique uses and aqueous solution of manganous chloride in a magnetic field to yield apparent specific gravities that range from 1.4 to >9 depending upon the strength of the field. Simultaneous gravity and magnetic separations are possible, but, as in the case of heavy liquids, this method is most appropriately used to refine rough concentrates prepared in some other way. Sodium paratungstate in water solution provides a non-toxic liquid with

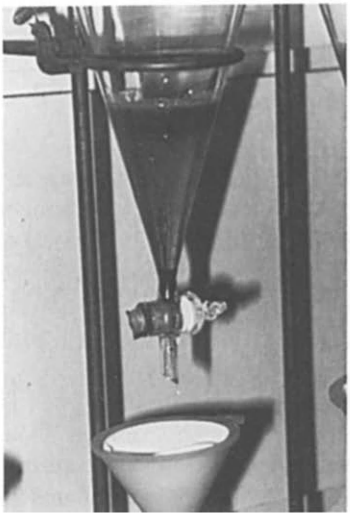

Fig. 6-6. Heavy-liquid separation of minerals in a rough-panned heavy-mineral concentrate (US Geol. Surv. laboratories, Denver, Colo.).

a specific gravity as high as 3.1 and can be used where tungsten is not being sought (Torresan, 1987).

The pan

The most commonly used method of preparing heavy-mineral separates is by "panning". There are several types of pans, such as the gold pan, the batêa,

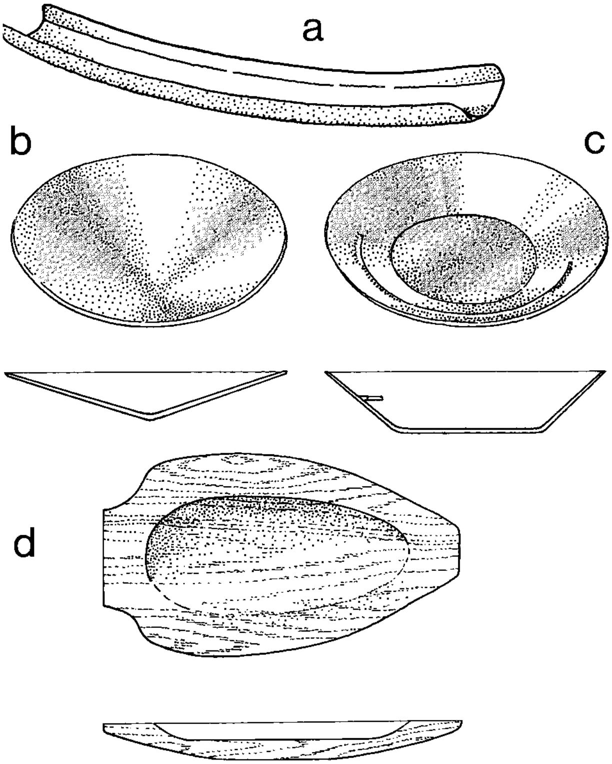

Fig. 6-7. Four types of pans for heavy-mineral separation: (a) the sax pan; (b) the Batêa pan; (c) the gold pan; and (d) the Freiburger pan.

the Freiburger pan, and the sax (Fig. 6-7). The vanning plaque of the assayer, or even a large watch glass, can be used to separate heavy minerals (Shepard and Dietrich, 1940, p. 122; Zeschke, 1961). Wash pans, frying pans, almost any vessel of appropriate shape have been used in double duty by prospectors.

The gold pan. The gold pan, also called the miner's, California, or riffled pan, is made in diameters of up to 40 cm measured at the rim. The flat base of the pan is two-thirds of the lip diameter, and the angle between the side and the base is about 140°. The standard gold pan is usually made of steel or stainless steel. Pans are also made of copper, to facilitate amalgamation of fine-grained gold (Mertie, 1954) and, more recently, of plastic. The "Asiatic ladle" (Sigov, 1939, p. 3) is essentially a gold pan with a handle. Almost any material stiff enough to resist bending or denting during use is suitable.

The batêa. The batêa, batell, or Brazilian batêa, is a cone-shaped pan. Pans called *dulong* or "chinaman's hat" (Hallenstein et al., 1981), used in Malaysia, have a round bottom. The standard batêa of Brazil has a diameter of about

50 cm, a depth of 6–8 cm, and a core-angle of 150°. For diamond washing in Brazil and Guyana, the batêas range from 75–90 cm in diameter, similar to some of the dulongs used to concentrate cassiterite in Malaysia. A small potable batêa, 8 cm deep, with an apical angle of 120°, and made of copper was used by Derby (1891). The batêa and dulong are often made from hardwoods, iron, or steel (Mertie, 1954; Von Putzer, 1968), specially fabricated aluminium (Stendal, 1978), or plastic.

The Freiburger pan. The Freiburger pan is oval and measures 25 × 40 cm (Von Putzer, 1968) with a more or less flat base, and is only a few centimetres deep. An elongated pan is also used in India, Nigeria, and Ghana, where it is called a calabash (Mertie, 1954). These are made of wood, a gourd (e.g., Calabash), or metal.

The sax type pan. The sax type ("banana skin") pan (Hintsteiner, 1977; Hallenstein et al., 1981) is narrow (10-cm wide), weakly arched, and 70–80 cm long, looking like a gutter with a nearly flat base with 2-cm-high edges. The pan is made in plastic and commonly used by Austrian prospectors.

Panning technique. According to Mertie (1954), "the operation of panning for heavy minerals cannot be adequately described; it must be seen and practised". Clay should be carefully washed from the sample before panning. All of the pans operate by repeated suspension and settling of the sample in water (Fig. 6-8). During repeated shaking cycles, the heavier and finer particles work their way downward while the lighter and coarser particles work toward the surface of the sample. By periodic skimming of the lighter material from the surface of the sample, the average specific gravity of the remainder is continuously raised. The process is repeated until a residue of heavy minerals is obtained. A highly skilled panner can carry the process to a nearly pure concentrate of gold (sp. gr. >15). For exploration purposes, it is more common to continue the process until minerals such as epidote, garnet, barite, or amphibole appear on the surface of the concentrate, giving a concentrate containing 30 to 50% of the minerals with specific gravities in the range 3 to 3.5 (Theobald, 1957). Most heavy-mineral programmes now consider the pan as a rough concentrating device and stop the process when the concentrate still contains 50 to 75% of quartz and feldspar. These concentrates are subsequently cleaned with heavy-liquid separations in the laboratory.

The major advantages of the pan are its low cost, portability (small pocket versions are available) and ease of operation. It allows the rapid reduction of 2 to 10 kg of sample to tens of grams of concentrate as the rate of 2 to 10 samples per hour, depending largely on the skill of the panner. Although requiring a high degree of manual dexterity, panning is easily learned and its precision and percent recovery are comparable to that of many of the more complex methods. Taking into account both the time to separate minerals and the time to clean up between samples, it is the fastest separating procedure.

Fig. 6-8. (a) Panning techniques using a gold pan. "Old West Collectors Series", published by Kustom Quality, P.O. Box 3459, El Paso, TX 79923.

Other techniques

Jigs, sluices, tables and a variety of mechanical panners have been used to separate heavy minerals for exploration. Jigs have been used primarily where large grains are to be separated, such as in exploration for cassiterite and the gem minerals, although specially designed jigs for material finer than 2 mm are available commercially. Jigs operate on the differential settling velocities of the particles in an oscillating water column, induced either by pulsing the water through the sample or pulsing the sample within the water. A very simple jig consists of a hand-held screen on which the sample is shaken in a pool of water. The heavier particles sink through the sample and are collected on the screen. Most jigs, however, require a power source and are best used from a fixed location in the field or laboratory.

Fig. 6-8. (b) Panning techniques using a batêa. Photo by H. Stendal.

Sluices are normally used in the economic recovery of placer minerals, but small versions such as the rocker (Averill, 1946) or the mechanical sluice, which is used by the Geological Survey of Sweden (Brundin and Bergström, 1977), can be adapted for exploration purposes. The sluice is essentially a long trough along which the sample is transported by water. The heavy minerals work their way to the bottom of the sluice where they are trapped in artificially prepared irregularities of the sluice bed called riffles. Sluices have been used at fixed, central locations in the field and in the laboratory (Brundin and Bergström, 1977).

A great variety of shaking tables is available in laboratory-sized models (Taggart, 1945, pp. 11–59 to 11–90). They have an oscillating motion across a sloping, riffled table on which the water flow is down the table, across both the axis of shaking and the riffles. The large range of possible combinations of feed mechanism and rate, water volume, slope, shaking motions and riffle designs provides flexibility in the use of tables for heavy-mineral separation.

The shaking tables are particularly useful in exploration for fine-grained gold where a conventional heavy-mineral concentrate can be collected from the end of the table and fine-grained gold can be collected in the slimes coming over the table (Mehrtens, 1986). Shaking tables require relatively permanent installation, preferably in a central laboratory.

There is a bewildering variety of mechanically panners, all of which combine some characteristics of sluices, tables and the gold pan. Some can be used for exploration (for example, Sale, 1983). The bulk and power requirements of the mechanical panners generally restrict their use to readily accessible field sites or to fixed locations such as a laboratory.

Magnetic separations

Magnetic separations of heavy-mineral concentrates serve three purposes: (1) it removes a large proportion of iron and titanium, which can cause interferences in many analytical procedures; (2) it removes many metal-enriched, rock-forming minerals; and (3) it upgrades the final concentrate by removing the bulk of the ferromagnesian minerals. At a minimum, the ferromagnetic minerals, mostly magnetic with some hematite and ilmenite, should be removed because this is often the largest and most iron-riched part of the concentrate, and can cause extreme trace-element variations. The ferromagnetic fraction of the concentrate can serve as a sample medium (Theobald et al., 1967; Granath, 1983) were platinum or metals commonly sorbed by magnetite are sought. The separation can be accomplished with an ordinary hand magnet.

Separations of paramagnetic minerals have been carried out with strong permanent magnets with intense magnetic fields. More commonly, an electromagnet is used in which the strength of the magnetic field is proportional to the amperage (A). The Frantz Isodynamic Separator has been extensively evaluated for use in mineral exploration. Hutchison (1974, p. 119), drawing on the work of Rosenblum (1958) and Flinter (1959), gives the magnetic susceptibilities of a variety of minerals commonly encountered in heavy-mineral concentrates based on the conventional configuration of the Frantz, with feed along a track mounted between the poles of the magnet (Fig. 6-9). In this configuration, optimum separation is obtained in a laboratory or research mode, but the process is slow. For routine separation of large numbers of samples, modification of the pole pieces and rotation of the electromagnet allows more rapid operation (R.B. Tripp, pers. commun., 1985; Fig. 6-10).

Individual minerals have fairly narrow ranges of magnetic susceptibility but may appear to have fairly wide ranges of magnetic susceptibility related to variations in the composition, intergrown minerals and inclusions. Nevertheless, routine isolation of magnetic separates has been valuable in amplifying contrast in geochemical exploration. Alminas and Watts (1978) analyzed two magnetic splits, one magnetic at 1 A but nonmagnetic at 0.1 A, and one nonmagnetic at 1 A, in which the more magnetic split was used to determine metals in mature, secondary iron and manganese oxides, whereas the less magnetic portion

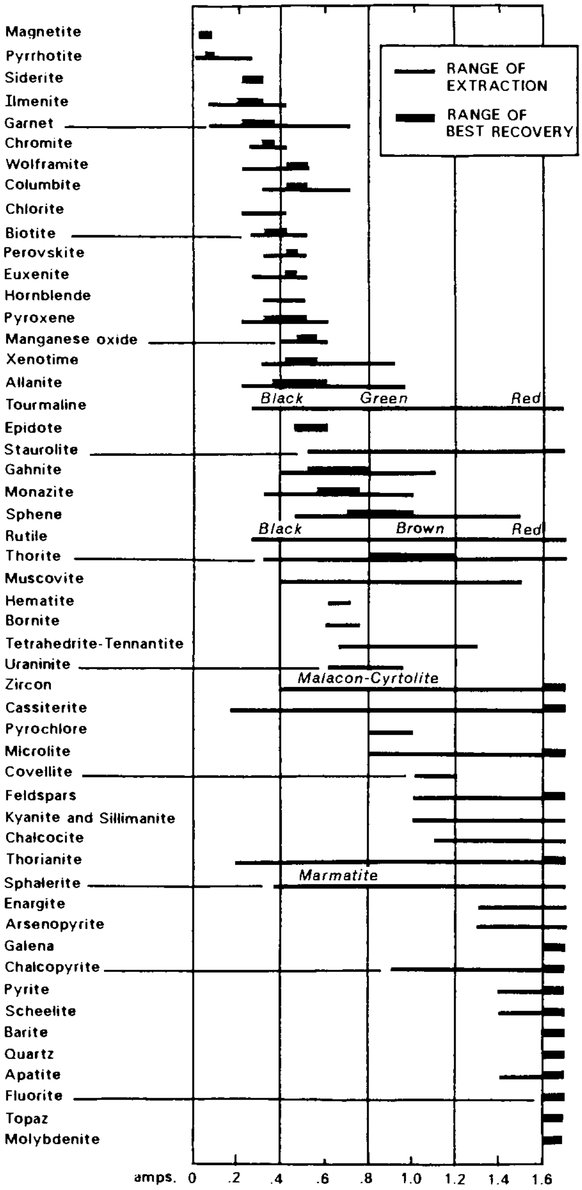

Fig. 6-9. Magnetic susceptibilities of selected minerals in Frantz Isodynamic Separator; data are for a side tilt of 15 to 25° and a forward tilt of 15 to 25° (modified and simplified from Rosenblum, 1958, and Flinter, 1959).

contained ore minerals and their immediate oxidation products. Brundin and Bergström (1977) analyzed five splits of heavy-mineral concentrates based on a combination of gravity and magnetic separates: the ferromagnetic fraction; magnetic and nonmagnetic fractions at 0.7 A for minerals with a specific gravity

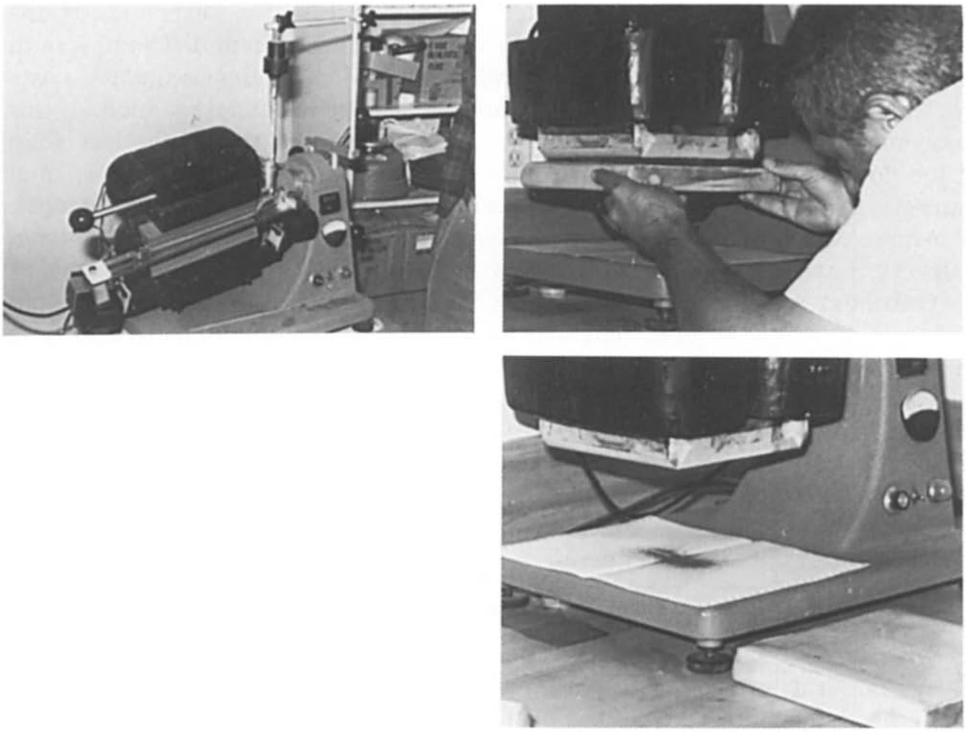

Fig. 6-10. Conventional Frantz Isodynamic Separator (top left) and a modified separator (right) used for routine separations in the US Geol. Surv. laboratories.

greater than 3.31; and magnetic and nonmagnetic fractions at 1.3 A for minerals with specific gravities between 2.96 and 3.31. Current routine separations in the US Geological Survey are at the equivalent of 0.2 and 0.7 A. In most instances, only the fraction which is nonmagnetic at 0.7 A is analyzed, although the intermediate magnetic split may also be analyzed where, for example, the presence of columbite is suspected. All of these routine schemes, which are designed for broadscale regional studies, involve considerable compromise between cost and reproducibility. Wherever possible, particularly in follow-up studies at larger scales, magnetic separation should be tailored to provide a more precise solution for particular exploration problems.

Sampling in the field

Location of site

The size of stream sampled should be based upon the length of the dispersion trains. Limited evidence from the literature suggests that chemically and mechanically resistant minerals, such as cassiterite, have long dispersion trains with anomalies recognizable for tens of kilometres downstream (Raeburn and Milner, 1927; Theobald and Thompson, 1959). Unfortunately, most of the ore minerals and their oxidation products are soft and brittle. Dispersion trains for these are short. In the example cited by Theobald and Thompson in Colorado, USA, the major ore mineral is molybdenite, the secondary hosts for molybdenum are ferrimolybdite and lepidocrocite, and the anomaly for molybdenum in the heavy-mineral concentrates can be traced for less than 1 km downstream from the source. For reconnaissance or small-scale regional surveys, big streams with large catchment areas may be used for some elements. For more detailed investigations, and for most of the elements even in regional surveys, smaller, first- and second-order active streams are preferred.

Optimum physiographic conditions for heavy-mineral exploration are in areas of moderate to high relief. In these areas, erosion is actively providing a good supply of detritus to the streams, and the irregularities in the eroding stream bed provide numerous traps for heavy minerals. Plateau or peneplaned landscapes are less suitable although, providing there is an adequate drainage system, the techniques are still useful. In areas completely covered by till (e.g., Finland), the till may be sampled instead of drainage sediments.

The sample should be collected from one or several heavy-mineral traps at each site. The heavy minerals behave like lighter grains of larger size. Thus, gravel or coarse sand provides the best sample medium. Fine sand, silt and clay deposits are selectively enriched in the finest grained, lowest specific gravity, tabular-shaped minerals, hence are less desirable sample media. The heavy minerals are concentrated by lag enrichment whereby finer and lighter minerals are winnowed from the head of bars. Heavy minerals generally filter to the base of alluvium where they are most concentrated in irregularities in the stream bed, behind obstructions, and on clay beds.

Ephemeral streams in semiarid and arid environments often present a uniform, almost planar, sand-floored channel. Where labour is cheap, these have been sampled by digging pits to bedrock. They can be sampled more practically near the surface at the head of minor scours, or by visually locating heavy-mineral pockets, streaks, or laminae.

Size of sample

The size of the sample varies with the purpose of the investigation. Most surveys collect 1 to 10 l of sediment at each site for concentration. Examples are Stendal (1978, 1980) for a 10 l sample, Hallenstein et al. (1981) for a 5 l sample, Rossiter (1976) for a 5 kg sample (approximately 2 l), Steenfelt (1985) for 1 to 3 l samples, and Ghisler et al. (1979) for a 1 l sample. Some surveys have sought a uniform size of concentrate, but this leads to varying amounts of dilution with light minerals that complicates interpretation of data, especially where analytical values are low.

Grain size of the sample

Some form of sizing of the samples takes place both in the field and in the laboratory. The nature of the sizing depends upon the nature of the problem and the methods of heavy-mineral separation employed. For conventional geochemical exploration using heavy minerals, sieving in the field at a fairly coarse size to remove gravel may be adequate. Theobald (1957) used a pair of nesting sieves to remove material coarser than 3 mm. Coats et al. (1980) pan the heavy minerals from the 0.15–2 mm fraction, Stendal (1978, 1980) used the <1 mm fraction, and Zantop and Nespereira (1979) and Hallenstein et al. (1981) used the <0.5 mm fraction.

This initial sieving reduces the bulk of the sample to be transported and processed and provides a more uniform feed for gravity separation. It can be disadvantageous where the heavy minerals sought are of coarse-grain size; for example, gem stones, wood tin, and even lead molybdenum in wulfenite (Rozelle, 1978). In these situations, special separation techniques may be necessary to evaluate size fractions coarser than normally used.

Further sieving is often needed to accommodate to gravity separation technique. Settling velocities are proportional to both the size and specific gravity of the particles; hence, the greater the uniformity of size, the greater the quality of the separation. Even for heavy-liquid separations additional sizing is required to prevent separation equipment from becoming blocked.

Mineralogy of the heavy minerals

In the field

Some simple tests for ore minerals can be carried out at the sample site or base camp. Preliminary examination by binocular microscope and the determination of magnetic and fluorescent properties and radioactivity are possible after drying the concentrates. A Wilke-magnet (Von Putzer, 1968, p. 33; Boenigh, 1983) can be used to separate martite, pyrrhotite, ilmenite, and sometimes monazite and hematite (Fig. 6-11). Where only the magnetic portion of the heavy mineral content of stream sediments is of interest, it is possible to collect this fraction directly from wet sediments with an automagnet (Callahan, 1975).

The nonmagnetic fraction can be examined for fluorescent minerals. Zeschke (1961, 1964) found about one hundred minerals that sometimes fluoresce under short-wave ultra-violet light, a few of which are of interest for exploration purposes. Scheelite and powellite are two well known examples (Greenwood, 1943), but other ore minerals such as willemite are sometimes encountered in heavy-mineral concentrates. As an indirect indicator of mineralization, Williams and Cesbron (1977) note that the bright orange fluorescence of apatite increases in intensity with "increasing degree of development of the porphyry system". A variety of portable and more powerful lamps are available and are described by Hintsteiner (1977).

A geiger counter or scintillation counter will identify concentrates containing radioactive minerals such as uraninite (pitchblende), secondary uranium minerals, thorium-oxides, thorite and monazite.

Several simple chemical tests are useful where specific elements or minerals are being sought. These provide for short term sample design control and also provide a morale boost for the field crews, increasing the overall efficiency.

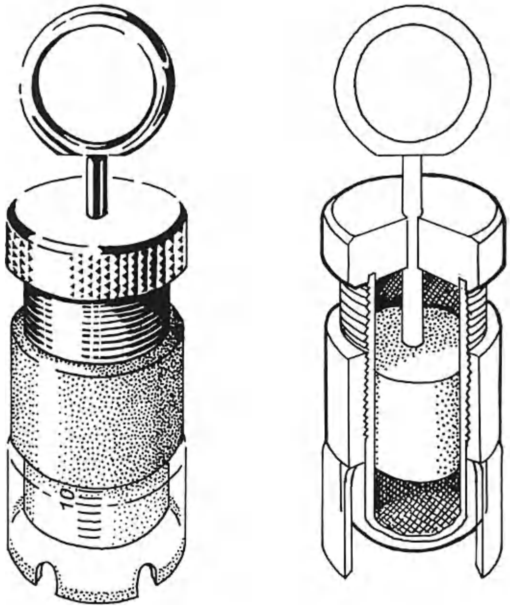

Fig. 6-11. The Wilke hand magnet can be used to separate to most magnetic minerals and some paramagnetic minerals.

Most of the standard microchemical techniques, described by Short (1940) and Guillemin (1953) and summarized in standard texts such as Cameron (1961) and Hurlbut (1971), are readily adaptable to the field identification of metal-rich minerals in heavy-mineral concentrates. The bead test is particularly useful for distinguishing minerals of the wolframite group in tungsten exploration. Several of the simple mineral staining tests (Reid, 1969) have been applied to the field determination of minerals in heavy-mineral concentrates. In particular, the ferricyanide–oxalic acid–diethylaniline method for zinc has been widely used (Fletcher, 1981, comments on the value of this method) and the hydrochloric acid–zinc method for identification of cassiterite has been used to estimate the frequency of tin minerals in heavy-mineral concentrates (Von Bernewitz, 1943).

In the laboratory

The mineralogical tests used in the field are equally suited to the laboratory, although more sophisticated equipment is normally available. The binocular microscope is particularly well suited to identification of minerals in heavy-mineral concentrates (Guigues and Devismes, 1969). In the process of release of the accessory minerals from the parent rocks, original grain boundaries are often preserved so that three-dimensional morphology can be determined. Properties such as crystal form, lustre and hardness can be critical to identification. Additional optical properties can be determined by single-crystal, oil-emission techniques under a petrographic microscope. The use of a spindle stage (Wilcox, 1959; Hutchison, 1974) facilities this approach and allows a simple, non-destructive method of analysis.

Concentrates may be more permanently mounted on a glass slide, preferable using one of the mounting media of higher than average refractive index, for conventional petrographic analysis. Parallel mounting of a fraction of the concentrate for a polished section is usually desirable because many of the minerals of most interest in exploration are opaque. Such permanent mounts are less suitable for concentrates being used in geochemical exploration because a fraction of the sample is lost prior to analysis. There is an increased possibility of errors from unrepresentative splitting, of the nugget effect, and of simply not having enough sample.

Determinations to confirm mineral identifications can be made by single-crystal, X-ray diffraction techniques. Additionally, chemical analysis of single or several grains can be made using a narrow X-ray beam for X-ray fluorescent analysis, or by laser-emission spectrography, scanning electron microscopy, or microprobe.

Criteria for the determination of heavy minerals are found in Hutton (1950); Stumpfl (1958); Milner (1962); and Boenigh (1983). Standard texts of petrography, optical crystallography and ore microscopy are useful.

Mineralogic information from heavy-mineral concentrates can be valuable aid to geochemical interpretation but it may not be practical to carry out such studies routinely on all samples. Three types of mineralogical analysis are appropriate for routine exploration. (1) Identification of the presence of distinctive minerals such as gold, cassiterite and scheelite. (2) Rapid analysis of the concentrates to identify major components and readily recognizable minerals. This provides considerable information on geological environments, identifies anomalous samples and can be of value in alerting the analyst to potentially difficult or extremely rich samples. (3) Mineralogical analysis following chemical analysis to identify minerals responsible for anomalous values. This approach is the most practical because it involves examination of relatively few samples.

Chemical analysis

Heavy-mineral concentrates provide a challenge for the analyst. Major problems are the extreme variation and unusual composition of the matrix and the limited size of the concentrates. In 1,300 nonmagnetic heavy-mineral concentrates from a reconnaissance programme in the southwest of the USA, for example, a single mineral constituted 50% or more of the concentrates in about a quarter of the samples. For practical purposes, this mineral constitutes the matrix for the sample in question. Although zircon and apatite are the most common single minerals in this category, 15 other minerals also dominate samples. These range from highly refractory minerals like topaz (AlF_2SiO_4) and rutile (TiO_2) to minerals such as fluorite (CaF_2), barite ($BaSO_4$), sphene ($CaTiSiO_5$), aragonite ($CaCO_3$) and celestite ($SrSO_4$). Where more magnetic fractions of the concentrates are used, Fe, Ti, Mn and Cr may be dominant matrix elements. An example of the type of problem that can arise is provided by a case where a minor chromium line was misread as an antimony line using emission spectrography (Theobald et al., 1967, fig. 3).

Most of the analytical techniques reviewed by Fletcher (1981) can be adapted for analysis of heavy-mineral concentrates, but extreme care and a skilled analyst are essential. The problems of matrix variation can be partly offset, for example, by dilution with an inert medium to approximate the composition of an "average" sample. This approach introduces another possible source of error and reduces the analytical sensitivity, thereby removing one of the advantages of using heavy-mineral concentrates.

Analytical procedures involving sample dissolution will rarely be total analyses in the case of concentrates because of the variation in their mineralogy. The major disadvantage of solution chemistry, and some of the direct instrumental techniques, such as some forms of X-ray fluorescence, is their requirement for a relatively large sample. In a survey in part of the southwestern USA, 1300 concentrates were each derived from about 2.5 kg of original sediment, but after concentration ranged in weight from less than 2 mg to 46 kg. Only 20% of the concentrates weighed 0.5 g or more, eliminating the use of analytical methods requiring large samples. Nearly 8% weighted less than 10 mg, the weight required for emission spectroscopy or neutron activation analysis.

Ideally, an appropriate analytical scheme must be designed by an analyst experienced with both heavy-mineral concentrates and chemistry. Moreover, the analyst should participate in the interpretation of the data.

Sample homogeneity

Heavy-mineral concentrates are, by their nature, inhomogeneous. Moreover, the metals of most interest in exploration are often present as major components of minor minerals. Where metals are present as a major or minor component of an abundant mineral there is less problem with homogeneity, although there can be problems in measuring differences within anomalous areas. Host minerals of low specific gravity are subject to erratic recovery during concentration, as is the case for some secondary hydrous Mn and Fe oxides. Hence, the homogeneity of a sample may provide valuable information on the source of anomalous metal, and the sample locality yielding the most erratic results may be the most important.

Some measure of homogeneity is desirable, particularly where the source of the variation results from sampling and preparation produces. Three sources of procedural variation can lead to gross variation in reported concentrations of elements in concentrates. There are (1) in field sampling, (2) in sample preparation and (3) in sampling the concentrate for analysis. There are often great differences in the composition of the heavy minerals derived from the bed load of the stream and from the suspended load or overbank deposits. A careless or poorly trained sampler can create variance that may appear systematically by collecting from the most readily accessible sites. Theobald and Allcott (1973) describe a situation where a sampler was asked to collect 25 samples at a single anomalous site, and intentionally left unsupervised, to establish site variance. The sampler collected a stratified set of samples, starting at the alluvial surface and terminating at the bedrock surface. The samples from the suite were all anomalous for W, although the range of values varied by more than an order of magnitude from less than 500 to more than 5000 ppm. Uniformity is best obtained when a trained geologist collects the samples, or is on site to supervise collection.

Sample preparation of concentrates is generally less of a problem than the other two sources of error. The major problem is in comparing data between laboratories or programmes rather than within programmes. Various organizations have designed their own heavy-mineral separation procedures which, although generally similar, are sufficiently different to cause pronounced systematic bias, cf. the schemes of Brundin and Bergström (1977) and Alminas (in Meyer et al., 1979, p. 427).

Few data are available to compare the various methods of separation, but from inhouse comparisons over the last few decades it appears that the most of the mechanical concentration devices yield similar recoveries (Theobald, unpublished data) which are similar to those obtained by gold panning. Theobald (1957) evaluated the factors affecting the variability of concentrates from a programme in the southeastern USA involving ten panners working in an area of complex geology and physiography. He concluded that recovery was most dependent upon mineralogy and grain size of the heavy minerals. No systematic difference could be measured between experienced panners. Stendal (unpublished data), however, evaluated the performance of four different panners working in similar geologic environments in southwestern Norway and identified a significant bias between the panners (Table 6-V), although some of this difference may be attributed to sampling procedures. The maximum variation between operators was 25%, which should not hinder recognition of most anomalies although it could affect the statistical identification of subtle anomalies. To overcome this bias, it is common to pan the bulk sample in the field to procedure a concentrate containing 50 to 90% of light minerals. This rough concentrate is further reduced under controlled conditions using a single operator (Hallenstein et al., 1981) or by heavy-liquid separation in the laboratory (Brundin and Bergström, 1977; Meyer et al., 1979).

Inhomogeneity affects the results in two ways. In most cases, the presence of rock-forming minerals subdues anomalous values, but obscures only the marginally anomalous values. A clean concentrate containing 1000 ppm Pb, for example, will still contain 500 ppm Pb if diluted with an equal volume of quartz but a concentrate containing 150 ppb Pb similarly diluted would contain an unimpressive 75 ppm. Nonuniform magnetic separations can have the reverse effect by creating anomalies. For example, a few grains of wolframite that are inadvertently included in the nonmagnetic concentrate can appear as several hundred ppm W that would be attributed to scheelite. Entrapment of a single flake of gold with the magnetic minerals can remove 100 ppm Au from the

TABLE 6-V

Average weight proportions of panned concentrates obtained by different panners

Panner	A	B	C	D
No. of samples	126	128	135	113
Panned concentrates (average g)	57.9	56.5	48.3	44.0
Heavy-minerals (g) (>2.96 g/cm^3)	45.7	41.3	35.5	32.9
Magnetic fraction (g)	22.4	17.7	15.5	15.5
Non-magnetic fraction (g)	23.3	23.6	20.0	17.7
Light fraction (g)	12.2	15.2	12.8	11.1
Light fraction (%)	21.1	26.9	26.5	25.2

nonmagnetic residue. The most critical need for uniformity is, thus, in the preparation of magnetic separates.

The final preparation of heavy-mineral concentrates is a source of much of the variation attributed to analytical error. Before grinding, a split of the coarse concentrate is often retained for mineralogical examination. This is an acceptable and valuable practice only when the concentrates are to be examined mineralogically after chemical analysis. Even under optimum conditions, splitting can only aggravate the nugget effect. If a sample contains two particles of gold, for example, there is one chance in four that both will go into the analytical split indicating the presence of several hundred ppm in the sample, while the mineralogist will see nothing. There is one chance in four that both flakes will go into the mineralogic split and the chemist will see nothing. So that in 50% of the cases will the chemist and the mineralogist agree! If the samples are to be split, the splitting must be done carefully with full recognition that the two parts will not be the same.

The concentrates must be ground carefully before analysis. This is probably the most critical step in the preparation procedure, particularly if the entire sample is not to be consumed for a single analytical procedure. Nor is the grinding of heavy-mineral concentrates a simple task. Minerals such as corundum and moissanite (silicon carbide, carborundum) are fairly common in concentrates and not only do they resist grinding and inhibit the grinding of the other minerals, but also they cause considerable damage to the grinding vessels. At the other extreme, the soft and malleable minerals such as gold may roll, ball, or flatten rather than grind, and in extreme cases may plate out on the grinding vessel. The effect is to enlarge rather than reduce the particle size and, in the instance of gilding of the vessel, to promote carry-over of metal from one sample to the next.

The best way to avoid inhomogeneity resulting from weighing of the chemical charge from the ground sample is to have a well-trained technician hand grind the concentrates and remove problem minerals from the sample for separate handling, following the standard procedures of the assayers (Shepard and Dietrich, 1940, p. 32).

Cost of heavy-mineral surveys

Heavy-mineral concentrates are more expensive to collect, process and analyze than conventional stream sediments. Where the cheaper techniques are adequate for the objectives of the survey, they should be used. Although more equipment is required for heavy-mineral surveys, the actual cost is best measured by the time required in comparison with cheaper methods.

Sample collection time varies with the type of logistic support and scale. At regional scales, a 2-man team on foot can sample about five sites per day whether sampling stream sediments alone or collecting heavy-mineral concentrates. With an adequate road network, the same team could average about ten heavy-minerals sites per day by car, as demonstrated in southwestern Norway (Stendal, 1978), in Spain (Zantop and Nespereira, 1979) and in the southeastern USA (Theobald, 1957). Conventional stream sediments could be collected at about twice this rate. Working with helicopters in terrain with reasonable good landing sites in the valley bottoms, an average of 20 sites per day per team was achieved in northern Alaska and southwestern Arizona. In the forested, high-relief terrain of central Arizona and the Colorado mountains, a rate of ten sites per day is more reasonable. With good access, about twice as many conventional stream sediments can be collected by helicopter, but with poor access the time is spent getting to the sampling site and the rate of collection is about the same for stream sediments or for heavy-mineral concentrate. In general, heavy-mineral concentrates can be collected at about half the rate of conventional stream sediments.

Processing of the heavy-mineral concentrates is an added cost over that for stream sediments. Preconcentration by panning will take 10 to 30 minutes, depending upon the proficiency of the panner and the nature of the sample. A consistent rate of 20 per man day is attainable. After preconcentration, heavy-liquid separations can be accomplished at a rate of 100 per man day in an efficient laboratory setup, magnetic separations at the rate of 50 per man day. Grinding and analytical time for heavy-mineral concentrates is slightly greater than for conventional stream sediments.

Thus, the overall cost in man days for collection, processing, and analysing of a single magnetic separate of a heavy-mineral concentrate is two of three times greater than that of a conventional stream sediment. Where several size, gravity, or magnetic splits are to be analyzed, or mineralogical data are required, the cost increases substantially primarily because of additional analytical cost.

SUMMARY AND CONCLUSION

The use of heavy-mineral concentrates derived from alluvial materials is increasing with the growing understanding of their value in improving the detection and characterization of anomalies. The sample medium is a concentration of the heavy, resistant minerals such as elemental gold and the

TABLE 6-VI

Examples of the use of heavy-mineral concentrates for exploration in a variety of climates

Climate	Target element	Minerals in panned concentrate	Elements	Region	Principal mineralization	Reference
Arctic/ subarctic	As	Arsenopyrite, galena, pyrrhotite, pyrite, ilmenite, scheelite, monazite	As, Pb, Sn, W, Ti, Zr	Central East Greenland	Vein and fracture-bound arsenopyrite	Stendal 1980, 1982
	Au	Gold, hematite, garnet, magnetite, arsenopyrite, galena, anglesite	Au, As	Yukon Territory	Vein and placer gold	Gleeson, 1963, 1970 Boyle and Gleeson, 1972 Gleeson and Boyle, 1980
	Cu	Chalcopyrite, covellite, bornite, chalcocite, native copper	Cu	North Greenland	Cu in sandstones, native Cu in basalts	Ghisler et al., 1979
		Chalcopyrite, tetrahedrite, pyrite, pyrrhotite, ilmenite, rutile, apatite, sphene	Cu, Ba, La, Ni, Zr	Central East Greenland	Strata-bound Cu in quartzites	Stendal, 1979, 1980 Stendal and Hock, 1981
	W	Scheelite, ilmenite, Zr, rutile, sphene, pyrite, pyrrhotite, arsenopyrite, apatite, monazite	Ti, Zr, W, As, Sn, locally Sb	Central East Greenland	Tungsten-skarn and vein	Stendal, 1980, 1982 Hallenstein et al., 1981
Temperate	Au	Gold, monazite, cassiterite	Nb, Ta, Th, U	South Island, New Zealand	Alluvial gold	Bradley, 1979
		Gold	Mo, Pt, Sn, W, Ag, Cu	USA, several localities	Different types	Antweiler and Campbell, 1977
	Ba	Barite, celsian	Ba, Pb, Zn	Scotland	Strata-bound barite	Coats et al., 1980, 1984b
	Nb	Pyrochlore, apatite	Nb, P	Finland	Carbonatite niobium and phosphorus	Vartiainen, 1976
	Pb–Zn	Phosphate plumbo-gummite, sphalerite	Pb	Scotland	Fracture-bound lead strata-bound Zn	Stone and Gallagher, 1984
	Sb		Sb, As	Scotland	Vein antimony, strata-bound arsenic	Stone and Gallagher, 1984

	Sn		Sn, W	New England, USA	Tin vein, beryllium skarn	Nowlan et al., 1985
	Sn–W	Cassiterite, wolframite, scheelite, gold, rutile, ilmenite, monazite, zircon		NW Spain	Hercynian granites migmatites and schist	Zantop and Nespereira, 1979
	W	Scheelite		SW Norway	Tungsten in amphibolites	Stendal, 1978
		Scheelite, tourmaline		N Norway	Tungsten in schist and vein	Petersen and Stendal, 1987
		Huebnerite	W, Mo, Sn, Mn	Colorado	Molybdenum porphyry	Theobald and Thompson, 1959
Subtropic/ tropic	All	Gold, cassiterite, columbite, wolframite	Mo, Nb, REE, Ta, Zr	Egypt	Nepheline syenites greisen	Bugrov and Shalaby, 1975
	Au	Gold (also more general exploration)	Au	SE USA	Vein, veinlets and volcanoclastic rocks; granites	Overstreet, 1962, 1963 Overstreet and Bell, 1960 Bell, 1976
		Gold, hematite (dominant), ilmenite–magnetite, chalcopyrite, pyrite	Au	South Carolina, USA	Submarine exhalative Cu and Au	Stilwell et al., 1983
		Gold	Au	Liberia and Surinam	Quartz-vein gold	Tooms, 1985
	Cu	Malachite	Cu	Northern Australia	Secondary Cu deposits from basic volcanics	Rossiter, 1976
	Sn	Cassiterite, topaz, wolframite, tantalite	Be, Cu, Li, Ta, U, W	Northern Australia	Greisen and veins	Rossiter, 1976
	U	Uranitite, monazite, scheelite, zircon, gold, magnetite, ilmenite	U, Au	Pakistan	Undifferentiated crystalline rocks	Zeschke, 1959
			U, Cu, Pb, Zn	Southern Sumatra	Volcanic and granatic rocks	Watters and Sagala, 1979
			U, Sn, Au	Indonesia and Sri Lanka	Various rock types	Watters, 1983

platinum group metals and alloys, monazite, cassiterite, the tungsten minerals, barite, fluorite, the oxides of iron and titanium, and silicates such as zircon, garnet, amphibole, pyroxene, epidote and sphene; in some environments primary sulphide minerals, and/or their oxidation products may be present. A general order of survival for the most commonly sought ore minerals is diamond (and the gem varieties of corundum) > cassiterite > chromite > iron–titanium oxides > the tungsten ores > pyrochlore > gold > barite > uraninite > fluorite > sulphides. Minerals as durable as gold will generally survive in most environments, whereas less durable minerals will have only short dispersion trains. Sulphides survive in moderate to high relief and arctic environments, but are less common in tropical environments, particularly in the arid environment.

Heavy-mineral concentrates have been used for exploration at all scales but their maximum advantage is at regional scales. At large scales they can often be replaced by less expensive, more direct techniques. Samples are collected preferable from first- and second-order streams to restrict the provenance, reduce dilution and accommodate the short dispersion trains for many of the less durable minerals. Material is collected from the active sediment in natural heavy-mineral traps. Preconcentration, most often in a gold pan or batêa, is commonly followed by a heavy-liquid separation and one or several magnetic separations. Where preconcentration is accomplished in the field, the presence of fluorescent, radioactive and readily identified minerals such as gold can be determined, thereby providing direct control for sampling. One or several of the fractions of the heavy-mineral concentrate may be analyzed chemically and/or mineralogically. Uniformity throughout the procedure is essential. Concentration factors are of the order of 10^4 so that, although some dilution can be tolerated, the effect of any contamination is greatly exaggerated. A great variety of size, gravity and magnetic subfractions of heavy-mineral concentrates has been used for exploration, the most useful for most metals being the nonmagnetic fraction.

Analysis of heavy-mineral concentrates solely for the element of interest will often establish the presence of an anomaly. Multi-element chemical and mineralogical analyses of at least anomalous samples, are generally recommended. Element associations and mineralogy may indicate the type of deposit present, while element associations can also provide information on the geology of the area and a basis for normalization of the data.

Some examples of the use of heavy-mineral concentrates in exploration are given in Table 6-VI; their advantages and disadvantages are summarized below.

Advantages

(1) Heavy-mineral concentrates are small in size but represent a large volume of original sample. Hence, they overcome some of the sampling problems inherent in stream sediment sampling.

(2) Contrast is often greatly enhanced, sensitivity increased, and dispersion trains extended.

(3) Metal-bearing, but not ore-related minerals can often be identified and excluded by careful selection of the heavy-mineral fraction to be used.

(4) On site examination of concentrates can provide a guide for the sampling programme.

(5) Mineralogical examination can indicate the presence of particular deposit types.

(6) Consideration of the morphology and grain size of durable minerals may indicate the proximity of a sample to its source.

(7) Organic material, which can complicate interpretation based on stream sediments in some areas, is excluded from heavy-mineral concentrates.

(8) Anomalies attributable to sorption by Fe and Mn oxides can usually be identified.

(9) Anthropogenic contamination of heavy-mineral concentrates may give similar patterns to those given by stream sediments, but is far more readily identified.

Disadvantages

(1) The preparation of heavy-mineral concentrates is expensive. A minimum of twice as much time is required in comparison with stream sediments.

(2) Specialized equipment and facilities to handle toxic liquids are required.

(3) Preconcentration techniques require an adequate supply of water, which may be difficult to acquire in remote, arid environments.

(4) A reasonable well-developed drainage system is required.

(5) Mineralogic examination of concentrates beyond the most simple techniques is an art mastered by few and specialized equipment may be required.

(6) Variance attributable to sampling and sample preparation can be high, particularly for anomalous samples where the element of interest is a major component of a minor mineral.

(7) Chemical analysis of heavy-mineral concentrates is more difficult than for most geologic materials. Samples may be small, have highly variable and unusual matrices and may be rich in interfering elements.

(8) Very fine grained particles require special care to be recovered effectively during concentration, so the technique is less well suited to exploration for deposits with a fine initial particle size.

(9) The nature of the detrital dispersion train requires that the ore or primary or secondary pathfinder minerals are eroded from the bedrock surface. Completely concealed deposits are not likely to be detected.

Heavy-mineral concentrates are gaining wide acceptance as a sample medium for geochemical exploration. Anomalies defined in concentrates have led to the discovery of major ore deposits. However, the great sensitivity of the technique has resulted in the discovery of vast numbers of minor occurrences of ore minerals. The technique requires judicious management and specialized expertise.

Drainage Geochemistry
edited by M. Hale and J.A. Plant
Handbook of Exploration Geochemistry, Vol. 6 (G.J.S. Govett, Editor)

Chapter 7

LAKE SEDIMENT SAMPLING IN MINERAL EXPLORATION *

EION M. CAMERON

INTRODUCTION

Lake sediment sampling is one of the most recently developed methods of exploration for metalliferous mineral deposits. Although the first attempt to use lake sediments was in 1938–40 (Lundberg, 1957), and Schmidt demonstrated the basis of the method in 1956, major investigation of this method only began in the late 1960's. These studies showed that, where used in appropriate terrain, lake sediment geochemistry was an effective and relatively uncomplicated means for rapidly surveying districts to outline areas for more detailed exploration. This promise led to large scale survey programs in northern terrains by government and industry, commencing in the early 1970's. Today, more than two hundred thousand samples of lake sediment have been collected and analyzed, representing about two million square kilometres, and the method has assisted in the discovery of several important mineral deposits and prospects. In addition, the data form an invaluable long term source of information on the chemical condition of the landscape.

The Precambrian shield areas of the northern hemisphere have long been a fruitful target for the prospector and geologist. After the Second World War they were joined by the geophysicist, who had developed means for surveying large areas from the air. However, no comparable technique in geochemistry had been devised. Several geochemical methods were available for detailed exploration within glaciated shield areas, but not for reconnaissance exploration. By the 1960's, stream sediment reconnaissance had become firmly established in most other regions of the world. This method could not be consistently applied to the northern shields because stream systems are often poorly developed and thick forest cover make access difficult and time-consuming.

While these regions are poorly endowed with streams, they do possess an abundance of lakes. At first sight, the use of lake sediments as an alternative to stream sediments looked unpromising. Sediment that could be seen along the edge of lakes seemed to be of quite local derivation, unsuitable for recording the geochemical signature of a drainage basin. Perhaps this material would have seemed more promising if the climate was warmer, allowing chemical

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* Manuscript of Chapter 7 received November 1985; revised January 1990.

weathering of minerals and the resulting transport of metals in solution to the lakes. But at that time it was widely perceived that chemical processes of weathering were not active in cold, glaciated terrain. The initial steps into lake sediment geochemistry proved this to be a fallacy. Chemical weathering of sulphide minerals forms a basis for the method. Sampling is now largely confined to centre-lake sediments, which are more homogeneous than near-shore sediments and contain a higher proportion of elements precipitated from solution. Moreover, centre-lake sediments are more readily sampled by helicopter.

The majority of lake sediment surveys have been carried out within shield areas of North America and Fennoscandia, in the northern Appalachians, and in Alaska. In all of these regions there is an abundance of lakes formed by glacial processes. While lake sediments can and have been used for geochemical exploration in other terrain, notably mountainous regions, their application in these regions is subsidiary to other methods, principally stream sediment sampling. Thus this chapter deals only with glaciated regions of low relief with a wealth of lakes. For reasons of familiarity, many of the principles that govern the use of lake sediment geochemistry for exploration are illustrated by Geological Survey of Canada (GSC) results, including those of the National Geochemical Reconnaissance (NGR) program.

Although the use of lake sediments for mineral exploration is relatively recent, they have had a long history of scientific study. In the course of this, limnologists have developed an extensive technical language to describe the various features of the lakes, waters and sediments. Since most readers of this chapter will be using the method to assist in a broader purpose, it is written with a minimum of these specialized terms. The classic texts in limnology are Hutchinson (1957, 1967), and recent reviews pertinent to the subject matter of this chapter are by Imboden and Lerman (1978); Jones and Bowser (1978); Ragotzkie (1978); Sly (1978); and Hakanson and Jansson (1983). Readers are also referred to an earlier review of lake sediment geochemistry applied to mineral exploration by Coker et al. (1979).

NATURE OF THE LAKE ENVIRONMENT

Formation of lake basins

Lakes are formed by a variety of processes. Some of the largest lakes, such as the Dead Sea and Lake Tanganyika, are due to tectonism, principally crustal extension. Lakes of volcanic origin tend to be smaller. Fluvial mechanisms produce many types of lakes, mostly small: in deltas, by fluviatile damming, as well as oxbow and levee lakes. The majority of lakes sampled during geochemical exploration surveys were formed by glacial action. Ice sheets moving over reasonably level surfaces produce large numbers of lakes by scouring. This action is not random, but is concentrated along faults and shatter zones, and within altered rocks and other recessive lithologies (Fig. 7-1). These are the

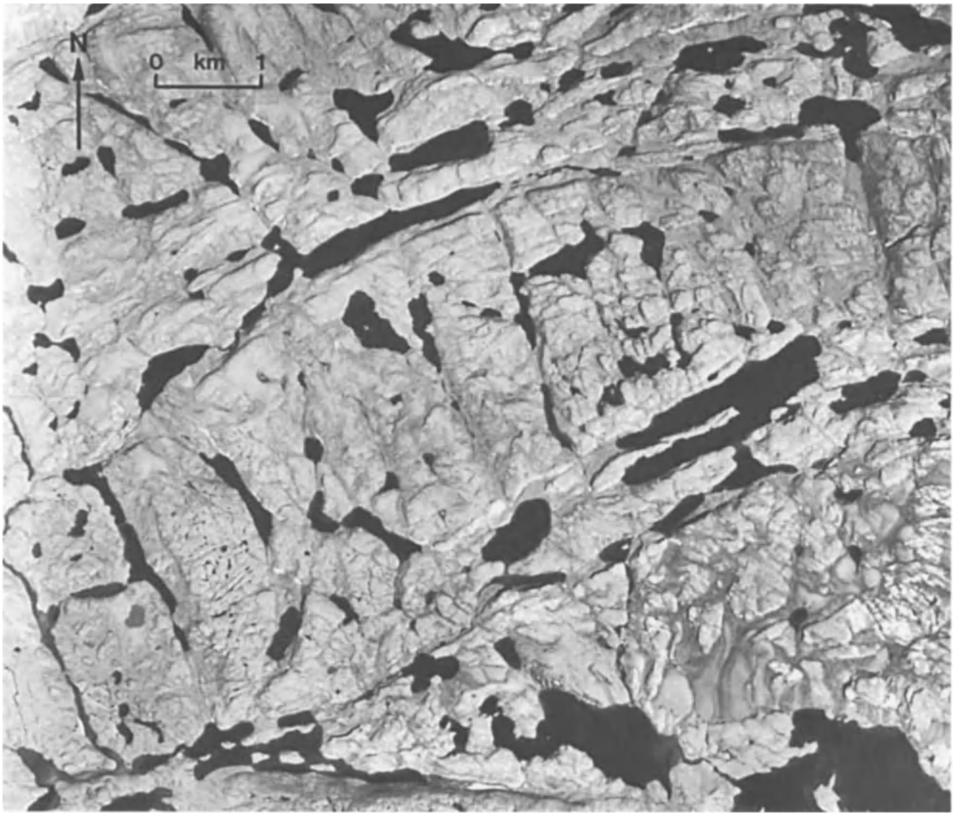


Fig. 7-1. Aerial view, Melville Peninsula, NWT. Note that in this region, where sedimentary rocks dip vertically, the distribution of lakes is determined by lithology and jointing.

same zones in which many mineral deposits occur. Apart from scouring, glacial lakes may form by moraine damming, while kettle lakes fill depressions in glacial drift that were originally occupied by residual ice. In mountainous areas, freeze-thaw effects at the head of the valleys produce cirque lakes.

In Alaska vast numbers of lakes have formed by local melting of permafrost. Here the permafrost is unstable, so that once melted, it does not reform. Destruction of vegetation exposes frozen ground for summer melting; melting is accompanied by a decrease in volume and the area of subsidence fills with water. Once formed, the lake steadily increases in volume.

Distribution of lakes

The greatest concentrations of small lakes suitable for geochemical exploration purposes occur in flat, glaciated areas, such as the shield regions of the northern hemisphere. Such lakes may cover as much as 75% of the surface area, as in the Quetico region of Ontario and Minnesota. Parts of the Canadian Shield have a lake density of 1 per 2 km^2 (Allan, 1971). In the Canadian Shield most lakes are small and shallow, less than 0.1 km^2 in area and less than 9 m deep (Cleugh and Hauser, 1971); lakes in Alaska are similar in size and depth. For geochemical reconnaissance, rather larger lakes, in the range of 1 to 25 km^2, are preferred, to represent a broader drainage area.

Thermal and density effects

In northern shield terrain there is seasonal ice cover on lakes. After the ice melts in the spring and the water attains a temperature of 4°C throughout, mixing by the wind can extend over the entire depth of the lake. This continues until heating by the sun makes the surface layer (epilimnion) sufficiently buoyant that it resists mixing with deeper, cooler, more dense water (hypolimnion). The lake water is now stratified. In late summer, there is cooling of water at the surface, which then descends convectively to cool the entire epilimnion. With progressive cooling, the buoyancy of the epilimnion decreases until, in the fall, the entire water column can mix by wind action. Whether or not a lake becomes stratified in the summer depends on several climatic and topographic factors, but is principally influenced by water depth and wind strength, with increase in the latter causing the depth of the epilimnion to expand. Stratified lakes, in which free circulation occurs twice a year, are termed dimictic. Dimictic lakes and unstratified lakes are the principal types found in those regions of the northern hemisphere with a high density of lakes. Hutchinson (1957) describes other, less common, types of stratification.

Stream or river water entering a lake may, at times, be more buoyant than the surface water, causing the inflow to disperse across the lake surface as a plume. Since stream water carries fine particles in suspension, this is an important mechanism for sedimentation in the central portions of lakes. In stratified lakes, density differences may cause suspended sediment to be retained in the epilimnion until the latter mixes with deeper water. In winter the entire water column is still and of similar density, so that fine suspended particles can settle.

Oxygen content

Stratification acts as a barrier to free exchange of oxygen between surface and deep water. In eutrophic lakes, i.e., those with a high flux of organic material, oxidation of organic matter causes a diminution or exhaustion of oxygen present in the hypolimnion, which may be accompanied by the formation of sulphide due to bacterial reduction of sulphate. This can have important effects on the solubility of metal ions in the water column, since heavy metals, such as Cu, Zn, Cd, Pb and Hg, form sulphides with low solubility products. Conversely, high concentrations of organic ligands in eutrophic waters can promote the solubility of some metals. In reducing conditions, alkylated species of Hg such as CH_3Hg^+ can form, leading to the mobilization of this metal. Stratification is, in part, controlled by depth and Schindler (1971) found that lakes <4 m deep in northwestern Ontario were unstratified and oxygen-saturated throughout the summer, while those >12 m were eutrophic. Those of intermediate depth showed an oxygen depletion in their bottom waters by the end of the summer.

pH, carbon dioxide, dissolved solids

The range of pH in 64,743 samples taken during NGR surveys of Canadian Shield lakes is 3.1 to 9.5, with a median value of 6.4 (Fig. 7-2, Table 7-I). Values near the median are typical of areas underlain by non-calcareous granitic or supracrustal rocks. Values near or above 7.0 generally come from areas of calcareous bedrock or till, while naturally acidic waters are derived from oxidizing sulphide minerals. For non-acidic waters, pH is buffered by the carbon dioxide–bicarbonate–carbonate system. In the hypolimnion, CO_2 is released by respiration and by the oxidation of organic matter, causing a decrease in pH. Conversely, CO_2 is consumed by photosynthesis in the epilimnion, increasing pH. Thus in a well stratified lake, pH declines down the water column, together with temperature and oxygen content (Fig. 7-3).

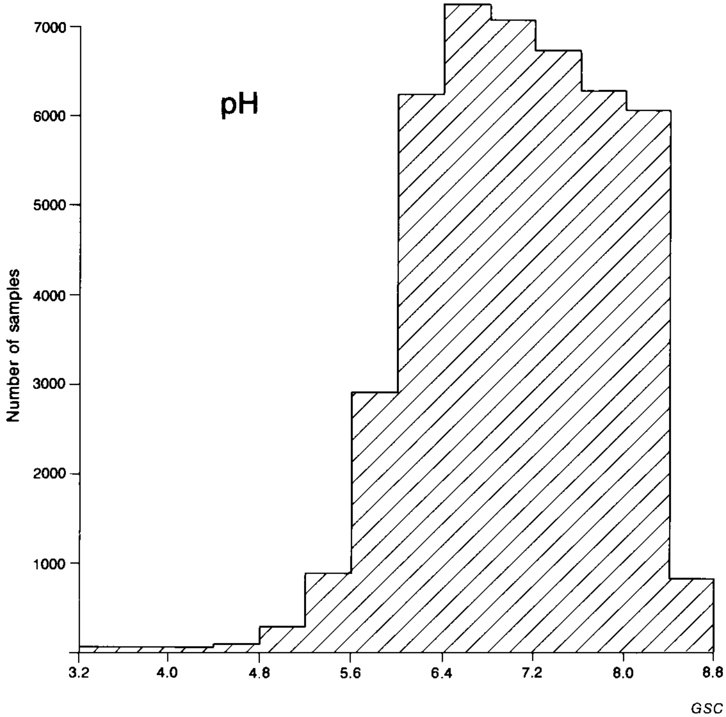


Fig. 7-2. Histogram of pH for 64,743 samples of lake water collected mainly in the Canadian Shield by the National Geochemical Reconnaissance program.

TABLE 7-I

Statistical data on the composition of all NGR lake sediment samples collected to the end of 1982 (compiled by D.J. Ellwood)

Element	Number of samples	5th percentile	Median	95th percentile
Zn, ppm	40,988	32	86	200
Cu, ppm	40,989	6	24	100
Pb, ppm	40,988	1	3	18
Ni, ppm	40,988	4	13	54
Co, ppm	40,986	2	7	24
Mn, ppm	40,986	60	240	1300
Fe, %	40,980	0.4	1.6	7.0
U_{SED}, ppm	41,028	0.6	4.6	35.9
Mo, ppm	40,966	1	2	11
Hg, ppb	29,174	12	50	140
Ag, ppm	40,989	0.1	0.1	0.2
As, ppm	40,845	0.5	0.5	7.0
LOI, %	40,861	4.5	29.8	69.8
U_{WAT}, ppb	29,730	0.005	0.05	0.43
F_{WAT}, ppb	24,432	10	34	140
pH	21,901	5.6	6.4	7.5

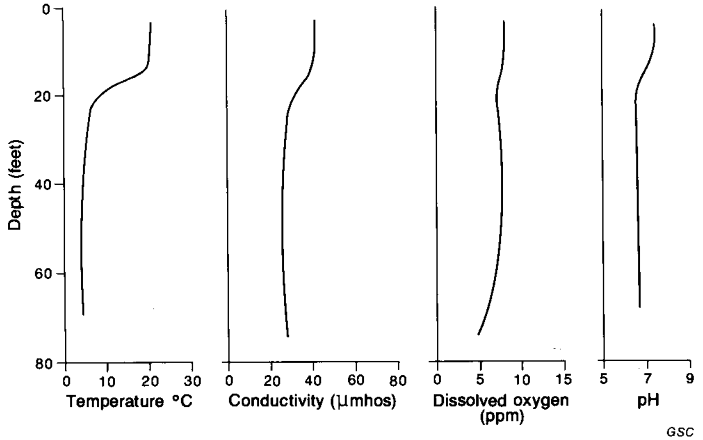


Fig. 7-3. Profiles of temperature, conductivity, dissolved oxygen and pH in the water column of a stratified lake (Lake 'A', Ontario, modified after Coker and Nichol, 1975).

Specific conductance is a measure of dissolved ions within waters. In most fresh waters, the major ions are SO_4^{2-}, Cl^{2-}, CO_3^{2-}, HCO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and silicic acid. Trace elements that serve as indicators for metallic mineralization, if present, are at low concentrations, in the range 0.01 to 100 ppb. The lowest values for specific conductance tend to occur in waters with pH near the median value of 6.4. Values increase in alkaline and in acidic waters, reflecting salts dissolved from carbonate rocks or released by the oxidation of sulphide mineralization.

Types of lake sediment

The three principal sedimentary environments in lakes are deltaic, nearshore, and deep. To this may be added a transitional environment between deep basins and shallower conditions where there is mixing of sedimentary types. Coarser particles, sand or silt, carried in stream and river water are deposited in deltas where these waters enter the lake. Nearshore sediments, which are derived by erosion of the shoreline and shallow bottom, are also relatively coarse, since the action of waves and currents removes fine particles to deep water, although fine material may also accumulate inshore in bays or in the lee of promontories. Wave and current action can cause longshore transport of the nearshore sediments.

It is the sediment of deep basins that is most often sampled for geochemical exploration purposes. This comprises clay- or fine silt-sized mineral and rock particles brought to the lake in suspension in stream waters, together with chemical precipitates produced within the lake by organisms and by inorganic reactions. This sediment is a gel that becomes increasingly watery towards the sediment/water interface. Its fluid nature causes it to be deposited in depressions within the lake bed. Thomas (1969) found a good correlation between the clay and organic carbon content of sediment from deep basins in the Great Lakes. Fine, organic-rich sediment may be referred to as gyttja. North of the treeline, fine sediment from deep basins may be poor in organic matter.

The distribution of sediments within Turkey Lake (Fig. 7-4) in the Canadian Shield shows that modern post-glacial sediment was deposited upon a floor of bedrock and glacial/proglacial sediment. In this lake, as in many others, nearshore sediment is poorly developed, except for sand deposited near the main inflow. The inshore bottom is mainly bedrock, mantled in places by till. It is common in glaciated terrain to find till forming the nearshore bottom and in permafrost regions this often shows the same periglacial features, such as patterned ground, as the onshore till (Shilts and Dean, 1975). The acoustic profile across Turkey Lake (Fig. 7-5) demonstrates that the fluid nature of the gyttja prevents its deposition on slopes.

Composition of lake sediment

There are three principal sources for the material forming lake sediment. The allogenic fraction is particulates transported by streams, as airborne dust, in rain, or derived by shore erosion. The mineralogical composition of this fraction largely reflects that of local bedrock or overburden and this applies to the clay-sized material, as well as to the coarser fractions (Jones and Bowser, 1978). There is little modification of well-crystallized silicates and oxides in the lacustrine environment. Clay-sized material that comprises a substantial part of centre-lake sediments is not all clay minerals; indeed, fine-grained quartz and feldspar make up more than half of this fraction (Timperley and Allan, 1974; Coker and Nichol, 1975).

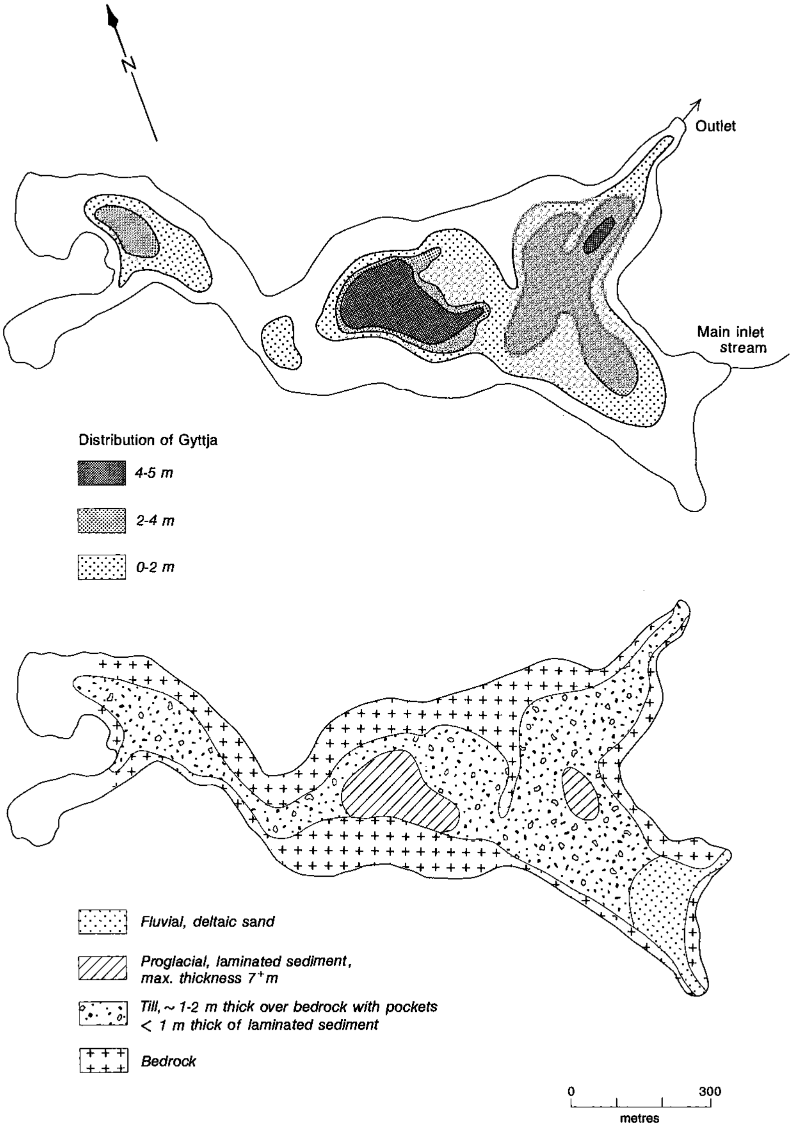


Fig. 7-4. Distribution of glacial/proglacial and modern lake sediments in Turkey Lake, Ontario (modified after Shilts and Farrell, 1982).

The endogenic fraction of sediments is formed within the water column, and includes biological remains. Whereas the distribution of the allogenic fraction is determined by physical factors in the drainage system, the endogenic fraction is chemically and biologically controlled. Despite this fundamental difference in origins, there are some strong relationships between the allogenic and

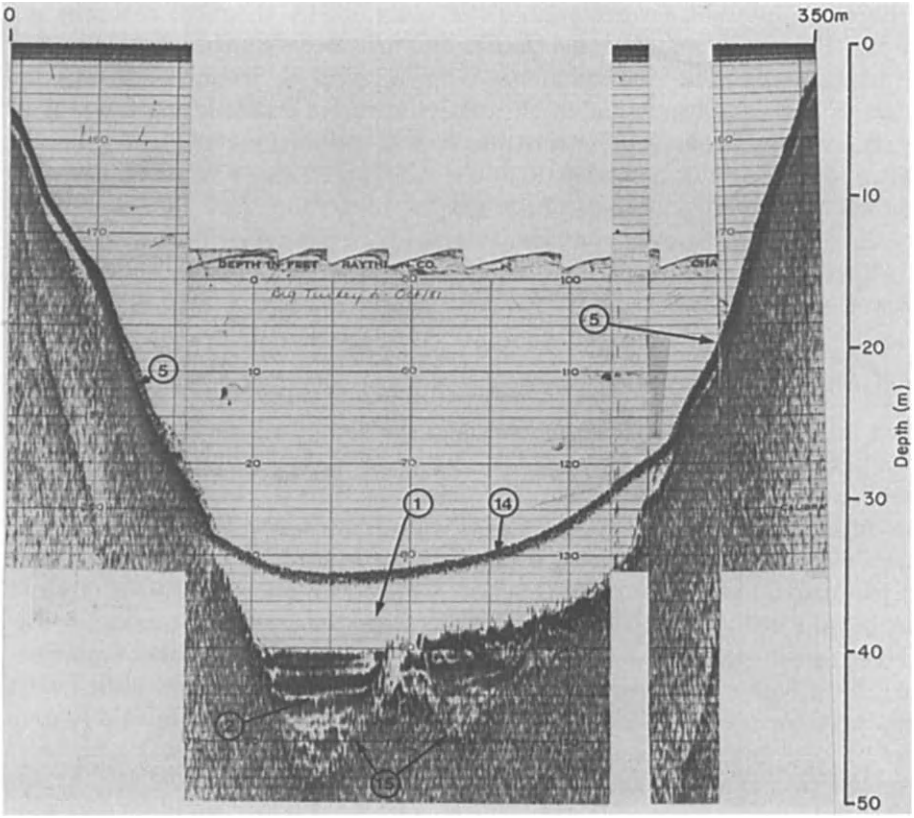


Fig. 7-5. Acoustic profile across Turkey Lake, Ontario (from Klassen and Shilts, 1982, Geological Survey of Canada, Department of Energy, Mines and Resources). Key to numbers: (*1*) Lake gel or gyttja; wattery, organic modern (postglacial) lake sediment; (*5*) Bedrock; (*14*) 200 kHz trace of "soft bottom", displaced 1.5 m above true position of bottom as defined by 3.5 kHz reflections (reproduced with the permission of the Minister of Supply and Services Canada, 1993).

endogenic fractions. For example, the correlation noted above between organic matter and clay content is determined by similar settling rates. The Fe and Mn oxides that are precipitated in the water column commonly coat fine-grained allogenic silicates. These oxide coatings, and organic coatings, provide important sites for the adsorption and co-precipitation of trace elements in solution (Jenne, 1977). The complex nature of the relationship between the endogenic fraction and fine-grained allogenic material make it hazardous to postulate, for example, that an element is organically-bound simply because its distribution correlates with that of the organic fraction. Notwithstanding the above remarks on chemical weathering of silicates, there is some dissolution of silicate minerals in lakes. This produces hydrated metal oxides, while free silica is commonly precipitated as diatom frustules.

Authigenic minerals, formed within the sediment by chemical reaction between the inorganic and organic solids and the pore fluids, are the third important component of lake sediments. The chemical environment within the sediment is different from that of the lake water; for example, pore water is usually more reducing and its concentration of solutes is greater. Thus minerals stable in the water column may be unstable in sediment and vice versa. Because of chemical gradients established between the pore fluids and the lake water there is a dynamic system of chemical interaction between sediments and lake water (Mortimer, 1971), which is strongly influenced by seasonal changes in lake water composition.

Organic content of deep lake sediment

Coker and Nichol (1975) and others have shown that there is a strong correlation between Loss on Ignition (LOI) and organic carbon in lake sediments, the relationship being LOI% = 2.4 × C% (Fig. 7-6). LOI not only reflects loss of carbon during combustion, but also loss of water bound with the clay minerals, the content of which is correlated with the organic fraction, and water bound with hydrous oxides. LOI has been used as a easily-measured proxy for organic carbon in lake sediment surveys. For 40,861 deep lake sediment samples collected during the early part of the NGR program, mainly from the Canadian Shield, the median LOI is 29.8% (Table 7-I), representing lakes both north and south of the treeline. Sediments from south of the treeline have a higher organic content because of greater organic input and because eutrophication reduces the rate at which this material is oxidized. In the Melville Peninsula, NWT, north of the treeline, only 13% of centre-lake sediment samples contained more than 20% LOI, compared to 88% for a large area in northwestern Ontario, which is well south of the treeline (Cameron, 1980).

North of the treeline, the lower organic productivity in lakes and drainage basins often allows the entire water column to remain oxygenated, even in stratified lakes. This, in turn, permits oxygenation of sediments. Thus Klassen (1975) found Fe and Mn oxides abundant in deep sediments from lakes in permafrost terrain. However, even in these lakes there is sufficient organic material that sediments become reduced at depth. There may also be a surface layer of oxidized material in southern lakes that are unstratified or where there is sufficient seasonal oxygenation of the bottom waters (Tenhola and Lummaa, 1979). It is the upward migration of Fe^{2+} and Mn^{2+} from reduced sediments that causes the precipitation of the oxides of these metals in the oxidized surface sediments. Moreover, there may be migration of other metals from deeper sediments, which are then precipitated on these oxidized surface crusts and nodules, together with metals from the water column. This may produce an upper zone of sediment, a few centimetres deep, with irregular metal contents (Coker and Nichol, 1975; Tenhola and Lummaa, 1979). The sampling equipment used for routine geochemical exploration surveys is designed to penetrate through and discard this surficial layer, which

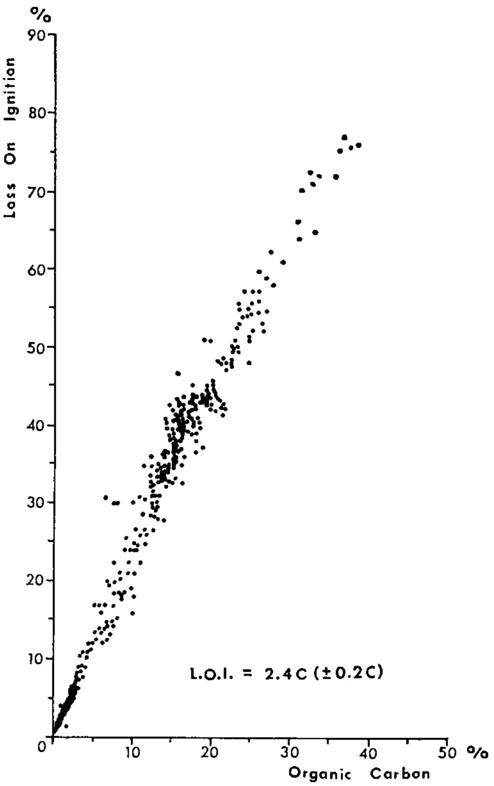


Fig. 7-6. Plot of LOI to organic carbon content for centre-lake sediments (reproduced with permission from Coker and Nichol, 1975, Economic Geology, 1975, Vol. 70, p. 207).

also, in places, may have been affected by pollution (Allan, 1974; Salminen, 1976).

DISPERSION OF ELEMENTS INTO LAKES

In shield terrain of low relief, clastic dispersion of metals from mineralization is less widespread than hydromorphic dispersion. This was demonstrated by Dyck (1974) and Levinson et al. (1978), who found that U in lake sediments from a uraniferous district of Saskatchewan is considerably out of equilibrium with its daughter products. Uranium was dispersed in solution along the drainage system, while Th, Ra and Pb produced by the decay of ^{238}U and ^{234}U, being relatively immobile, were retained in the rocks and soils near the mineralization. In this section the factors which most influence dissolution of metals, their stabilization in solution, and eventual precipitation are discussed, followed by a consideration of the factors influencing clastic dispersion.

Element mobility

The primary control on hydromorphic dispersion is the chemical properties of the elements. Of particular importance is the behaviour of elements during oxidation of mineral deposits containing sulphides; their solubility in waters of varying pH; and their reactions with organic materials, metal oxides and other materials. A secondary control on dispersion is the nature of the environment. There have been relatively few comparative case histories of element mobilities in lake drainage systems. Cameron (1977b) found that during oxidative weathering of a massive sulphide deposit in an acidic, permafrost environment, Au, Hg, Pb and Ag are immobile and were retained in soils near the mineralization; Fe, Cu, and As are of intermediate mobility, deposited in the proximal parts of the drainage system; while Zn was widely dispersed in the lake system. On the basis of a number of case histories from the Canadian Cordillera (Bradshaw et al., 1975) and Canadian Shield (Boyle et al., 1975), an empirical order of mobility can be derived: Zn > Cu > Ni > Mo > Ag > Pb > Au. Many surveys have shown U to have a high mobility, comparable to or greater than that of Zn (Cameron, 1980). It is emphasized that environmental variation will modify any generalized order of mobility.

pH

The pH has a major influence on the extent of hydromorphic dispersion. In the absence of carbonate near sulphide mineralization, acidic waters produced by oxidation of sulphide minerals are not neutralized. This allows the waters to attack other primary minerals, hastening their decomposition. Many metals are highly soluble in acidic waters and are readily dispersed down-drainage in solution. Carbonate need not be present in the rocks to inhibit metal dispersion. For example, over large areas of the southern Canadian Shield, exotic, carbonate-rich till derived from Phanerozoic rocks along the margin of Hudsons Bay mantles carbonate-poor granitic and supracrustal rocks of Archean age. This has a marked effect on the dispersion of metals in these areas (Coker and Shilts, 1979; Shilts, 1981; Friske, 1985).

Although most metals of interest to the exploration geochemist tend to become less soluble with increasing pH, two important exceptions are U and Mo. The solubility of U in alkaline waters is due to the formation of uranyl carbonate and hydroxy complexes. In lake waters the amount of dissolved U is probably limited by adsorption on various organic and inorganic compounds, rather than by the solubility of any particular U-bearing mineral. The pH range of minimum solubility for U, weakly acidic to neutral water, is also the range for maximum sorption of uranyl ion on inorganic adsorbents, such as ferric oxyhydroxide (Langmuir, 1978), or on organic materials, such as humic materials (Fig. 7-7). In acidic water Mo is insoluble as $HMoO_4^-$, but at pH 6 or greater it becomes soluble as MoO_4^{2-}.

The effect of pH on the solubility of U has considerable practical signifi-

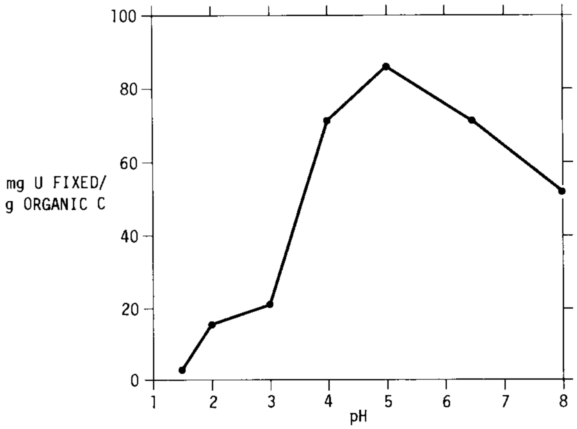


Fig. 7-7. Effect of pH on the adsorption of uranium by organic material (reproduced from Bloomfield and Kelso, 1973, J. Soil Science, 1973, Vol. 24, p. 375, by permission of Oxford University Press).

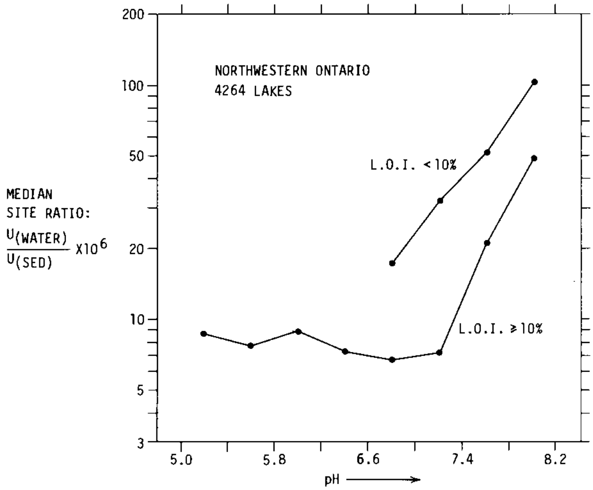


Fig. 7-8. Median site ratio, uranium in water to uranium in centre-lake sediment for different classes of pH. Lake sites in northwestern Ontario (from Cameron, 1980).

cance in lake sediment geochemical surveys (Maurice, 1977; Coker and Closs, 1979). For a large area of northwestern Ontario, median values of site ratios $U_{water}/U_{sediment}$ are plotted for different classes of pH (Fig. 7-8). This shows that partitioning of U between sediments and overlying water is generally constant when the pH of the water is near neutral or less. In alkaline waters there is a marked shift in the partitioning ratio in favour of waters. Figure 7-9 demonstrates that the shift is a function of increased content of U in water, rather than decreasing ability of the centre-lake sediments to fix U.

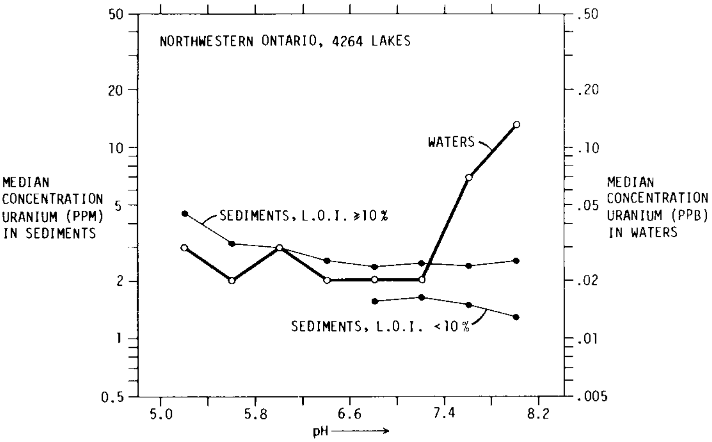


Fig. 7-9. Median concentrations of uranium in water and uranium in sediment for different classes of pH. Lake sites in northwestern Ontario (from Cameron, 1980).

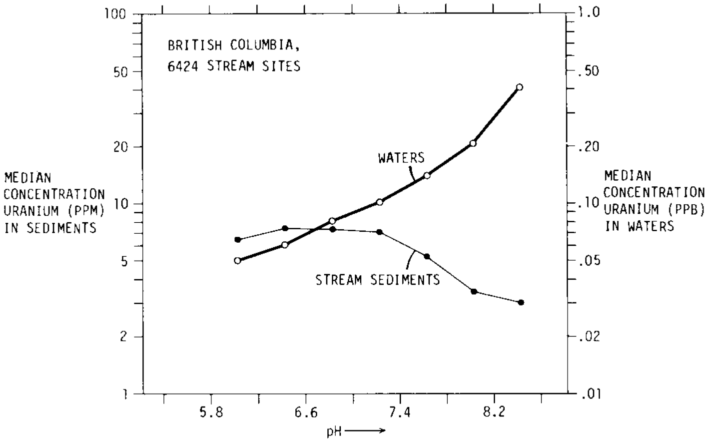


Fig. 7-10. Median concentrations of uranium in water and uranium in sediment for classes of pH. Stream sites in southeastern British Columbia (from Cameron, 1980).

For these relatively organic-rich sediments, there is little change in U content with changing pH. The partitioning ratio $U_{water}/U_{sediment}$ is greater for organic-poor sediments (Fig. 7-8), reflecting lower content of U in sediments (Fig. 7-9). Further, stream sediments, which contain much less organic material, show a marked decline in U content as the pH of the water increases (Fig. 7-10). These data demonstrate the strong affinity of U for organic material.

Iron and manganese oxides

Hydrous oxides of Al, Fe and Mn are important sinks for heavy metal ions and organic compounds in lake systems. Conversely, when Fe and Mn oxides are dissolved in reduced, eutrophic waters, they are a source of metal ions and dissolved organics. Precipitation of Fe and Mn oxides takes place at four main chemical interfaces: where reduced groundwater mixes with more oxidizing stream or lake water; where acidic waters are neutralized; at the interface between reduced hypolimnion waters and the epilimnion; and at oxidized surfaces above reduced sediments. The cycling of Fe and Mn between solid and soluble phases near the epilimnion/hypolimnion boundary can cause lateral movement of these metals (Tessenow, 1974) and also, possibly, of the trace metals that they fix (Stumm and Baccini, 1978). In general, Mn^{2+} is less readily oxidized than Fe^{2+}, so that precipitates of these metals tend to become separated in drainage systems.

The adsorption of metal cations on hydrous oxides is dependent on a number of factors, one of the most significant being pH (Fig. 7-11). The adsorption sequence for metals, in order of increasing pH, is correlated with the decreasing tendency for the cations to hydrolyse in solution. Adsorption is essentially complete at pH values less than the first hydrolysis constant of the metal (Forbes et al., 1976). As is shown in Fig. 7-11, Cu and Pb in solution are adsorbed at lower pH on Fe oxides than Zn and Co, thus enhancing the mobility of the latter. Adsorption of metals occurs at lower pH on Mn oxides (Rao Gadde and Laitinen, 1974).

An example of the effect of pH and oxide precipitation on element mobility is given by Cameron (1977a, b) for the Agricola Lake area, NWT. Here ele-

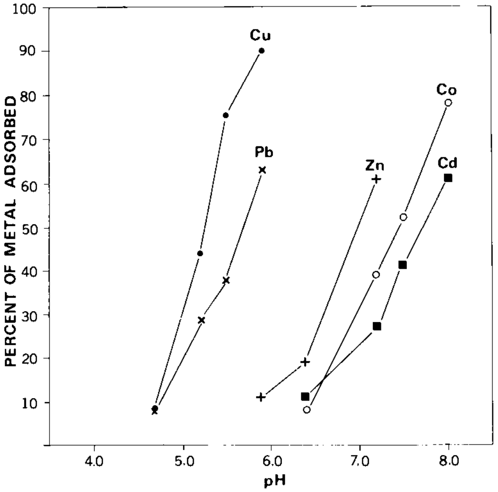


Fig. 7-11. Adsorption of certain metal cations on goethite (compiled from Forbes et al., 1976).

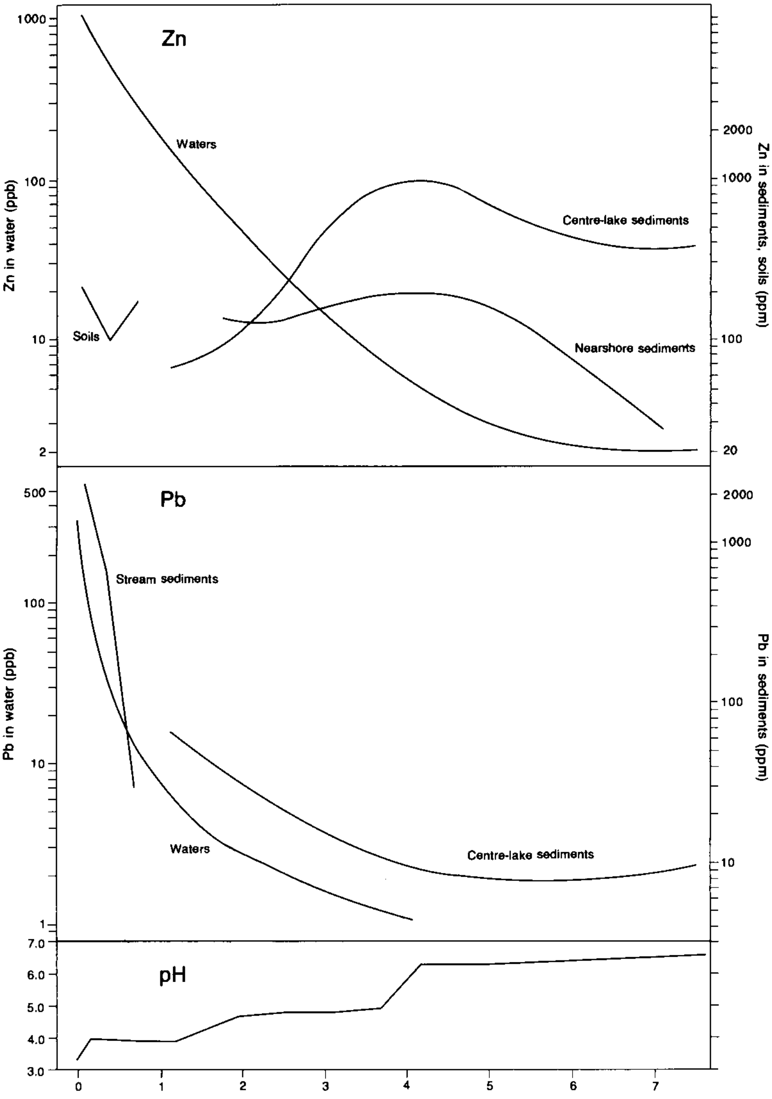
ments are being dispersed down-drainage from massive sulphide mineralization through a chain of lakes with interconnecting streams. This is permafrost terrain, with a minimum of organic material in the drainage system. There is a near absence of carbonate in bedrock or glacial till, so that oxidation of sulphides has produced strongly acidic waters, as low as pH 2.4 in soils overlying the mineralization, and pH 3.4 in a spring issuing from the deposit. These pH values increase down drainage by dilution with less mineralized waters and neutralization by rare carbonates.

There are three major locations in this drainage system exhibiting precipitation of Fe oxides. The first is an intermittent stream channel proximal to the mineralization. This contains coarse, rounded fragments of goethite grown by accretion in the metal-rich stream waters. The pH is $\sim$ 4, which is low, but sufficient for oxide precipitation in the highly oxygenated stream environment. At this site there is a close correlation between Fe content and that of Cu and As, indicating that the latter were adsorbed onto the fresh oxide precipitate. There is little Zn adsorption at this pH; the bulk of this element continues further down the drainage in solution. Correlations between Fe and Pb, Ag and Hg are poor, since these elements, along with Au, are the least mobile and are largely retained in the soils overlying the deposit.

The second locus for precipitation of Fe oxides is a shallow pond 2 km down drainage. Here the pH is $\sim$ 4.7, still insufficient for major precipitation of Zn, which remains below 200 ppm in the lake sediment (Fig. 7-12), while Cu is strongly anomalous at 340 ppm.

The third locus is in centre-lake sediments of Agricola Lake, 4.5 km down drainage. These Fe oxides may, in part, have been precipitated further upstream near the shallow pond and been carried downstream in suspension. In this lake the pH is $\sim$ 6.3 and there has been strong fixing of Zn, with values for the centre-lake sediments of more than 1000 ppm. Maximum values for Zn in nearshore sediments are also found in this lake. Since the particulate material forming the nearshore sediments has a local origin in the tills and was not carried down-drainage in suspension, this suggests that precipitation of Zn has occurred in this lake. Centre-lake sediments remain anomalous in Zn for several kilometres down drainage from Agricola Lake, as a result of particulate transport, while nearshore sediments fall off sharply in Zn content, in parallel with the Zn content of the waters.

At Hackett River, north of Agricola Lake, there is a similar occurrence of mineralization. Here, however, the bedrock contains abundant limy beds, which maintain the pH of the waters near neutrality. Zinc retains a reasonable mobility in these waters (Allan et al., 1973a; Cameron and Ballantyne, 1975), because the neutral pH has not permitted solution of Fe which, on precipitating, would fix Zn. In the Sturgeon Lake area, northwest Ontario, Coker and Nichol (1975) found that the dispersion of Zn was restricted where stream waters of pH $\sim$ 7 mixed with alkaline (pH $\sim$ 8) lake waters.



GSC

Fig. 7-12. Dispersion of zinc, lead and pH down a chain of lakes from Agricola Lake massive sulphide deposit, NWT (from Cameron, 1977a).

Organic matter

Organic material has a major influence on the dispersion of metal ions. In freshwater environments this may be classified into three types: humic acid, which is soluble in basic solutions; fulvic acid, which is soluble in acid and basic solutions; and humids, which are insoluble. Humic and fulvic acids behave as negatively charged species. Neutralization of this charge, by metal cations, by metal oxide colloids, or by clays, can cause their flocculation and precipitation. This is a major factor in reducing the concentration of dissolved organic compounds in water and causing precipitation of trace metals. Conversely, colloidal metal oxides may be stabilized in solution by sorption of dissolved organics (Stumm and Bilinski, 1972). It is this phenomenon that permits high concentrations of Fe to exist in the strongly coloured, organic-rich waters. Organisms may also concentrate trace metals in their living parts. Where the organisms are abundant in lake waters, as in the case of algal blooms, this may have a significant effect on the behaviour of the metals (Trollope and Evans, 1976).

In low, forested terrain, there is an abundance of organic matter along the drainage system, most notably in swamps. This may have a positive effect on dispersion by forming soluble metal-organic complexes (Jackson and Skippen, 1978) and organic acids have a strong solubilizing effect on various minerals, invluding sulphides, oxides and silicates (Bondarenko, 1968; Baker, 1973; Singer and Navrot, 1976). A negative effect is the formation of insoluble metal-organic complexes. Further negative effects of swamps on the dispersion of metals are the precipitation of sulphides, the presence of metal-fixing oxide crusts and films, and quiet water which permits trace metal-bearing fine particulates to settle. Overall, organic-rich environments appears to inhibit the dispersion of base metals, since the movement of the more mobile of these, such as Zn, seems greater north of the treeline than in the south. An interesting case history of the restrictive effect of swamps on base metal dispersion is given by Bogle and Nichol (1981).

The complex nature of interactions between various organic species and major and trace inorganic ions in waters (e.g., Jackson and Skippen, 1978) make it difficult to generalize about the relationship of special metal ions to organic material. One of the few studies to attempt this for the shield lacustrine environment is by Jonasson (1976a). He found that the order of bonding strength for certain metal ions onto humic and fulvic acids was: $UO_2^{2+} > Hg^{2+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Ni^{2+} > Co^{2+}$. The strong bonding of U with these organic acids may serve to both mobilize and precipitate this element. Thus U which migrates in this form will be fixed when the humic colloid is flocculated by increase in Ca^{2+} (Jackson et al., 1978). However, in Ca-rich alkaline environments, the decrease in the solubility of U as organic complexes may be compensated by its increased solubility as bicarbonate complexes. Lee and Jonasson (1983) found that the affinity for organic complexing in natural waters was Cu > Ni > Co. Complexes of the latter two metals are relatively stable in solution and permit their ready migration. By contrast, the Cu complexes are more easily coagulated, restricting its dispersion.

Timperley and Allan (1974) showed that the fixing of dissolved metals in reducing sediments was mainly by organic complexing and sulphide precipitation. The importance of sulphide precipitation for divalent metal cations is in the order: Cu > Pb > Co = Ni > Zn > Fe > Mn. For organic fixing it is: Cu > Ni >

$Pb > Co > Fe > Zn > Mn$. The balance between the two models is determined by the sulphide ion content of the organic sediments. Iron and Mn oxide crusts and nodules are enriched in the metals that are least strongly fixed by sulphide and organics: Fe, Mn, Co, Ni, Zn.

In centre-lake sediments a good correlation has been noted between organic carbon (represented by LOI) and several elements that are principally dispersed by hydromorphic processes. Garrett and Hornbrook (1976) drew attention to the relationship between LOI and Zn for a large group of centre-lake sediments from Saskatchewan (Fig. 7-13). For samples in the range 12% to 50% LOI, there was an adequate adsorption capacity in the sediment, and their Zn contents adequately reflected the Zn chemistry of the drainage basin. Below 12% LOI there was insufficient adsorption capacity in the sediment, so that in this range the content of Zn partially depended on the organic carbon content. Above 50% LOI they suggested that the increased organic load diluted a fixed flux of Zn. A useful function of their plot is to show that over the most frequent range of LOI, the Zn content is not dependent on LOI, i.e., organic content. Figure 7-13 shows that U bears a similar relationship to LOI.

A different form of presentation is used to compare the dependence of Fe, Mn and U on LOI for a large group of sediments from northwestern Ontario (Fig. 7-14). The variation of U is essentially similar to that of Zn and U in the preceding figure. However, Fe and Mn are quite different with maxima in the 10–20% LOI class, above which the contents of these elements fall off rapidly with increasing organic matter. The rate of decrease is consistent with dilution of Fe- and Mn-bearing minerals by organics. However, it is also possible that some of these metals were reduced to soluble Fe^{2+} and Mn^{2+} when buried in organic-rich sediment. Once in solution, these metals would tend to be precipitated near the boundary between aerobic and anaerobic conditions on the lake bottom. Sediments with LOI contents in the range 10–20%, which show maxima for Fe and Mn, may well represent these boundary conditions. The curves shown in Fig. 7-14 suggest that neither Fe or Mn have significant influence on the distribution of U in lake sediments.

A note of caution should be given regarding interpretation of element variables that correlate with LOI. The LOI term does not simply reflect variation in organic content, but also in a number of correlated variables. These variables, although not measured, may have influenced the metal content of the sediments. In addition to clays and other hydrated minerals that directly contribute to LOI, there is a relationship between LOI and the depositional environment. Samples low in LOI occur more frequently in aerobic environments, while samples with >50% LOI are more common in low, swampy terrain where metals are less easily mobilized from bedrock.

Clay minerals

Clay minerals have long been considered a prime material for the adsorption of trace metals. However, Jenne (1977) advanced the proposition that the clays

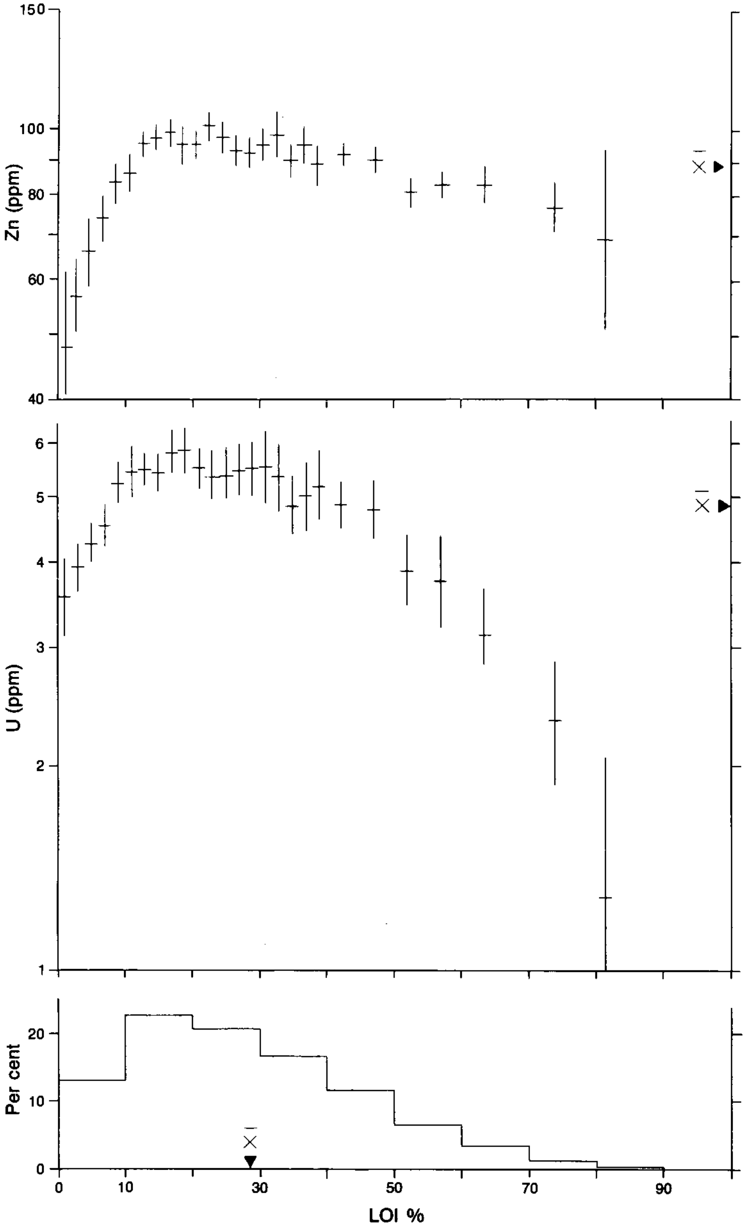


Fig. 7-13. Relationship between LOI and zinc and uranium; histogram of LOI. For 3815 centre-lake sediment samples from Saskatchewan (modified after Cameron and Hornbrook, 1979; Garrett and Hornbrook, 1976).

themselves are relatively unimportant trace element sinks. Instead, they act as mechanical substrates onto which organic materials, Fe and Mn oxides, sulphides and carbonates precipitate, and it is these which act as the sinks.

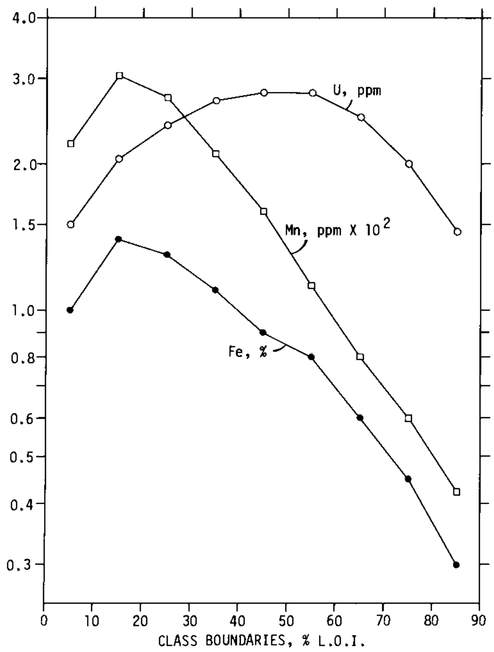


Fig. 7-14. Median contents of uranium, manganese and iron for classes of LOI, centre-lake sediments, northwestern Ontario, 4268 samples (from Cameron, 1980).

Whether or not this is the case, it is clear that an important component of trace metal dispersion within the lake system may take place on fine suspended soils formed by precipitation. Fixing of trace metals onto these fine particulates may take place either in the lakes or in the surface waters that feed the lakes.

Effect of permafrost

A significant portion of the terrain that is likely to be explored using lake sediment geochemistry is underlain by partial or continuous permafrost. At one time this was viewed as a major impediment to the chemical weathering of sulphide mineralization and the dispersion of indicator metals. However, even in winter and within frozen ground, the presence of thin water films along grain boundaries allows ionic movement (Anderson and Morgenstern, 1973). The solubility of oxygen in water increases as temperature falls. In permafrost terrain, dissolved oxygen is less likely to be depleted by organic activity. Many of the oxidation reactions of sulphides are exothermic. Liberation of heat from these reactions causes thawed channels to develop in permafrost around oxidizing sulphide bodies. It is the writer's observation that oxidation of sulphide mineralization in the Canadian Shield is more rapid north of the permafrost boundary than in the south.

Clastic dispersion in lakes

The preceding discussion has emphasized the importance of the dissolution of elements in facilitating their widespread dispersion in the lake system. However, centre-lake sediments contain a variable, often substantial, allogenic component derived from nearby bedrock or surficial materials. In mineralized areas, this may include particles of primary ore minerals or secondary, insoluble minerals derived from the ore. For example, there may be clastic dispersion from outcrops of gossan that contain high contents of immobile elements, such as Pb and Au.

Following storms, it is common for lake waters to be turbid from contained fine-grained suspended material. This comes from streams that carry a greater suspended load after heavy rainfall and from the action of waves on the nearshore sediments and banks of the lakes. In permafrost, frost boils in the nearshore sediments bring to the surface till that has not been winnowed by waves or currents. The suspended, allogenic material that settles in the centre of the lake is more representative of the drainage basin of the lake than individual samples of nearshore sediment, till, or rock. Centre-lake sediments from a mineralized area may contain anomalous amounts of elements that are the product of both hydromorphic and clastic dispersion.

In routine surveys it will usually not be possible to determine whether anomalous metal contents were contributed by clastic or hydromorphic processes. Detailed studies have, however, identified instances where primary minerals are a principal source of an anomaly in centre-lake sediments. Rogers and Garrett (1987) made separates of heavy minerals from centre-lake sediments that earlier had been identified as strongly anomalous for Sn. Examination of these separates by scanning electron microscopy showed fine, angular grains of cassiterite. Cassiterite is the principal ore mineral of the East Kemptville tin deposit, ~ 10 km distant; it has been widely dispersed in tills throughout the region before being carried into the lakes. Also in Nova Scotia, Rogers (1988) identified fine particles of native gold in centre-lake sediments that contain anomalous concentrations of this element.

Glacial dispersion

The East Kemptville area is but one example of the widespread dispersion of minerals by glacial action. These minerals may then be transported into lakes either in clastic form or in solution. Glacial dispersion is capable of transforming a small primary target in bedrock into a much larger and more easily discovered target in till.

This mechanism is responsible for one of the most spectacular anomalies yet found in lake sediments, down-ice from the Key Late uranium–nickel deposit in northern Saskatchewan (Figs. 7-15, 7-16). Glacial erosion of the deposit formed an extensive blanket of mineralized till, which in places contains minable quantities of U. The till was then cut by an esker that transported

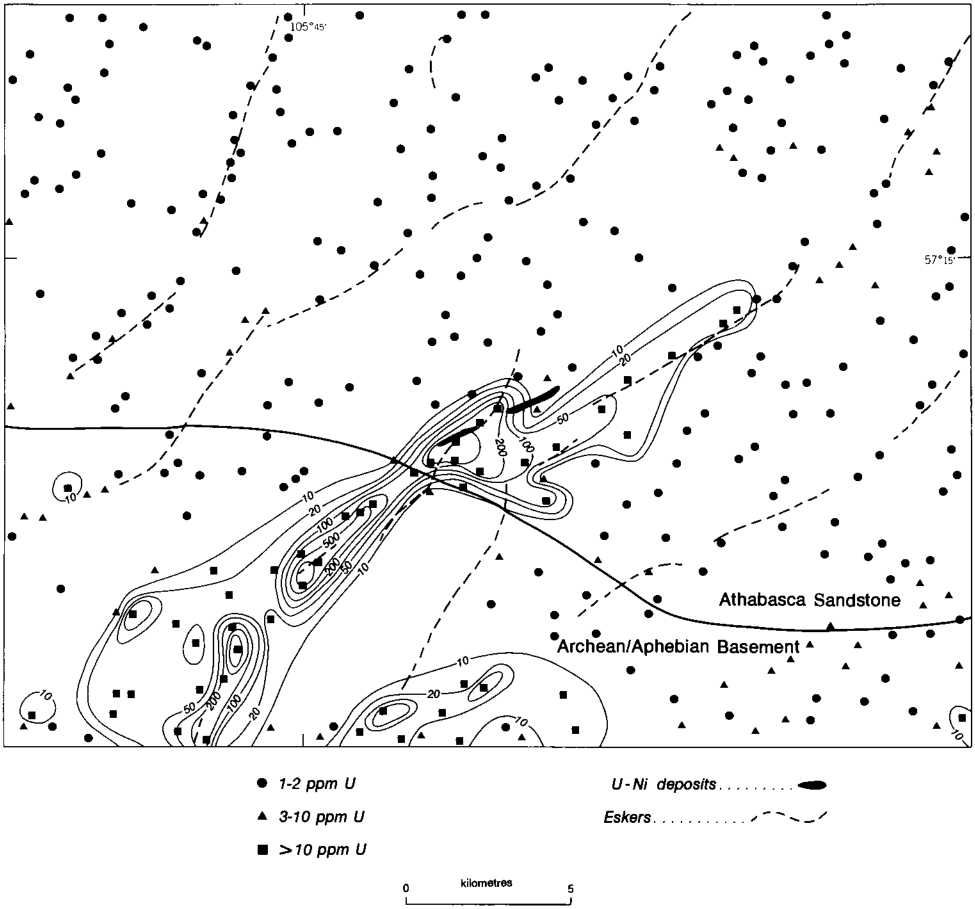


Fig. 7-15. Uranium in centre-lake sediments near the Key Lake uranium–nickel deposit, Saskatchewan (modified after Maurice et al., 1985).

mineralized clasts up to 10 km to the southwest. The U and Ni are now being dispersed to the lakes, where they are fixed in the sediments (Maurice et al., 1985). Anomalous contents of U in waters down-ice from the mineralization were discovered in 1969 (McPherson, 1969). Subsequent detailed geochemistry, including lake sediment sampling (Tan, 1977) and boulder tracing, led to the discovery of the deposit in 1975. The strongly anomalous contents of U in the lake waters indicates the hydromorphic nature of the dispersion of this element from till to lake. A rather less spectacular, but still widespread, lake sediment anomaly of similar origin is found down-ice from the Rabbit Lake U deposit, Saskatchewan (Cameron and Ballantyne, 1977).

In Labrador, follow-up investigations of NGR lake sediment and water data (Geological Survey of Canada, 1979) led to the discovery of the Strange Lake Zr–Y–Nb–Be–REE deposit (McConnell and Batterson, 1987). A number of

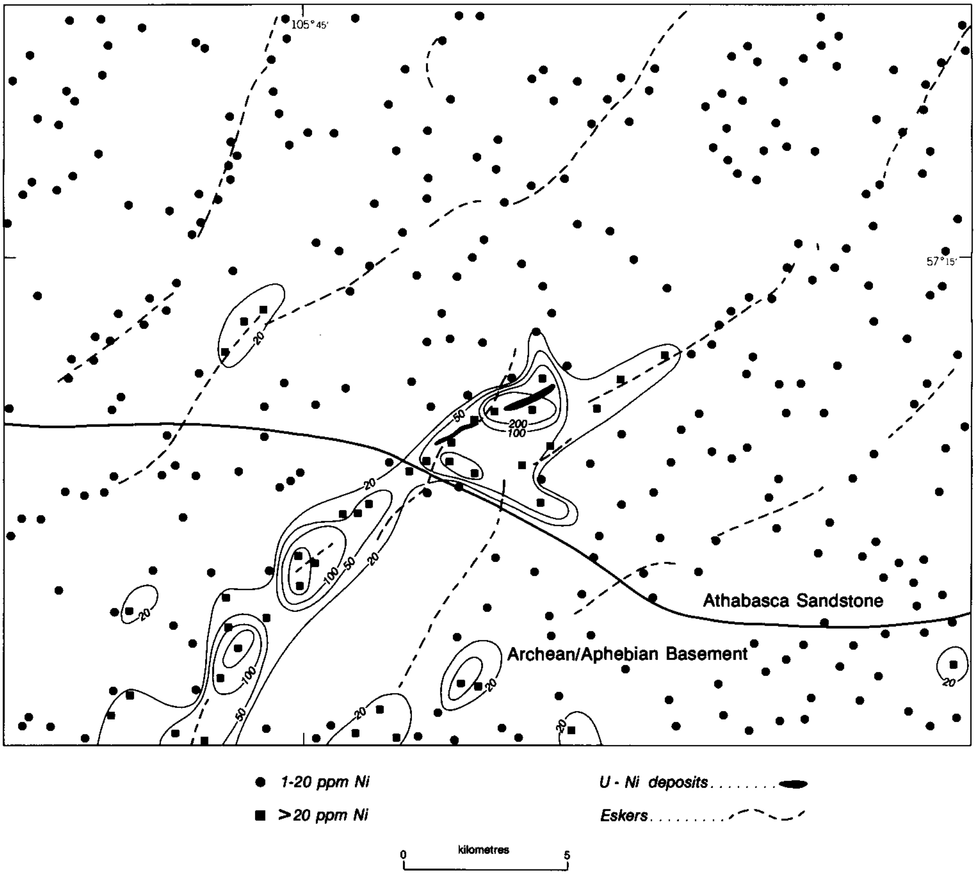


Fig. 7-16. Nickel in centre-lake sediments near the Key Lake uranium–nickel deposit, Saskatchewan (modified after Maurice et al., 1985).

other elements are associated with the mineralization and with the peralkaline granite that is its host. Till containing fragments of the mineralization has been dispersed up to 40 km down-ice, from which indicator elements have migrated into the local drainage systems. This has produced extensive anomalies for several elements, including Pb in lake sediment (Fig. 7-17) and F in waters. The F represents hydromorphic dispersion from the till, whereas it is likely that the Pb migrated from the till to the lakes in clastic form.

It is pertinent to add that, while glacial action may significantly enhance geochemical exploration using lake sediments, it may also have a negative effect. Impermeable glacial lake clays that mantle bedrock act as a barrier to the weathering of mineralization and subsequent hydromorphic dispersion of indicator elements (Gleeson and Hornbrook, 1975).

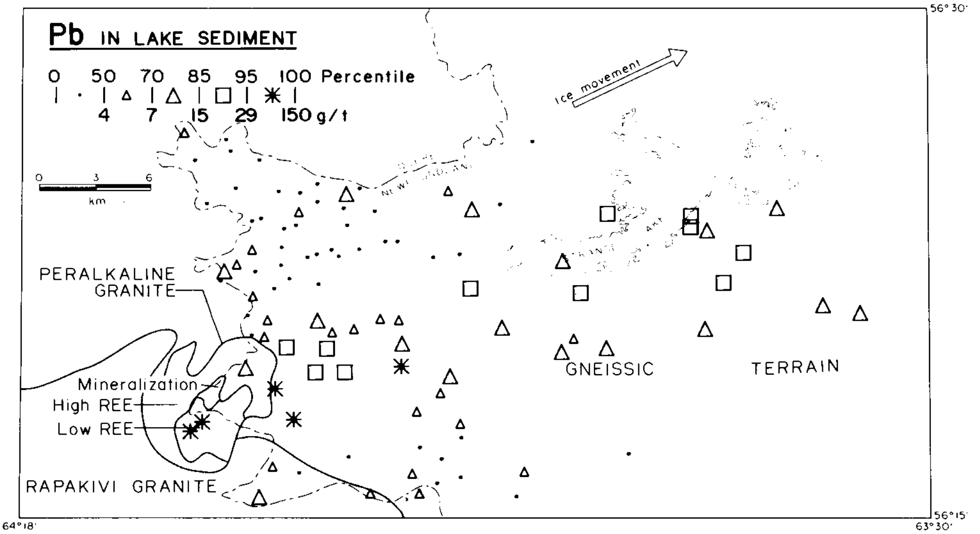


Fig. 7-17. Lead in centre-lake sediments down-ice from the Strange Lake deposit, Labrador (from McConnell and Batterson, 1987).

Dispersion from gold mineralization

The question of hydromorphic versus clastic dispersion is of particular importance in considering the use of Au as an indicator for gold deposits. The early years of lake sediment geochemical surveys — the 1960's and 1970's — coincided with a strong interest in exploration for uranium and base metal deposits. The lake sediment method, using mobile elements such as U and Zn, is well adapted to the search for these commodities. In the 1980's there was a marked shift to exploration for gold.

The two approaches to the use of centre-lake sediments in exploration for gold deposits are to determine Au directly or to determine a pathfinder element other than Au. The most frequently used pathfinder element is As, since it is enriched in many deposits and is moderately mobile. Unfortunately, As is also enriched in other geological environments unrelated to gold, such as black shales. Epithermal gold deposits often contain a wide range of other elements, including the "volatile" elements Sb, Hg and Tl, which can be used as pathfinders. However, glaciated shield terrain is predominantly associated with mesothermal gold deposits, which have a more restricted element assemblage (the Hemlo deposit, near Marathon, Ontario, is an exception with high levels of Mo, Sb, Hg, Tl and V; Cameron and Hattori, 1985). For these reasons there has been a continuing effort to determine Au directly in lake sediment surveys.

One difficulty in using Au as a tracer for gold deposits is that the detection limit of ~ 2 ppb using most commercially available analytical methods is close to its crustal abundance of ~ 3 ppb. Most samples report values that are either below or slightly above the detection limit. Analysis near the detection limit entails a high level of analytical variance, which is compounded by the high sampling variance that frequently characterizes this element. An analytical method that provides high sensitivity for Au at reasonable cost utilizes a graphite furnace-atomic adsorption spectrophotometer (GF-AAS). Gold is first extracted by HF-aqua regia attack, then separated into a small volume of MIBK and analyzed by GF-AAS. This has been used extensively by the Geological Survey of Finland (Kontas et al., 1986) and is capable of a detection limit of 0.1 ppb Au on 1 g samples (E. Kontas, pers. commun., 1988). Using a similar method on 15 g samples, G.E.M. Hall and J. Vaive (in Cameron, 1989) report values as low as 0.04 ppb.

Given an analytical method of reasonable sensitivity, a remaining difficulty in using Au as a tracer in lake sediment surveys is its limited mobility, which is shown by its frequent retention in gossans. However, there is evidence that Au may be dispersed into lakes both in particulate form and in solution. Rogers' (1988) discovery of particulate Au in centre-lake sediments was noted above. Also H.R. Schmitt (pers. commun., 1989) found a pyrite grain containing native gold in a sediment sample from Waddy Lake, Saskatchewan, that was previously found to contain 65 ppb Au.

One indication that Au also travels in dissolved form is the success of humus surveys for Au (Curtin et al., 1968). This requires that the Au be concentrated in the humus after its migration in solution. Baker (1978) found that Au can be transported as a complex with humic acid. Taisaev and Plyusnin (1984) investigated the dispersion of Au in surface waters from Au mineralization in a mountainous area of Siberia. At one locality they found that the metal existed in true solution close to the ore body, but it did not migrate further than 300 m in this form. From this distance up to 1 km, Au moved principally as a colloid. From 1 to 2 km, it moved mainly as a microsuspension.

Evidence for the dispersion of Au into lakes in a mobile form has also been reported by Gregoire (1985), who found the highly anomalous value of 280 ppb Au in a composite organic lake sediment sample from Red Lake, Ontario. Moreover, 91% of this Au could be chemically extracted with the organic fraction. In Moose Lake, near the Hemlo deposit, he reported only 6 ppb Au in organic sediment, although sediment from a stream draining into the lake contained 53 ppb Au, more than half of which is present in the organic fraction. The lake sediment value of 6 ppb Au is anomalous when compared to the regional geometric mean content of <1 ppb Au in centre-lake sediments (P.W.B. Friske, pers. commun., 1985).

The first comprehensive attempt to measure the Au content of centre-lake sediments was by Coker et al. (1982). They found anomalous values up to 34 ppb Au, and a mean content of 6 ppb Au, for 281 samples from the Reindeer Lake area of Saskatchewan, which contains gold mineralization. The Au did not disperse into the central, deeper portions of the lake, which the authors attribute to fixing on organic-rich nearshore sediment. The limited mobility of

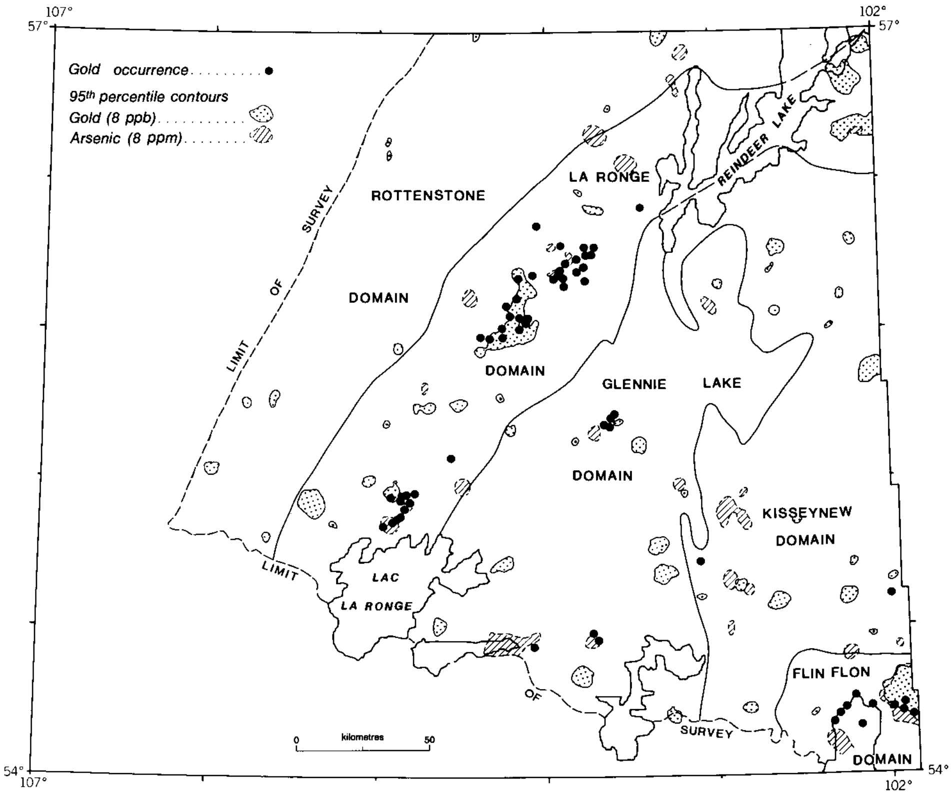


Fig. 7-18. Gold and arsenic in centre-lake sediments, east-central Saskatchewan (reproduced from Schmitt et al., 1985, Geological Survey of Canada, Department of Energy, Mines and Resources, with the permission of the Minister of Supply and Services Canada, 1993).

Au led the authors to conclude that a high sampling density, i.e., every lake, was required to detect gold mineralization.

A reconnaissance survey using the Au content of centre-lake sediments over a large area of Saskatchewan that includes the Reindeer Lake area has been reported by Schmitt et al. (1985). The sampling density was one per 13 km^2 and the geometric mean content of 3512 samples, 1 ppb Au. The results of this survey are summarized in Fig. 7-18, which indicates that there is a good spatial correlation between some of the major Au anomalies, i.e., >8 ppb, and the occurrence of known Au mineralization. The seemingly very low background concentration of Au in lake sediments from this region should be placed in the context of Shaw et al.'s (1976) average value of 1.8 ppb for rocks of the Canadian Shield.

A detailed study of dispersion of Au into lake systems was carried out by Schmitt (1989) near Foster Lake, Manibota, where gold mineralization occurs along the Johnson shear zone (Fig. 7-19). Much of the area is covered by till,

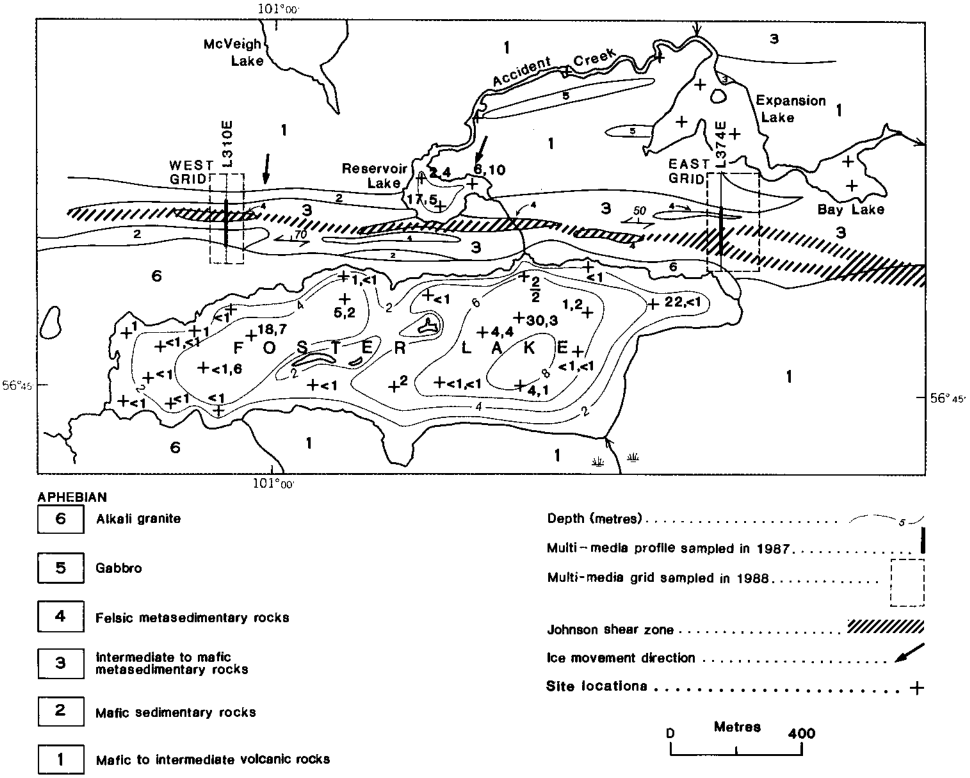


Fig. 7-19. Distribution of gold (ppb) in lake sediments, Foster Lake area, Manitoba (reproduced from Schmitt et al., 1985, Geological Survey of Canada, Department of Energy, Mines and Resources, with the permission of the Minister of Supply and Services Canada, 1993).

which may be up to 2 m thick. Reservoir Lake, closest to the mineralization, has organic-rich sediments. It is clearly anomalous in Au (Fig. 7-19), compared to regional background of 1 ppb. The larger Foster Lake is mainly floored by non-organic sediments which contain mostly background concentrations of Au. Organic sediments occur in two basins; a number of samples collected from these basins are anomalous in Au (Fig. 7-19). Schmitt also found till, peat and vegetation samples near to the mineralization to have anomalous amounts of Au, as did some samples of surface waters, suggesting dissolution of Au.

The above data suggest that both clastic and solution processes may be involved in the dispersion of Au into lakes. Even a transitory stage where it passes into solution may be important. This can permit the element to be adsorbed onto fine-grained, suspended particulates and carried to the lake centre. "Solution" is here used in its broadest sense, to include the colloidal form or as an organic complex, as well as in ionic solution. Clastic dispersion of particulate gold may lead to erratic results from replicate analyses of lake sediment samples. An interesting demonstration of this is by Hornbrook (1989).

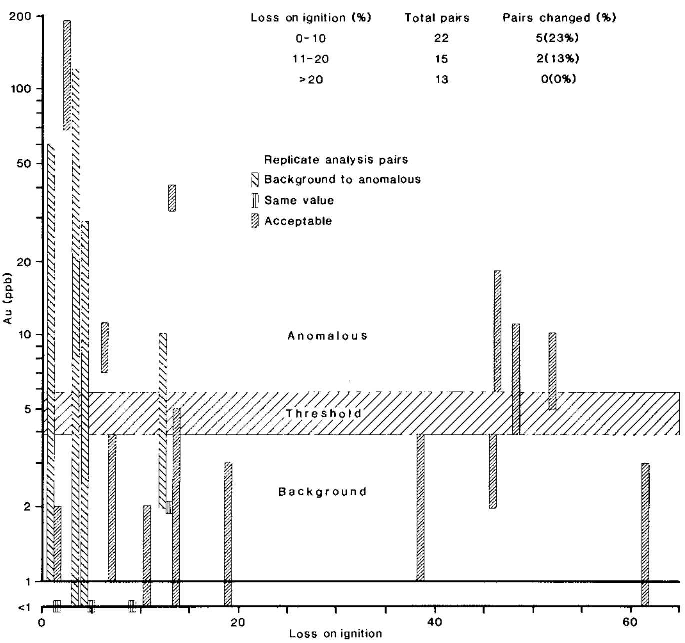


Fig. 7-20. Replicate pair Au analyses in relation to the organic content of lake sediment samples. The vertical bars represent the separation between replicate analyses of the same sample. Of 22 samples with less than 11% LOI, 5 had repeat values where Au changed from background to anomalous or vice versa. Where LOI values exceeded 20%, no change occurred after replicate analysis of 13 samples (reproduced with permission from Hornbrook, 1989).

Figure 7-20 shows that the organic-poor samples give the most erratic results, which may cause a change in the classification of a sample from anomalous to background or vice versa.

Lake waters

Lake waters are a useful medium for geochemical exploration, either independently or in conjunction with lake sediment surveys. Costs of lake water surveys are less than for lake sediments, because waters may be sampled more rapidly and preparation time is shorter. However, for many elements, higher sampling densities are required to give equivalent information to sediment surveys (Cameron, 1978). Thus, at a reconnaissance scale, the overall cost of a lake water survey may be similar to or greater than a lake sediment survey. Lake water surveys are useful for detailed exploration, particularly during follow-up of lake sediment surveys. Because of the close links between lake waters and sediments, chemical data on the water significantly assist in the interpretation of lake sediment survey results. A good example of the complementary nature of the two types of data is given by Coker and Dunn (1983).

Practical model for geochemical dispersion in lakes

The foregoing discussion has indicated the complexity of processes that determine the dispersion of elements into lakes. In planning a lake sediment survey and in interpreting the resulting data, it is impractical to consider these interacting processes in detail. This section summarizes the more important considerations.

For the more mobile, and hence more useful indicator elements, initial stages of transport are principally in solution. This may be followed by sorption onto particulates which are chemically reactive, such as organic solids, or which have reactive coatings, such as the Fe and Mn oxides and organics precipitated on surfaces of clay minerals. Elements are then carried further on particulates before settling to the lake bottom. Those elements that do not have a dissolution stage, however short, are required to travel as fine particles of primary minerals or the residual products of weathering. An example of the latter is Pb, the sulphides of which weather to insoluble sulphate minerals. A generalized model for element dispersion into lakes is given in Fig. 7-21. This suggests that lake sediments are anomalous for a greater distance down-drainage from mineralization than are lake waters, reflecting the final stage of transport on suspended solids.

During dispersal there are a number of chemical and physical obstacles that may cause a given trace element to be fixed before it enters the lake. These include:

(1) *impermeable barriers* to migration, e.g., extensive glacio-lacustrine clay cover on rocks;

(2) *low physical relief*, which causes suspended particulates to settle in ponds before reaching the lakes;

(3) *carbonate minerals* in rocks or overburden, which neutralize the acidic

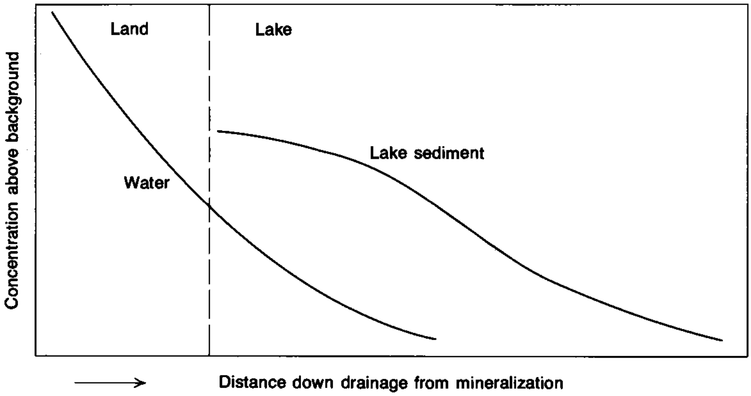


Fig. 7-21. Model for the distribution of mobile trace elements in lake drainage systems when dispersion is initially in solution, followed by adsorption onto suspended particulates, further transport in this form, then sedimentation of the fine particulates.

waters produced by oxidizing sulphides in which many metals are highly soluble (although some elements, e.g., U, Mo, are readily soluble in neutral to alkaline waters and are thus more mobile than in carbonate-rich terrain);

(4) *reactive substances*, such as organic matter and metal oxides, that are stationary in the stream channel and which fix trace elements, e.g., Mn oxide coatings on boulders;

(5) *redox changes*, such as those found in swamps, which may cause the direct precipitation of metals;

(6) *mixing* with water of different composition, causing precipitation, e.g., coagulation of soluble U-organic complexes by Ca^{2+}.

The greatest impediment to the dispersion of mobile elements into lakes are swamps, since they combine obstacles (1), (2), (4), (5), and sometimes (6).

LAKE SEDIMENT SURVEY PROCEDURES

Nearshore versus centre-lake samples

In the early years of the lake sediment surveys, nearshore sediments were widely sampled. Experience showed that homogeneous element distributions could be obtained from organic, centre-lake sediments, both across the lake (Fig. 7-22) and vertically in cores (Allan, 1974; Tenhola, 1976), whereas nearshore sediments are less uniform and generally contain smaller concentrations of indicator elements. The greater homogeneity of element distributions in centre-lake samples reflect their more uniform mineralogical composition, particularly the content of organics (Coker and Nichol, 1975). In the case of nearshore sampling, it is sometimes necessary to examine several sites before a suitable fine-grained sample can be obtained. Almost invariably it is possible to obtain a

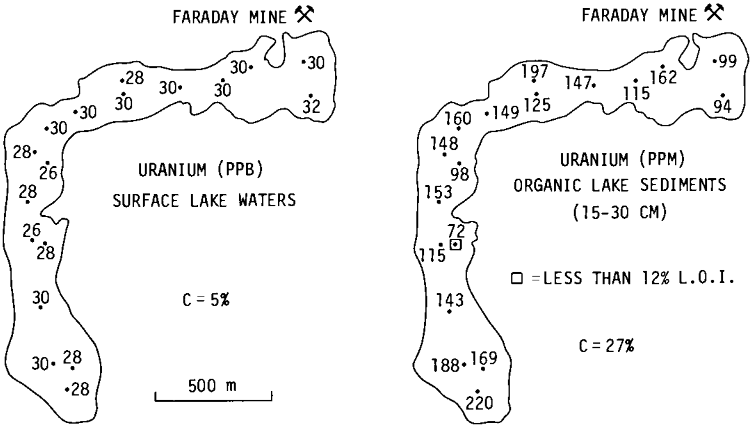


Fig. 7-22. Uranium in surface lake waters and centre-lake sediments, Bow Lake, Ontario; *C* = coefficient of variation (from Cameron, 1980; based on data by W.B. Coker).

good sample from the centre of a lake. In recent years lake sediment sampling has been almost exclusively of centre-lake material.

Centre-lake sediment sampling device

Development of a simple, efficient sampling device was essential for the success of the lake sediment method. The apparatus must be capable of rapid sampling of sediment from below the upper layers. It is desirable to avoid sampling the upper few centimetres, which may be inhomogeneous, containing, for example, oxide nodules or crusts. The sampler varies both in purpose and design from the types used by limnologists. The model currently used by GSC (Fig. 7-23) was designed by E.H.W. Hornbrook. It is a hollow pipe, 6.4 cm inside diameter, of 0.5 cm mild steel, with a butterfly valve in the lower section to retain the sediment. The nose is beveled inwards to compress the sediment, with the valve hinged 2 cm up from the nose. A lead collar on the outside, together with the two fins, ensure a nose-down attitude during free-fall and increased penetration. The upper section is 44 cm long, but from 14 cm up there is a large port in the wall to permit the upper few centimetres of sediment, which are to be discarded, to be washed out of the sampler during retrieval. The two sections of pipe are joined at a screw joint, allowing the lower section to be replaced when the beveled nose or valve is damaged. The length of the lower section may be varied to collect different quantities of sample. That shown in Fig. 7-23 is 16 cm long. A 30 cm lower section is currently used for NGR surveys, which retains 1.2 kg of lake sediment; the weight of the entire device is 7.1 kg.

Sampling method

Sampling is usually carried out from a light turbine helicopter equipped with floats. A navigator/data recorder sits beside the pilot, with the crew member responsible for sampling in the rear. Upon landing, the first task of the latter is to collect a water sample before the water can be contaminated by the sampling device. This is done while kneeling on a wooden platform attached to the top of the float assembly. Then, when the helicopter is stationary on site, the sampling device is dropped vertically into the water and recovered with the aid of a hand-operated winch attached to the side of the helicopter. It is essential that the helicopter does not drift during sampling and to this end all crew members are linked by a voice-actuated intercom. As the sampling device is recovered, the top-layers of sediment are washed out through the port. Then a plastic scoop is inserted into the port, the entire device is inverted, and the sediment is collected in the scoop by banging the head of the device against the platform. The sample can then be transferred to a paper bag. During collection, the sampling operator communicates a description of the sample and the sampling depth to the navigator. Cards for recording this information have been described by Garrett (1974). Using this procedure at a sampling density of one per 13 km^2, an average of 15 sites can be sampled per hour.

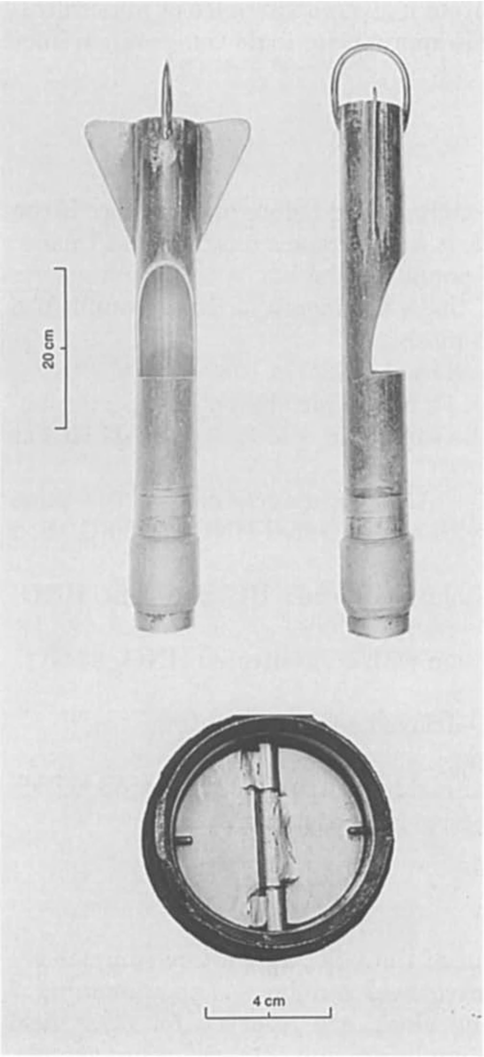


Fig. 7-23. Centre-lake sediment sampler.

Choice of lakes

As described above, the lake sediment method of geochemical exploration is based on the dispersion of metals in solution and as fine, suspended particulates. Thus, wherever possible, lakes with active inflow and outflow should be sampled. Moderately sized lakes, 1 to 5 km in length, are preferred, since they will be deeper than smaller lakes and more likely to contain organic-rich sediment. Sampling will usually be from the centre of these lakes. Bigger lakes usually drain a larger area; the greater flux of material from the larger drainage area will tend to dilute the metal signal from a given occurrence of mineralization. If a larger lake must be sampled, it is appropriate to do this from an inlet bay that has a profundal basin.

Sample preparation and analysis

It is essential that the sample be thoroughly dried before preparation. If the sample is of the correct, organic-rich type, it will become a hard, compact mass. This is broken into small fragments by pounding the bag with a hammer on a steel plate. An appropriate volume of these fragments is then ground in a ceramic ball mill and sieved to minus 200-mesh.

The analytical procedures routinely used by the GSC in 1989 are:

(1) Zn, Cu, Pb, Ni, Co, Ag, Mn, Cd and Fe by atomic absorption spectrophotometry (AAS) following dissolution of the sample in 4 M HNO_3 – 1 M HCl at 90°C;

(2) As and Sb by hydride evolution — AAS, As determined on the same solution as (1), Sb following extraction with concentrated HNO_3 at 90°C, then concentrated HCl at 90°C;

(3) Hg as vapour by AAS following dissolution in conc. HCl plus conc. HNO_3 and reduction by stannous sulphide;

(4) Mo and V by AAS following extraction with concentrated HNO_3 at 90°C, then with concentrated HCl at 90°C;

(5) U by neutron activation analysis — delayed neutron counting;

(6) LOI by ignition at 500°C for 4 hours;

(7) Commencing in 1989, Au is determined by instrumental neutron activation analysis on 10 g samples to give detection limit of 2 ppb.

Quality control

During sampling carried out on behalf of the GSC, 17 routine samples are collected within a block of 20 consecutive field numbers. The remaining 3 numbers, in random position within the block, are reserved for (1) a field (site) duplicate sample, (2) an analytical duplicate, and (3) a reference sample. Samples (2) and (3) are inserted during the post-field, sample preparation phase. Once the analytical data have been received, their quality may be evaluated using the procedures described by Garrett et al. (1980) and Fletcher (1981). The GSC has prepared a series of lake sediment standard samples that may be used to monitor the accuracy of survey data.*

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* These samples may be obtained from: Coordinator, CCRMP, Energy, Mines and Resources Canada, 555, Booth Street, Ottawa, Ont. K1A 0G1, Canada.

Reliability of method

Assessing the reliability of data is an essential part of any lake sediment survey. A qualitative indication that data are, indeed, meaningful is the patterns seen in most geochemical maps. Anomalous areas are not usually defined by single samples, but by a cluster of high or low values that bear a discernible relationship to the underlying geology.

A useful, qualitative measure of the reliability of lake sediment surveys has been made by Garrett and Goss (1979). These workers used a sampling and analytical system broadly similar in principle to that described above in the quality control section. They divided survey areas into blocks, each containing 16 cells, 13 km^2 in area. One centre-lake sediment sample was taken from each cell, except for one, where two lakes were sampled. From one of these two lakes two samples were collected, one of which was split to give an analytical duplicate. By use of an appropriate analysis of variance procedure, the different components of variance can be estimated. If the lake sampling method is to be effective, the analytical variance and the variance between samples taken from the same lake should both be small. There should be greater variance, on average, between lakes within the same cell, and the greatest variance should be between cells, i.e., regional variance. This is, indeed, the case for the example shown in Fig. 7-24.

Sampling density

One of the most vexing and important questions in planning a geochemical survey of any type is the sampling density. The choice is subjective and is difficult to evaluate even with posterior knowledge of mineralization within an area. Sampling density is related to the geological nature of the mineralization

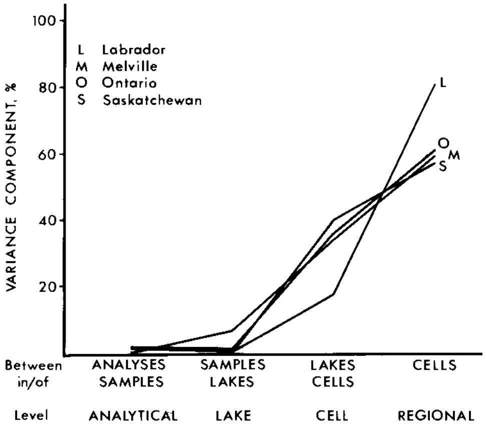

Fig. 7-24. Components of variance plot for uranium in centre-lake sediments from four large survey areas in the Canadian Shield (reproduced with permission from Garrett and Goss, 1979).

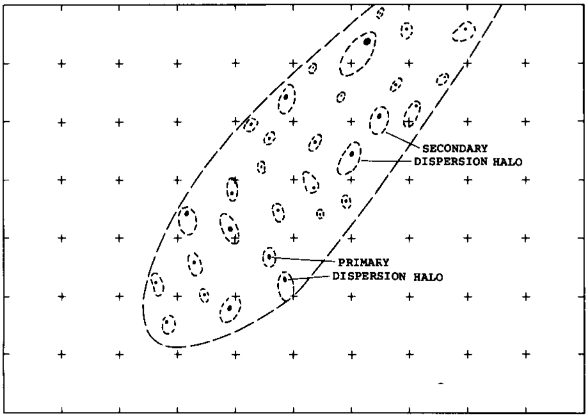

Fig. 7-25. Relation of sample grid spacing to the detection of a mineralized belt (reproduced with permission from Cameron and Hornbrook, 1979, International Atomic Energy Agency, Exploration for Uranium Ore Deposits, p. 242).

sought, the mobility of elements which are likely to occur within this mineralization, and the effect of the local environment on the mobility of the elements. All of these factors have been discussed in the earlier parts of this chapter, but are difficult to quantify.

Lake sediment surveys are generally reconnaissance in nature, i.e., they are designed to outline favourable areas for more detailed follow-up, rather than find specific deposits. This approach is based on the knowledge that mineral deposits rarely occur as single entities. Instead, they tend to occur in clusters, in association with more numerous minor occurrences of no economic value (Fig. 7-25 and Hornbrook et al., 1975). Orientation surveys should thus consider mineralized areas, rather than single deposits.

Garrett (1977) has attempted to use quantitative methods to evaluate sampling density. The basis for this is that areas containing mineral occurrences have positively skewed frequency distributions. Montecarlo techniques were applied to data from survey areas to incrementally reduce the sampling density and compare the frequency distributions at these densities with the starting distributions. The minimum effective sampling density for a given element is reached when the frequency distributions generated for that density can no longer be considered a valid sub-sample of the starting frequency distribution. Garrett applied this method to U distributions in seven NGR areas in the Canadian Shield, for which the nominal survey density was one sample/13 km^2. For six of these areas he found that the sampling density could have been reduced to one/26 km^2 with no significant loss of information. For one area in southeastern Ontario in the Grenville Geological Province, the sampling density could not have been reduced below one/13 km^2. This is an area of complex geology, poorly developed drainage systems, and frequent variation between carbonate-rich and -poor bedrock lithologies.

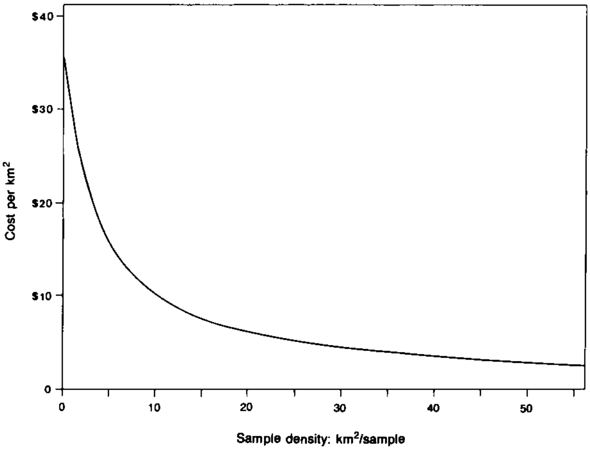

Fig. 7-26. Estimated total costs in 1985 Canadian dollars to carry out centre-lake sediment and water surveys at different sampling densities (modified after Cameron and Hornbrook, 1979, and reproduced with permission from International Atomic Energy Agency, Exploration for Uranium Ore Deposits, p. 257).

Survey costs

A chart illustrating approximate costs for lake sediment surveys is shown in Fig. 7-26. The costs, current in 1989, are derived from sampling, sample preparation, and analytical contracts tendered by successful contractors to the GSC, plus internal costs for data processing and presentation. These are average costs; they will be lesser for areas with good access and greater for remote areas. One of the features shown by the chart is that with varying sampling densities, costs do not remain proportional to the number of lake sites sampled. As the sampling density declines, a decreasing number of sites can be visited each hour of flying time and thus per cost per site increases. At a sampling density of one/13 km^2, 15 sites can be visited each hour. At a density of one/1.2 km^2, Maurice (1977) averaged 21 sites per hour.

Interpretation and follow-up of lake sediment survey results

Lake sediment surveys are usually regional in scope and the data, after plotting on a map, should be examined in conjunction with other maps at the same scale of bedrock geology, surficial geology, aeromagnetics and gravity. Because of the considerable influence of pH on element mobility, a map of this parameter in lake waters is an essential adjunct to the interpretation. Similarly, topographic maps show the distribution of swamps that may impede the dispersion of elements into lakes. The integration of geological and geophysical information with lake sediment geochemical data is usually done by visual comparison. However, an interesting mathematical approach to the integration of these variables was given by Bonham-Carter and Chung (1983). This paper includes a signal processing technique which improves the ability of the lake sediment data to predict the occurrence of known U mineralization. This approach has been further developed by Bonham-Carter et al. (1990). For the Meguma terrain of Nova Scotia they combined eight mapped variables to "predict" the occurrence of known gold mineralization. A contrast measure, C, is used to estimate the relative effectiveness of the different features. The four most effective predictors, with C values greater than 1, are: presence of Goldenville Formation (1.8); anticlinal axes (1.3); Au anomalies in balsam fir (1.2); and multielement lake sediment anomalies (1.1).

In considering the use of statistical methods of interpretation, it should be recognised that rocks, mineralization, and surficial processes within a large survey area give rise to a large number of overlapping and mixed populations of geochemical data in the lake sediments. Care should be taken in applying statistical methods designed to treat single populations of data, such as factor and discriminant analysis. Because of the several populations of data within any survey area, it is useful to plot the different associations of elements across a survey area. This may be done most easily by showing, for each sample site, those elements that occur in amounts greater than the 90th or 95th percentile. This can be supplemented by displaying on the same map sites which contain unusually high (>90th percentile) or low (<10th percentile) amounts of those components that may affect the fixing of trace elements (Fe, Mn, LOI).

Much of the broad, spatial variation shown by lake sediment geochemical maps is related to the varying abundance of trace elements in different rock types. For example, Cu will usually be more abundant in sediments collected over mafic igneous rocks than over felsic rocks, while the converse will be true for U. These relationships become most apparent when the geochemical maps are compared with geological and geophysical maps (e.g., Maurice, 1984). Indeed, as well as contributing to mineral exploration, lake sediment data may be able to contribute to the better understanding of the geology of a region (Allan, 1978). These topics are addressed in detail elsewhere in this volume.

After data interpretation, a number of targets for follow-up investigation will have been identified. A full description of follow-up is beyond the scope of this chapter, since it usually involves a mix of geological, geochemical and geophysical studies. However, in the writer's experience, a great deal can be achieved in classifying the relative importance of targets by an initial brief field visit to examine the geology. Provided that there is moderately good exposure, this can be done at the outset of the field campaign to determine the order in which anomalous areas should be investigated. In some cases it may be apparent that the anomalous values are unrelated to mineralization and do not merit further study.

In choosing geochemical methods for follow-up, the principles governing the lake sediment method should be considered. The model for element dispersion given in Fig. 7-21 stresses the importance of transport of mobile elements in solution, followed by adsorption onto suspended particulates and further dispersion in this form. Using this model, the method of choice for follow-up of anomalies of mobile elements, such as U, Zn and Cu, is to analyze the waters of the anomalous and adjoining drainage basins for the same elements. Portable instruments are available that permit the analysis of waters for U and several base metals in the field (Robbins, 1978; Castledine and Robbins, 1983; Mann and Lintern, 1984) allowing the source of metals within a target area to be rapidly identified. Hydrogeochemical methods of follow-up have been described by Cameron (1978). Alternatively, since mineralization usually contains a mix of elements of differing mobility, sediments from the proximal portions of the drainage system and soils may be analyzed for less mobile elements.

Availability of lake sediment survey data

Large areas of the northern hemisphere have now been covered by lake sediment surveys. Much of this was by government organizations and can readily be accessed, providing information for exploration in these areas for many years to come. In North America there are a large number of unpublished surveys by exploration companies. Coker et al. (1979) compiled a comprehensive list of surveys published to that time.

In Alaska, approximately 500,000 km^2 has been covered by lake sediment surveys at a sampling density of one/23 km^2 by the US Energy Research and Development Administration. These results have been compiled into a geochemical atlas of Alaska (Weaver et al., 1983), which gives relevant references to the work.

In Canada, approximately 1,200,000 km^2 has been surveyed using organic, centre-lake samples at one sample/13 km^2, mainly in the Canadian Shield and northern Appalachians. These surveys are part of the National Geochemical Reconnaissance (NGR) program (referred to as the Regional Geochemical Reconnaissance program in some publications) and were carried out by cooperative agreement between the Geological Survey of Canada and governments of the Northwest Territories and the provinces of Saskatchewan, Manitoba, Ontario, Nova Scotia, and Newfoundland and Labrador. Prior to establishment of the NGR in 1975, a 93,000 km^2 area of the Northwest Territories was covered using nearshore sediment samples at one sample/26 km^2 (Allan et al., 1973b) and 34,000 km^2 in Ontario was covered at one/8 km^2 using centre-lake material (Hornbrook and Gleeson, 1972). In Newfoundland 12,000 km^2 has been sampled at densities of one/2.7 to 5.3 km^2 (e.g., Davenport et al., 1975), again using centre-lake samples.

In Fennoscandia, there has been a number of surveys using centre-lake samples. This has principally been by the Geological Survey of Finland commencing in 1973. To 1984 an area of 80,000 km^2 had been completed at an average spacing of one sample/5 km^2 (Tenhola, 1988).

SUMMARY

The ideal sampling medium for any type of geochemical exploration survey has a relatively uniform matrix composition, contains chemically reactive minerals to fix trace elements, and can be rapidly and economically sampled by persons with no specialist training. Organic, centre-lake sediments meet all of these criteria. This permitted the rapid development of the method in the late 1960's and early 1970's, followed by routine reconnaissance surveys that have covered almost two million square kilometres of the northern hemisphere.

Terrains that contain the abundance of lakes required for these surveys are almost invariably of low relief. Wide dispersion of elements from the source of mineralization to a lake bottom several kilometres distant is more likely for elements that are transported in solution and/or on fine, suspended particulates. For most mobile elements this would appear to be a two-stage process: initial dispersion in solution, followed by adsorption onto fine particulates, which then travel further in suspension. The more immobile elements may disperse as fine particulates of primary minerals or the residual products of weathering. The prior dispersion of fragments of mineralization by glacial action can substantially increase the size and intensity of lake sediment anomalies.

A number of physical and chemical phenomena can restrict the dispersion of elements to lakes in solution and on fine particulates. These include a pH which is unfavourable to the solution of the element; organic and inorganic adsorbents along the drainage; redox changes which cause precipitation of insoluble compounds; and low relief which permits the particulates to be dropped from suspension before reaching the lake. Many of these phenomena are represented in organic-rich swamps, so that, in general, lake sediment surveys tend to be more effective north of regions of heavy forest cover.

Lake sediment surveys were undertaken to assist in mineral exploration and in resource evaluation. Since this work was commenced in the late 1960's, there has been increasing interest in the chemical condition of the environment. The survey results and the stored samples now provide an invaluable environmental database, the importance of which can only appreciate with time.

ACKNOWLEDGEMENTS

I am indebted to colleagues at the Geological Survey of Canada with whom I worked on the development and application of lake sediment surveys: Rod Allan, Bruce Ballantyne, Bill Coker, Chris Durham, Willy Dyck, Bob Garrett, Gwendy Hall, Don Hornbrook, Ian Jonasson, John Lynch, Greig Lund, Yvon Maurice and Mike Timperley. I am further grateful for the good company of Rod Allan and Chris Durham during field work in the northern Shield. In hindsight, lake sediment surveys appear to be a fairly obvious approach to mineral exploration. However, this was not the case when the work commenced. In this regard I wish to acknowledge the contribution that Arthur Darnley made to obtaining necessary financial support. In preparing this chapter I have benefited from the previous review by Bill Coker, Don Hornbrook and myself, published in 1979. David Ellwood, Peter Friske, Don Hornbrook, John Lynch, Rolf Schmitt and Bill Shilts have kindly supplied material for incorporation in the text. Finally, Peter Friske and Yvon Maurice took the time to read the manuscript and suggest how it might be improved.

NOTE ADDED IN PROOF

Since the time that this chapter was prepared and revised, lake sediments have taken an increasingly imporant role in geochemical mapping and in defining the natural geochemical background for environmental purposes. A recent presentation of these topics is Davenport et al. (1993).

Drainage Geochemistry
edited by M. Hale and J.A. Plant
Handbook of Exploration Geochemistry, Vol. 6 (G.J.S. Govett, Editor)

Chapter 8

NATURAL WATERS AS SAMPLE MEDIA IN DRAINAGE GEOCHEMISTRY

ANGELA GIBLIN

INTRODUCTION

The advantages of natural waters as sample media in exploration geochemistry derive from their chemical reactivity with crustal rocks and soils, coupled with their physical mobility. Natural waters migrate at or below the Earth's surface along drainage pathways where the chemical and physical products of weathering may accumulate. As a result, some of the rock constituents are dissolved by the water, which is subsequently responsible for the migration and redistribution of many elements in the surface and near-surface environments. In areas of high topographic relief and shallow or exposed basement, stream sediments, which comprise detrital and secondary minerals and precipitates, are probably the best medium in which to detect a geochemical expression of the rocks crossed by the drainage path. Sub-surface water is the most appropriate medium where dispersion into a surface drainage system is limited or non-existent due to low topography and/or arid climatic conditions. For example, terrain that is today arid may have a blanket of transported overburden which conceals drainage channels developed during an earlier pluvial period. Nevertheless, groundwater flowing in such palaeo channels may carry dissolved metals from concealed mineral deposits or their palaeo dispersion patterns.

Element abundances vary in natural waters according to the solubility of their source minerals and the availability of surface active particulates, which remove solutes from solution by adsorption or chemical complexation. The solubility of source minerals is controlled by acidity (pH), redox conditions (Eh) and salinity (total dissolved solids (TDS)) of the natural water. The effect of variations in these water properties on a mineral solubility can be summarised by phase diagrams which identify the most thermodynamically stable phase of the principal element under specific pH, Eh and TDS conditions. The calculations involved in the preparation of these diagrams also provide theoretical abundances of all soluble forms of the element under the designated conditions. Abundances of solutes are measured by "activity", which may be regarded as an effective concentration in natural waters with total dissolved solids not exceeding 0.5%. In addition to true solutes, particles that are smaller than 0.5 μm, such as colloids, are also mobile because they can pass through soils and along

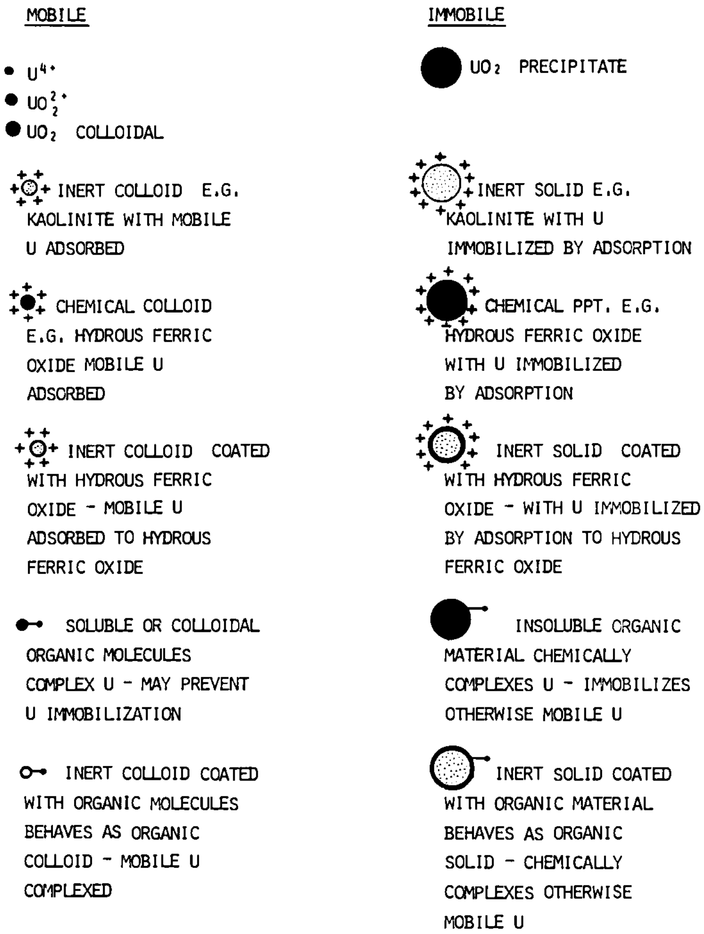

Fig. 8-1. Mobile and immobile species of U which can occur in natural waters. Mobile species are those for which particle sizes are less than 0.5 μm. Both groups include species that result from interactions among natural water constituents, products from which both increase and decrease the aqueous mobility of U in an equilibrated U–H_2O system.

grain boundaries in rocks. Some interactions among natural water constituents can increase or decrease the aqueous mobility of an element from that determined by concentrations of thermodynamically soluble species, as illustrated using U as an example in Fig. 8-1. Laboratory measurements of mobile U that greatly exceed the U concentrations predicted from thermodynamic equilibrium models of U solubility are explained by some of the processes referred to in Fig. 8-1 (Giblin et al., 1981). The aqueous mobility of Th, determined in some natural waters by Langmuir and Herman (1980), is also much higher than would have been predicted from considerations of the theoretical solubility of ThO_2 in these waters. This is attributed to the formation of soluble Th complexes and adsorption of Th onto colloidal clays or organic particles.

During interaction with rocks that contain potentially economic minerals, natural waters acquire not only traces of ore elements, but also traces of pathfinder elements such as As, Sb, Bi, which are pathfinders to Au mineralization, and elements leached from host rocks such as Mn, which is associated with shale hosted deposits. In general, geochemical halos associated with particular types of ore deposits should be reflected in some way through the composition of natural waters draining the mineralization. Vandelannoote et al. (1985) confirm that abundances of elements F, V, Fe, Ni, Cu, Sr, Y, Sb, Ba and I in local surface waters reflect the presence of Zn–Pb ore in Brittany. On a regional scale, in an area approximately 25,000 km^2 in eastern maritime Canada, Dyck et al. (1976) demonstrated systematic regional patterns for well water contents of U, Rn, He and F in 2000 samples, indicating broad regional belts of U enrichment which are leached by circulating groundwaters. A study by Rose et al. (1983) of groundwaters associated with small U and Cu–U occurrences near Monticello, NY, also identified anomalous groundwater levels of these elements. Statistical methods were used to identify the anomalies and to determine the nature of the processes affecting groundwater composition, and hence the prospectivity of individual aquifers. Halos may also reflect the distribution of secondary products of present day weathering of ore minerals; for example, sulphate, Fe and acidity halos in waters emanating from the vicinity of oxidizing base metal sulphides.

The value of waters as geochemical exploration samples has increased during recent years due mainly to the development of new analytical instruments and procedures that have lowered analytical detection limits, facilitated the handling of large batches of samples, and expanded the range of elements which can be determined routinely. Many elements, such as Ti, Zr and Cr, previously considered insoluble in natural waters because of relatively high analytical detection limits, can now be determined on a routine basis. Methods for the determination of low levels of Au in the range of 0.001–0.036 μg Au/l in natural waters have also been reported by Hamilton et al. (1983) and McHugh (1984), indicating the feasibility of using natural waters as sample media in Au exploration. Instrumentation for analytical techniques such as spark source emission spectroscopy, neutron activation, inductively-coupled plasma spectrometry (ICP), ICP linked with mass spectrometry, graphite furnace atomic absorption spectrophotometry and ion chromatography have all contributed to the range and quality of routine analytical data currently available for water samples collected in geochemical exploration programs. In some cases sophisticated analytical technology has also been incorporated into field portable analytical instruments (Mann and Lintern, 1984; Fig. 8-2), providing an on site method of analysis for a range of elements including Cu, Pb, Zn, Cd and Au.

THEORETICAL CONSIDERATIONS

In the cycle of natural waters, rain and snow initially interact with crustal rocks and soils and subsequently collect in surface streams and rivers, or enter

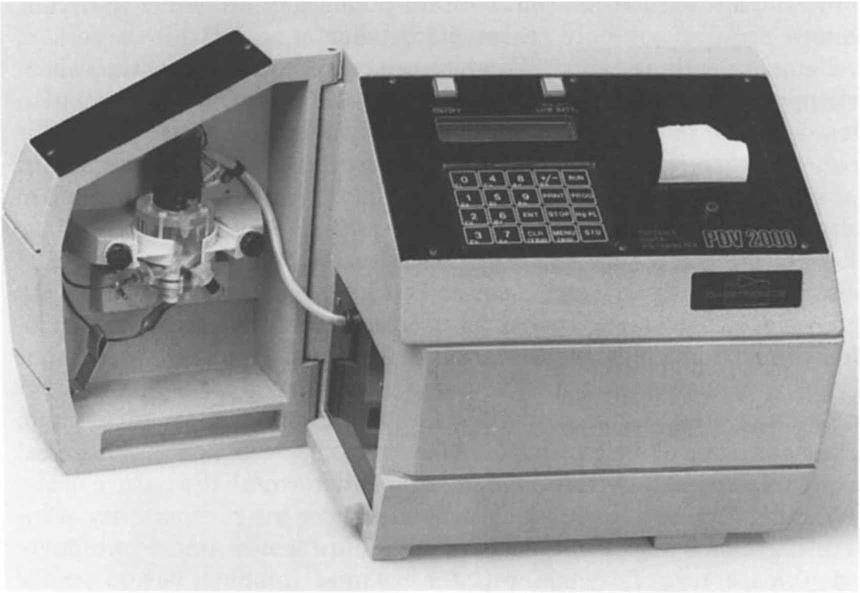

Fig. 8-2. Chemtronics PDV 2000, a portable digital voltammeter with which Cu, Pb, Zn, Cd, Au, and Hg can be easily measured in natural waters either at the sample site or in the laboratory, at detection limits in the 1–10 μg/l range for base metals, 50 μg/l for Au and 300 μg/l for Hg.

subsurface systems, either being incorporated into groundwater, or collecting in pore spaces and open cracks in rocks. Most surface water eventually flows into the ocean, although a small proportion flows into continental lakes or inland seas. From the ocean and lakes, water returns by evaporation to the atmosphere and subsequently completes the cycle by falling as precipitation. The total Earth surface natural water load is distributed between the atmosphere, in streams and lakes, ice, groundwaters and the ocean. The chemical composition of a natural water at each stage in its cycle depends upon the type of rocks previously traversed, local topographic relief, climate and the length of the drainage path, which determines the water–rock contact time.

Groundwaters

Immediately below the Earth's surface is a zone in which rock and soil voids are incompletely filled by water (unsaturated zone), but in a deeper zone all spaces are completely filled (saturated zone). The boundary between these zones is the water table, and is generally within a reasonable sampling distance (<100 m) from the surface. In the saturated zone various forces act on the groundwater, causing it to flow through transmissive rocks which are described as aquifers. Flow paths and rates are controlled by hydraulic head, the total amount of void space in a particular rock volume (porosity), and the extent of void interconnection and flow path diameter (permeability). Degrees of aquifer transmissivity decrease from the highest levels found in unconsolidated overburden, through layered sedimentary rocks to the least permeable crystalline rocks in which fractures, joints and grain boundaries provide groundwater flow paths. Each stratigraphic unit beneath the water table constitutes a discrete aquifer, with waters from neighbouring units mixing at flow path junctions, and impervious formations acting as barriers between separate groundwater flows in the transmissive units. Over time aquifer transmissivities may change, for example crystalline rocks may become more permeable as a result of tectonic events which cause fracturing or highly fractured units may become less permeable as a result of chemical deposits blocking cracks or fissures in the flow path. Because groundwater studies traditionally relate to rural and domestic water supply requirements, certain low permeability rock types (e.g., shales) have been erroneously described as impermeable. In a geological context and time scale all rocks have some permeability, even if limited to capillary movement along minute cracks and grain boundaries.

Rock–water interactions in both the saturated and unsaturated zones control the solute composition of groundwaters. Interactions may be full mineral dissolution, incongruent aqueous alterations of minerals or dissolution of salts in the unsaturated zone by downward moving surface waters or upward moving groundwaters. Geochemical exploration programs using groundwater as the sample medium apply techniques for identifying the possible presence of ore in concealed aquifer rocks from the solute composition of groundwaters. Even slowly seeping groundwaters can provide this information for the large volumes of rocks surrounding and underlying the sample collection site. If a concealed target formation can be identified via a groundwater sample, then it is likely that the formation is within an economically exploitable depth of the ground surface, unless aquifers beneath this depth comprise highly transmissive rocks. However, it is unlikely that deeply buried high grade deposits within deep formations would be preserved if they are contacted by highly transmissive aquifers.

Since water–rock contact times in groundwaters are greater than in stream or other surface waters, groundwaters have a better chance of accumulating solutes up to analytically detectable levels than do normal surface waters. Groundwaters also penetrate further into the crust than surface waters, and provide a vertical component to geochemical samples; this is uniquely useful for the detection of mineral deposits which lack a surface or near-surface expression and in areas where mechanical or chemical dispersion of a target ore deposit is limited at surface because of arid climatic conditions or low topographic relief. These latter conditions are common throughout much of the inland areas of large continents such as Australia (Fig. 8-3). Figure 8-3 also demonstrates that traditional exploration methods in Australia have to date been more successful where ore deposit host rocks are exposed or only covered by shallow overburden. Clearly exploration techniques need to “see” beneath vast areas covered by deep barren overburden. A similar problem prevails in

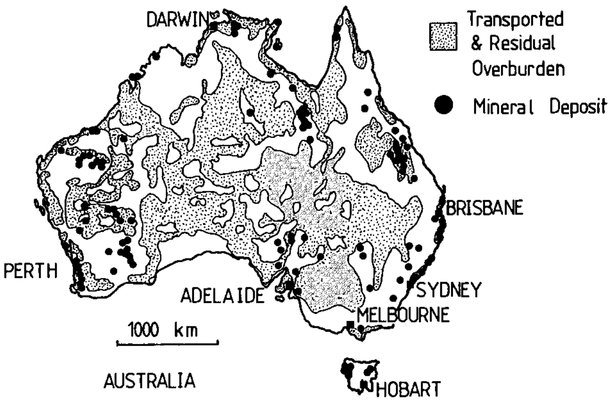

Fig. 8-3. Distribution of established mineral deposits in Australia related to areas of deep transported and residual overburden (reproduced with permission from Haynes, 1979).

regions covered by deep glacial overburden such as large areas of Canada, where Levinson (1974) has suggested that groundwater could be used to sample terrain covered by glacial deposits.

Surface waters

In regions of high rainfall and well developed drainage systems, surface waters may be the most appropriate sample medium, particularly where the elements to be determined have a high aqueous mobility. In most surface water systems, however, trace solutes are distributed between solid and aqueous phases, and most tend to be concentrated on the surfaces of particulate material such as clays, hydrous metal oxides (mostly those of Fe and Mn), and organic particles or coatings on solids. As a result, stream or lake sediments concentrate trace elements and are usually more useful for exploration than water, in which trace solutes are at such low concentrations that they are difficult to detect by standard analytical methods. Exceptions occur when surface waters are so acid or alkaline that surface adsorption or organic complexation of minor solutes is restricted because of competition for adsorption or complexation sites by hydrogen or hydroxyl (H^+ or OH^-) ions. This is illustrated by the data of Forbes et al. (1976) (Fig. 7-11), which show marked decreases in the degree of metal solute adsorption onto a hydrous ferric oxide (goethite) with decreasing pH. The data demonstrate variations in the pH values of maximum adsorption for different metals. They also show that below pH 4.5 all metals are predominantly in solution.

Cameron (1977b) compared variations in pH with abundances of Cu, Pb, Zn, Fe and Mn in lake waters and centre-lake sediments in the Agricola Lake area of Canada; the pH varied from 3.8 to 6.6 (Fig. 8-4). Increased levels of Cu, Zn, Fe and Mn in sediments correlate with decreased levels in lake water

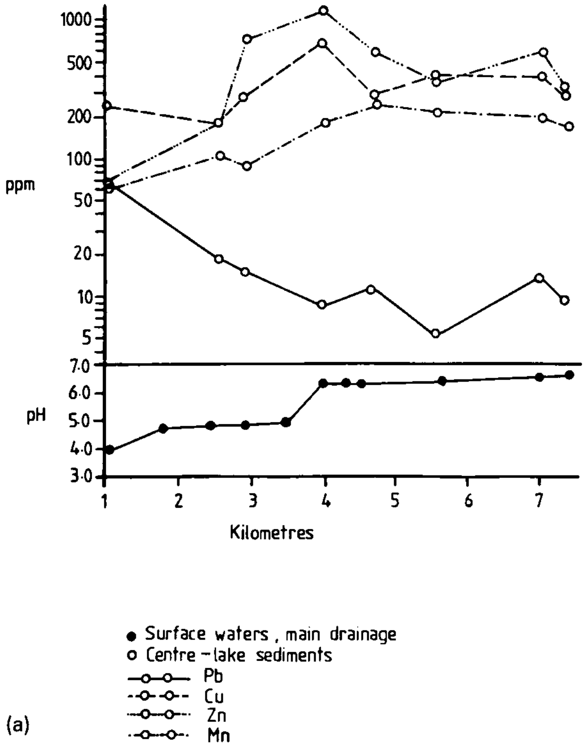

Fig. 8-4. (a) Variations with pH in abundances of Cu, Pb, Zn, Fe and Mn in centre-lake sediments in the Agricola Lake area of Canada (from Cameron, 1977b).

over a 6.3 km section of a drainage system; lead is immobilized early in the drainage system, even at pH 3.8, so that very little Pb moves into centre-lake sediments. Controls on dispersion in the area are discussed further in Chapter 7. The data demonstrate a correlation between pH and the distribution of metals between lake waters and sediments, and hence the relative usefulness of the two sample types at different points in the drainage system. The data suggest that a selection can be made between lake water and sediments for the best Cu–Zn exploration medium using a simple in situ pH measurement of the lake water: below pH 4 lake water would be chosen; and above pH 4 sediments comprise the better exploration sample.

Regardless of these findings, the convenience of surface water as a sample medium may outweigh the disadvantage of the very low concentrations of geochemical indicator elements at near neutral pH values. Rapid sample collection can keep costs relatively low (see Chapter 7, this volume), the uniformity of the sample medium can compensate for any additional analytical effort, and low background solute concentrations increase the definition and contrast of anomalies. Cameron (1978; Chapter 7, this volume) has demonstrated the rel-

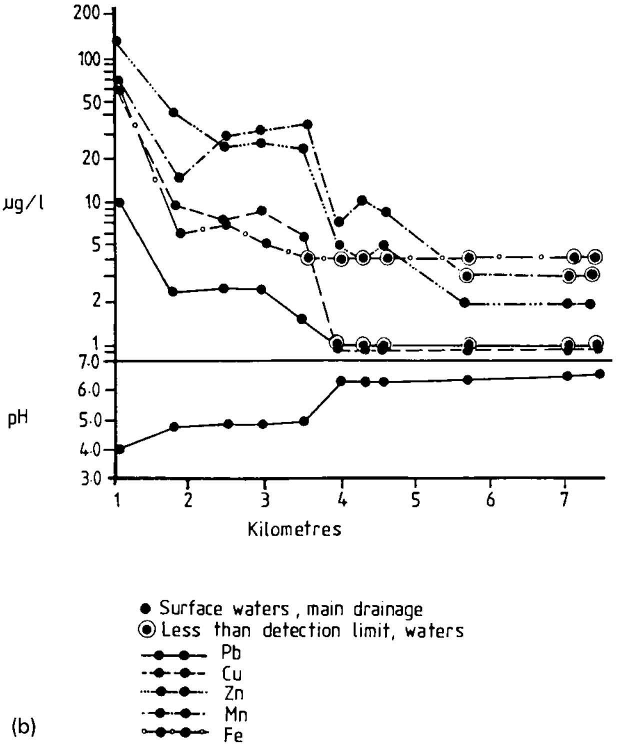

Fig. 8-4. (b) Variations with pH in abundances of Cu, Pb, Zn, Fe and Mn in lake waters in the Agricola Lake area of Canada (from Cameron, 1977b).

atively limited areal extent of lake water base metal anomalies compared with equivalent lake sediment anomalies and suggested that the former are appropriate for detailed exploration, whereas the latter should be used for broad scale, regional geochemical reconnaissance.

PROPERTIES AND CONSTITUENTS OF NATURAL WATERS: APPLICATION TO EXPLORATION

Release of major ions from rocks into natural waters is dominated by hydrolytic alteration of silicate minerals such as feldspars. Probably the most effective agent of decomposition of rocks into soluble species is dissolved CO_2 from atmospheric and soil organic matter sources. Solution of CO_2 in water provides the necessary H^+ (for hydrolytic alterations) by a reaction which is summarized as: $CO_2 + H_2O = H^+ + HCO_3^-$. Consumption of H^+ during mineral alteration results in a build up of HCO_3^-, balanced by cations such as Ca^{2+}, Mg^{2+}, Na^+ and K^+; Cl^-, SO_4^{2-} and traces (<1%) of many other ions are also released together with water soluble organic substances and some gases.

pH and redox potential

Natural water exhibits degrees of acidity or basicity which are usually expressed as pH, and water is relatively oxidizing or reducing depending on its redox potential (Eh). The precise nature of both of these variables is well documented in many texts including Rose et al. (1979) and Hem (1985). For this discussion it is sufficient to identify pH as a measure of H^+ concentration and Eh as dependent upon the concentration ratio, in an equilibrated solution, of oxidizing to reducing solutes (electroactive species). Eh and pH are fundamental to any study of natural waters as they together reflect concentrations of species which directly or indirectly affect all chemical reactions in a natural water system. As a result, the equilibrium solute composition of any natural water at a particular point in its drainage path is directly related to the pH and Eh of the water. Whereas pH is easily measured in situ in natural water systems, true Eh values are difficult to measure, particularly in O_2-containing surface waters, and may have to be calculated from the ratio of concentrations of electroactive species such as those of Fe III and Fe II.

Control of mineral solubility

The major influence on water composition is whether or not specific minerals, including ore minerals, are soluble or insoluble at equilibrium in a particular natural water. This is not only a function of the water pH and Eh, but also of temperature, and the concentrations of other ions with which the mineral elements may form soluble complexes. Pourbaix (1949); Garrels and Christ (1965) and many authors since have demonstrated the preparation of pH–Eh diagrams which are in essence maps showing pH–Eh ranges of values within which particular species of an element are predominant when temperature and concentrations of other constituents are fixed. These diagrams have particular value in defining pH–Eh fields in which the dominant species of an element is either soluble or insoluble. Figure 8-5 shows how pH–Eh fields of dominantly soluble Cu species change position when the compositions of complexing anions are varied. Hence in exploration programs it is essential that the overall composition of groundwater is considered as well as pH and Eh. Figure 8-6 illustrates the ranges of pH–Eh values where various Fe, Mn and S containing minerals dissolve. Boundaries are drawn where concentration (activities) of soluble species $= 10^{-6}$ M.

Field measurement of pH and Eh

In exploration programs, field measurements can be made of both pH and Eh. Although they are both useful, fundamental differences apply to what each measurement actually represents. Because pH is a measurement of a specific species, the physical measurement can be equated to the overall H^+ concentration (activity) in the water system. Although field "Eh" readings can be made, the reading does not apply to the water system as a whole, because a non-equilibrium system has no unique Eh. Nevertheless, measurements of apparent

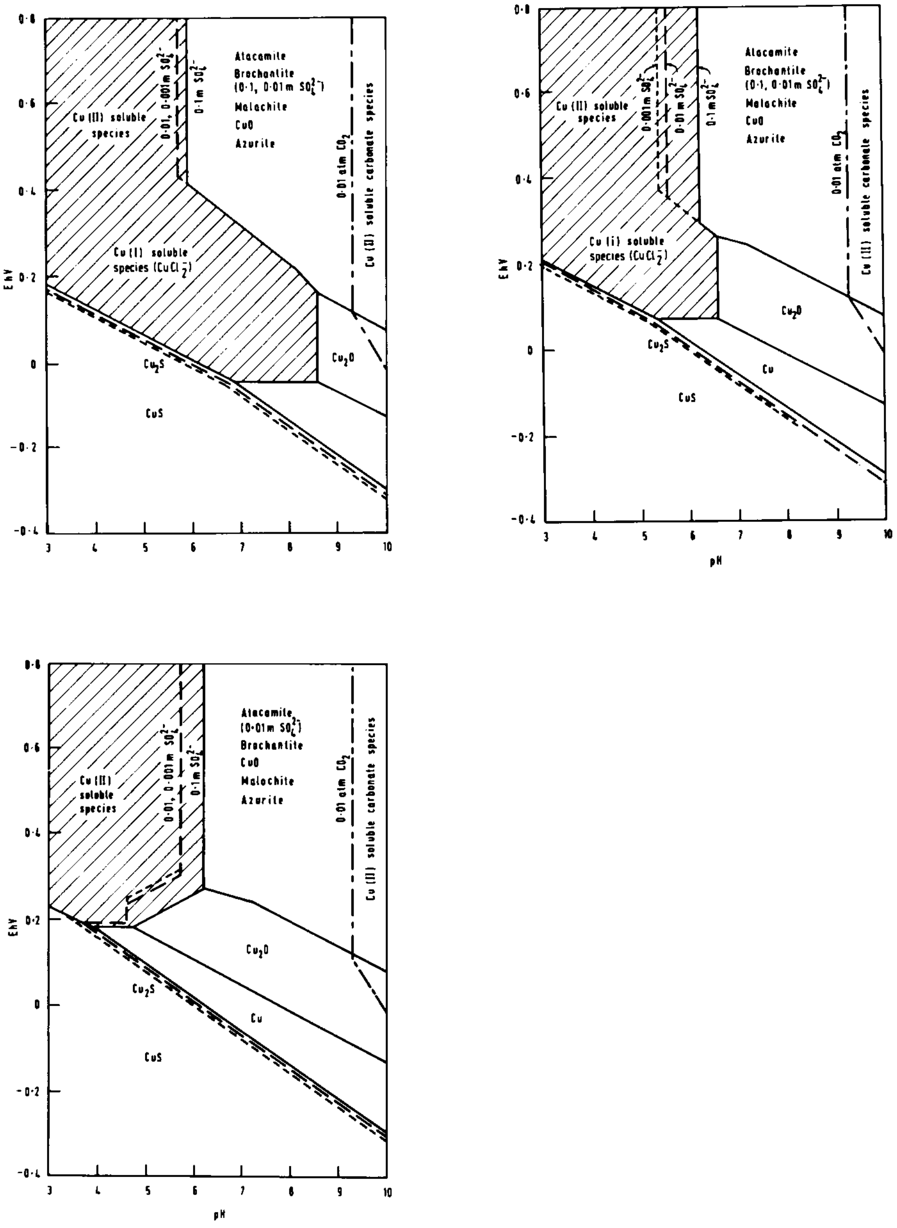

Fig. 8-5. Thermodynamic equilibrium predominance diagrams showing varying pH–Eh fields of soluble Cu species at 25°C in aqueous solutions with Cl^- compositions of 0.01 M, 0.1 M and 1.0 M. Marginal effects of variable levels of SO_4^{2-} and CO_2 species are also shown.

"Eh" of natural waters have been found useful in exploration programs. These values often relate to whichever natural water reaction is dominant, that is the reaction involving the highest concentration of electroactive species, or the

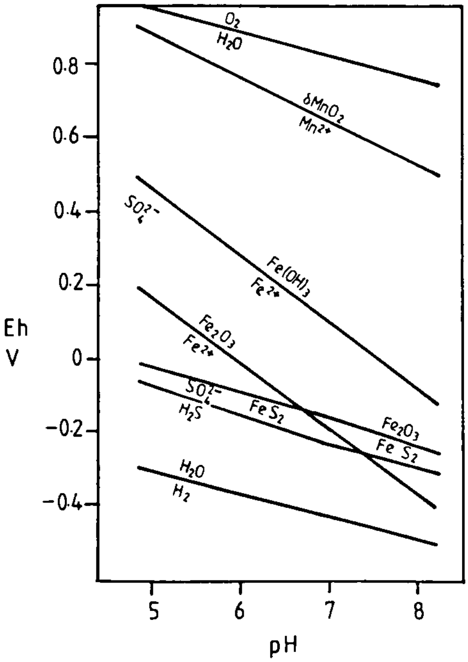

Fig. 8-6. pH–Eh boundaries between constituents of some redox reactions in an aqueous system. At each boundary the concentration (activity) of soluble constituents equals 10^{-6} M (modified after Drever, 1982).

reaction which is occurring at the fastest rate. Any of the constituent reactions depicted in Fig. 8-7 could buffer the overall redox conditions in the system and so dominate "Eh" measurements. In surface waters the supply and consumption of atmospheric O_2 is usually the dominant redox influence and controls the apparent "Eh". If sulphide ore minerals are associated with a groundwater they will constitute significant consumers and producers of electroactive species and so be the dominant influence on apparent "Eh".

Applications of pH and Eh

Even in the absence of information identifying dominant redox reactions, a series of groundwater "Eh" measurements gives a range of relative values which illustrate how redox conditions in a natural water system vary from one location to another. This can be of great value in exploring for redox-front controlled U mineralization. Figure 8-7 illustrates an approach for locating a redox front within a drill-hole pattern in a sedimentary basin using pH and "Eh" conditions in drill-hole waters. These values are plotted on a pH–Eh diagram which delineates fields of insoluble U minerals in a U–H_2O–CO_2 system with a boundary drawn where the concentration of soluble U species equals 240 μg/l U. The boundaries of the graded fields of varying pH–Eh,

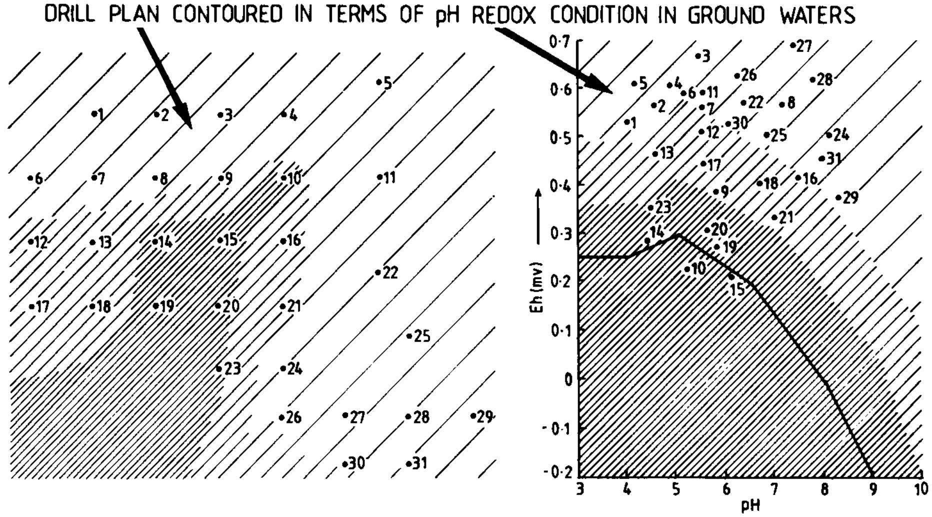

Fig. 8-7. Locating a redox front on a drill-hole plan using pH–Eh conditions in drill-hole waters (hypothetical example).

shown by different depths of shading, are arbitrarily chosen as the diagram is intended to illustrate pH and Eh trends from one location to another, rather than absolute values. As the shading deepens, the pH and Eh conditions in the groundwaters approach the redox front between the field in which U is dominantly soluble and that in which it is dominantly insoluble as UO_2, a potential ore mineral.

The main application of pH–Eh diagrams in exploration is in the identification of concealed environments where economic deposits could be preserved, compared with environments where chemical conditions favour neither ore mineral deposition nor preservation. Although measured "Eh" values have large uncertainties, they provide a general indication of the extent to which dominant redox conditions would allow the preservation of ore minerals. Figure 8-8 shows plots of pH and "Eh" for a series of groundwaters from an area of known Cu mineralization (A), and an area where extensive exploration drilling demonstrated the absence of any Cu mineralization (B). Each diagram shows the calculated boundary for the pH–Eh field where theoretical Cu ore mineral solubility would produce Cu levels in groundwaters in excess of 6.4 mg/l (unshaded zone). Calculation of each boundary includes consideration of a range of Cu minerals and the average water composition (in terms of complexing anions) measured in each area. Figure 8-8a is clearly indicative of an environment, where Cu ore minerals would be preserved, whereas Fig. 8-8b shows waters that would dissolve any Cu minerals in their path. A set of diagrams such as these, including variations in Cl^-, SO_4^{2-} and total carbonate (TCO_3) species, could be prepared for each target element of interest in a mineral exploration

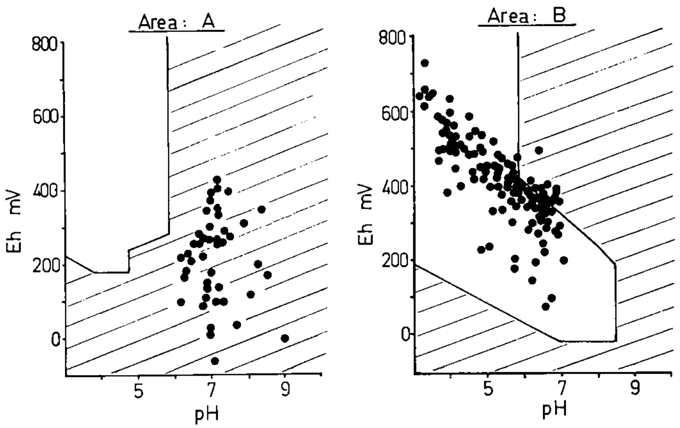

Fig. 8-8. Plots of physico-chemical conditions summarised by pH and Eh in groundwaters from the vicinity of a major base metal sulphide deposit (A) and an area of dispersed non-economic low grade sulphide mineralization (B). Unshaded areas illustrate the pH–Eh fields within which Cu solute concentrations (activities) exceed 6.4 mg Cu/l if the waters are in equilibrium with Cu ore minerals. Differences in shaded area boundaries between A and B are due to differing anion compositions (A = 350 mg Cl^-/l, 98 mg SO_4^{2-}/l and 640 mg HCO_3^-/l; B = 35,000 mg Cl^-/l, 980 mg SO_4^{2-}/l and 640 mg HCO_3^-/l).

program; diagrams for important pathfinder trace elements such as As would also be useful.

Sulphide mineral oxidation

Natural waters in the drainage path of oxidizing sulphide minerals are characterized by increased acidity, enhanced sulphate levels compared with regional values and the presence of detectable Fe^{2+} in solution (Deutscher et al., 1980; Giblin and Dickson, 1984; Robbins and Chenoweth, 1984; Everdingen et al., 1985). These variables are all soluble products of sulphide mineral oxidation, Fe^{2+} deriving from pyrite or from Fe incorporated in other sulphide minerals. Low pH and increased Fe^{2+} levels are the most immediately useful because they can be measured in the field. In order to detect local enhancements in SO_4^{2-} abundances, it is important to normalize SO_4^{2-} concentrations by a factor related to the overall concentration of dissolved salts in each sample.

Major element solutes

Although the major element content of a water is initially controlled by the relative ease of dissolution of various rock forming minerals, effects of subsequent processes, such as ion-exchange, adsorption-desorption, degassing, mineral precipitation, evaporation and water recharge, modify the major element composition from that observed at a particular location and time. Figure 8-9 illustrates the extent to which the major element composition of surface wa-

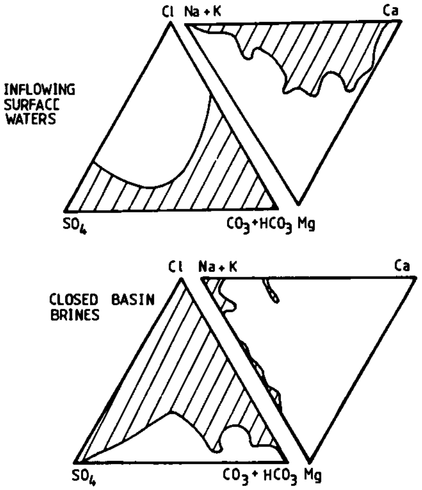

Fig. 8-9. Trilinear composition diagrams in which shaded areas demonstrate the range of compositions of (i) surface waters flowing into a closed basin, and (ii) the brines into which inflowing waters evolve (modified after Eugster and Jones, 1979).

ters flowing through a variety of lithologies into closed inland basins is modified during the evolution of the waters into saline basinal groundwaters (data from Eugster and Jones, 1979). Removal of reaction products from the system as a result of many of these processes limits the relevance of an equilibrium model description for many natural water systems.

Controls on major element abundances in natural waters

Major ions exhibit a range of susceptibility to removal processes in natural waters, those least affected accumulating in the water as "conservative" solutes. Results from a study area covering 8000 km^2 in inland Australia demonstrate a decreasing order of conservatism for major ions, viz. $Na^+ = Cl^- > Mg^{2+} > SO_4^{2-} > Ca^{2+} > K^+ > TCO_3$ (Fig. 8-10). Each plot in Fig. 8-11 shows how concentrations of a solute ion vary among a set of 316 samples with changes in levels of total dissolved solids expressed as ionic strength (I). A high degree of correlation (percent variance explained) is evident between ion concentration and I for conservative ions Na^+, Cl^-, and Mg^{2-}. Progressively lower correlations relate I to concentrations of SO_4^{2-}, Ca^{2+}, K^+, TCO_3. This order of conservatism principally reflects the relative ease of formation of $CaCO_3$ and $CaSO_4$ and loss of CO_2 compared with other precipitation or degassing reactions. Many natural waters are close to saturation with $CaCO_3$ and $CaSO_4$, and Fig. 8-11 illustrates how waters from different exploration areas can be compared and contrasted on the basis of how close each set of waters is to saturation with these minerals (Giblin, 1987). Sulphate can also be removed from natural waters by reduction to insoluble sulphides, a process that is important in saline waters in which anoxic conditions are more easily attained because the solubility of O_2 decreases

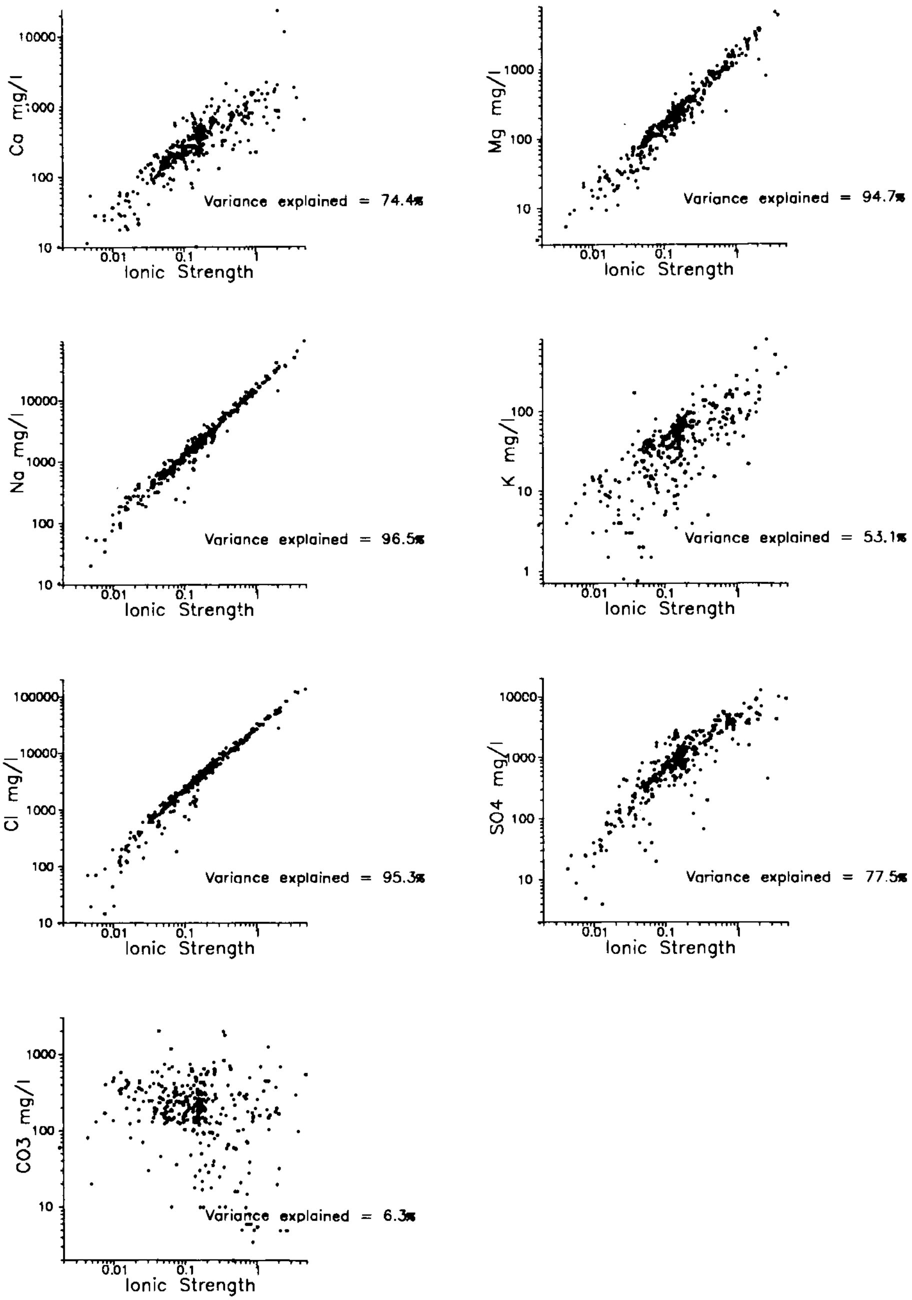

Fig. 8-10. Concentrations of major ions plotted against ionic strength (I) of 316 samples from a study area covering 8000 km^2 in inland Australia. Degrees of correlation between ion concentrations and I demonstrate a decreasing order of conservation of major ions in natural waters of Na$^+$ = Cl$^-$ > Mg^{2+} > SO$_4^{2-}$ > Ca^{2+} > K$^+$ > TCO^3.

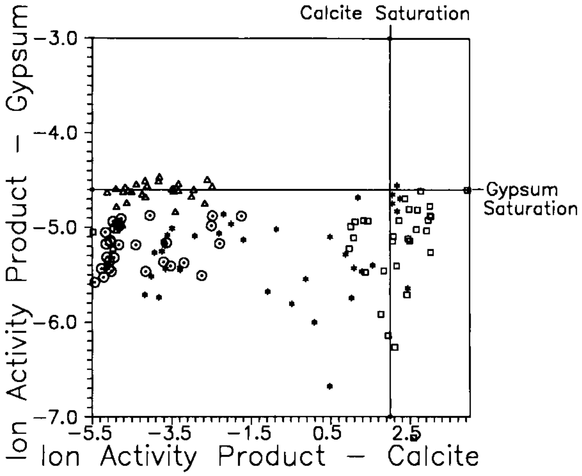

Fig. 8-11. Scatter plot of calcite and gypsum ion activity products for groundwater samples from four different exploration areas (from Giblin, 1987). Samples depicted by open squares are from the vicinity of a U ore deposit, while all others are from non-mineralized or sub-economic prospects. Samples which plot above 1.99 on the log (activity Ca^{2+} × activity HCO_3^-) + pH scale are saturated with respect to calcite, and those which plot above −4.60 on the log (activity Ca^{2+} × activity SO_4^{2-}) scale are saturated with respect to gypsum. Samples from the area containing the ore deposit are distinguished by their saturation with both calcite and gypsum while others are only saturated with gypsum.

as salinity increases (Drever, 1982). In Fig. 8-10 loss of K^+ from natural waters because of preferred adsorption, or ion exchange of K^+ on clay minerals, is also demonstrated by K^+ abundances which are two orders lower, and far more variable than those of Na^+, although Na occurs in rock forming minerals at comparable levels to K.

Major element abundances in natural waters as reflections of lithologies in the drainage path

Understanding the relative conservatism of major ions in natural waters is important if lithologies in the drainage system are to be identified. First, if an ion is conservative then any unusually high levels in a water, acquired by leaching rocks of elevated concentration, will be clearly anomalous in comparison to regional values. For example, gangue minerals near the Pine Creek Geosyncline deposits in northern Australia are greatly enriched in Mg^{2+} so that groundwaters draining these deposits contain Mg^{2+} as the dominant cation (Giblin and Snelling, 1983). Second, depleted levels of less conservative ions may not only indicate limited contact by the water with original source minerals, but also may indicate processes of removal of these ions. For example, depleted SO_4^{2-} concentrations in natural waters may reflect the formation of $BaSO_4$, which is highly insoluble.

Waters may be classified by aquifer or similar aquifer rocks by means of sig-

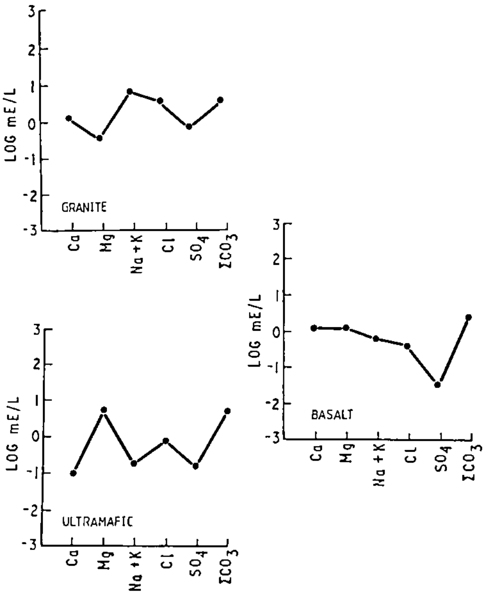

Fig. 8-12. Composition plots of groundwaters from three distinct aquifer lithologies.

natures provided by major solute concentration graphs. These graphs are drawn by plotting major solute concentrations, according to the procedures originally suggested by Schoeller (1935). Each point represents the log concentration of a major solute (in milli-equivalents/litre (mE/l)) in a water, plotted in the order Ca^{2+}, Mg^{2+}, $Na^+ + K^+$, Cl^-, SO_4^{2-}, and TCO_3. The slope of each line joining the points in order represents the ion concentration ratios Ca/Mg, Mg/(Na + K), (Na + K)/Cl, Cl/SO_4, SO_4/TCO_3 respectively, and the resultant shape that derives from these ratios constitutes the signature of the major solute content of the water. General similarities in major element plot shapes, apparent for waters from aquifers of particular lithological type, are principally controlled by cation relativities. For example, Fig. 8-12 shows signatures for waters from a granitic aquifer, a basaltic aquifer and an ultramafic aquifer. Although waters from all granite, basalt and ultramafic aquifers do not conform exactly to these shapes, lithologies are often identifiable from the ratios of major ion concentrations, particularly those of the cations. Cation relativities consistently observed include: Na^+ and $K^+ > Ca^{2+}$ and Mg^{2+} in waters from felsic igneous aquifers such as granites; Ca^{2+} and $Mg^{2+} > Na^+$ and K^+ in waters from mafic igneous aquifers such as basalts; intermediate relationships for waters from aquifers with compositions between these extremes; and $Mg^{2+} > Ca^{2+}$, Na^+ and K^+ in waters from ultramafic aquifers.

For each of these igneous groups there is a group of sedimentary rocks that are equivalent in terms of bulk chemistry. Major solute relativities in groundwaters from aquifers in sediments are indistinguishable from those from chemically equivalent igneous sources. Distinctive groundwater groups that

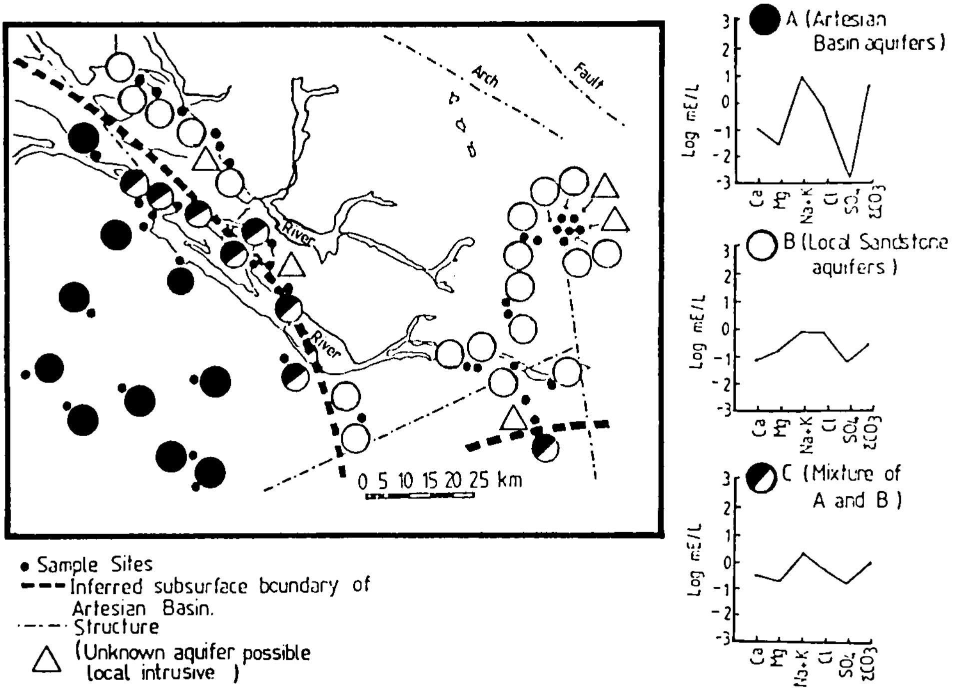

Fig. 8-13. Location of a concealed sub-surface lithological boundary using plots of the major element compositions of groundwaters.

are identified in a region that has been geologically mapped are assigned to specific aquifers on the basis of lithologies in the region. Alternatively, the number of groups into which a set of groundwaters is classified on the basis of major element compositions indicates the degree of aquifer rock diversity in an area. Cation relativities typical of each group of waters suggest possible aquifer lithologies, thereby increasing information on the exploration area. Figure 8-13 illustrates the use of major element compositions of groundwaters to locate a concealed lithological boundary in an area of exploration between two main aquifers. The compositions of waters from drill-holes located between the principal formations comprise a mixture of waters from both sources.

Other graphical methods of representing the major element composition of a water are described by Hem (1985). Of these the various trilinear plots are useful for classifying groundwaters although they do not provide the pictorial impact of Schoeller plot signatures.

Applications of major element abundances in natural waters to exploration

The major element composition of natural waters can indicate the presence of a group of rocks which has been identified from previous ore discoveries to be favourable for a particular type of ore deposit. This has considerable value when host formations are concealed too deeply beneath sedimentary cover to

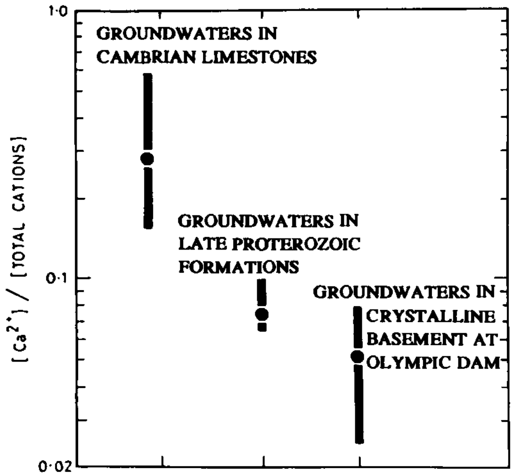

Fig. 8-14. Range and mean value for normalized Ca (NCa) in groundwaters from three stratigraphic levels in the vicinity of the Olympic Dam Cu–U–Au ore deposit, Australia.

be identified by traditional exploration methods, such as airborne geophysics. A good example is illustrated by waters in contact with the crystalline basement which hosts the Olympic Dam deposit in South Australia. These waters have normalized Ca^{2+} (NCa), the ratio of Ca^{2+} concentrations (expressed in mE/l) to the total of all cation concentrations (in mE/l) of less than 0.08, whereas waters in overlying Late Proterozoic sediments have NCa values around 0.1 and waters in younger formations such as Cambrian limestones have NCa > 0.1 (Fig. 8-14). Low NCa values confirm that the host of Olympic Dam ore has a dominantly granitic composition. Determinations of NCa in groundwaters in the region provide a means for identifying aquifers which could also be of the same granitic character as the formation which hosts the Olympic Dam deposit.

Volcanogenic base metal deposits are associated with enrichments and depletions in major cations in their surrounding host rocks (see Chapter 2). Wellmer (1983) lists the type of alteration which has been documented for volcanogenic deposits of Archean to Silurian age. In nearly all cases, alteration includes depletion of Na and Ca and enrichment of Mg. Govett (1989) also found that Na depletion and Mg enrichment is common in volcanogenic deposits of Archean to Tertiary age. The alteration can be identified from the composition of groundwaters. Figure 8-15 illustrates enrichment of Mg^{2+} and depletion of Na^{+} in groundwater from the Silurian Woodlawn deposit, Australia compared with groundwater from barren Silurian sediments in the same region. Sulphate is also enriched in waters draining this ore deposit, reflecting leaching and oxidation of sulphide minerals. Although Ca is depleted in the altered volcanic host rocks, this is not reflected in the associated groundwaters, this response being masked because acidity derived from sulphide oxidation increases the solubility of any $CaCO_3$ in the vicinity.

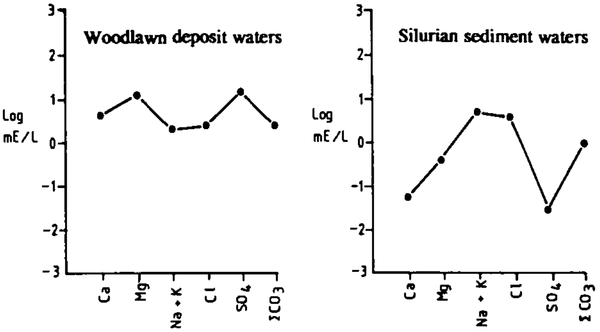

Fig. 8-15. Major element composition plots which illustrate contrasts between groundwaters from aquifers hosting the Silurian volcanogenic base-metal deposit at Woodlawn, Australia, and groundwaters from barren Silurian sediments in the same region.

During a study of the application of groundwater geochemistry to exploration for Mississippi Valley style base metal deposits in northwest Ohio, Deering et al. (1983) found that major constituents Ca^{2+}, Mg^{2+}, SO_4^{2-} and total dissolved solids reflected the chemistry of the bedrock. They concluded that this groundwater approach could be used in this region in the reconnaissance and detailed survey stages of exploration for Mississippi Valley type base metal deposits which occur in aquifer systems.

Magnesium enrichment occurs in the natural waters in the vicinity of the Pine Creek Geosyncline uranium deposits in the Northern Territory of Australia (Fig. 8-16) (Giblin and Snelling, 1983). Normalized Mg^{2+} (NMg, the ratio of Mg^{2+} concentrations expressed as mE/l to total cation concentration in mE/l) is now used to identify waters draining these uranium deposits, as waters from these deposits have NMg values in excess of 0.8.

In general, Mg^{2+} is also enhanced in groundwaters in contact with ultramafic rocks. Calculations using the compositions of spring waters from ultramafic rocks in the western USA (reported by Barnes and O'Neil, 1969) indicate that these waters have NMg > 0.9. The spatial association of magnesium ultramafics with gold in the Pilbara region of Western Australia has made Mg^{2+} enrichment of groundwaters a clear indicator to gold deposits of this type (Giblin, unpublished data).

Trace element solutes

Trace element levels in natural waters sometimes reflect the presence of an ore body or of a potentially mineralized formation, or they may merely reflect the natural background of these elements in rock forming minerals locally. In this last case trace elements are useful in identifying different rock types. For example, high levels of U and F are common in groundwaters draining felsic igneous rocks, while Ti and Mn are high in groundwaters draining basic rocks and Ni, Co and Cr in groundwaters draining ultramafic rocks. Particular

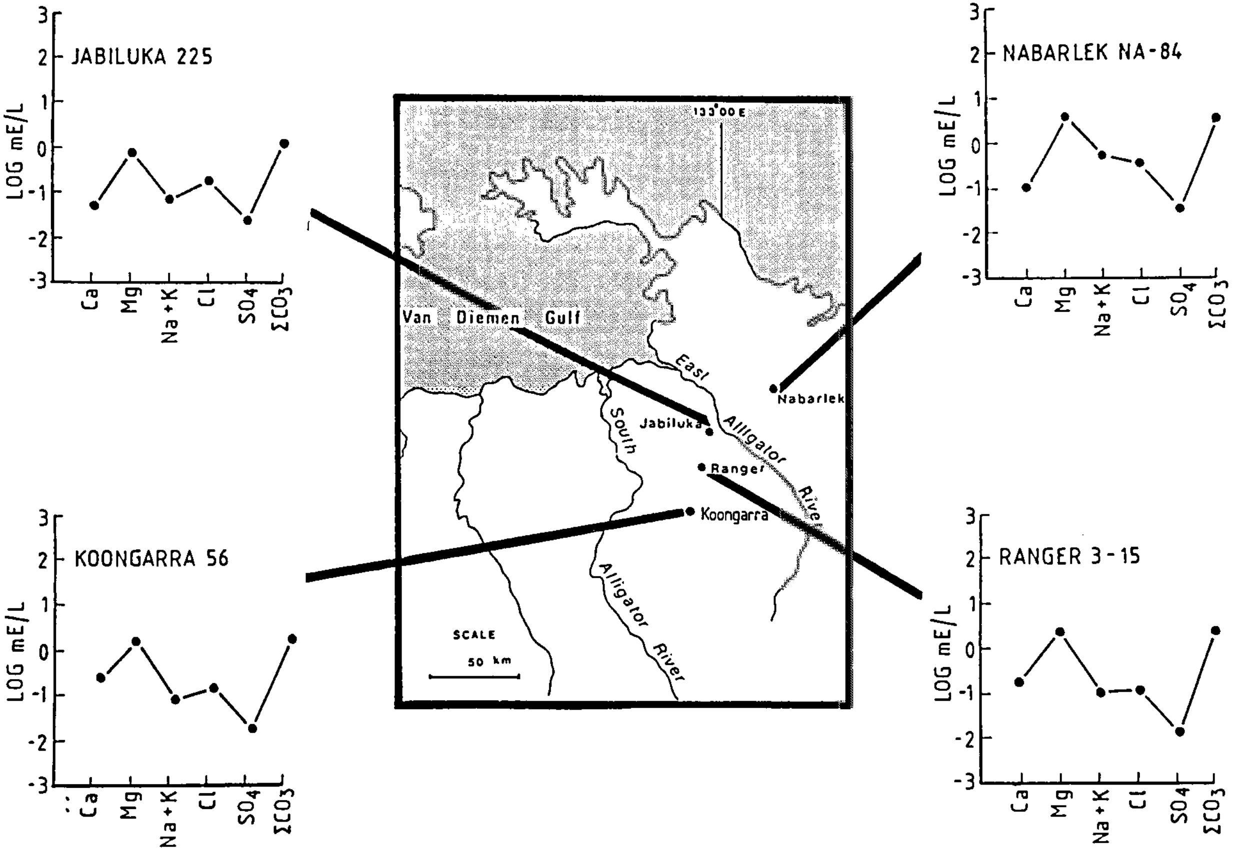

Fig. 8-16. Typical shape of major element composition plots of groundwaters from the immediate vicinity of four major U deposits in the Alligator Rivers Province of the Pine Creek Geosyncline, northern Australia, which constitutes a mineralized aquifer "signature" for this style of ore deposit.

rock formations may also give rise to unusually high trace element levels; for example, Li is high in groundwaters draining the Carnmenellis granite in southwest England (Edmunds et al., 1984).

The ease with which a trace element is dissolved from rocks by a natural water depends upon how the element is bound to constituent minerals, the aqueous stability of the host mineral and the chemical composition of the water. Ease of dissolution decreases with the strength of bonding of trace elements in the solid phase as follows: (i) adsorbed to a mineral grain, e.g., clay, hydrous metal oxide or an organic coating on a mineral; (ii) a trace constituent of a poorly crystalline mineral, e.g., Co or Cu co-precipitated in Fe or Mn oxides, or Zn in the strongly bonded octahedral sites of a montmorillonite clay; (iii) a trace constituent of a well crystallized mineral, e.g., Zn in magnetite, Pb in K-feldspar or Cu in biotite; or (iv) a major constituent of a well crystallized mineral, e.g., Pb in galena or anglesite or Cu in chalcopyrite or malachite (Rose et al., 1979). In some cases trace elements are released into the water because the mineral hosts are totally dissolved, or they merely may react with the water, losing trace elements to the aqueous phase in the process and possibly changing from one solid phase to another. In general the solvent power of waters increases with total concentration of dissolved salts (salinity), and varies with pH-redox conditions, the dissolution of many trace elements being most intense in acid oxidizing conditions.

If trace elements occur within minerals which are particularly resistant to aqueous dissolution (e.g., Ti in rutile, Cr in chromite and B in tourmaline), they will be released only by groundwaters containing high concentrations of dissolved salts, or which are highly acid or alkaline.

Some trace elements form insoluble products with major groundwater constituents of natural waters. Consequently concentrations of these trace elements are not only controlled by source minerals, but also by concentrations of the species with which they react to form solid phases. For example, Ba is controlled by the content of sulphate in the water with which it forms barite, while P is controlled by the Ca^{2+} content of the water, with which it forms insoluble Ca phosphates, and Fe levels are controlled by available oxygen which forms hydrated Fe III oxides. Soluble species of Al form only under exceptionally low or exceptionally high pH conditions.

Sources and abundances of trace elements in natural waters

Table 8-I lists common mineral sources and average fresh water contents for a range of trace elements. This information is culled from various authors, in particular Rose et al. (1979), Levinson (1980), and Hem (1985). Table 8-I also lists calculated concentrations for each element in a simulated river water and a simulated arid groundwater, which in each case is equilibrated with a mineral that contains the trace element as a dominant constituent. In the case of trace elements that are exploration targets, ore minerals are used in the calculations. These calculated values provide a benchmark for trace element concentrations in low and high salinity natural waters which could be indicative of an ore

TABLE 8-I

Typical concentrations of trace elements in natural waters

Trace Element	Common mineral sources	Average fresh water content	Concentrations in natural waters equilibrated with source minerals (calculated)	
			River	Arid groundwater
Ag	Native Ag	0.3 ppb	0.019 ppb	40 ppb
Al	Most silicate minerals, gibbsite	0.1–0.01 ppb	320 ppb	320 ppb
As	Arsenopyrite, sulpharsenides	2 ppb	>1000 ppm	>1000 ppm
Au	Native Au	0.002 ppb	<0.000001 ppb	<0.000001 ppb
B	Borates, tourmaline	10 ppb	>1000 ppm	>1000 ppm
Ba	Barite, K-feldspar	20 ppb		
Be	Beryl, mica, feldspar	5.5 ppb	0.4 ppb	0.9 ppb
Bi	Polymetallic, sulphides	0.005 ppb	10 ppm	3.8 ppm
Cd	Mafic silicates, sphalerite	0.032 ppb	2.2 ppm	>10 ppm
Co	Mafic silicates, Cu–Ni sulphides	0.1 ppb	12 ppm	3.5 ppm
Cr	Chromite	1.0 ppb	<0.01 ppb	<0.01 ppb
Cu	Mafic silicates, Cu sulphides	3.0 ppb	5.5 ppb	7 ppb
Fe	Mafic silicates, Fe oxides, Fe sulphides	100 ppb	17 ppb	17 ppb
Hg	Cinnabar, sphalerite	0.07 ppb	<0.001 ppb	0.002 ppb
La	Rare earth phosphates, rare earth carbonates	3.0 ppb	1.5 ppb	2.8 ppb
Mn	Most mafic minerals	15 ppb	3.2 ppm	1.0 ppm
Mo	Molybdenite	1.5 ppb	20 ppm	3.0 ppm
Nb	Niobates, Ti minerals	1.0 ppb	<0.01 ppb	<0.01 ppb
Ni	Mafic silicates, Ni sulphides	1.5 ppb	>10 ppm	>10 ppm
Pb	Galena, K-feldspar	3 ppb	400 ppb	80 ppb
Pd	Ni–Cu–Cr sulphides		40 ppb	45 ppb
Pt	Native Pt, Ni–Cu–Cr sulphides		<0.0001 pg/l	<0.0001 pg/l
Sb	Stibnite, Cu–Sb sulphides	2.0 ppb	0.2 ppb	0.2 ppb
Sn	Cassiterite, stannite, biotite	0.09 ppb	<1 pg/l	<1 pg/l
V	Mafic silicates	2.0 ppb	>1000 ppm	>1000 ppm
W	Scheelite, wolframite	0.03 ppb	5 ppm	450 ppb
Y	Rare earth phosphates, rare earth carbonates		180 ppb	40 ppb
Zn	Sphalerite, mafic silicates	20 ppb	3 ppm	5 ppm
U	Uraninite	5 ppb	6 ppm	1000 ppm

deposit. However, exploration decisions should not be made solely on the basis of these values, as other processes could be active that affect the concentrations, for example, adsorption onto clays or other water system solids.

Calculations of trace element concentrations in Table 8-I are made using the program THERMODATA (Turnbull and Wadsley, 1984), which produces thermodynamic equilibrium phase diagrams for soluble trace element species dissolved from a mineral host by a water containing major anions at concentrations which model either the river water (3.6 mg Cl^-/l, 9.6 mg SO_4^{2-}/l, 61 mg HCO_3^-/l) or the arid groundwater (3550 mg Cl^-/l, 960 mg SO_4^{2-}/l, 610 mg HCO_3^-/l). Calculations used are analogous to those that produce pH–Eh diagrams, and total activity of all the soluble species of a particular element are calculated for the model waters at pH = 7 and Eh = 200 mV. Activities are transformed to concentrations, which are more practical in exploration programs, using activity coefficients calculated by an extended Debye–Huckel equation.

Calculations such as those used to produce concentrations listed in Table 8-I can also demonstrate what ranges of pH and Eh cause maximum dissolution of each host mineral, and what effect increases in concentrations of each of the major anions have on levels of trace element concentration. In some cases increased anion concentrations reduce trace element concentrations due to the formation of insoluble compounds, whereas in other cases higher anion concentrations result in the formation of soluble complexes of the trace element, thereby increasing the overall concentration.

Trace elements leached from ore and associated minerals

Trace elements derived from the direct leaching of ore minerals by natural waters include major constituents of ores, such as Cu, Pb, Zn, U, Au, Ni, Co, W, S, and minor constituents commonly associated with various types of ore minerals, such as As, Sb, Bi, Cd, Ba, Mo, Mn, Be, B, Li, Cr, F and Sr. The latter group of trace elements may be useful as geochemical pathfinder elements if they are more mobile in natural waters, or more easily determined than the ore elements with which they are associated.

The application of water sampling to exploration depends upon an understanding of ore-forming mechanisms and ore-mineral associations. Since both of these commonly involve trace elements, the trace element content of water samples is in many cases a valuable indicator of proximity to an ore deposit. For example, the compositions of 5000 groundwater samples from 21 mines in a 2000 km^2 section of the Abitibi region, Quebec, showed that groundwater abundances of As, Mo, and F were indicative of base metal mineralization, and that increased levels of As, Ni, F(Cl) and Mn were related to Au mineralization (Lalonde, 1983). The study of Deering et al. (1983) in northwest Ohio, USA, also showed that groundwater abundances of F, Sr and Ba, correlate with the locations of Mississippi Valley style base metal mineralization. Exploration in ultramafic terrain demonstrates the importance of understanding the trace element content of ore mineral host rocks when using groundwaters in exploration. Ultramafic rocks can be identified by unusually enhanced concentrations of the trace elements Cr, Co, Mn, Ti and Ni in associated groundwaters. If ore grade accumulations of these trace elements occur in an ultramafic terrain, groundwater concentrations would have to be high enough to contrast against background values if the mineralization is to be identified.

Interpretation of natural water trace element abundances

In geochemical exploration drainage programs based on water sampling of areas that are unrelated to known ore deposits, it is essential to distinguish sources for any ore elements identified in the natural waters. One discrimination test is based upon observations that trace elements leached from rock forming silicate minerals are accompanied by other elements which were also part of the host mineral. Because Zn can substitute for Mg in ferromagnesian minerals, the extent to which Zn^{2+} is leached from these minerals directly relates to the release of Mg^{2+} from the same source. In practice, the best indicator that Zn solutes are derived from silicates is a strong correlation between concentrations of Zn^{2+} and abundance ratios of Mg^{2+}/Ca^{2+} in a set of groundwater samples (Fig. 8-17; Giblin, unpublished data). The basis of this relationship is probably the positive correlation between Zn^{2+} and Mg^{2+} leached from similar silicate lattice sites, associated with a negative correlation between Zn^{2+} and Ca^{2+} which occupy different silicate lattice sites because of the dissimilarity of their ionic radii.

Because U and F are both hosted by apatites and biotites, U is leached proportionately with F from felsic igneous rocks. Fig. 8-18 illustrates a sample set of groundwaters in which U abundances clearly relate to F concentrations, indicating the likelihood of a common source for the two elements (Giblin, 1987). At Olympic Dam, fluorite is associated with U ores and moderately high F levels (~ 3.5 mg/l) are present in associated groundwaters. Nevertheless because U and F are not constituents of the same mineral phase, no correlation is found between U and F abundances in Olympic Dam groundwaters (Giblin, unpublished data).

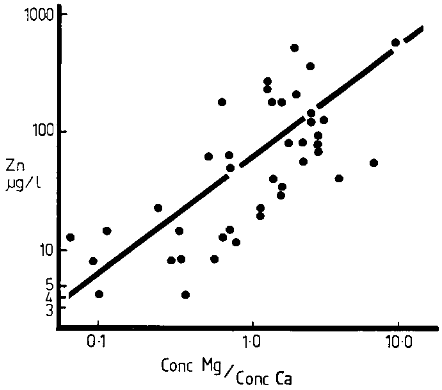

Fig. 8-17. Correlation between dissolved Zn^{2+} and abundance ratios of Mg^{2+}/Ca^{2+} in a set of groundwaters suggests that non-economic ferro-magnesian minerals are the source for the Zn^{2+}, rather than Zn ores.

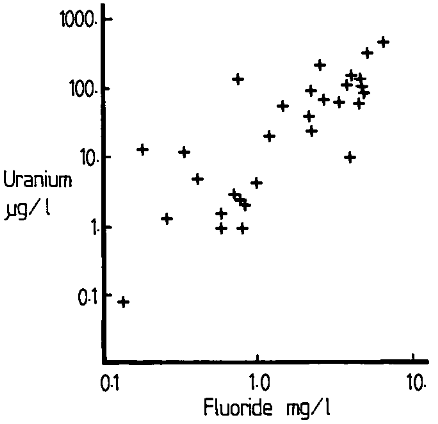

Fig. 8-18. Correlation between U and F abundances in groundwaters which co-leach these elements from felsic igneous aquifers.

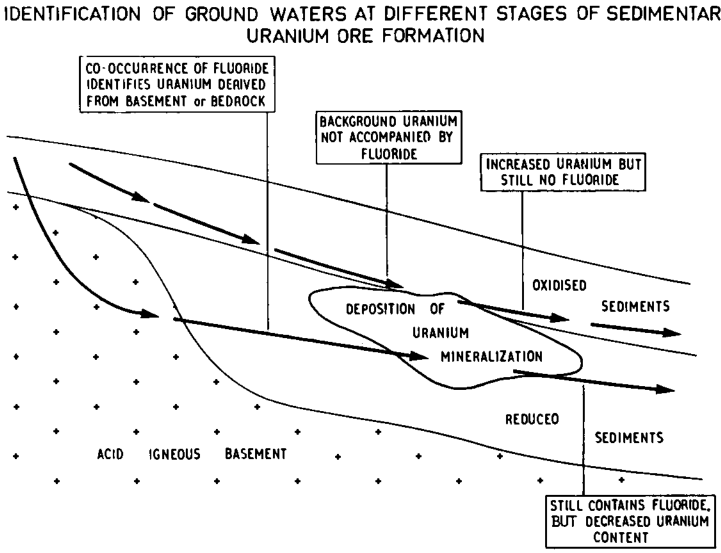

Fig. 8-19. U–F relationships at various locations in the drainage path, in waters which leach U from felsic igneous source rocks and then deposit U in a redox trap in a sedimentary basin.

In a particular exploration area variations in U : F abundance ratios in groundwaters can identify different stages of sedimentary U ore formation (Fig. 8-19). In reducing sediments U previously leached from felsic igneous rocks is deposited in a redox trap, and U : F ratios can be used to identify waters up and down flow of the deposit. Up flow of the deposit, correlation between groundwater U and F concentrations indicates a felsic igneous basement source for both elements. Down flow of the deposit a decrease in the U : F ratio

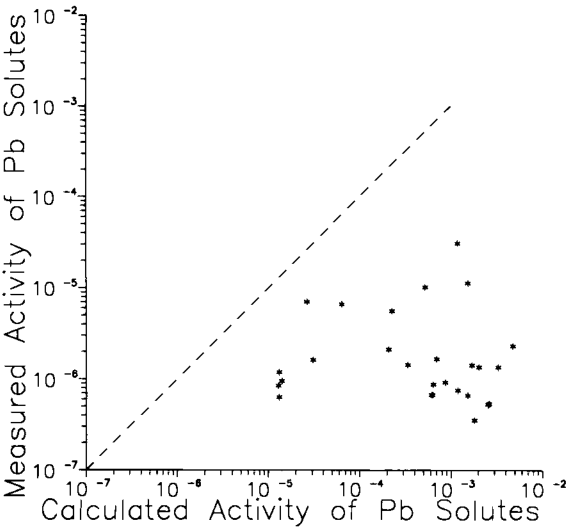

Fig. 8-20. Activity of Pb solutes (calculated from measured concentrations) in groundwaters sampled at "Prospect II" (from Giblin, 1987) compared with the theoretical activities of Pb solutes which would have been present if the groundwaters at "Prospect II" were in equilibrium with galena. The dashed line demonstrates an equivalence trend for measured versus calculated values of Pb activity. Measured values are clearly too low for galena to be the source of Pb solutes in "Prospect II" groundwaters.

demonstrates loss of U from the groundwater at the deposition site, but retention of F in solution. In oxidizing sediments, on the other hand, waters leaching the deposit are identified by increases in U concentration down flow of the deposit without any associated increase in F concentrations.

In a natural water system, the solubility of minerals, pH-redox conditions and the major element composition of the water can be used to predict concentrations of trace elements. Hence it is possible to deduce the extent to which enhanced trace element abundances in natural water derive from leaching of potential ore minerals. For example, Fig. 8-20 shows that Pb concentrations up to 27 mg/l in groundwaters in a study area in an extremely arid region in Australia, when translated into activities, are still below the theoretical activities which would be present if the waters sampled were in equilibrium with galena. Data used to calculate Fig. 8-20 are published in Giblin (1987), where the study area is described as "Prospect II". The dashed line in Fig. 8-20 demonstrates a theoretical equivalence trend for the relationship between measured and calculated values of Pb activities in groundwaters which are in contact with galena, and which have compositions as found at "Prospect II". Measured values of Pb are clearly too low for galena to be the source of the Pb solutes. Groundwaters from "Prospect II" are highly saline so that activities of all ions, including Pb are much smaller than measured concentrations.

Solubility (saturation) index (SI) calculation is a method for determining whether minerals in contact with a natural water system are precipitating or dissolving. If the system is at equilibrium and the mineral in question is stable as a solid, a solubility product (K_{sp}) has a constant value at a particular temperature and is the product of the concentrations (or more correctly the activities) of ions released from the mineral into the water. For example, dissolution of $CaSO_4$ produces Ca^{2+} and SO_4^{2-} and at equilibrium K_{sp} $CaSO_4$ = Act. Ca^{2+} × Act. SO_4^{2-}. If, however, the mineral is still precipitating or is dissolving the ion activity product (IAP analogous to K_{sp}) will be respectively greater or smaller than K_{sp}. The SI equals the ratio of IAP to K_{sp}. Values of SI equal to, or in excess of 1 imply equilibrium or over saturation, and thus preservation of the mineral, whereas values less than 1 imply dissolution or non-preservation of the mineral (if present). Since pH-redox changes control the dissolution of most ore minerals, such as sulphides, pH–Eh diagrams provide a more impressive demonstration in exploration programs of the potential stability of a target ore mineral in its aqueous environment (Fig. 8-8) than do SI calculations. In addition, pH–Eh diagrams allow assessments of waters from several locations to be compared on one diagram.

In many cases it is easier, however, to establish a range of background concentrations empirically for each element in waters with compositions typical of specific exploration regions, rather than by calculations which are restricted by a presumption of equilibrium between the waters and all relevant minerals. Different mineral sources and water compositions result in published abundance ranges which are highly variable, and data relating to one geographic or climatic region are rarely applicable to another. For example, a compilation by D. Langmuir and H.L. Barnes of data for 8000 groundwater samples held in the US Geological Survey data bank shows median values for Cu and Pb of 3 μg/l, and 20 μg/l for Zn (Rose et al., 1979). The same reference contains data from groundwaters in the USSR that are consistent with the USGS data. In contrast, a set of groundwaters from an inland region of Australia, where topography and climatic conditions are markedly different from those over most of the USA and USSR, has median abundance values of 15 μg/l for Cu, 100 μg/l for Zn, and limited data for Pb suggest a median of <3 μg/l (Giblin, unpublished data). Similarly, Benson and Leach (1979), describing U transport into a drainage terminus in California (Lake Walker), report only a tenfold increase in U in solution from the input flow of 14 μg/l U to 130 μg/l U within the lake. In similar studies in Australia, concentrations of U which exceed 10 mg/l have been recorded in ponded groundwaters in regions where the U content of inflowing groundwaters is in the range of 10–100 μg/l U (Giblin, unpublished company reports).

Two variables which directly affect interpretation of natural water trace element abundances are total dissolved solids (TDS) and the concentration of dissolved organic matter (DOM). If the source of a dissolved trace element is background levels in silicate minerals, it will be leached from those minerals at more or less the same rate as the major elements, and the trace element concentration in the water will correlate with the total of leached elements or TDS. Figure 8-21 illustrates the correlation between U and TDS in a collection

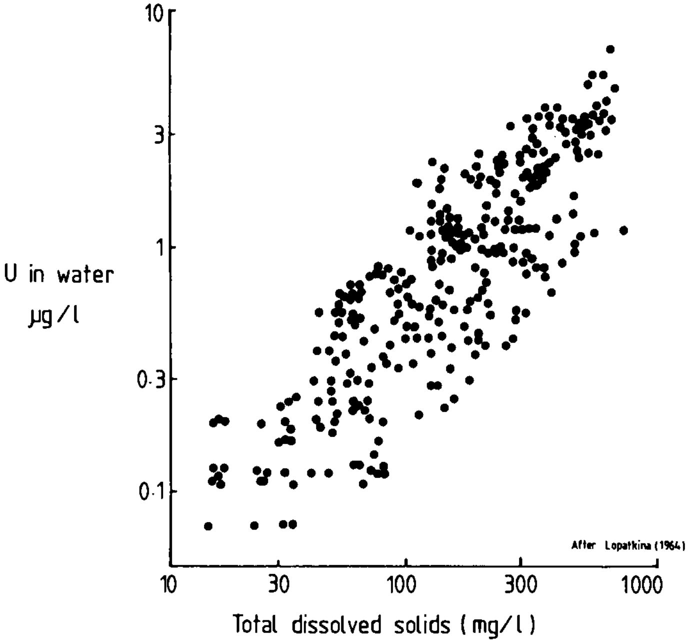

Fig. 8-21. Correlation between U concentrations and total dissolved solids in surface waters from the USSR (reproduced with permission from Lopatkina, 1964).

of surface waters from the former USSR (Lopatkina, 1964; Rose et al., 1979). To identify a water sample in this set which derives from U mineralization, its U concentration would have to be either significantly higher or significantly lower than the U : TDS trend. In general, if apparently anomalous trace elements concentrations in a set of natural waters vary directly with TDS, then it is reasonable to assume a non-economic source for the trace element solutes.

Similarly, apparent trace element anomalies can occur in natural waters due to complexing of trace elements by DOM. These are identified by correlations between trace element abundances and concentrations of DOM, indicating that apparently anomalous trace element concentrations are merely background levels which have been enhanced due to their persistence in solution as DOM complexes. Lee and Jonasson (1983) demonstrate the implication of the effects of DOM complexation of Ni, Co and Cu in hydrogeochemical exploration procedures in Canada and recommend caution in the interpretation of water borne trace element anomalies without consideration of the local effects of DOM.

On the other hand, DOM complexing of sparingly soluble elements, such as Au, may enhance the natural water abundances of such elements into the range of analytical detection. Indeed, Au has such very low background concentrations in rock forming minerals and such low aqueous solubility that even DOM complexing will not produce easily detectable Au concentrations in natural waters unless discrete Au mineralization occurs in the drainage system.

Isotopic variation in natural waters

A degree of natural isotopic variation is inherent in many elements which constitute and are dissolved in natural water. The variation arises from the different chemical, physical and biochemical behaviour of isotopes of the same element resulting from differences in their atomic weights. Isotopic ratios of H and O in natural waters are initially determined by the isotopic ratios of local rainwater. Subsequently interactions with bedrock and the mixing of waters from different sources can introduce variability into isotopic ratios. Sources such as surface water, seawater, or fossil water trapped in marine sediments, together with various secondary processes which occur beneath the water table, systematically alter isotopic ratios of H and O (Fig. 8-22). Information regarding a water's previous rock associations may therefore be obtained from a study of variations in the water's H and O isotopic abundances. This has value when using groundwaters in exploration as it assists in sorting groundwater samples into aquifer groups.

In specific geological provinces, variations in the isotopic ratios of Pb and Sr constitute unique geochemical halos in the environment of particular types of ore mineralization. Measurement of these ratios during case history studies is used to establish an empirical range for these parameters, which is indicative of that particular type of ore. Gulson (1986) has measured Pb isotopic ratios in groundwaters which are associated with the locations of previously identified exploration anomalies, and demonstrates the value of this additional information to exploration programs. McNutt (1987), in a review of Sr isotopic data for saline groundwaters from the Canadian Shield, shows that Sr isotopic ratios in groundwaters directly reflect rock isotopic ratios. A Sr isotopic ratio identified as typical for a style of ore deposit will be then be identifiable from associated natural waters.

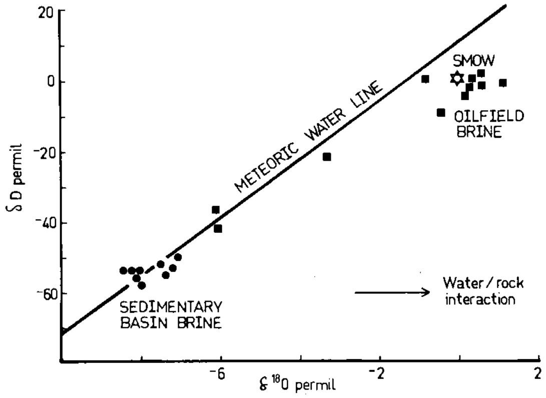

Fig. 8-22. Correlation between H and O isotopes (^{2}H or Deuterium D and ^{18}O) in groundwaters which have a meteoric source. Deviations from this line can indicate history of the water since reaching the ground surface, and other contributory sources of H and O (from Fritz and Frape, 1982). SMOW is an average ocean water.

Measurements can be made in natural waters of Ra isotopes, most often ^{226}Ra and ^{228}Ra, which, as daughters of U and Th respectively, suggest that the water has come into contact with the parent elements. Whether or not the U and Th were derived from ore minerals or are from rock forming minerals requires careful interpretation (Bloch and Key, 1981; King et al., 1982; Dickson, 1985). In many cases local soil accumulations of Ra (identified by air-borne or surface radiometrics) occur because Ra is complexed or adsorbed in organic rich clays associated with the natural water, or is incorporated into evaporitic gypsum or diagenetic barite. The parent elements, U and Th may have no physical association with the location of the radiometric anomaly, Ra having been transported there in solution after its release from parent elements. Dickson et al. (1987) shows how to use Ra concentrations in groundwaters to assess the economic significance of Ra sourced radiometric anomalies.

PRACTICAL CONSIDERATIONS

Procedures for sampling and analysis of natural waters in an exploration program can be as complex and sophisticated as is warranted by the subtlety of anomaly definition needed in the specific program. In all cases, however, definition of a geochemical anomaly requires standardized procedures for handling samples. Since standardization of procedures is inversely related to their degree of complexity, methods should be simple, robust and not easily distorted by commonly experienced difficulties in the field or analytical laboratory. Such methods will produce useful exploration data at costs comparable to other exploration methods.

Sample collection

Sample sites

In regional exploration programs natural water sample sites can be specifically selected only if the area is one in which the cost of drilling to the water table is allowable within the exploration budget. Generally, locations of surface drainage systems, lakes, stock bores, wells, exploration drill holes or natural springs control the selection of sample sites in regional programs. Samples from different sources will not be comparable directly with each other and differences in sample type should be recorded, as these differences are considered during data interpretation. For example, exploration drill holes may include water from much deeper aquifers than stock bores and wells which utilize aquifers containing groundwaters with the lowest solute levels available. If samples can be collected within a restricted area of pattern drilling, systematic sampling is possible, and a greater degree of statistical interpretation of data is warranted than in regional programs in which data sources are clearly heterogeneous.

Even if all samples derive from a single aquifer, differences in composition will still be evident because the chemical composition of any large body of groundwater will vary from place to place due to chemical interactions with rocks and inputs of waters from other sources. In exploration these variations could be the very information which could lead to the discovery of a new ore deposit. Nevertheless, if the exploration program requires it, some degree of homogeneity may be achieved by preliminary pumping from a groundwater sampling point before sample collection. If the groundwater body is large this could be a very expensive process, as it would be pointless unless continued until constant groundwater compositions were achieved. In many instances in arid regions, groundwater movement is very slow, and recharge times are too long for preliminary pumping to be practical. Standardization of pumping procedures between equipment and operators might also be a problem. The compositions of natural waters will also vary with climate and season, the effects of seasonal variations being more pronounced in areas of high rainfall. All data in a moderate to tropical rainfall area, for a specific program, should be collected over as short a period as possible, during one particular season.

Sample collection methods

To maintain simplicity in exploration procedures, samples in general are neither filtered nor acidified in the field, and bottles used are new and only prewashed with the water sample itself. These procedures would not be suitable for research programs as there is no doubt that trace element concentrations in natural water samples do change on storage in sample bottles. These changes can be inhibited by field filtration at 0.45 μm, followed by acidification with metal-free HNO_3 to pH < 1.6. However in an exploration program, there are other considerations, as follows.

(1) Trace elements which are mobile at near neutral pH values in natural waters are the most useful indicators of proximity to an ore deposit. Cameron (1978) records insignificant differences, after several months, in Zn and Cu contents of lake water samples, between those which were filtered and acidified, and those which were untreated.

(2) If less mobile elements, such as Pb, are present in a particular sample, then either the water is already naturally acid, or it contains a high concentration of complexing anions which are mobilizing the trace element. In both cases acidification is unnecessary.

(3) "No" field treatment of samples is the only truly standard procedure which eliminates operator variability and other possibilities of contamination.

(4) Experience from completed exploration programs (for example, Cameron, 1978) has shown that pre-washing new linear polythene sample bottles with the water sample is adequate container preparation. Cameron (1978) does, however, recommend testing of representative samples of each batch of containers for possible contaminants, in particular for Zn.

It is recommended that laboratory filtering of part of the sample at 0.45 μm, followed by acidification with metal-free HNO_3 of the filtrate be carried out in the laboratory as soon after collection as possible. The major hazard in field acidification is when it is applied to improperly filtered samples. False anomalies may result due to dissolution of trace elements from mineral grains.

An argument can be made for more complex sample treatment in specialized follow-up studies; for example, with samples with low solute concentrations in which trace element levels might be lowered below detection limit by adsorption onto the bottle walls. In these cases some form of field preconcentration is required, such as the addition of an appropriate trace element complexing agent to a measured volume of sample (for example, 100 ml), followed by collection of trace element complexes on a solid phase column, such as C18 bonded silica gel cartridges. Subsequent elution in the laboratory of the trace elements into a lesser volume provides preconcentration of the trace element resulting in a proportionately lower analytical detection limit. Watanabe et al. (1981) describe the application of this procedure to the determination of trace elements in seawater. A procedure in use in the Australian CSIRO, Division of Exploration and Mining, uses sachets of activated carbon to preconcentrate Au from 1 litre water samples. A 1000 times reduction in the analytical detection limit for Au is achieved by using neutron activation analysis of the charcoal.

Groundwater samples are usually collected with a chemically inert tube sampler which has one-way flow valves. One-way valves allow water to flow through the tube as it is lowered down a sampling hole, but prevent water leaving the tube when the sample is returned to the ground surface. The water collected is a sample from the lowest depth reached by the tube. Calibrated survey cable wound onto a hand held reel is used to suspend the sampler and to measure the depth to standing water and the sample depth. A standard sample depth of 5 m below the water table provides samples unaffected by atmospheric contact. If a pump (wind or diesel powered) is fitted to a bore or well that is to be sampled, flowing water is collected. At all sites two 500 ml samples are collected; one for immediate field measurements and for rinsing the sample bottle, the other for subsequent laboratory analyses.

Chemical analysis of water samples

Field analyses

Some properties of natural waters change rapidly after a sample has been removed from the water body it represents. Unstable properties of interest in exploration programs are pH, Eh, reduced iron (Fe^{2+}) and temperature. In situ measurements are the ideal solution to this problem. Whereas suitable probes are commercially available for measurements of pH, Eh, temperature and salinity in surface waters, similar measurement in groundwaters require slimline probes, connected by tens of metres of cables to the instruments which record the readings. Although electronic difficulties with this system are now largely solved, appropriate devices are not yet commercially available and measurements of unstable properties are made on groundwater samples in the field immediately after collection.

Salinity, measured as "conductivity", although not an unstable water property, is useful to know in the field as it provides a field classification of samples into those that may have the same source, compared with others that are completely different.

Field measurement of Fe^{2+} is performed on a 10 ml (filtered if not clear of suspended matter) sample of water to which is added 1 ml of 0.2% aqueous solution of 2-2′ Diquinolyl. This reagent promotes a distinctive red coloration to the water if Fe^{2+} is present. The depth of colour is directly related to the solution concentration of Fe^{2+} using field colorimeter or visual comparison with prepared standards.

Laboratory analyses

The following analytical regime is that which is used successfully in the Australian CSIRO, Division of Exploration and Mining laboratories. Samples for analyses of major and trace constituents are returned to the laboratory where a portion is filtered through a 0.45 μm filter and acidified (10 ml/l) with high purity concentrated HNO_3. The acidified samples are analyzed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) for the major elements Ca, Mg, Na and K, and trace elements Al, Si, Fe, Mn, P, Ti, B, Ba, Be, Li, Sc, Sr, V and Zn. The acidified samples are also analyzed for Sb, Bi, W, Ag, Co, Cr, La, Mo, Ni, Rb, Cs, Tl, Cu, Pb, U, Th and Zr by ICP coupled with Mass Spectrometry (ICP-MS).

Using the unacidified portion of the samples, Cl^- and S are determined by ion chromatography; total carbonate (TCO_3) with a thermal conductivity analyzer; As with a hydride generator coupled with quartz tube AAS; F with an ion selective electrode using a buffer to compensate for the presence of high levels of dissolved Al, Cd and Hg.

Analytical detection limits vary between 0.1 and 20 μg/l. These limits are lower than are presently available commercially, but will probably be generally available in the near future.

CONCLUSIONS

Natural waters constitute effective sample media in certain exploration programs, particularly those where information is required about deep formations (including ore deposit host rocks) concealed beneath transported overburden and in situ weathered rocks. In such environments subsurface groundwaters are the only dispersing agents active at the present day which can be used in exploring for deeply buried targets. Natural waters also integrate the chemistry of all of the rocks in their drainage path, and their trace and major element contents are of direct geological relevance.

Surface waters may be appropriate geochemical exploration samples of lithologies upflow of a sample point in regions where high rainfall and topographic relief incorporate shallow or outcropping basement.

Surface water sample sites are governed by the location of surface drainage systems, whereas a groundwater sampling plan is controlled by the availability of sampling points such as natural springs, wells and boreholes, or exploration drill holes.

Interpretations of drainage flow path lithologies from the geochemical composition of natural waters can be applied to:

- identifying ore deposit host formations;
- deducing the suitability of particular environments for the presence of ore deposits; and
- providing information on rock or soil geochemical halos associated with particular types of ore deposits.

Sample collection, and field and laboratory analytical procedures in any program are initially those found successful in previous programs, with improvements incorporated as seems justified. Water properties measured in the field include pH, Eh, conductivity (a measure of total dissolved solids), reduced Fe and temperature. A further suite of major and trace elements can be measured in the laboratory routinely. Many of these measurements are obtained at low cost by simultaneous determination using ICP-AES and ICP-MS. Samples from strategic areas can also be subjected to more expensive measurements of relevant isotopic ratios, in particular where age and previous patterns of groundwater flow have exploration significance, and are not evident from other data.

All of the data can be compiled and the relevance and value of each parameter to exploration for the ore deposit(s) in question assessed. Methods for assessing the significance of the chemistry of natural water data include graphical presentations of major element compositions and the identification of trace element solutes typical of specific lithologies. Some identifications may be immediately obvious from the data, whereas in other cases subtle relationships may require statistical appraisal using multivariate techniques. Major element variations in natural waters can indicate host rock alteration in halos such as those around volcanogenic base metal deposits, or trace element enrichment associated with specific types of mineralisation, for example:

- Mn enrichment around major base metal mineralization;
- As enrichment around various types of gold mineralization; and
- low pH with Fe^{2+} and sulphate enrichments reflecting the secondary dispersion of sulphide mineralization around base metal deposits.

Theoretical predictions of the trace element compositions of natural waters can also be made by assuming thermodynamic equilibrium between a water and rock forming economic minerals in the flow path. A compilation of theoretical concentrations of major and trace element constituents of principal ore mineral exploration targets in waters of varying concentrations of major ions can be prepared (Table 8-I), and consulted during interpretations of whether a trace element abundance reflects the presence of ore minerals in the flow path. In practice empirical compilations of background trace element concentrations for waters in a specific exploration area may be more relevant to identification of anomalous concentrations of trace elements in a water sample.

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Chapter 9

DRAINAGE GEOCHEMISTRY IN GLACIATED TERRAIN

A. BJÖRKLUND, P. LEHMUSPELTO, R.T. OTTESEN and A. STEENFELT

INTRODUCTION

Finland, Denmark, Norway and Sweden (the countries of Fennoscandia) share a common Quaternary glacial history and include a range of different surface environments varying from deeply dissected mountain chains in western Norway to low-lying Precambrian shield areas covered by till sheets in eastern Sweden and Finland. Geochemical exploration has been carried out over the region since early this century and modern regional geochemical maps based on the collection of several different types of samples have recently been completed over northern Norway, Sweden and Finland as part of the Nordkalott project (Bölviken et al., 1986). The region is thus ideal for studying the application of geochemical exploration methods in glaciated terrain and in particular for evaluating the advantages and disadvantages of alternative sample media. The information presented should also be of assistance in developing methods of exploration suitable to similar terrains in Canada and Russia.

The early interest in geochemical exploration in Fennoscandia was, at least in part, due to a close acquaintance with the pioneering work of the Norwegian geochemist V.M. Goldschmidt and of the Soviet scientists W.J. Vernadsky and A.E. Fersman in fundamental geochemistry. Kauranne (1986) has given a comprehensive review of the development of exploration geochemistry in Finland, which closely follows that of the other Fennoscandian countries. In addition to a similar Quaternary glacial history, Finland, Norway and Sweden also have similar bedrock geology, which comprises the crystalline rocks of the Precambrian Fennoscandian Shield and Lower-Paleozoic Caledonian mountains, both of which contain metalliferous deposits. Such deposits are absent from the Mesozoic and Cainozoic sediment cover in Denmark, but are found in Precambrian and younger terrains in Greenland, which is administratively linked to Denmark. Therefore, geochemical exploration has been carried out in Greenland but not in Denmark.

The first geochemical methods to be used in mineral exploration in Fennoscandia were based on biogeochemistry (Brundin, 1939; Rankama, 1940). Subsequently, peat was tested as a sampling medium in Finland by Salmi (1955) and the application of till geochemistry was initiated by Hyvärinen (1958) and Kauranne (1958, 1959) in the 1950's. Stream-sediment geochemistry was first used in the late 1950's in Norway (Bölviken, 1967) and during the 1960's mineral stream sediments began to be used widely in mineral exploration throughout Fennoscandia. The minus 0.18 mm fraction has normally been used in routine geochemical mapping, whereas coarser fractions are collected mainly for studies of heavy minerals. In the 1970's Swedish geochemists developed an exploration technique based on decomposed organic material in streams (Brundin and Nairis, 1972) and the technique was later adopted in a slightly modified form in Finland. In Sweden the use of organic stream sediment has recently been replaced by the use of roots of Carex species as a sampling medium (Brundin et al., 1987). In 1985 Norwegian geochemists introduced sampling of overbank sediment, the material deposited during periods of abnormally high water levels, as an alternative to lake- and stream-sediment samples for regional geochemical mapping.

Although a large number of drainage-sediment samples has been collected during the past 30 years, only limited research has been done in Fennoscandian countries, and relatively few case histories have been published. A review of the use of stream sediment has been compiled by Steenfelt (1987). The following text is largely based on unpublished data and on the personal experience of the authors.

CLIMATE AND PHYSIOGRAPHY

Fennoscandia comprises an area of approximately 1 million km^2 and is located between 55° and 71° north and 5° and 32° east. It is bordered by the North Atlantic and the Arctic Oceans to the west and north, by the Baltic Sea and the eastern North Sea to the south and by the former Soviet Union to the east. The climate, especially in the west, is strongly affected by the proximity of the sea and in particular by the warm Gulf Stream of the North Atlantic, which gives rise to a relatively high precipitation of more than 2000 mm annually (Fig. 9-1) and a warmer climate than is suggested by the northern latitude. In the east the climate is dry and continental with annual precipitation below 600 mm. Mean temperatures vary from +10 to +15°C in summer to −10 to −40°C in winter.

The topography of Fennoscandia varies from the deeply eroded Precambrian Fennoscandian Shield in the east to the younger Caledonian mountain range in the west. The region can be divided into three physiographically different areas as follows: a coastal low-lying area mainly in southern Sweden and along the coasts of the Baltic Sea, the Gulf of Finland and the Gulf of Bothnia; an upland area between 100 m and 1000 m a.s.l. and; the Caledonian mountain range above 1000 m a.s.l. (Fig. 9-1).

The coastal lowland consists of two types of terrain: an area of gently undulating forested landscape (Fig. 9-2) in which the range in elevation is normally less than 50 m, and flat areas covered by glacial and postglacial lacustrine and marine sediments. Much of the lowland region of central and

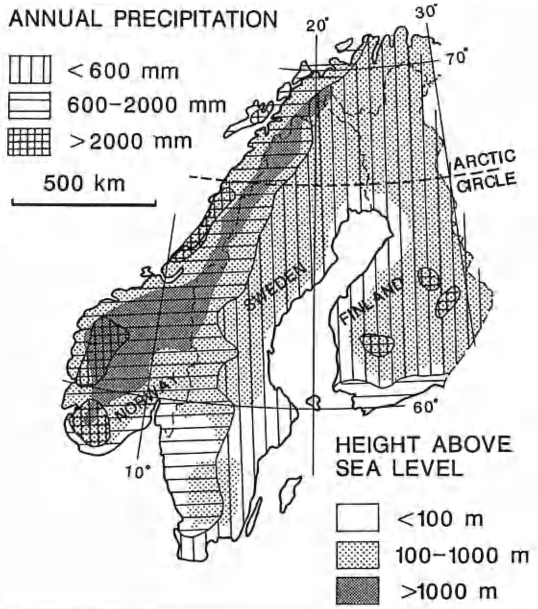


Fig. 9-1. Precipitation and elevations in Fennoscandia.

Fig. 9-2. Landscape of low relief and impeded drainage, western Finland. Photo by E. Iisalo.

Fig. 9-3. Dissected terrain, southeastern Finland. Photo by A. Hartikainen.

northern Fennoscandia is characterized by extensive peat cover and impeded drainage. In some parts landowners have carried out considerable ditching of forested areas, which has caused changes to the natural drainage pattern.

The upland region is in general more deeply dissected with a well-developed drainage pattern and with relative differences in elevation up to 200 m (Fig. 9-3). In northern Lapland smooth hills rise up to 600 m a.s.l. Large parts of the upland comprises relatively flat peneplains, however, with impeded drainage and extensive peat cover (Fig. 9-4). In southern central Finland the upland mainly comprises hilly terrain with abundant lakes.

The Caledonian mountain range of western Fennoscandia has summits rising to about 2500 m a.s.l. (Fig. 9-5). Windows of Precambrian rocks form peneplains, or "vidda", with rolling topography and few mountains (Fig. 9-6). The largest plateaus are Hardangervidda in southwestern Norway and Finnmarksvidda in northern Norway.

In Greenland there are several different types of geological and physiographical terrains. The continent is covered by an ice cap except for a coastal zone less than 200 km wide. The topography is moderate to steep with well-developed drainage systems (Fig. 9-7) except in parts of western Greenland where lowlands with numerous lakes prevail.

Most of Fennoscandia is covered with coniferous forest. Deciduous forest dominates only in southern Sweden. Greenland and northern Fennoscandia lie in the tundra zone which is characterized by bare mountains and fells and a low vegetation of birch and willow bushes in valleys and along the coast.

Fig. 9-4. Peneplain in the uplands of Finnish Lapland. Photo by M. Kontio.

Fig. 9-5. The Caledonian mountain range, central Norway. Photo by R.T. Ottesen.

Fig. 9-6. Finnmarksvidda, northern Norway. Photo by R.T. Ottesen.

GEOLOGY AND MINERAL DEPOSITS

The Fennoscandian Shield

Gaál and Gorbatschev (1987) divide the Fennoscandian Shield into three domains (Fig. 9-8) which reflect their geological history. These comprise the Archean domain in the northeast, a central early- to mid-Proterozoic Fennoscandian domain, and a late-Proterozoic Scandinavian domain in the southwest. The following summary of the geology and metallogeny of Fennoscandia is based on Vokes (1978, 1987), Frietsch (1986), and Gaál and Gorbatschev (1987).

The Archean domain comprises high-grade gneisses in the east, dominated by tonalitic to granodioritic intrusions with subordinate metasediments. The western area comprises late-Archean to early-Proterozoic greenstone belts between areas of Archean tonalites, trondhjemites, and granites (Gaál et al., 1978). The greenstone belts are dominated by volcanic rocks of tholeiitic to calc-alkaline composition, with occasional komatiites. An early-Proterozoic granulite complex (Merilainen, 1976) separates the high-grade gneiss from the granite-greenstone province and consists of high-grade flysch-type metasedimentary rocks intercalated with mafic volcanites and intruded by intermediate to ultramafic plutonic rocks. The few ore deposits which occur are associated with supracrustal rocks and late-Archean greenstones in Finland

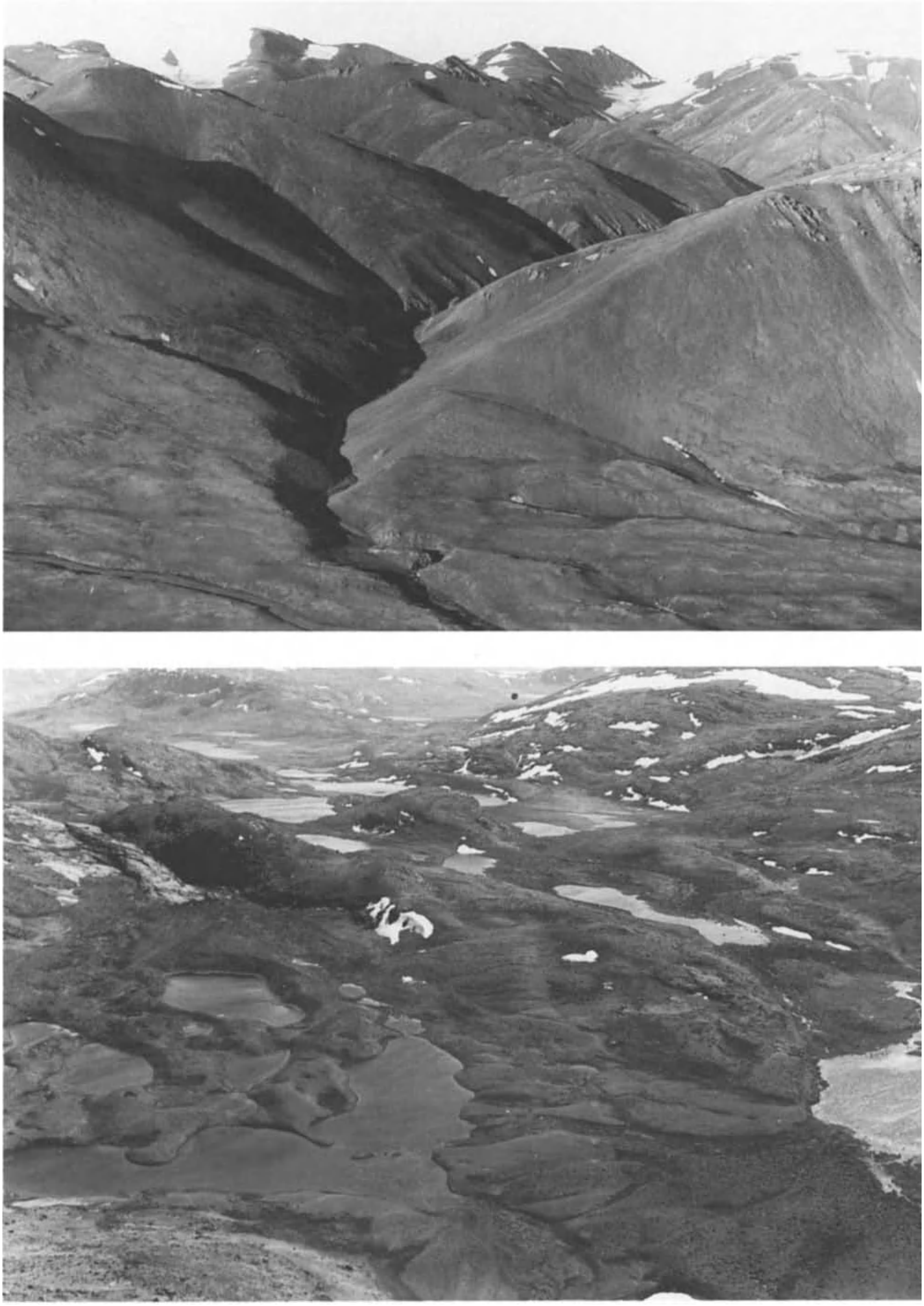


Fig. 9-7. (Top) Dissected terrain without vegetation typical of north and northeast Greenland. (Bottom) Rolling plateaus typical of southern west Greenland. Photos by A. Steenfelt.

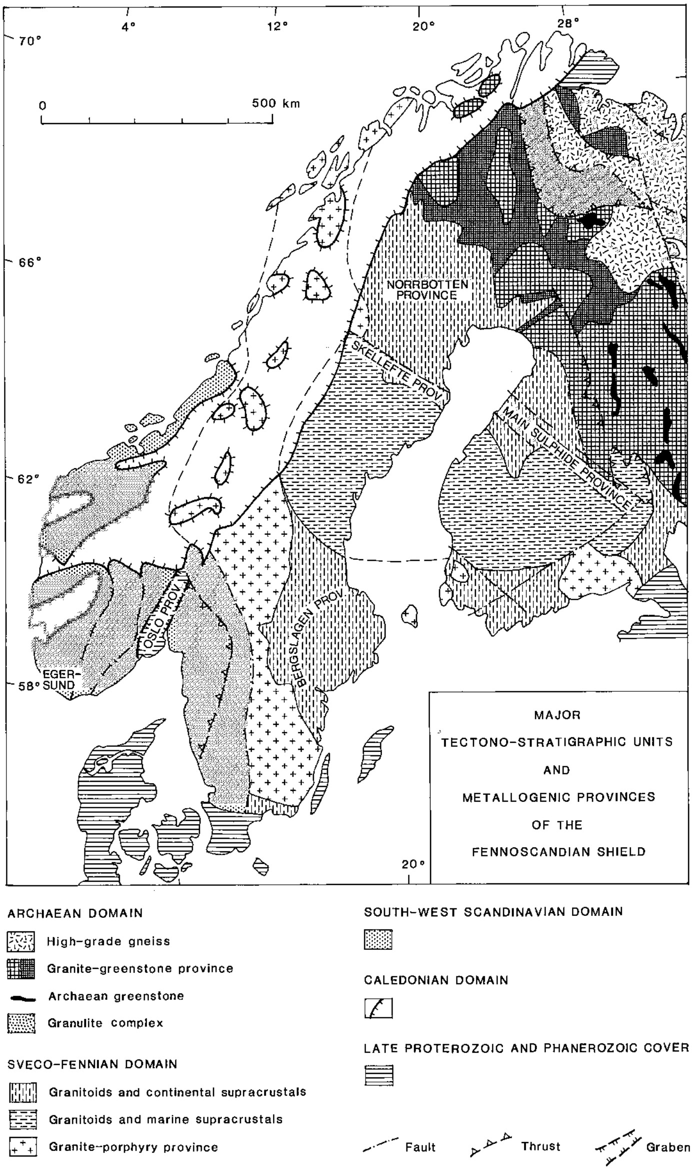


Fig. 9-8. Major tectono-stratigraphic units and metallogenic provinces of the Fennoscandian Shield (modified after Gaál and Gorbatschev, 1987).

and Norway, and contain quartz-banded iron formations and Ni–Cu deposits.

The Fennoscandian domain comprises a central province, dominated by metagreywacke and metapelite, and surrounded to the north, east and south by an arcuate zone of mainly continental and shelf sediments and calc-alkaline volcanics. Extensive areas of tonalitic to granitic plutons of early- to mid-Proterozoic age occur throughout the area. The early calc-alkaline intrusions are thought to be mantle-derived whereas the late-Svecofennian granites are assumed to be crustal (Patchett et al., 1987). The granite-porphyry province comprises felsic volcanites and intrusions of monzodiorite, monzonite and granite with pronounced syenitic trend (Lindh and Gorbatschev, 1984). The intrusive rocks give ages from 1750 to 1550 Ma (Wilson et al., 1985). The economically most important provinces in the Fennoscandian Shield occur in Lower-Proterozoic rocks of the Svecofennian domain (Fig. 9-8). In the Norrbotten province veins and disseminations of chalcopyrite with Au occur in intermediate volcanic and pyroclastic rocks and the Kirunavaara iron–apatite deposit occurs in the same region. In the Skellefte province and in the Main Sulphide Ore Zone of Finland, stratabound Cu–Zn–Pb(–Au) sulphide deposits occur in felsic-intermediate volcanic rocks. In the Bergslagen province and its possible continuation in southwestern Finland, felsic volcanic rocks host stratabound Fe, Mn and Cu–Zn–Pb(–Ag) deposits. Several deposits are also associated with Proterozoic intrusions; layered ultramafic-mafic intrusions contain Ni–Cu sulphides and V-, Ti-, Cr- and PGE-bearing oxides, whereas granites in Sweden host Cu–Mo–W–(Au)–U deposits and Sn-mineralization.

The southwest Scandinavian domain was accreted to the Fennoscandian Shield during the mid-Proterozoic and comprises medium- to high-grade ortho- and paragneisses overlain by low-grade platform-type supra-crustal rocks and mid-Proterozoic tonalites and granodiorites with sparse soda granites. The area was affected by two main episodes of metamorphism and magmatism during the late-Proterozoic. The emplacement of large volumes of granite magma was interrupted by a period characterised by the intrusion of anorogenic pyroxene-syenite, monzonite and alkali-granite complexes. Mineral deposits are restricted to granite-hosted molybdenite occurrences, polymetallic vein deposits, and norite- and anorthosite-hosted magnetite–ilmenite deposits in Egersund, southern Norway.

The Caledonides

The Caledonian domain mainly comprises Proterozoic crust reworked during the Caledonian orogeny between 600 to 400 Ma. Allochthonous nappes mainly consisting of late-Proterozoic to Palaeozoic sediments and volcanites also include a large proportion of disconnected slices of Precambrian basement. The Caledonian orogeny was accompanied by the intrusion of plutons of gabbroic to granitic composition. Ore formation was associated with the evolution of the pre-Caledonian ocean basin and Vokes (1987) distinguishes four types of ore deposits.

(1) Stratabound sulphide deposits including: disseminated to semi-massive Pb(–Zn) in late-Precambrian to lower-Cambrian sandstone; massive Cu–Zn sulphide in basaltic volcanites; and massive to disseminated Cu–Zn(–Pb) sulphides in a sequence of bimodal volcanites and sediments.

(2) Bedded sedimentary Fe and Fe–Mn oxide ores in nappes of the northern Caledonides.

(3) Magnetite ores in volcanic rocks in the central Caledonides.

(4) Deposits of Ni–Fe(–Cu) sulphides associated with syntectonic ultramafic to mafic intrusions, low-grade Mo–Cu deposits of apparent porphyry type, and Au–Ag vein-type deposits associated with Caledonian granites.

Platform sediments

Late-Proterozoic and Phanerozoic platform sediments cover southern Sweden, Denmark, and the Permian Oslo graben. Several mineral deposits occur in the Oslo Province related to the magmatism and hydrothermal activity associated with the rifting. They include endomagmatic apatite–ilmenite–magnetite ores, base metal sulphides, native Ag and Ni–Co arsenides in veins, and Mo-bearing porphyry.

GLACIAL AND POSTGLACIAL GEOLOGY

Glacial geology

The Quaternary glaciation has followed approximately the same pattern throughout Fennoscandia. The latest or Weichsel glaciation dominates the glaciogenic formations of the region but relics from older phases of glaciation have been observed. The main spreading centres of the Scandinavian ice sheet were in the Caledonian mountains and the most prominent glacial features of the topography, such as the Salpausselka marginal formation in Finland, can be followed from one country to the other (Fig. 9-9). The glacial geology is highly complex (Kujansuu, 1985; Saarnisto, 1985; Hirvas and Nenonen, 1987). The Salpausselka marginal formation in Finland is a marker in the history of the deglaciation of the last Pleistocene ice sheet. According to Hirvas and Nenonen (1987) the till stratigraphy south of the Salpausselka zone comprises two till beds with unknown age difference. The Salpausselka marginal formation depicts the outer limit of a re-advance which deposited till on varved clays and sorted sediments. The till stratigraphy north of the Salpausselka zone becomes more complicated towards the ice-divide zone in Lapland and in the Caledonian mountains. Hirvas and Nenonen (1987) describe six till beds of different age in northern Finland.

The late- and post-glacial development of the Baltic Sea is closely associated with the post-glacial geology of Finland and parts of Sweden, whereas ocean-level changes have affected the post-glacial geology of Norway and southwestern Sweden. Water-lain sediments dominate the Quaternary stratigraphy outside the Salpausselka zone and have a decreasing significance towards areas above the highest postglacial sea level. Peat-bogs cover 30% of the land area in Finland, less in Sweden and significantly less in Norway. In Finland results of

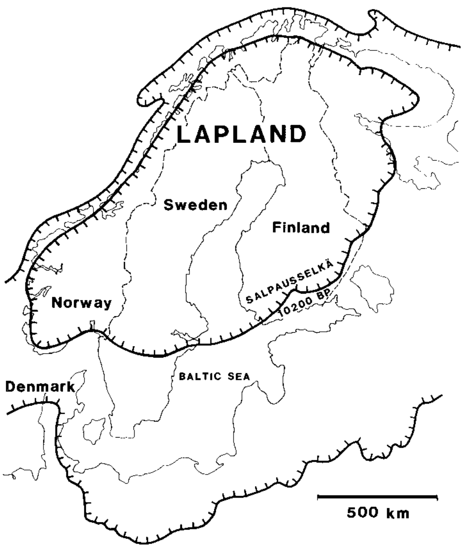


Fig. 9-9. The largest extent of the Weichsel Glaciation (compiled from data from Hirvas and Nenonen, 1987) and the position of the end moraines of the Salpausselka phase (compiled from data from Hyvärinen, 1975).

drilling give an arithmetical mean of 8.64 m, and a median value of 6.7 m for the depth of overburden. Most of this material consists of till. The figure is lower in Norway and somewhat higher in Sweden.

Soils

In general the bedrock is more widely covered with overburden over large parts of Finland and Sweden than over most of Norway. The soil has mainly formed since the last glaciation; only rarely have soil profiles from interstadial and preglacial periods survived the glacial erosion. The most frequent, fully developed soil types are podsol, brown earth and swamp soils. In addition, there are small areas of saline soils and rendzina or rendzina-like soils. In the mountains there are large regions of mountainous lithosols (Låg, 1967a, b). On the barren summits of mountains there is often a layer of frost-heaved rocks, forming a boulder field. In the mountain areas of high relief, the upper valley slopes are commonly blanketed with thick locally derived scree deposits.

Fluvial erosion

The traditional model for denudation based on supply and removal of fresh weathering products, fails to describe the overall denudation activity in Fennoscandia (Nilsson, 1972; Nordseth, 1976; Bogen, 1986). The stream sediments are derived from Quaternary deposits which commonly were transported and

TABLE 9-I

Probable types of sediment sources in Fennoscandian streams of different environments. From Nordseth, 1974; J. Bogen, pers. commun., 1980, 1982, and 1984; and Mansikkaniemi, 1982

Environment	Areal extent	Sediment Source	Representativity of stream sediment for the drainage basin
Glacier area	Minor areas	Sheet erosion (?)	Whole drainage basin reflected
High alpine region	Minor areas	Sheet erosion (?)	Whole drainage basin reflected
Alpine region (above tree limit)	Large areas	Point sources – undercutting of adjaject slopes – channel erosion in segments of streams	Parts of drainage basin reflected
Forested till areas	Dominating environmental type	Point sources – undercutting of adjacent slopes – channel erosion in segments of streams – farmfields	Parts of drainage basin reflected
Clay districts below the highest post-glacial marine limit	Small areas	Point sources – channel erosion in segments of streams – farmfields	Parts of drainage basin reflected

reworked before the fluvial processes took over. Thus, the present regional pattern for the supply of sediments closely coincides with the distribution of Quaternary deposits. The supply of particulate organic matter to streams probably depends on overburden geology. Mansikkaniemi (1975) reports that in Finland the percentage of particulate organic matter is highest in the forest-peat areas with till deposits and lowest in areas of argillaceous deposits.

True sheet erosion can be observed only during occasional heavy rainstorms. Generally the major part of the stream sediments originates from limited sources within the drainage basins. Table 9-I lists some of the sediment sources in different environments in Fennoscandia. One very important point source develops where a stream undercuts an adjacent slope containing fine-grained sediments (Fig. 9-10). Mass movement may be induced during rising water discharges (Bogen, 1980). Different types of land use, for instance intensive cultivation, also provide important point sources (Mansikkaniemi, 1982). The chemical weathering varies with the composition of the bedrock and the overburden, as well as with the atmospheric supply of corrosive components (Nilsson, 1972; Nordseth, 1974, 1976; Wright and Henriksen, 1978). In amount the dissolved load does not vary as much as the suspended load. Aqueous dispersion is most important in regions where the amount of suspended particulate matter

Fig. 9-10. A point source of stream sediments where the stream undercuts an adjacent slope. Photo by R.T. Ottesen.

is small, such as in forested till areas (Nordseth, 1976). A generalized picture of the total denudation can be obtained from the specific loss of suspended and dissolved inorganic matter in some Norwegian streams (Table 9-II).

Heavy minerals and oxides

One of the effects of selective erosion and accumulation is heavy mineral enrichment (Chapter 6, this volume; Sundborg, 1967). Not until grain sizes on a river bed are reduced to such an extent that a large portion of the grains are individual mineral particles does the process of sorting and heavy-mineral enrichment become effective (Sundborg, 1956). However, when the heavy minerals are very fine-grained and are transported in suspension together with other fine-grained particles, no pronounced enrichment takes place (Ljunggren, 1958).

Precipitated oxidates of Fe and Mn (see Chapter 5, this volume) are generally believed to be common as coatings on the surfaces of stream-bed material in shallow, rapidly flowing, well areated segments of streams (e.g., Goldschmidt, 1954; Rose et al., 1979), as local enrichments down-stream from bog areas (e.g., Nichol et al., 1967; Nowlan, 1982), and as deposits around springs or ground-water seepages (e.g., Whitney, 1981). However, there are data to indicate that these oxidates are not ubiquitous and that they show large-scale regional distribution patterns (Ottesen and Volden, 1983; Ottesen et al., 1985; Bölviken et al., 1986). None of the existing theories on the genesis of oxidates can

TABLE 9-II

Specific yield of suspended and dissolved inorganic sediments in some Norwegian streams. From Nordseth, 1976

River/year	1[a]	2[b]	3[c]
Glacial outlets			
Hellstugubreen, 1972–74	6	6700	–
Vesledalsbreen, 1967–72	4	155	–
Erdalsbreen, 1967–72	11	1442	–
Trollbergdalsbreen, 1970–72	2	3033	–
Glacial streams			
Bøyumselv, 1966	61	51	–
Suphelleelv, 1966	61	155	–
High-mountain streams			
Dirdalselv, 1969	160	5	19
Low-land streams			
Verkenselva, 1971	27	2	32
Gryta, 1971	21	5	13
Lierelv/Oppdal, 1970	223	–	31
Mønsterelv, 1970	7	450	17
Finnstadbekken, 1971	2	8	23

[a] 1 = Catchment area, km^2.
[b] 2 = Specific yield of suspended matter, tons/km^2/year.
[c] 3 = Specific yield of dissolved matter, tons/km^2/year.

satisfactorily explain the existence of continental-scale oxidate provinces. The hypothesis that methane and other gases reduce and mobilize Fe and Mn at depth in certain regions of the crust, with migration upward and oxidation and precipitation at the surface as a consequence (Malmqvist and Kristiansson, 1981), has not yet been substantiated.

Atmospheric input

Geochemists and agronomists have long recognized that the atmosphere provides a major source of input of material to the Earth's surface (Meybeck, 1983). The material transported by the atmosphere originates from the oceans, wind-blown dust, vegetation aerosol release and anthropogenic sources. The consistent coast-inland gradient of Se in overbank sediments, apparent in Fig. 9-11, indicates an atmospheric supply from the marine environment. The southern and southwestern parts of Fennoscandia receive a considerably higher input of long-range transported atmospheric pollutant from Europe than other parts of Fennoscandia. This applies in particular to Pb, Cd, As and Sb, for which the deposition rates are about tenfold the corresponding figures for more northerly parts. This results in a very pronounced regional geochemical pattern in the soils (Bölviken and Steinnes, 1987).

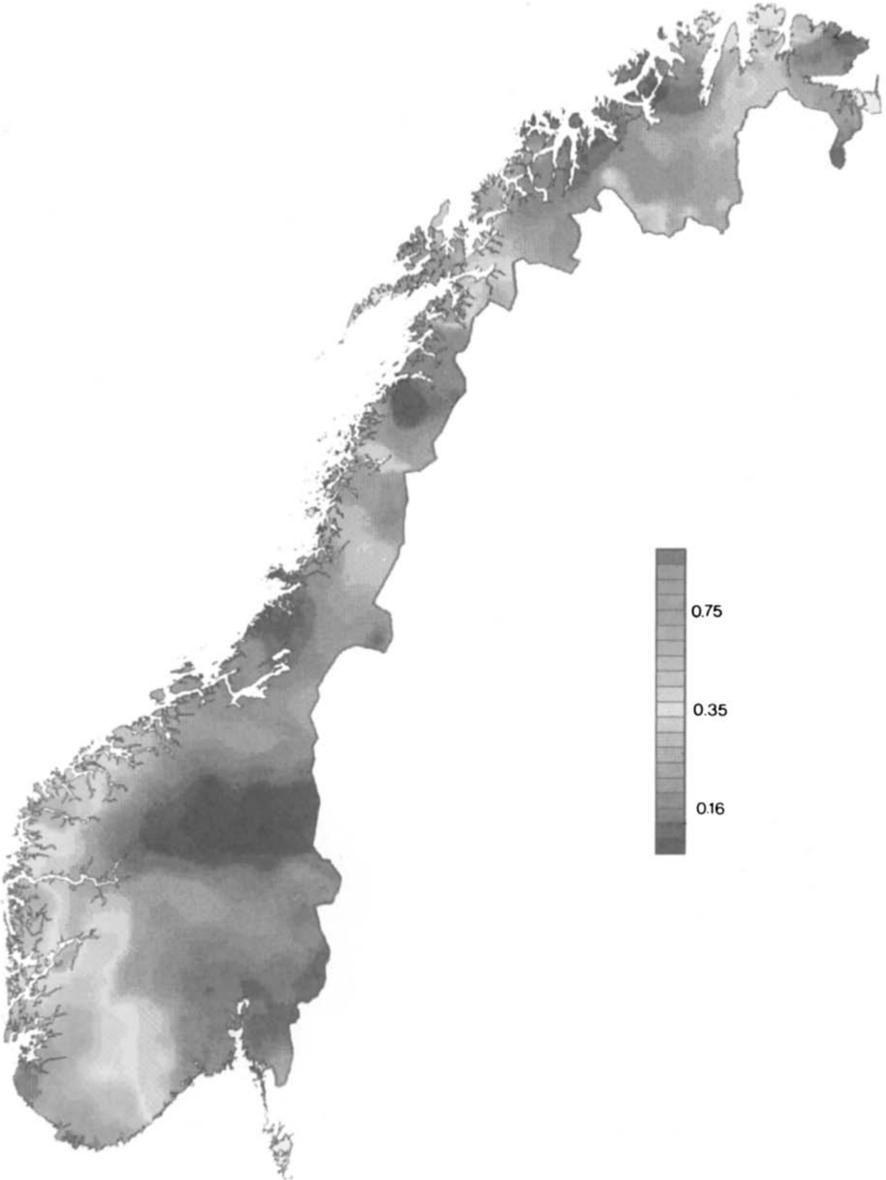


Fig. 9-11. Content of acid-soluble Se (ppm) in overbank sediments from Norway.

METHODS

Sample media

At present, five major types of sample are being collected from streams in Fennoscandia for geochemical exploration: mineral stream sediments; overbank sediments; stream organic matter (also called stream organic material, stream peat, or organic stream sediment); stream moss; and the roots of Carex species.

The term mineral stream sediment refers to unconsolidated material mainly composed of mineral grains and rock fragments with varying amounts of organic matter and oxidates. The material normally collected is active subaquatic stream sediment. Overbank sediments are deposited on the river plains above the normal stream channel during major flooding, when the water discharge exceeds the quantities that can pass through the normal river channel (bankful discharge). The thickness of layers of such sediments varies from a few millimetres to several decimetres. A vertical section through overbank sediments shows the sedimentation history, and a composite sample of such a section gives an integrated picture of the chemical and mineralogical conditions representative of the whole drainage basin over long periods of time. Samples from deeper parts of a section may reflect natural dispersion, while samples from the uppermost part may, in addition, reflect anthropogenic pollution, In some cases such material may have been subjected to soil-forming processes, however, so that its chemical composition may differ from its composition at the time it was dispersed.

Approximately 15–29% of the total sediment load of streams in Fennoscandia is of organic origin. The organic matter is a fine-grained heterogeneous mixture of plant, animal and other organic detritus in various stages of decomposition, as well as precipitated inorganic matter (Fig. 9-12). Organic stream sediments have been collected for analysis in many exploration programs throughout Finland and Sweden.

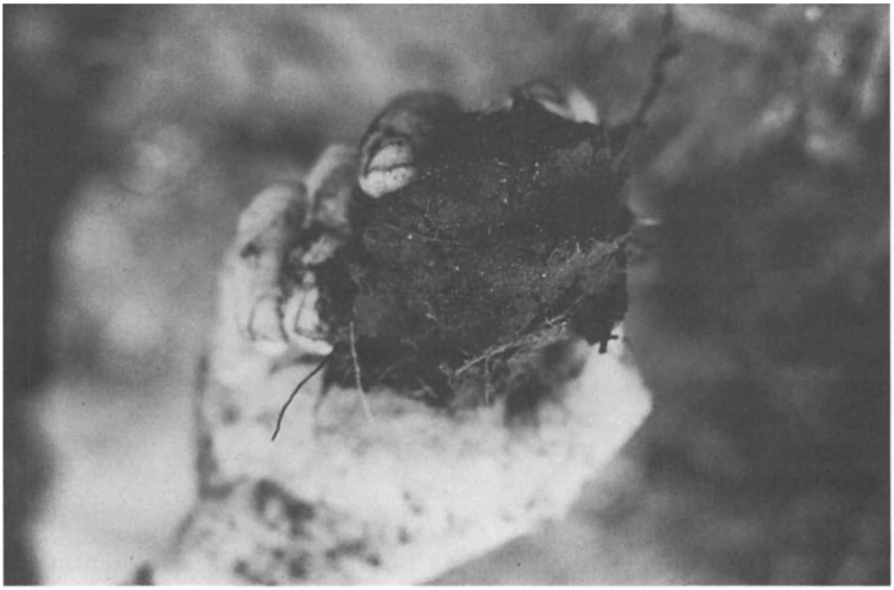


Fig. 9-12. Stream organic matter. Photo by M. Kontio.

Fig. 9-13. Aquatic bryophytes (stream moss) on washing bowl. Photo by P. Lehmuspelto.

Stream moss consisting of mixtures of various species of aquatic bryophytes (Fig. 9-13) growing on stream beds have been sampled especially in Norway. Roots of living plants from the narrow boggy areas which are normally developed on both sides of most Fennoscandian streams are commonly collected in Sweden; the species sampled are Carex juncella and Carex rostrata.

Sampling

The main stages of the sampling and sample preparation procedures are summarized in Table 9-III. Whenever possible, material is collected by hand using protective gloves. However, in the case of mineral-sediment sampling a spade or scoop is often used.

Mineral stream sediments are usually wet-sieved through 0.6 and 0.18 mm sieves in the field (Fig. 9-14). Normally only the 0.18 mm fraction is collected, but in some programs also the 0.18–0.6 mm fraction is retained.

Organic matter is available over most of Fennoscandia, providing the opportunity of acquiring homogeneous samples with only slight compositional variations. The type of samples of organic matter collected from streams differs in different organizations, however. In Finland a well-decomposed organic mud is preferred, whereas Swedish geochemists collect a less decomposed sample of peat from the stream banks. All organic samples are collected and squeezed by hand to be as dry as possible.

TABLE 9-III

The main stages of the sampling and preparation procedures for drainage samples

Material	Sampling		Preparation
	Equipment	Procedure	
Mineral stream sediment (including overbank sedim.)	Spade, sieves	Wet-sieving	Drying (dry-sieving)
Stream organic matter	Spade, gloves	Squeezing	Drying, ashing
Stream moss	Gloves, perforated washbowl	Washing	Drying, ashing
Roots	Gloves	Washing	Drying, ashing

Fig. 9-14. Sieves for wet-sieving in the field. Photo by P. Lehmuspelto.

Stream moss is collected from stones and the banks of streams. Tests indicate that there are no systematic differences between different species, but mosses below the water surface usually have metal contents twice as high as mosses on the bank above the water surface. Copper and Pb contents, however, seem to be independent of the habitat. The mosses are thoroughly washed clean of all mineral and dead organic material during sampling and are squeezed dry. The roots of Carex species, which are collected from the stream banks, are also thoroughly cleaned at the site.

To increase sample representativity, 3–20 subsamples are normally collected along a 50–100 m section of the stream and these are sued to prepare composite

TABLE 9-IV

Some examples of the number of stream-sediment samples collected in Fennoscandia and Greenland in 1978–1987

Year	Finland		Greenland	Norway	Sweden
	Geol. Surv.	Others			
1978	20400			5803	
1979	23600			4485	
1980	15000			6700	
1981	11900			4290	
1982	17600	12330	800	6200	4300
1983	13100			5990	
1984	7500			3700	
1985	2900			3391	
1986	500			1901	
1987	200	580	14	317	2500

samples. Typical sample sizes are 0.1–0.5 l of the fine fraction of mineral stream sediments, 0.5–1 l for stream organic matter and 1–2 l for stream moss and roots.

Table 9-IV shows examples of the total number of samples collected from streams in Fennoscandia and Greenland in 1978–1987. In Finland and Sweden organic sediment is the main type collected, while mainly mineral samples are collected in Norway, where the trend is to collect fewer but larger samples.

Sample preparation

Mineral sediment is normally wet-sieved in the field. After drying, sieving is occasionally done to improve the data quality. In most cases the coarse fraction (0.18–0.6 mm) is used for heavy-mineral studies and is, therefore, cleaned and separated by heavy liquids and magnetic separators. Iron and Mn oxidates are sometimes common in the coarse fraction, and are occasionally separated and analyzed.

Organic material is usually ashed in an oxidizing atmosphere for 12 hours at 500°C. The temperature is high enough to complete the ashing and low enough to prevent the volatilization of most metal compounds (Vaananen, 1979). In most cases loss on ignition (LOI) is determined.

Analysis

A number of analytical techniques are used on a routine basis in geochemical exploration, among which the most common are X-ray fluorescence, ICP emission spectrometry, optical emission spectrometry, atomic absorption spectrophotometry and neutron activation (Table 9-V). At present a clear trend is to analyze the samples for a large number of elements with several ana-

TABLE 9-V

Techniques most commonly used for analysis of drainage sediments in Fennoscandia

Location	Analytical method[a]
Finland	ICP, AAS
Greenland	XRF
Norway	ICP, AAS, XRF, NAA
Sweden	OES, XRF

[a] AAS = Atomic absorption spectrometry; ICP = ICP emission spectrometry; OES = Optical emission spectrometry; NAA = Neutron activation; XRF = X-ray fluorescence.

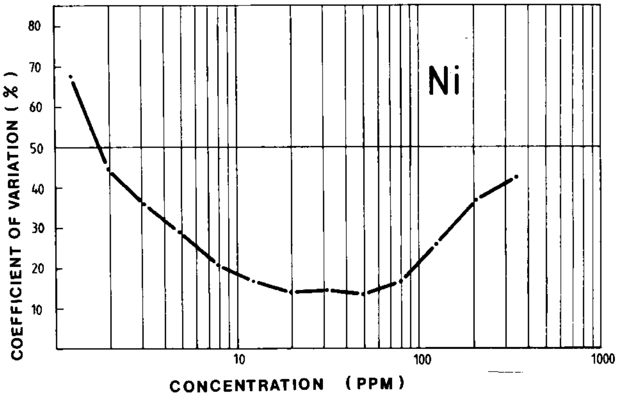


Fig. 9-15. Average total relative error for acid-soluble Ni versus the Ni concentrations.

lytical techniques. At the Geological Survey of Norway samples are analyzed in random order. Often both acid-soluble and total contents of the elements are determined. A large number of duplicate samples have been collected and analyzed for acid-soluble metals (Bölviken et al., 1983). Figure 9-15 shows the relative total error in relation to the concentrations of Ni. An example of a typical analytical program used in regional geochemical mapping is shown in Table 9-VI.

Data processing

Data processing and presentation on maps has generally followed long-established procedures used in exploration geochemistry worldwide, including classification based on standard deviations or percentiles of the frequency distribution of metal contents, with each class represented by a symbol, or in Norway by dots of increasing size with increasing contents. A modification of the Norwegian technique has recently been developed (Björklund and Gustavsson, 1987) which has largely replaced other methods.

One specialized style of data processing was adopted in Sweden after recognition of a strong correlation between Fe–Mn and several base metals in organic

TABLE 9-VI

Analytical methods used and elements determined in stream sediment samples from regional geochemical mapping in Norway

Method	Grain size (mm)	Elements	Total/Acid soluble
X-ray fluorescence	<0.18 0.18–0.6 HM *	Al,Ba,Ca,Cl,Co,Cr,Cu,Fe,K, Mg,Mn,Mo,Na,Nb,Ni,P,Pb, Rb,S,Sn,Sr,Ti,V,Y,Zn,Zr	Total
ICP emission spectrometry	<0.18	Ag,Al,Ba,Ca,Ce,Co,Cr,Cu,Fe, K,La,Li,Mg,Mn,Mo,Na, Ni,P,Pb,Sc,Ti,V,Zr,Zn	Acid soluble
Neutron activation	<0.18	As,Au,Ba,Br,Cs,Fe,La, Na,Rb,Sb,Sc,Sm,Th,U	Total

* HM = heavy mineral concentrate.

stream sediment. Brundin and Nairis (1972) showed that the spatial relation between anomalies and known mineralization was improved by the use of residuals from regression analysis. Based on this finding, the Geological Survey of Sweden has routinely performed regression analysis on heavy-metal contents of organic stream matter and has plotted maps of residuals rather than measured concentrations for a number of elements (Selinus, 1983).

SURVEY DESIGNS

The use of drainage sediments and the methods of sampling and analysis in geochemical mapping and mineral exploration have to some extent followed common lines in the different Fennoscandian countries, but there are some differences in approach and in methods applied. In part this is due to differences in physiography and extent of the glacial cover; it is also due to the fact that methods developed somewhat independently in the different countries.

Norway

In Norway, which mainly comprises the Caledonian mountain range and where strong mechanical dispersion occurs along streams, mineral stream-sediment sampling has been the principal method used in regional geochemical exploration. Sampling has been carried out at scales from one composite sample per 30 km^2 during reconnaissance to hundreds of samples per km^2 in follow-up work. In the early 1980's overbank sediment was successfully tested for regional sampling in the Oslo district (Ottesen et al., 1989) and during 1984–1985 Norway has been covered at a density of one such sample per 500 km^2. The technique is now replacing the use of mineral stream sediment at reconnaissance scale.

Soil sampling and, occasionally, sampling of bedrock and glacial drift have been done at local scales to complement and follow up the results of stream-sediment surveys.

Sweden

In areas of subdued relief and impeded drainage, typical of large parts of Sweden, erosion and mechanical dispersion in the streams is limited. Mineral sediments, even where they are present, contain varying amounts of organic compounds and limonite, which are strong metal collectors and which cause high variability of the contents of heavy metals. Stream peat was the only drainage-sediment type sampled in regional work in Sweden during the 1970's (Larsson, 1976). In the 1980's, stream peat was replaced by roots of Carex species in the streams for detection of hydromorphically dispersed elements from natural and anthropogenic sources (Selinus, 1988). Geochemistry of heavy minerals and of the fine fraction of till, as well as sampling of peat along the edges of bogs, have been the main techniques used in follow-up work.

Finland

In Finland mineral stream sediments have been used in exploration since the early 1960's (Wennervirta, 1968). Following the development of the use of organic stream matter in Sweden, this material was also included in most geochemical sampling programs in Finland. Sampling programs carried out by the Geological Survey include the collection of both types of material at every sampling site, whenever possible. The type of organic sample is, however, different from that used in Sweden, and comprises a totally decomposed organic mud from the bottom of the stream bed, normally termed an organic stream sediment. In the early 1980's the Geological Survey of Finland, in the preparatory stages of a national geochemical survey based on a sampling density of one per 4 km^2, showed that the fine fraction of till (<0.06 mm) was superior to organic and mineral stream sediment in the reliability of detecting geochemical anomalies and patterns related to geological features. Stream-sediment sampling has therefore been replaced by till sampling at densities of one composite sample per 4–300 km^2. The number of stream sediments collected in Finland had decreased from some 30,000 samples in 1982 to less than 1000 in 1987.

Greenland

Mineral stream sediment is the preferred sample medium in regional mineral exploration and geochemical mapping in Greenland, where the terrain is mountainous and the amount of overburden is limited. The Geological Survey of Greenland produces geochemical atlases at the scale of $1 : 1,000,000$ based on multielement analysis of the <0.1 mm fraction of stream sediment collected at a density of one sample per 20–50 km^2. The rate of coverage varies since sampling is tied to geological mapping programs, but it averages about 8000 km^2 per year (Steenfelt, 1987). In addition, stream sediments (supplemented by soil and, occasionally, stream moss and plants) are collected at higher density for mineral exploration purposes over small areas. Reconnaissance sampling using panned concentrates has been carried out over much of the supracrustal belts of West Greenland.

COMPARISON BETWEEN MEDIA IN LOW-DENSITY SURVEYS

In recent years exploration geochemistry has largely been applied in the Fennoscandian countries as part of multimedia, multielement and multipurpose surveys covering large regions with very low sampling density. The geochemical maps resulting from such surveys illustrate the large-scale geochemical background variation in which geochemical provinces and trends can be recognised and used together with other information to distinguish geological environments which are favourable to ore formation. At this large scale, element-distribution patterns are not sensitive to effects of glaciation (Bölviken et al., 1986).

The Nordkalott Project

The Nordkalott Project, an extensive mineral resource assessment project sponsored by the Nordic Council of Ministers, was carried out from 1980 to 1986 through co-operation between the Geological Surveys of the Fennoscandian countries. The project comprised geological, geophysical, and geochemical mapping over the northernmost 300,000 km^2 of Finland, Norway and Sweden. Composite samples of stream sediments, stream organic matter, stream moss, humus and till were collected at a density of one site per 30–50 km^2 (Bölviken et al., 1986). For some analytical methods samples were combined to give one bulk composite sample per 150 km^2. The 0.18 mm fraction and the heavy minerals of the 0.18–0.6 mm fraction were analyzed from the mineral sediments.

The geochemical atlas prepared as a result of the Nordkalott Project (Bölviken et al., 1986) provides an excellent basis for evaluating the applicability of different sample media for geochemical mapping of lithological and structural changes as well as metallogenetic provinces. The sample media and methods used are documented in Table 9-VII.

The element concentration levels obtained in the different media over the entire Nordkalott area are illustrated for several elements in Fig. 9-16. The concentration ranges for the heavy mineral concentrates of till (the 0.062–0.5 mm fraction) and stream sediment (the 0.18–0.6 mm fraction) are very similar, and a comparison of the maps of the atlas shows that these two media give almost identical spatial information. The concentration ranges for the fine fraction of stream sediment are generally lower than for the fine fraction of till and stream organic matter, but this reflects the use of partial extraction for the analysis of stream sediment, whereas total analysis was used for the two other media.

TABLE 9-VII

Analytical methods used and elements determined in the Nordkalott Project. After Bölviken et al. (1986)

Sample type	Fraction (mm)	Method[a,b]	Lab.[c]	Elements
Till	<0.062	OES,T,R	GSF	Co,Cr,Cu,K,Mg,Mn,Ni,Pb,Ti,V,Zn
	<0.062	NAA,T,C,B	TRCF	As,Au,Ba,Br,Cs,Fe,La,Na,Rb,Sb,Sc, Sm,Ta,Th,U,W
	0.062–0.50 HM[d]	XRF,T,C,B	SGAB	Al,Ba,Ca,Cl,Co,Cr,Cu,Fe,K,Mg,Mn, No,Na,Nb,Ni,P,Rb,Si,Sr,Th,Ti,V,Y, Zn,Zr
Stream sediments	<0.18	ICP,HNO_3,R	GSN	Ag,Al,Ba,Ca,Ce,Co,Cr,Cu,Fe,K,La,Li, Mg,Mn,Mo,Ni,P,Sc,Sr,V,Zn,Zr
	0.18–0.60 HM[d]	XRF,T,C,B	SGAB	Al,Ba,Ca,Cl,Cr,Cu,Fe,K,Mg,Mn,Na, Nb,Ni,P,Si,Sn,Sr,Ti,V,W,Y,Zn,Zr
Stream organic material	<0.1 Ash	XRF,T,C,B	SGAB	Al,Ba,Ca,Cl,Co,Cr,Cu,Fe,K,Mg,Mn, Mo,Na,Ni,P,Rb,S,Si,Sr,Th,Ti,U,V,Y,Zn
Stream moss	<0.1 Ash	NAA,T,C,B	TRCF	As,Au,Ba,Br,Co,Fe,La,Lu,Mo,Sb,Sc, Sm,Th,U

[a] Methods: ICP = inductively coupled argon plasma spectrometry; NAA = Neutron activation analysis; OES = Optical emission spectrometry; XRF = X-ray fluorescence.
[b] T = Totals; HNO_3 = Acid-soluble; C = Combined samples; R = Analyzed in random order; B = Analyzed in batches in order of sample number within eath batch.
[c] Laboratories: GSF = Geological Survey of Finland; GSN = Geological Survey of Norway; SGAB = Swedish Geological Company; IRCF = Technical Research Centre of Finland.
[d] HM = Heavy mineral fraction (>2.96 g/cm^3).

The element-concentration ranges for the fine fraction of till and stream organic matter are fairly similar with respect to K, Mg, Ni, P, Ba and Cr, whereas the ranges for Co, Cu, Fe, Mn and Zn in the organic matter are wider and displaced towards high concentrations. This demonstrates the effect of adsorption of some trace elements by the organic matter.

Although the measured element-concentration ranges in the fine fraction of both till and stream sediment and in the organic stream sediment display differences, the spatial distribution patterns of each element in each of the media are generally similar. By contrast, the spatial distribution of trace elements indicated by fine fraction of till and stream sediment frequently differs from that of the corresponding elements determined in heavy mineral concentrates.

Figure 9-17 illustrates how the distribution of Al, Mg and Nb in the heavy minerals of stream sediment each distinguishes one of the three major tectonostratigraphic units of the Fennoscandian Shield (see Fig. 9-8). The Al-rich province covers the Archean gneiss terrain and, in particular the granulite complex. The high Al content is attributed to the abundance of garnet, biotite

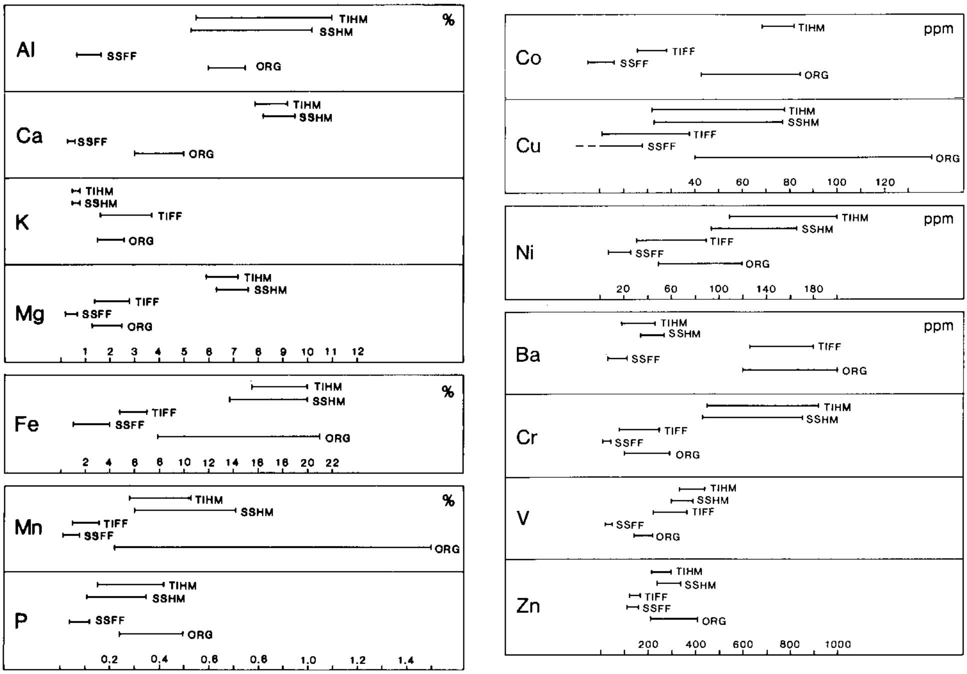


Fig. 9-16. Concentration ranges of elements in samples from the Nordkalott Project (TIHM = heavy minerals in till; SSHM = heavy minerals in stream sediments; TIFF = fine fraction of till; SSFF = fine fraction of mineral stream sediment; ORG = stream organic matter; the bars represent the interval from the 50th to the 95th percentile of the frequency distribution of the contents of the elements).

and possibly sillimanite in the amphibolite- to granulite-facies terrain. The zone of high Mg follows the granite-greenstone terrain, reflecting the presence of ferro-magnesian silicates. The elevated Nb level in the southwest reflects the abundance of Proterozoic granites enriched in incompatible elements. A Nb anomaly in the east marks the occurrence of a carbonatite complex and the slightly elevated contents in the southern Finnish area are associated with a Proterozoic granite complex in the Archean domain.

The content of Cu in three different drainage media and in till is compared in Fig. 9-18. In heavy minerals the distribution pattern of Cu is similar to that of Al in heavy minerals (see Fig. 9-17) and, therefore, Cu in heavy minerals is thought to reflect lithological units in which a Cu phase occurs mainly in amphiboles or micas. In the fine fraction of stream sediment and in the organic matter the distribution patterns of Cu are similar, although not identical, and differ from that in the heavy minerals. The high Cu contents are associated with districts of mineral deposits of Cu sulphides. The Cu patterns in the fine fraction of till appears to represent a combination of the patterns of the three types of stream sediments, suggesting that this material contains both silicate-related and sulphide-bound Cu.

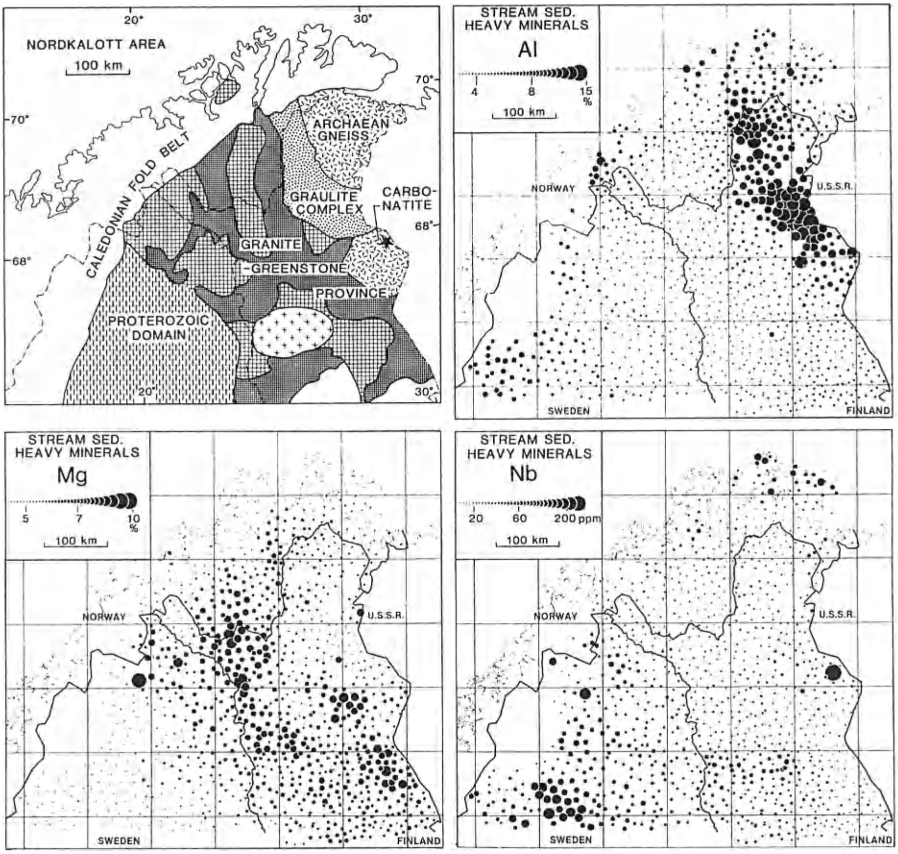


Fig. 9-17. Major tectono-stratigraphic map of the Nordkalott area (simplified from Fig. 9-8) and distribution patterns of the contents of Al, Mg and Nb in heavy minerals of stream sediment (from Bölviken et al., 1986).

Ostrobothnia, western Finland

The Geological Survey of Finland recently initiated a program to redraw maps of metal contents in mineral and organic stream sediments collected during the past 15 years using a uniform method of presentation for the whole country. This gave the opportunity of evaluating the ability of stream sediments to outline well-known ore provinces. In Figs. 9-19–9-21 maps are presented for an area in central Ostrobothnia, western Finland, which partly covers the Main Sulphide Ore Zone of Finland, and in these Ni contents in drainage sediments can be compared to those in till. The Main Sulphide Ore Zone in the northeastern part of the area is reflected by aqua-regia extractable Ni in the fine fraction of till at two sampling densities: one composite sample per 300 km^2 (Fig. 9-19, upper, small insert to the left); and one composite sample per 4 km^2 (Fig. 9-19, upper). A number of major and trace elements delineate

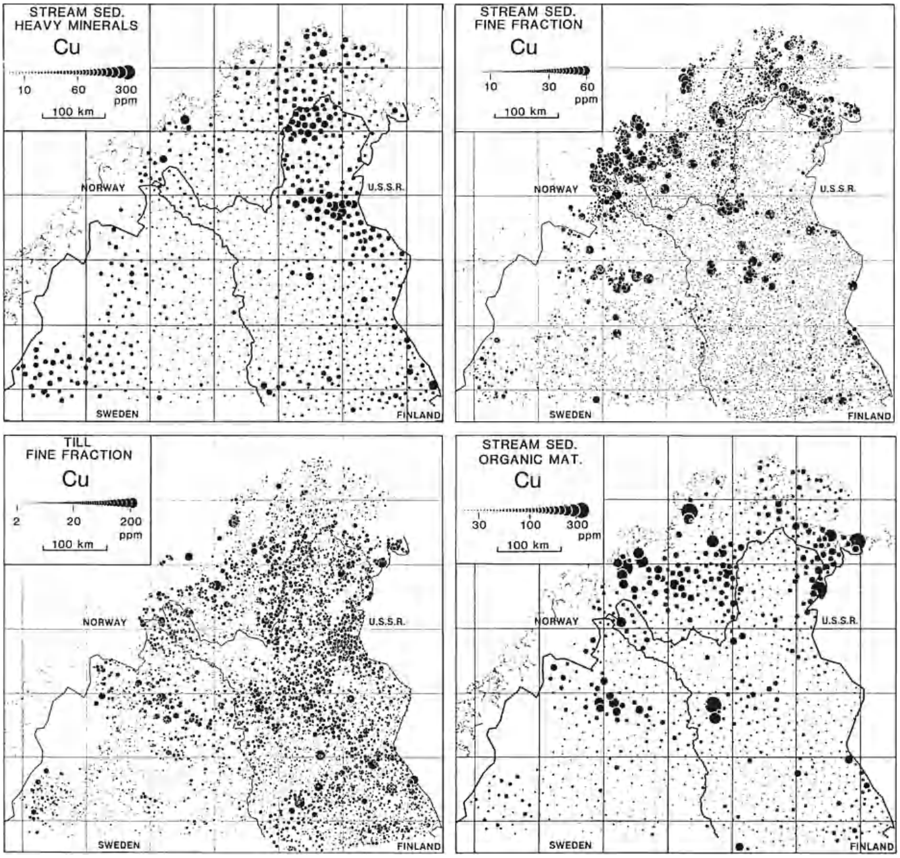


Fig. 9-18. Distribution patterns of the contents of Cu in the heavy minerals, in the fine fraction of stream sediment, in the fine fraction of till and in the ash of stream organic matter (from Bölviken et al., 1986).

the zone as well as or better than Ni. The anomaly contrast is low but the consistency of high values makes the anomaly clear. Björklund (1988) argues that such regional patterns are related to the geochemistry of crustal fluids. In the southwestern part of the zone a new prospect, which is presently being evaluated as a mine, was identified by till geochemistry.

Figures 9-20 and 9-21 illustrate that the presence of the ore zone in the northeastern corner of the area is difficult, if not impossible, to detect using the contents of aqua-regia extractable Ni in mineral or organic stream sediments, despite having a sampling density four times higher than that for till. The same is true for the other heavy metals analyzed (Cu, Co, Pb and Zn). The reason for the failure of the stream sediments to indicate the ore zone could be the modification of the low-contrast anomaly pattern by processes of the secondary environment, or it could be the failure of the analytical method used to extract an anomalous phase in the stream sediments.

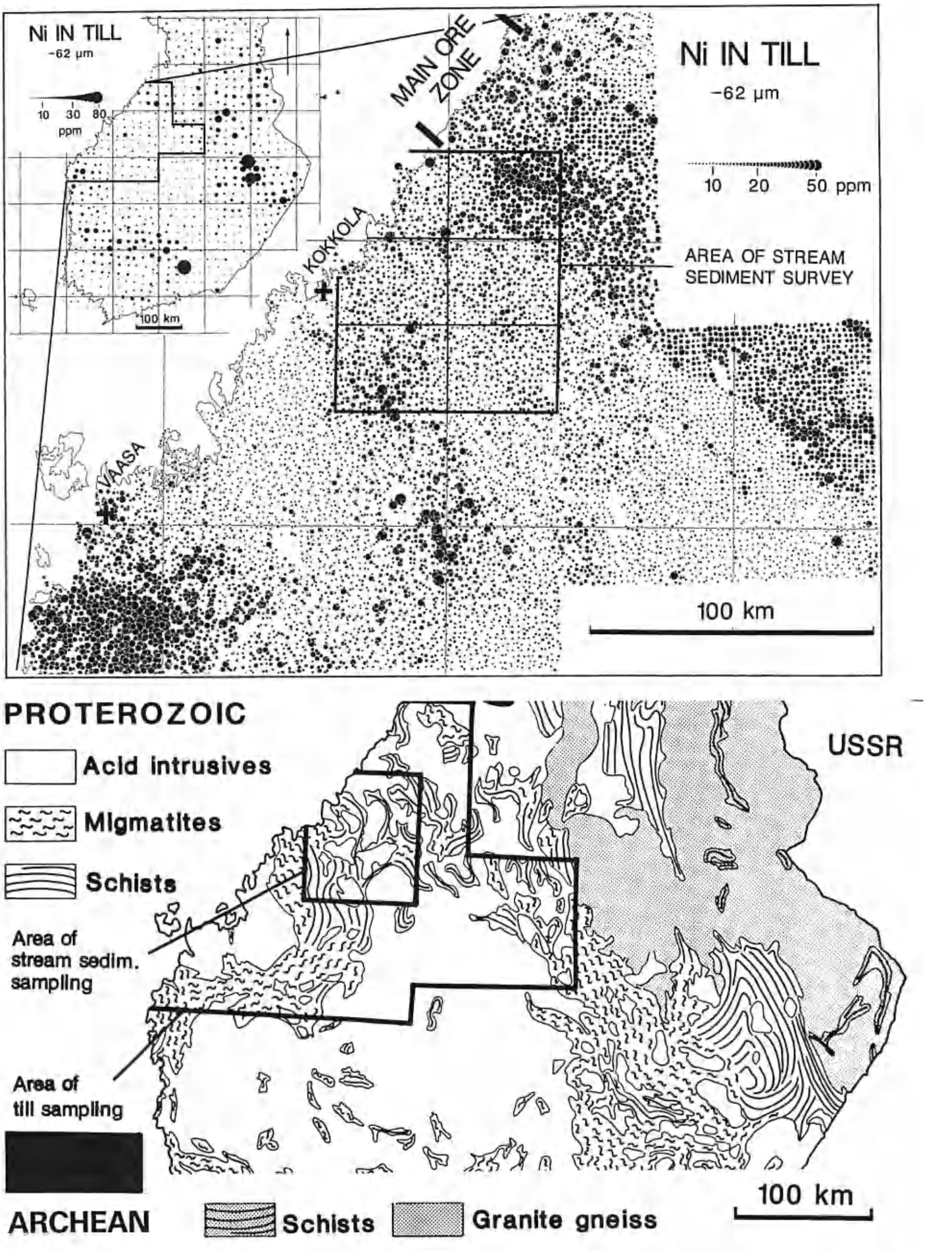


Fig. 9-19. *Lower half:* Bedrock map of southern Finland after Simonen (1980). The area of the upper half of the figure and the area of stream sediment samples of Figs. 9-20 and 9-21 are indicated. *Upper half:* The map of the Ni contents in the <0.062 mm fraction of till from the southern and central parts of the Geochemical Atlas of Finland is inserted on the left. The main map (the area is indicated in the lower half of the figure) shows the Ni contents in some 9000 till samples from Ostrobothnia. Maps from the archives of the Geological Survey of Finland.

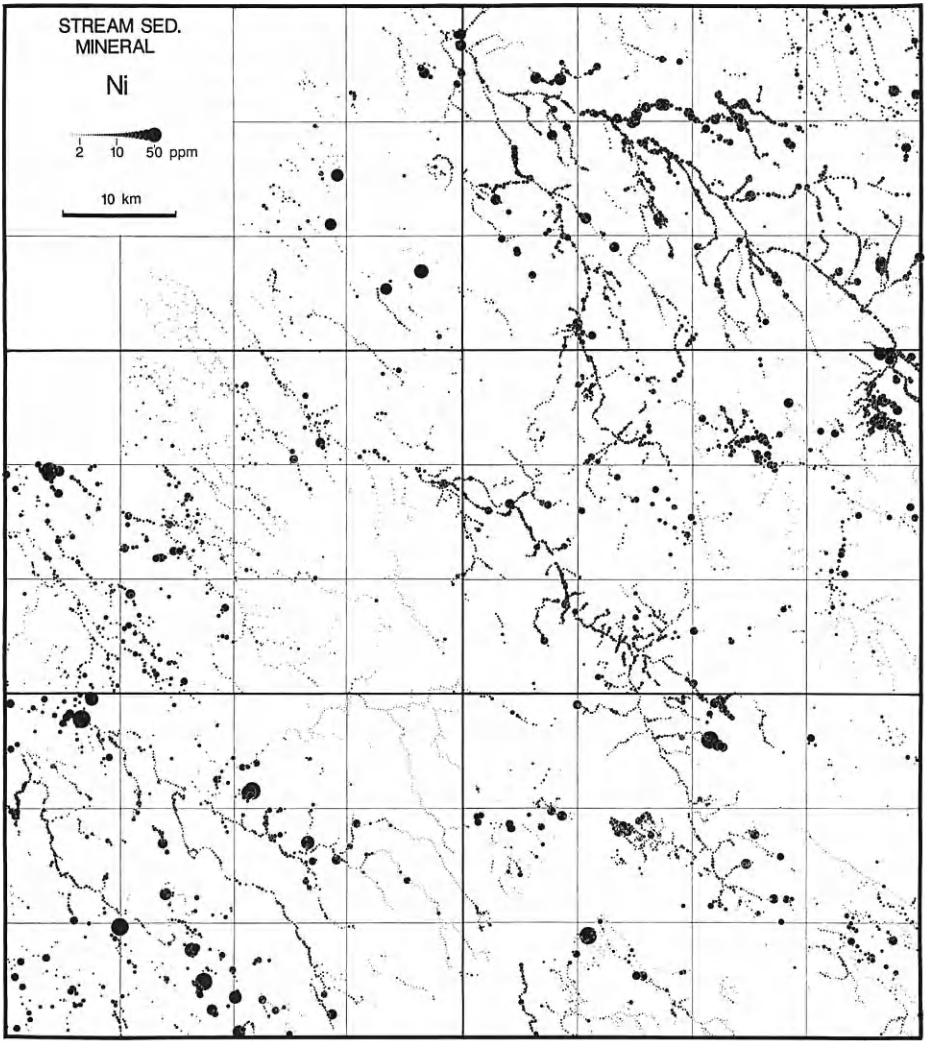


Fig. 9-20. Nickel contents in the <0.18 mm fraction of some 8000 mineral stream-sediment samples from central Ostrobothnia. The location of the area is indicated in the lower half of Fig. 9-19. Maps from the archives of the Geological Survey of Finland.

EXAMPLES OF TECHNICAL SUCCESS

In general there is a paucity of cases in Fennoscandia where the geochemistry of drainage sediments has played a major role in the discovery of mineralization, and there is no example of detection of an economic ore deposit. The highest rate of success has been achieved in Norway, where a large number of prospects have been found. In Sweden a number of uranium prospects have been located with

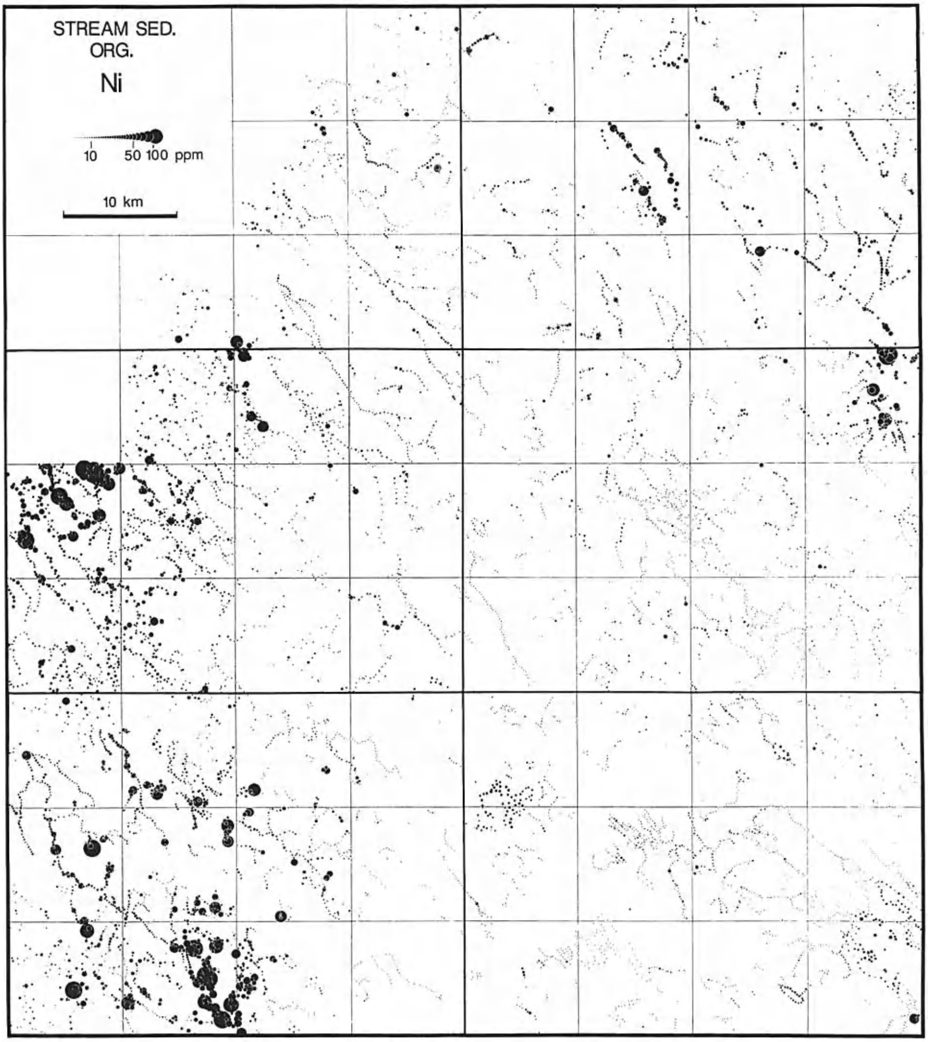


Fig. 9-21. Nickel contents in the ash of some 8000 organic stream-sediment samples from central Ostrobothnia. The location of the area is indicated in the lower half of Fig. 9-19. Maps from the archives of the Geological Survey of Finland.

drainage geochemistry, whereas the success in exploration for base metals has been minimal. In Finland the only example of the detection of mineralization using drainage geochemistry prior to the Nordkalott project was the detection of the subeconomic base-metal mineralization at Pahtavuoma, Lapland, in the 1960's. The three case histories below come from Finland and Norway.

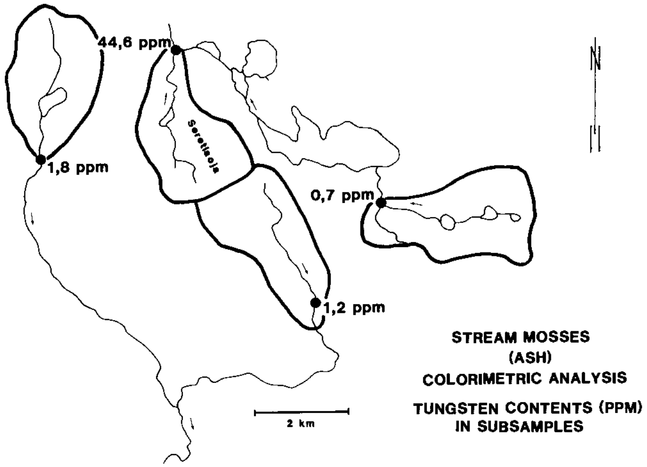


Fig. 9-22. Tungsten contents in the ash of stream moss from the Soretiapulju area, northern Finland.

Gold exploration at Soretiapulju, northern Finland

Neutron activation analysis of the ash of stream moss displayed a high anomaly of 12.8 ppm W in the Kittila area, western Finnish Lapland (Bölviken et al., 1986). The anomalous sample consisted of a composite of four original samples. In re-analysis of each sample separately, one taken from the Soretiaoja catchment area contained 44.6 ppm W, whereas the other three samples represented background values of around 1 ppm (Fig. 9-22). A follow-up study using organic stream sediment and stream moss at a density of one sample site per km^2 gave the highest W anomaly in the central part of the catchment area. Till sampling at an interval of 100 m along four profiles across the anomaly indicated W–Cu–Au-mineralization, in which Au proved to be the most important metal. Subsequent exploration discovered several mineralizations, but so far all are subeconomic (Johansson et al., 1986; Keinanen et al., 1988).

Baryte prospecting in northern Norway

The heavy mineral fraction (s.g. >2.96 g/cm^3) of stream sediment collected in the Nordkalott Project from the northern parts of the Fennoscandian Shield and the Caledonides show distinct Ba enrichment (Fig. 9-23). In a follow-up project, 400 stream-sediment samples were collected within a Ba province and the heavy mineral fraction was analyzed. Strong Ba anomaly (30% BaO) was detected in the western part of the survey area and barite was the main mineral in the heavy mineral fraction. Subsequent geological mapping and drilling located barite mineralization in bedrock.

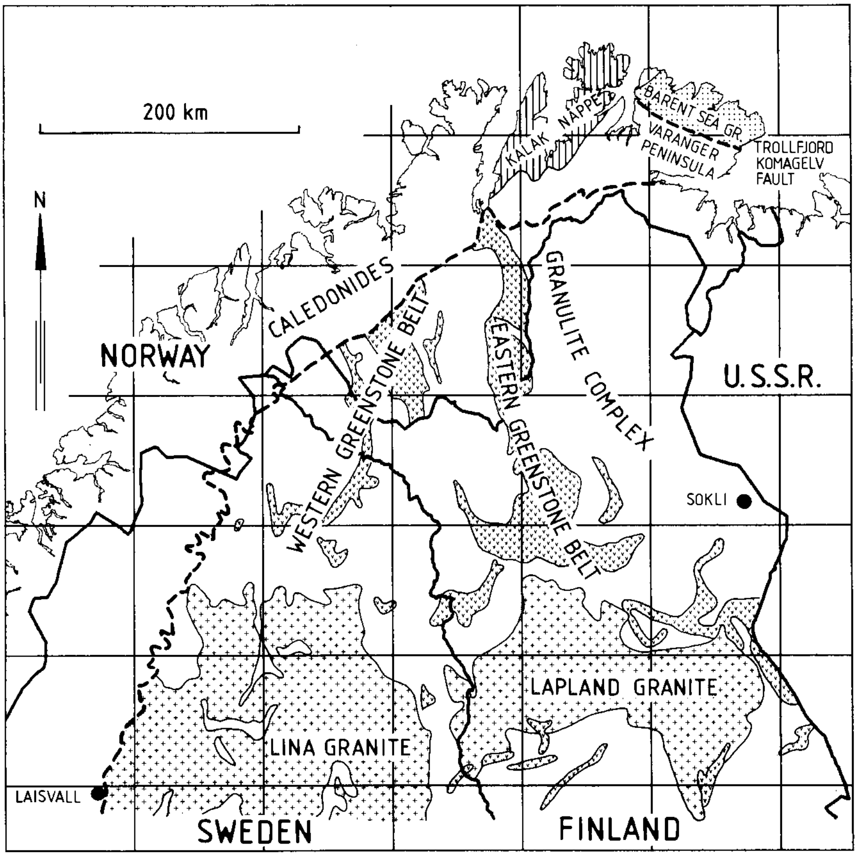


Fig. 9-23. (a) Main geological units in the northernmost part of the Nordkalott project area (from Bölviken et al., 1986).

Molybdenum prospecting in the Oslo Graben

During recent years there has been intense prospecting activity for Mo in the Oslo region, which has led to the discovery of several Mo occurrences, possibly of porphyry type.

The regional geochemical mapping programme based on stream sediment showed the existence of a large Mo province in the northern part of the Oslo graben. However, the large Nordli Mo mineralization is not reflected in the sediment samples although numerous mineralized boulders are found in the stream running across the deposit. This paradox prompted a study in which sediments, organic matter, heavy mineral concentrates and water were collected in the stream draining the Nordli mineralization and in a reference stream outside the mineralized basin. None of these sample media reflected the mineralization, although it is indicated in the geochemistry of overburden.

Studies of fluvial erosion, which were carried out in cooperation with the Nor-

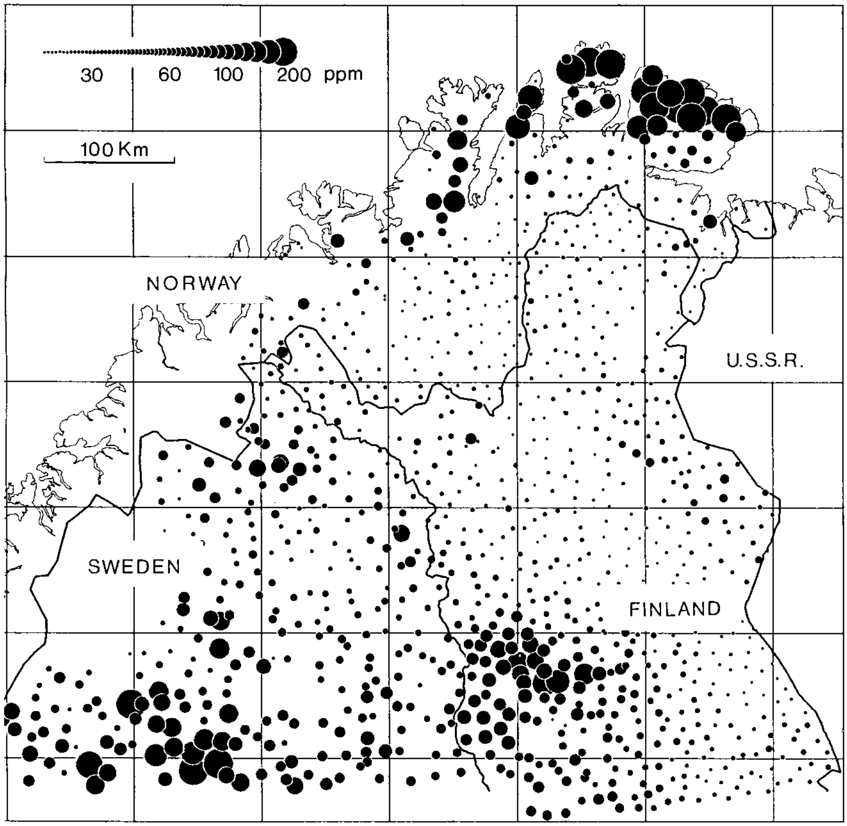


Fig. 9-23. (b) The Ba content in the heavy minerals of stream sediments in the northernmost part of the Nordkalott project area (from Bölviken et al., 1986).

wegian Water Resources and Energy Administration, concluded that present active erosion in the stream is limited by large boulders which armour the stream bed and banks. The only place where sand and silt enter the stream is upstream from the mineralization, where the overburden has a very low Mo content. Formerly, however, other sediment sources, including the mineralized areas, were actively eroded and material from these can be found in overbank sediment and in the delta where the stream enters Lake Going. The delta and overbank deposits have Mo contents 10–20 times higher than the average Mo content in Norwegian overbank sediments. Thus by understanding the erosion processes and by adopting the appropriate sample media in the drainage basin it was possible to indicate the mineralization (Ottesen et al., 1989).

CONCLUSIONS

In the mountainous parts of Norway mineral stream sediments in most cases depict the geochemistry of bedrock units and mineralized structures in a satisfactory way. However, the major part of the stream sediments originates from sources of limited extent in the drainage basin. Thus, the stream can pass mineralization without picking up material, whereby no anomaly is developed in the sediment. For this reason sampling of overbank sediments is preferred in regional surveys, whereas soil and till sampling is commonly applied at local scales.

In Greenland the topography is normally rugged with a well-developed drainage system, anthropogenic contamination is negligible, and the bedrock is generally well exposed. Low-density stream-sediment sampling has been used successfully to outline large-scale lithogeochemical patterns, including metallogenic provinces and potential ore zones (Armour-Brown et al., 1983; Steenfelt, 1987).

In the flat-lying areas of Sweden and Finland the effectiveness of stream sediment in mineral exploration is, in general, limited. However, in Sweden the use of stream organic matter has been useful in uranium exploration. The limited success in the use of stream sediment for base-metal exploration, together with a diminishing interest in uranium exploration, has led to sharp decrease of sampling of such sediment in Sweden.

In Finland experience from extensive work over the past 15 years has indicated that stream sediments do not reliably reflect regional geochemistry and, depending on the environment, may or may not reflect local sources of high metal contents. Geochemistry of the 0.06 mm fraction of till, used at reconnaissance and regional scales, has successfully outlined known and also previously unrecognized large structures with potential for Au and base metals. The present trend in Finland is towards an abandonment of drainage sediments as a sample medium and an increase in the use of the fine fraction of till at all scales of exploration for precious and base metals.

In summary, no deposit of economic importance has been discovered in the Fennoscandian countries using mineral or organic stream sediment, despite the collection of hundreds of thousands of samples over large areas. In areas of high relief and well-developed drainage systems, stream-sediment geochemistry normally delineates mineralized areas at all scales, although for regional and reconnaissance work overbank sediments are preferred. However, the geochemistry of the fine fraction of till, where present, also gives a good response. In areas of low relief and impeded drainage, the metal contents of the fine fraction of till reflect mineralization in the bedrock more reliably than metal contents in drainage sediments, especially at regional and reconnaissance scales. Therefore, the geochemistry of the fine fraction of till is increasingly being used in mineral exploration at all scales.

Drainage Geochemistry
edited by M. Hale and J.A. Plant
Handbook of Exploration Geochemistry, Vol. 6 (G.J.S. Govett, Editor)

Chapter 10

DRAINAGE GEOCHEMISTRY IN TROPICAL RAIN FOREST TERRAINS

J.D. APPLETON and J. RIDGWAY

INTRODUCTION

The term tropical rain forest was first used by Schimper (1898) to describe the evergreen forest which is the characteristic vegetation of the wet tropics. Such forests occupy, or formerly occupied, all land surfaces with a sufficiently hot climate and a sufficiently heavy and well-distributed rainfall (Richards, 1952). Excellent descriptions of tropical rain forests and their environment are given by Richards (1952) and Whitmore (1984). In this chapter the physical conditions and general geology of the rainforested regions are briefly discussed, followed by an examination of the development of their topography and drainage systems. Weathering and methods of geochemical dispersion, including a discussion of soil formation and the soil-stream sediment link, are then considered before moving on to deal with sampling media and the practical problems of working in tropical rain forest. Finally, a number of case histories are presented and some problems for future research highlighted.

Vegetation

Typical rain forest has a wide variety of plant species arranged in distinct forest tiers or layers. Trees are dominant and the canopy layer may be over 40 m high, individual trees commonly reaching over 60 m, with two lower tree layers, each having its own characteristic range of species. Below the trees is a shrub layer and finally ground plants such as herbs, ferns and mosses. Many of the taller trees have flange-buttressed trunks and are relatively slender. Climbing plants, chiefly woody lianes, and epiphytes are abundant and characteristic of the rain forests.

Mature primary rain forest is not usually difficult to penetrate because the dense upper foliage prevents much light reaching the ground, thus inhibiting plant growth. However, on river banks and in clearings, which receive more sunlight, the undergrowth can be extremely dense and almost impenetrable.

Climate

The development of tropical rain forest is favoured by uniformly high temperatures throughout the year and a plentiful supply of water. Typically daily temperatures might range between 24°C (75°F) and 32°C (90°F) averaging about 27°C (80°F), and there is little seasonal variation.

Rainfall is more variable but generally totals at least 190 cm per year and may reach over 500 cm per year in places. Variations in monthly rainfall tend to increase with distance from the equator so that in some areas distinct wet and dry seasons are produced although the dry season is merely less wet and vegetation growth continues throughout the year. Rain tends to fall in sudden downpours, sometimes with a regular pattern of afternoon thunderstorms but often with no particular rhythm. Cloud cover is an important feature of the humid tropics and plays a major part in limiting the diurnal temperature range. The wind is rarely strong in tropical rain forest areas but in some areas occasional cyclones can uproot the often shallow-rooted trees.

Distribution

The tropical rain forests form a belt, lying generally between the tropics of Cancer and Capricorn. Owing to the presence of mountain ranges and plateaux and to the irregular distribution of the controlling climatic factors the belt is not continuous, however, and rather more of the area lies in the northern than in the southern hemisphere.

There are three major zones of rain forest. The most extensive is the American rain forest, centred on the Amazon basin. The Indo-Malaysian rain forest covers the second largest area but this has been extensively disturbed by timber extraction and the development of agricultural activities. To the south and east the forest extends into the Melanesian archipelagos, Micronesia, Polynesia and northeastern Australia. The African rain forest, centred on the Congo basin and extending along the north coasts of the Gulf of Guinea, with outliers in Uganda, is the least extensive and contains the fewest species. There are a few relicts of rain forest on the east coast of Madagascar and on the islands of Mauritius, Reunion, Rodriguez and the Seychelles (Whitmore, 1984).

The boundaries of the rain forest where it extends into mountainous regions, drier and more seasonally wet climatic zones and areas where man has interfered with the natural vegetation are difficult to define, and authorities differ on the exact extent of true tropical rain forest. This chapter includes reference to regions that are not covered by tropical rain forest sensu stricto.

REGIONAL GEOLOGY AND MINERAL DEPOSITS

Approximately 40% of the area covered by tropical rain forest is underlain by Precambrian rocks and 20% by post-Palaeozoic mobile belts (Fig. 10-1). Eco-

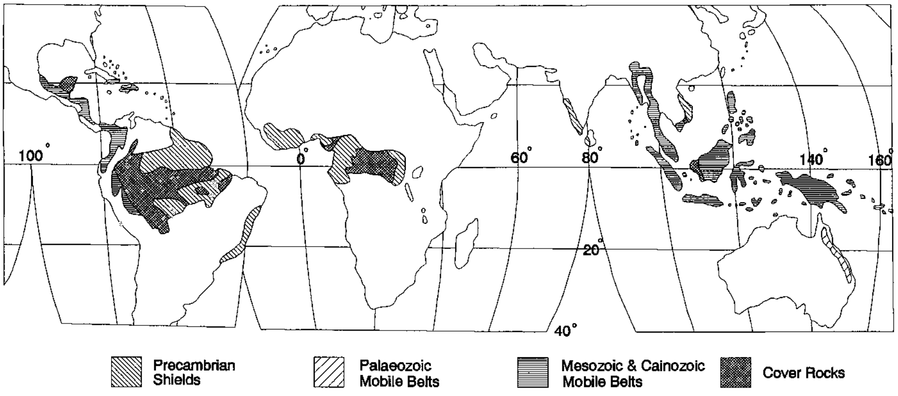


Fig. 10-1. Regional geology of tropical rain forest terrains (compiled from Dixon, 1979, Derry, 1980, and Whitmore, 1984).

nomically, porphyry copper deposits within mobile belts are the most important type of mineral deposit in tropical rain forested regions, but epithermal and other types of gold mineralization are rapidly increasing in importance. Nearly half of all exploration geochemistry case histories from tropical rain forest areas deal with porphyry copper deposits.

Precambrian shield

Within the South American continent, the Precambrian shield area of the Guyana Craton, to the north of the River Amazon, contains alluvial gold and tin, and metasedimentary iron and manganese deposits, whereas to the south, banded iron formation deposits, manganese, and copper together with alluvial gold deposits occur in the Carajas area of the Guapore Craton. In Rondonia, at the western margin of the Guapore craton, important tin and tungsten mineralization is associated with 940 Ma granite, alaskite and rhyolite intrusive complexes.

Most of the tropical rain forested regions of west and central Africa are underlain by Precambrian rocks. Mineral deposits in these regions include chromite and iron in Sierra Leone, iron and gold in Liberia and the Ivory Coast, and lode gold deposits in the Archean greenstone belt of Ghana. Gold deposits also occur in the Cameroon, Gabon, the Central African Republic and Zaire, while minor tin–tungsten mineralization is found in eastern Zaire and uranium and manganese deposits in Gabon. Kimberlites intruded into the Precambrian shield contain diamonds in the Central African Republic and Ghana.

The narrow belt of rain forest along the west coast of India is underlain by Precambrian rocks in which iron and manganese mineralization occurs.

Mesozoic, Tertiary and Quaternary sediments cover large tracts of Precambrian rocks in the Amazon and Congo basins and there are few recorded ore deposits in these areas.

Palaeozoic

Within the Palaeozoic mobile belt that underlies the thin strip of tropical rain forest in Queensland, Australia, is the Mt. Morgan copper–gold deposit, associated with 500–200 Ma intrusive plugs or volcanic pipes. In the same part of Australia, lateritic nickel deposits occur west of Townsville. In Burma, massive volcanogenic Pb, Zn, Ag, Sb sulphide mineralization occurs in late-Cambrian–early-Ordovician rhyolite meta-volcaniclastics at the Bawdwin Mine.

Younger mobile belts and island arcs

Parts of the northern Andes, Central America and the Caribbean covered by rain forest contain important porphyry copper and epigenetic gold and silver deposits. Small lead–zinc–silver deposits are located along the eastern margin of the Andes in Peru.

The Mesozoic and Cainozoic rocks of the Indonesia–New Caledonia mobile belt also contain major porphyry copper deposits including the Ok Tedi deposit in Papua New Guinea and the Panguna deposit in Bougainville. In the Philippine Islands, chromite deposits occur associated with ophiolites; copper, lead and zinc occur in volcanic massive sulphides; and porphyry copper deposits and epithermal gold and silver mineralization are associated with the younger volcanic centres. Similarly, in the Fiji Islands, Pb, Zn, Cu and Au mineralization is associated with young volcanic rocks — the gold being associated either with porphyry copper deposits or occurring in high-grade epithermal veins. Recent exploration in Papua New Guinea and the Melanesian archipelagos has also led to the discovery of several epithermal gold–silver deposits.

The important tin–tungsten deposits of Southeast Asia are associated with extensive granite intrusions in Malaysia, Thailand and Indonesia.

Recent

Recent residual mineral deposits include bauxite in Guyana, Surinam, Brazil, and the Cameroon, and secondary garnieritic nickel deposits developed over ultramafic rocks in New Caledonia, Sulawesi, Queensland (Australia) and Cuba.

GEOMORPHOLOGY AND THE DEVELOPMENT OF DRAINAGE SYSTEMS

The interplay of climate, lithology and tectonic regime gives rise to a variety of processes and landforms in the humid tropics. A useful summary is given by Chorley et al. (1984) and the following discussion draws heavily on their work.

Topography

Within areas of tropical rain forest relief varies greatly from the broad tracts of lowland of the Amazon basin, which are developed on the Precambrian rocks of the Guapore and Guyana shields and their covering sediments, to the rugged, mountainous terrain of the modern island arcs of the East Indies and southwest Pacific (Fig. 10-2).

In areas of recent tectonic activity steep slopes (often >40 degrees) rise abruptly from valley floors and are separated by knife-edge ridges which are maintained by the parallel retreat of the slopes. Douglas and Spencer (1985, p. 67) describe Papua New Guinea river beds as "narrow, mostly cut into bedrock with the river occupying nearly the entire width of the bed. Side slopes are very steep and straight and there are few lower slope concavities, as most of the debris transported to the foot of the slopes is quickly removed by the rivers. Strongly oversteepened profiles are also rare as slope processes keep pace with the rate of incision." As more mature landscapes develop rivers with a low gradient flowing through wide, flat or gently undulating lowlands are common and floodplains may be several kilometres wide. Where stream erosion is not rapid a sharp break between plains and hillslopes is common (Thomas, 1974, p. 213) even in areas of high relief.

Although the above features are characteristic of presently rain forested regions some landforms near their margins may be relicts of earlier, slightly different, climatic regimes.

Slope processes

Several factors are thought to be important in maintaining the steep forested slopes characteristic of areas of high relief in tropical rainforested terrain. Chemical weathering gives rise to a mantle of fine-grained debris even on steep, heavily vegetated slopes. The dense vegetation cover decreases the impact of rain on the ground although the thick humus layer promotes infiltration and inhibits surface run-off. Overland flow and creep and hence erosion are thus diminished and bare rock outcrops are consequently comparatively rare. Occasional catastrophic slope failures due to landslides, earthflows, soil avalanches and mudflows then steepen the slopes directly.

A number of conditions in the humid tropics are particularly favourable to slope failures where steepness has been maintained by a dense vegetation cover:

(1) The dense, shallow rooted vegetation maintains a steep slope only until the threshold of stability is exceeded. Heavy rain or earthquakes may trigger mass movement or the weight of growing vegetation itself can be sufficient to cause a landslide.

(2) The steep slopes themselves are both the effect and cause of slope failure, particularly after prolonged periods of heavy rain. Chorley et al. (1984) observed that approximately 200 slides of about 0.4 ha each occurred in an area of 39 km^2 in the basaltic Koolau Range on Oahu (Hawaii) over a period of eight years.

(3) Heavy rains, sometimes associated with tropical cyclones, increase unit mass and porewater pressure and moisten clays, leading to loss of cohesion between bedrock and weathered cover. The effects of catastrophic landslides and mudflows are illustrated by the huge fossil mudflow of the Kaugel Valley,

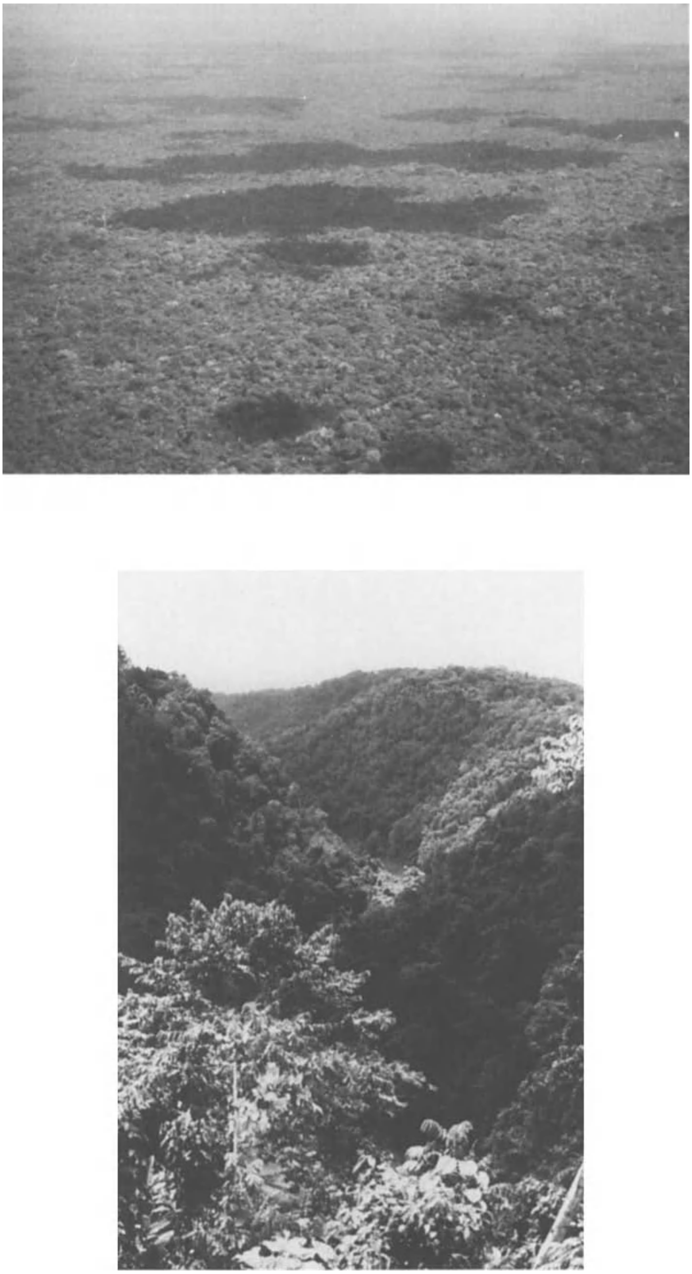


Fig. 10-2. (a) Subdued (eastern Bolivia) and (b) mountainous (Solomon Islands) topography in tropical rain forest regions.

Papua New Guinea, which occurred 20,000–30,000 years BP and removed approximately 65 cm from 345 km^2 to produce a mudflow of 3.5 m average thickness over 64 km^2 (Pain, 1975).

(4) About 18% of tropical rain forests lie in tectonically active zones (Garwood et al., 1979) and earthquakes are significant in causing landslips in these areas.

(5) The most unstable slopes appear to be those where weathering has progressed only far enough to produce montmorillonite and illite, which change their properties more than kaolinite under the influence of moisture. Instability also seems to be favoured by the presence of thin layers of weathered material lying on unweathered bedrock.

Drainage characteristics

Within tropical rain forests, drainage densities are influenced by bedrock lithology and rainfall. Areas underlain by rock types that produce permeable weathering products (e.g. granites and sandstones) generally have convex slopes and lower drainage densities than those where the soil has a higher clay content (e.g. derived from schists or shales) and slopes are more concave. Drainage densities also increase generally with increasing mean annual rainfall.

Despite the inhibiting effect on surface run-off of the dense vegetation cover, drainage densities in the humid tropics are generally greater than in humid temperate regions. The precise mechanism whereby first order channels are initiated in the humid tropics is poorly understood, but some probably derive from gullies produced by occasional high-intensity storms, while others develop from slides and sub-surface solution and washout. On permeable volcanic rocks in Hawaii the first channel to cut down to the water table captures groundwater from others and rapidly develops into a major valley (Chorley et al., 1984).

Although the average concentration of dissolved material in tropical rivers is much lower than that in extratropical ones, the higher discharges per unit area mean that the solution denudation rates may be greater (Levinson et al., 1969). For example, 22% of the silica weathered from Hawaiian basalts is removed in solution compared with 1–3% of that weathered from rocks in the Mississippi basin (Chorley et al., 1984).

Mountain rivers, in contrast with those of lowland areas, carry greater amounts of coarse material with higher proportions of quartz and montmorillonitic clay minerals, whereas the load of the rivers in lowland regions is characterised by the presence of suspended kaolinite and dissolved material. Lowland rivers are thus less able to erode their channels and are often characterised by reaches of low gradient separated by rapids (Chorley et al., 1984). There are, however, deeply incised valleys in the humid tropics and Sparks (1972) has suggested that this may, in part, be due to deep weathering processes beneath valley floors.

Rivers flowing in the rain forest, if unaffected by human activity, generally have relatively low sediment concentrations, but high-magnitude or catastrophic events give rise to episodes of high sediment yield (Kesel, 1985). Chorley et al. (1984) suggest that on average 2% of the highest discharges remove 50% of the total solid load, while according to Turvey (1975), Ei Creek, Papua New Guinea, transports 99% of its annual solid load in less than five days. There may also be significant changes in sediment concentration in streams and rivers due to daily rainfall cycles. Streams which are clear in the morning may be clouded with sediment in response to afternoon rainstorms.

Douglas and Spencer (1985) point out that coarse quartzite and limestone gravel (in the Strickland River, Papua New Guinea) can be found up to 100 km downstream from where the stream leaves the mountains. This is in contrast to the findings of other authors, chiefly commenting on more lowland areas, who note that gravel bedload is transported only short distances before being comminuted by chemical weathering and abrasion (Bakker, 1957; Budel, 1982; Segovia and Foss, 1984).

In the lower reaches of rivers, valley floors are subject to frequent flooding and entire floodplains are commonly affected by high-velocity flood flows. Debris from the valley slopes is frequently removed even where river terraces flank the floodplain.

WEATHERING AND DISPERSION PROCESSES

Weathering and soil formation

In general, a humid tropical climate provides almost optimum conditions for chemical weathering and dispersion, although in areas of strong relief, mechanical dispersion is also important. Deep chemical weathering is aided by: (1) the generally high rate of infiltration caused by the dense forest cover and high humidity leading to almost complete saturation of rocks for long periods; (2) the insulating effects of the layered forest canopy coupled with the heat generated by rotting vegetation, which gives rise to high ground surface and soil temperatures; and (3) the highly acid soils and groundwater, caused by the decomposition of humus, which reacts with bedrock (Tricart, 1972). Karst-like features can develop on igneous and metamorphic as well as carbonate rocks as a result of strong solution weathering (Garner, 1974).

When chemical weathering is complete, the alkalis and alkaline earth metals are totally leached together with a large proportion of silica, whereas iron and aluminium concentrate in situ as oxides and hydroxides (Zeegers, 1979). Kronberg (1979); Kronberg et al. (1979); and Kronberg et al. (1987) note that soils developed over granulitic and amphibolitic rocks in the Amazon Basin are essentially a hydrated refractory oxide assemblage of quartz, kaolinite, gibbsite, goethite and hematite containing 95% SiO_2–Al_2O_3–Fe_2O_3–H_2O (compared with 85% in bedrock) and with Na, K, Mg and Ca reduced to trace element levels. The main clay mineral formed, in the prevailing conditions of acid pH and intense leaching in the mature flat topography of the Amazon, is kaolinite. Under the extreme conditions of humid tropical weathering, silica is relatively mobile. Ferralitic soils (oxisols and ferralsols) found in tropical rain forest areas are characterised by the extreme and complete weathering of parent material to kaolinite and Fe–Al oxides (Rose et al., 1979). These soils have extremely low cation exchange capacities. In the Cameroon, U in shallow (1 m thick) ferralitic soils developed over syenite is strongly depleted from 54 ppm U in bedrock to 12–18 ppm in the soil profile where the major part of the U remains in resistant minerals rather than kaolinite or Fe and Al sesquioxides (Gueniot et al., 1988).

However, chemical weathering is not always as intense. Zeegers (1979) observed that 80% of soil samples collected from rain forest in French Guyana contained <30% Fe_2O_3, <20% Al_2O_3 and >50% SiO_2, suggesting that ferralitic weathering had attained only low to medium grade.

Data for ten highly weathered areas in Brazil (Kronberg et al., 1979) show that trace element enrichment is largely confined to the biologically important elements (B, Cl, Mo, As, Se, Sn, Sb, and I), to refractory metals such as Sc, Zr, Nd, Nb, Gd, Tm, Hf, Th and Bi whose oxides tend to be highly insoluble, and to elements such as Y, Ce, La, Ti B and Sn that occur principally in resistate minerals. Other elements such as Na, Mg, K, Cu, Ni and Sr are usually severely leached (Kronberg et al., 1979). In the kaolinitic environment of the Amazon, Ag, Pb and U may be adsorbed onto organic debris. Minor element enrichment tends to be associated with complex clay minerals such as montmorillonite, chlorite, and illite, and enrichment diminishes as these minerals are altered into simpler clay minerals as a result of desilication, as for example in the kaolinitic terrains of the Amazon basin and the gibbsitic aluminium oxide terrains of Goiás, Brazil.

Continuous chemical leaching may lead to vast accumulations of refractory oxides, as in the bauxitic deposits in the Amazon and the garnieritic nickel deposits in Cuba, Dominican Republic, New Caledonia and Sulawesi (Topp et al., 1984). However, according to Matheis (1980) and Kronberg et al. (1982) the development of laterites in tropical rain forests is relatively rare. True laterites (duricrusts) develop under conditions of strongly contrasting seasonal rainfall, although in tropical rain forest they may occur as relics of former weathering cycles under less humid conditions. Indeed, most humid tropical areas have been subjected to a seasonally humid peritropical climate (Budel, 1982) that has produced an intensely leached, often lateritic regolith which may have developed over millions of years since the Cretaceous or early Tertiary. According to Tardy and Nahon (1985), a typical ferricrete lateritic profile usually comprises five distinct horizons: (1) fresh parent rock at the base of the profile is overlain by (2) coarse saprolite in which primary minerals are partly disaggregated and transformed into smectite and kaolinite. In the saturated zone below the water table, the fine saprolite horizon (3), in which feldspars and ferromagnesian minerals are entirely transformed into kaolinite, halloysite and goethite, has suffered only minor leaching of iron and aluminium. This is overlain by a mottled zone (4) in which iron is now mobilized and concentrated in clay rich areas, forming mottles that are precursors of concretions. Finally, at the top of the profile, a few metres thick layer of ferricrete (5) is composed of hard cemented nodules. Progressive removal of silica produces a ferricrete in which goethite, hematite and kaolinite are the dominant minerals. If the deeply weathered profile has been subjected to further intense leaching under tropical rain forest conditions, many of the more mobile geochemical pathfinders will be almost totally impoverished. Thus an understanding of past as well as present weathering conditions is critically important (Butt and Zeegers, 1989), especially when developing geochemical exploration models (Butt, 1987).

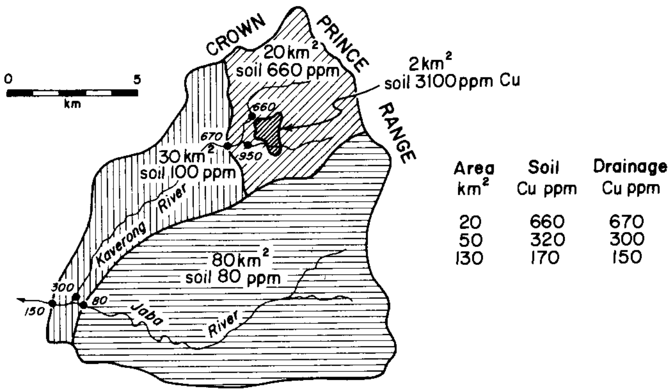
Although acid groundwaters tend to increase element mobility and leaching (Hansuld, 1967), clay minerals and hydroxides retain some of the elements (Clarke, 1970). Studies by Zeegers (1979) in French Guyana and Matheis (1983) in southwest Niger suggest that many of the trace elements remain more or less at their bedrock concentrations during soil development as a result of sorption as metal hydroxide and other inorganic complexes onto colloidal oxide/ hydroxide systems. Metal mobilization by humic chelating agents is depressed by the relatively fast decomposition of organic litter. Although trace elements are liberated and moved by percolating solutions and by run-off, the weathering mantle acts as an ion-exchange column in which repeated eluviations and ion-exchange processes give rise to fractionation of elements, the more soluble being removed and others being enriched. In areas of subdued terrain, movement of cations tends to be vertical rather than lateral, so that soil chemistry is often a good indicator of underlying bedrock (Matheis, 1981, 1982). In the Amazon region of Brazil, soil and bedrock compositions are similar although soil profiles average up to 20 m in thickness and range up to 115 m thick (Mazzucchelli, 1986). In the rain forest of west Africa, the Cr, Co, Cu, Ni and Mn contents in the B horizon of lateritic soils can be used to predict the location of ultramafic rocks in greenstone belts while Rb, Cs, Mg/Li and K/Rb in soils indicate the location of pegmatite host rocks of rare metal ore associations (Matheis, 1983). Zeegers (1979) showed that soils over ore can retain anomalous amounts of Cu and Pb while Zn may be completely leached, although Cu may also be leached over deposits rich in sulphides and pyrites.

The progressive upward decay of the Au–Ag–As–Bi–Mo–Pb–W geochemical signature of Au mineralization in deep lateritic weathering profiles was described in eastern Cameroon by Freyssinet et al. (1989a). Although pathfinder element levels vary considerably through the weathering profile, all are significantly anomalous in the surface soil, even though absolute levels are extremely low. In stream sediments collected at 0.5 km from the mineralization, only Pb is anomalous. Dispersion of gold from a narrow, rather coarse grained gold bedrock source in Gabon is considered to result from the dissolution of gold particles and the reduction in thickness of the weathering profile leading to the production of a mushroom-shaped anomaly of fine-grained gold (Lecomte and Colin, 1989). This has important implications for stream sediment sampling as it is probable that in such conditions the fine fraction is likely to contain more Au than the coarse fraction or heavy mineral concentrates. Freyssinet et al. (1989b) also concluded that lateritization processes in southern Mali were strong enough to mobilize gold. Dissolution and reprecipitation of gold in lateritic weathering profiles promotes the development of extensive secondary dispersion halos (Freyssinet et al., 1989a, b).

Soil-stream sediment link

As discussed in the previous section, unless weathering has proceeded to the stage of advanced kaolinization, soil chemistry will generally reflect bedrock composition, although geochemical signatures may be muted in low lying areas. Stream sediment samples derived from the erosion of such soils normally closely reflect bedrock geology. Relatively mobile elements such as Ni, Cu and Zn, once fixed by secondary Fe oxides, are unlikely to be re-dissolved in stream channels. MacKenzie (1977) showed that for a series of porphyry copper deposits, drainage values directly reflect average soil values for their drainage basins (Fig. 10-3). In a study of the Karang copper lode prospect in Borneo (Walker and Tooms, 1963), the copper content of stream sediment was shown to be directly related to that of copper in bank material. Copper derived from groundwater draining the mineralization is thought to have precipitated on secondary iron hydroxides in stream bank seepages. Davies et al. (1989) found that Cu, Zn and Co levels in auriferous horizons of laterite profiles overlying gold mineralization in a greenstone belt in northern Sierra Leone correlate closely with values in adjacent stream sediments.

Zeegers (1979), however, identified contrasts in the chemistry of soils and stream sediments in French Guyana. Mean values for Si, Mn, Co, Ni, Cu, Zn and Ba are higher in sediments while Al, Fe, V, and Cr are higher in soils from the region (Table 10-I). Detrital concentrations of quartz in stream sediments are reflected by higher SiO_2 values while Mn, Co, Ni, Cu and Zn are higher as a result of adsorption, although total Fe is lower than in soils. In east Bolivia (Appleton and Llanos, 1985), B, Ba, La, Sr, U, Y and Zr are higher in drainage sediments than in soils.



Area km²	Soil Cu ppm	Drainage Cu ppm
20	660	670
50	320	300
130	170	150

Fig. 10-3. Relationship between catchment area, soil, and stream sediment values, Panguna, Papua New Guinea (reproduced with permission from McKenzie, 1977).

TABLE 10-I

Comparison of geometric mean values for stream sediments and soils from east Bolivia (Appleton and Llanos, 1985) and French Guyana (Zeegers, 1979)

Element/Oxide*	East Bolivia		French Guyana	
	Stream sediments	Soils	Stream sediments	Soils
SiO_2	–	–	74.4	59.7
Al_2O_3	–	–	8.9	13.3
Fe_2O_3	1.0	1.2	9.2	16.9
MgO	–	–	0.7	0.6
Na_2O	–	–	0.3	0.3
K_2O	–	–	0.9	0.6
B	25	33	22	20
P	–	–	321	271
Ti	–	–	9668	10,660
V	–	–	122	175
Cr	28	30	135	172
Mn	112	107	320	200
Co	7	6	11	7
Ni	8	9	33	28
Cu	5	5	38	26
Zn	22	19	37	24
As	3	3	10	11
Sr	85	40	21	22
Y	42	30	–	–
Zr	676	575	162	144
Nb	22	21	–	–
Mo	1	1	2	2
Sn	3	3	22	24
Ba	234	154	178	99
La	62	44	–	–
Pb	19	20	25	26
Bi	–	–	5	5
U	6	4	–	–
N	6936	1251	3029	6315

* Oxides = %; Elements = ppm.

Although silica is relatively mobile under extreme tropical weathering conditions, many pure quartz river sands occur in watersheds with Precambrian rocks in the Amazon Basin (Franzinelli and Potter, 1983). The problems associated with the dilution effect of sand and silt size quartz on trace element levels in tropical forest drainage sediment is briefly discussed in the section on sampling media.

Dispersion and anomaly formation in drainage samples

The range of chemical, biological, mechanical, and environmental factors and mechanisms that control secondary dispersion have been described by Levinson

(1980, p. 348) and Plant and Raiswell (Chapter 3, this volume). Of these, the following factors appear to exert the greatest control in the rain forest environment: (1) hydromorphic dispersion and adsorption by Fe and Mn oxides, clay minerals and organic material; (2) mechanical dispersion of both detrital minerals and adsorbed material; (3) topography and local drainage conditions; and (4) temporal climatic variations.

Hydromorphic dispersion and adsorption

Extreme chemical weathering of sulphide deposits, which is common in the tropical rain forest environment, generally produces low pH (<5) groundwater in which the aqueous mobility of many metals is relatively high. The relative stability of elements will affect the extent of their hydromorphic dispersion. Fleming and Neale (1979) found that arsenic and to a lesser extent molybdenum were more stable than copper in the soils of the Yandera porphyry copper prospect so that copper had a greater hydromorphic dispersion leading to a more extensive anomaly in drainage samples. According to Learned and Boisson (1973), gold in porphyry copper deposits tends to form much more limited anomalies than copper suggesting that gold is a more suitable indicator for detailed surveys as it will not have been removed to the same extent as copper and molybdenum. This was partly confirmed by Andrade et al. (1991) who investigated the extent and mechanism of gold mobility from the Salobo Cu–As and Bahia Au–Cu sulphide deposits in Brazil. Low Au values in surface waters indicate that gold mobility is restricted to the soil zone in the subdued deeply weathered lateritic terrain of the Bahia area. This may be related to the scavenging effects of Fe and Al oxides and the low concentrations of complexing ligands such as chloride. Elevated concentrations of dissolved Au in the Salobo area may reflect the shallow lateritic cover, steep terrain and disturbance due to mining (Andrade et al., 1991).

Dissolved metals are prone to precipitation by several mechanisms after groundwater reaches the surface drainage system:

(1) *Secondary iron and manganese oxides.* For chemically mobile elements, such as Cu, U, Mo and Zn it is generally accepted that adsorption by Fe and Mn oxides is the main fixing process in the tropical weathering cycle and that this is generally more important than adsorption onto clay minerals or organic material (Griffitts and Ward, 1970; Ukpong and Olade, 1978; Watters and Sagala, 1979; Gibbs, 1982; Laville-Timsit et al., 1983; Pollack and Zeegers, 1983; Watters, 1983; Topp et al., 1984; Learned et al., 1985; Samama et al., 1989; Appleton and Greally, 1990; Appleton and Llanos, 1992). Soluble elements rapidly re-precipitate as secondary minerals and are consequently less mobile in the tropical environment than in a temperate climatic zone (Magnusson, 1983).

Studies of trace element speciation using sequential extraction methods (Pollack and Zeegers, 1983; Learned et al., 1985) have shown the high proportion of mobile elements adsorbed by crystalline and amorphous iron oxides. Pollack and Zeegers (1983), working on lode-type copper mineralization grading 1% over a width of a few metres and a strike length of 200 m in Surinam, determined that 40% of total copper occurred in residual phases such as silicates and clays, 30% in crystalline iron oxides, probably derived from the weathering of sulphides and mechanically transported in the drainage system, and 30% in amorphous iron oxides formed by precipitation in drainage channels. As only about 10% of the total iron is amorphous it must be very enriched in copper. Learned et al. (1985) showed that for the eight most anomalous samples downstream from the Rio Tanama porphyry copper in Puerto Rico, 35% of total copper occurred in the amorphous iron oxides and approximately 10% in crystalline iron oxides. Learned et al. (1981, 1985) found that the copper held in amorphous iron gave a significantly better anomaly to background ratio than total copper.

Watters (1983) maintains that there is normally a close relationship between U and Fe in the tropical rain forest environment and recommends the analysis of heavy mineral concentrates to improve anomaly contrast when U occurs mainly in secondary iron oxide minerals, or the fine ($<75\ \mu$m) fraction, when U is co-precipitated with Fe and Mn hydroxides in coatings of clay-size particles.

Gibbs (1982) and Appleton and Llanos (1992), concluded that the detection of low-grade copper mineralization is enhanced by the use of regression on Fe to screen out the effects of adsorption and variations in bedrock lithology. Appleton and Llanos (1992) illustrated how the adsorption of the mobile elements Cu, Pb, Zn and U onto Fe oxides and organic material could produce apparently false anomalies in eastern Bolivia, and recommended a two stage interpretation based on simple graphical regression of trace elements against Fe and then against loss on ignition (Fig. 10-4), which is generally accepted as a reasonable indicator of the content of organic material (Larsson, 1976). Magnusson (1983), used stepwise regression analysis to correct trace metal data for the effects of adsorption by Fe, Mn and organic material in stream sediments in Indonesia. At the Eagle Mountain Mo prospect in Guyana, Griffitts and Ward (1970) found that Mo correlated strongly with Fe in stream sediments, indicating adsorption onto secondary Fe oxides. Montgomery (1971) came to the same conclusion and recommended that Fe be used to detect high Mo related to adsorption.

In Gabon, Samama et al. (1989) noted that uranium generally occurred in hydroxide coatings to clay minerals and was not adsorbed directly by organic material or clays. Total iron content could not be used to correct for adsorption effects due to the different oxidation states in which U occurred and for which partial extraction data were non-specific and unreliable. However, regression of U against sample surface area, which indicated abundance of hydroxide and therefore the adsorption capacity of the sample, could be used to distinguish between samples containing high U related to mineralization and those with high U solely caused by adsorption.

Cluster analysis on data from nearly 9000 stream sediment samples from the island of Choiseul, Solomon Islands (Fig. 10-5) showed a generally low level of similarity between manganese and other elements, suggesting that adsorption by Mn oxides is not an important process in this particular environment (Ridgway and Coulson, 1987).

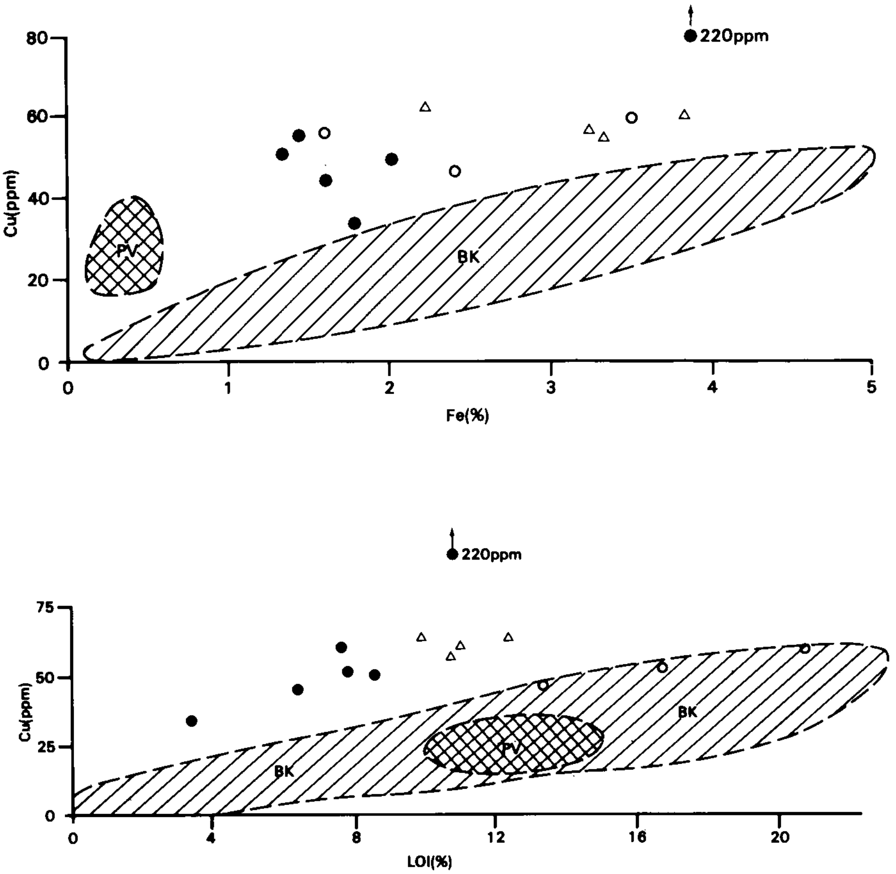


Fig. 10-4. Cu vs. Fe and Loss on ignition (LOI) for (1) background stream sediment samples from the San José de Chiquitos, Concepción and Santo Corazon areas (BK); (2) samples from Puerto Villazón (PV) and Concepcion (open circle) with high Cu/Fe ratios caused by adsorption onto organic material; and (3) anomalous samples derived from mineralised rocks in the San José (filled circle) and Concepción (open triangle) areas, east Bolivia (reproduced with permission from Appleton and Llanos, 1992).

(2) *Clay minerals.* Although clay minerals are thought to adsorb mobile elements by cation exchange (Levinson, 1980), they may also contain high levels of trace elements as a result of coating with iron hydroxides containing co-precipitated trace elements (Watters, 1983). Montgomery (1971) referred to the low sorptive capacity of clays and the relatively high Fe in the clay size-fraction, suggesting Mo is adsorbed by Fe rather than directly onto clay. Sorption onto coatings on clay-size particles is possibly the dominant mode of dispersion of several metals, although further research in tropical environments is required as most studies have been carried out in temperate regions.

(3) *Organic material.* Even though adsorption onto organic material exerts a

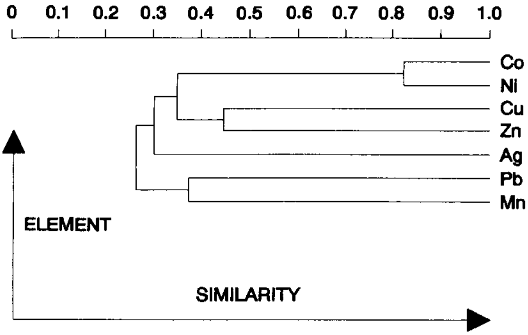


Fig. 10-5. Dendrogram for cluster analysis of 8846 stream sediment samples from the island of Choiseul, Solomon Islands (reproduced with permission from Ridgway and Coulson, 1987).

considerable influence on mobile element dispersion under temperate climatic conditions (Larsson, 1976), Watters (1983) considered that its influence is relatively restricted under tropical rain forest conditions, with mobile elements such as labile uranium being mainly adsorbed by secondary iron and manganese oxides. However, Laville-Timsit et al. (1983); Magnusson (1983); and Appleton and Llanos (1992) have shown that in tropical rain forest environments, Cu, Pb, Zn and U are all adsorbed to some extent by organic material and that false anomalies can be produced.

Mechanical dispersion

Although dispersion of mobile elements in the weathering profile of tropical rain forest environments is mainly hydromorphic, dispersion in drainage is dominantly mechanical (Watters, 1983). Metals adsorbed and precipitated with Fe and Mn in near surface soil subsequently enter the drainage system as a result of slumping or mechanical erosion. The greater importance of mechanical relative to chemical dispersion is confirmed by the longer dispersion trains for copper in stream sediments than in waters (Fig. 10-6; Learned et al., 1985).

Residual minerals and metals, such as cassiterite, wolframite, chromite, and gold are generally enriched in the weathering profile relative to bedrock and normally enter the drainage system by mechanical transfer, although there is some evidence that gold may move partly in solution (Freyssinet et al., 1989a, b; Lecomte and Colin, 1989). Dispersion of cassiterite and gold in the drainage systems of tropical rain forests is discussed by Sampattavanija (1963), Singh (1969), Garson et al. (1975), Johari et al. (1981), Hamidsyah and Clarke (1982), Watters (1983), Fletcher et al. (1987), Sirinawin et al. (1987), and Tooms (1987). Some relatively insoluble supergene minerals also tend to be mechanically dispersed. For example, Laville-Timsit et al. (1983) found that, in French Guyana, secondary lead phosphate, sulphate and phosphosulphate minerals, developed under deep ferralitic weathering conditions from galena, were mechanically

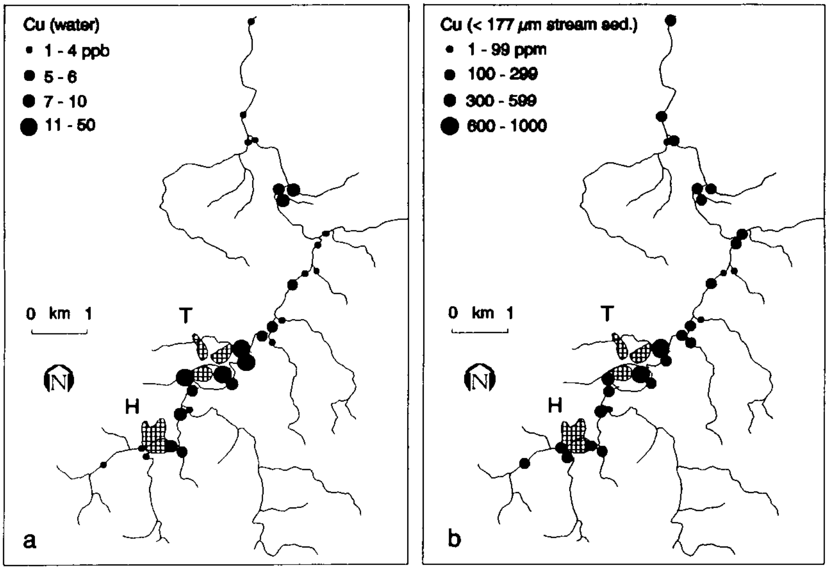


Fig. 10-6. Comparison of dispersion for (a) Cu in water; and (b) Cu in <177 μm stream sediment in the Rio Tanama porphyry copper district, Puerto Rico (shaded areas: *T* = Tanama deposits, *H* = Helecho deposit; modified after Learned et al., 1985).

dispersed whereas zinc from the same sulphide mineralization was chemically dispersed, being associated with organic material as well as with secondary iron hydroxides.

Influence of topography

Weathering and soil formation under tropical rain forest conditions are influenced not only by the zonal climatic characteristics of high temperature and rainfall but also by the topography and the history of landscape development. Greater leaching has occurred in the flat, mature topographic terrains of the Amazon basin and the Congo basin than in the relatively recent mountainous mobile belts of western South America, the Caribbean and the Indonesia–New Caledonia area. The saprolite zone of weathered rock below the B horizon is often more than 100 m thick in areas of flat topography, whereas in mountainous areas, the bedrock may be only a few metres below the surface. In mountainous tropical rain forest, chemical weathering proceeds incompletely before the partly weathered material is stripped off by slumping and landslides, leading to mechanical dispersion of the weathered material towards drainage channels.

Although there are obviously intermediate cases, the effects of the azonal topography factor on dispersion can best be studied by describing the two extreme cases: (1) mountainous terrain, and (2) the subdued topography.

Dispersion in mountainous terrains

In mountainous terrain in areas such as Papua New Guinea and Solomon Islands, hydromorphic dispersion followed by the fixing of mobile elements by iron oxides is the major mechanism of dispersion in soils, and dispersion in the drainage systems is predominantly mechanical. Torrential rainfall followed by flood run-off, sometimes accompanied by mud slides on steep slopes, is characteristic of such areas. The combination of flood discharge and steep gradients results in extensive mechanical dispersion. Mineralized float from major porphyry copper deposits, such as Ok Tedi and Tiflamin in Papua New Guinea, occurs tens of kilometres downstream from mineralization (Jones, 1973), indicating the tremendous power of flood water as an agent of mechanical dispersion. For stream sediments, downstream mechanical dispersion from major porphyry copper deposits extends for 16 km at Luzon, Philippines (Govett and Hale, 1967), 28 km at Panguna, Bougainville (Joyce, 1984), and at least 40 km at Ok Tedi in Papua New Guinea (Jones, 1973).

These extensive dispersion trains from porphyry copper deposits are caused by the large volume of mineralized rock associated with this type of deposit and by the importance of mechanical dispersion as a result of the steep terrain and torrential rainfall. In the case of smaller bodies of mineralization, dispersion is more restricted, extending often to only 1000 to 2000 m (Vasquez, 1972; Rose et al., 1979). Dispersion of only about 300 m was recorded by Walker and Tooms (1963) for the Karang Lode in north Borneo.

Stream sediment mixing at confluences often restricts the detection of dispersion. For example, Young and Johari (1978) showed that in the case of the Tangse copper–molybdenum prospect in northern Sumatra, downstream dispersion is restricted to approximately 3 km as the sediment from streams actively eroding the porphyry mineralization is diluted on entering a major river. A similar example is quoted by Jones (1973) from the Woitape prospect in Papua New Guinea, where anomalous concentrations in stream sediment of 2100 ppm Cu in the discovery creek decline to 55 ppm Cu where the creek joins the main river. In the vicinity of the Tiflamin porphyry copper prospect in Papua New Guinea (Jones, 1973), sediment in tributary drainage to the relatively large Elam River contains 100–500 ppm Cu above a regional background of 10–20 ppm, but no stream sediment anomaly occurs in the Elam River itself. Dilution of anomalous sediment from tributary streams by the sediment load of the main river has masked the anomaly even though mineralized float boulders are observed in the Elam river. Thus the length of dispersion trains strongly depends on the number and relative size of anomalous and barren streams as well as the size of the deposit.

Dispersion in areas of subdued terrain

The Precambrian shield of eastern Sierra Leone is a typical tropical rain forested area with low relief and mature drainage. Streams and rivers flow in broad gentle valleys; major rivers are incised in alluvium, whereas minor rivers and streams flow through colluvium. Stream sediment in areas of duricrust mainly consists of laterite fragments, and in areas of non-indurated duricrust the sediment contains a large component of weathered rock fragments. Precambrian granites and metamorphic rocks produce mainly siliceous sediments with minor mica and feldspar. Garrett and Nichol (1967) concluded that in this environment stream sediment geochemistry effectively defines areas of higher mineral potential as well as indicating changes in bedrock lithology.

Ukpong and Olade (1978) showed that there is a strong association of Cu, Pb and Zn with Fe, Mn and organic material in the stream sediments of the lead–zinc mineralized south Benue trough area of Nigeria, indicating the predominantly hydromorphic nature of dispersion in the region. Zinc has the more extensive hydromorphic dispersion, and lead the strongest anomalies related to weathering of residual secondary minerals. However, in contrast to the case of dispersion trains from porphyry copper deposits in mountainous areas, the metals are relatively strongly bonded, requiring a relatively strong acid leach (hot 4M HNO_3) to liberate them into solution for analysis (Ukpong and Olade, 1978). As the clay and silt fraction is the predominant host of adsorbed elements, the finest fraction (<125 μm) yielded the most consistent results.

Anomalies in low relief tropical rain forest may be very subdued (Overstreet and Marsh, 1981). Strong surface leaching over the Tartana deposit in Queensland, Australia, which grades 0.8–0.95% Cu, produces soil anomalies of 1000–2000 ppm Cu whilst stream sediments are anomalous at only 80–120 ppm (Rawlins, 1980). Pollack and Zeegers (1983) illustrated the restricted nature of stream sediment anomalies derived from lode copper mineralization grading 1% Cu over a few metres width and 200 m strike length in the relatively subdued topography of Surinam. The mineralization was originally discovered by the identification of a 500 × 200 m soil anomaly, with >400 ppm Cu rising to >1500 ppm Cu, and the results of an IP survey over an airborne geophysics anomaly. The maximum stream sediment anomaly was only 215 ppm in the <177 μm fraction and dispersion was restricted to a few hundred metres. Size fraction analysis showed that the best geochemical response should be in the <63 μm fraction (Fig. 10-7); geochemical response in the <177 μm fraction is diluted by barren quartz.

Previous erosion cycles may influence dispersion in areas of mature topography. For example Hamidsyah and Clarke (1982) report that some tin dispersion patterns in Indonesia are related to reworking of Tertiary fossil placer deposits rather than primary mineralization. Thus, in the case of resistate minerals such as cassiterite it may be difficult to locate a primary source for anomalous stream sediments that have gone through several erosion and deposition cycles. In this particular case the cassiterite derived from the Hatapang Granite passed through Tertiary fluviatile deposits and Pleistocene alluvium before entering the active stream sediments. Mobile elements in areas that have been subjected to various erosion cycles may be completely lost (Watters, 1983). In other areas, the geochemical response is blanketed by extensive laterite cappings developed during previous climatic regimes when rainfall was more seasonal (Singh, 1971).

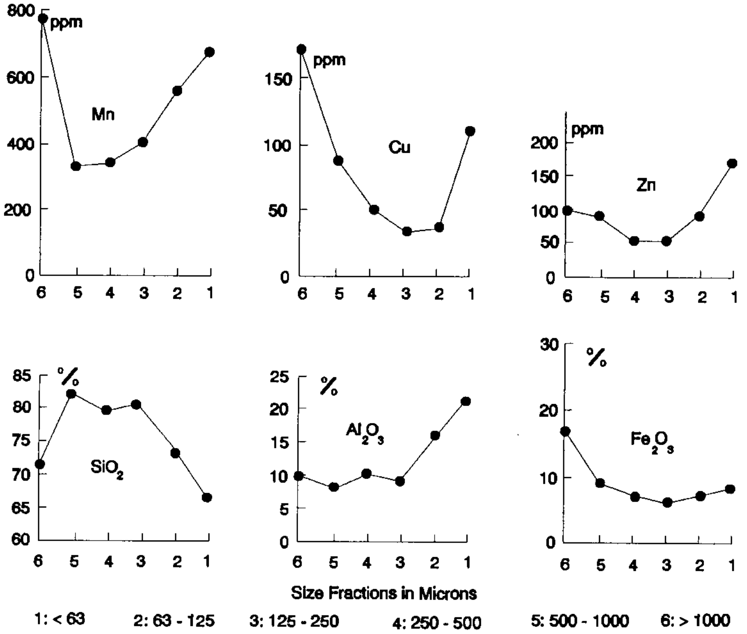


Fig. 10-7. Size fraction analysis of stream sediments at Kalebo, Surinam (redrawn with permission from Pollack and Zeegers, 1983, Editions BRGM, BP 6009, 45060 Orléans Cedex 2, France).

Griffitts and Ward (1970) and Montgomery (1971) both noted that mobile elements such as Mo could be stripped out of stream water by adsorption onto organic material and hydroxides in swamps. In areas of impeded drainage, such as topographically low areas where groundwater comes to the surface, smectites such as montmorillonite may form and retard the solution of Fe, Mn and other cations that may be adsorbed onto the clay minerals.

Influence of temporal climatic variations

Anomaly reproducibility in the silt fraction of stream sediments in the Solomon Islands has proved problematic: during follow-up of anomalies in the New Georgia group, samples collected after a period of heavy rain gave 400–500 ppm Cu, compared with values from the initial sampling campaign of approximately 1000 ppm (P.N. Dunkley, pers. commun., 1986). A copper anomaly on Guadalcanal was subsequently sampled at monthly intervals over a 15 month period and showed ranges of 20–135 ppm for cxCu, 130–240 ppm Cu and 150–240 ppm Cu for hot concentrated nitric acid and hot concentrated hydrochloric acid extractions respectively, while total Cu determined by XRF was 140–280 ppm (Fig. 10-8). The temporal variations appear not be strictly seasonal, but are instead related to long term changes or catastrophic events. Figure 10-8 shows variations in Co, Cu, Fe, Mn, Rb, Sr, Ti, V and Zn at one site for a period of 15 months. The peak in rainfall for March 1985 records the passage through Guadalcanal of the tail of a cyclone and is clearly linked to major changes in the stream sediment chemistry: total Fe, Mn and V all increase together with Ti whereas Rb and Sr are substantially depleted and Zn is slightly lower. This may reflect the introduction of magnetite rich sediment into the drainage system from landslide material (Ridgway and Midobatu, 1991).

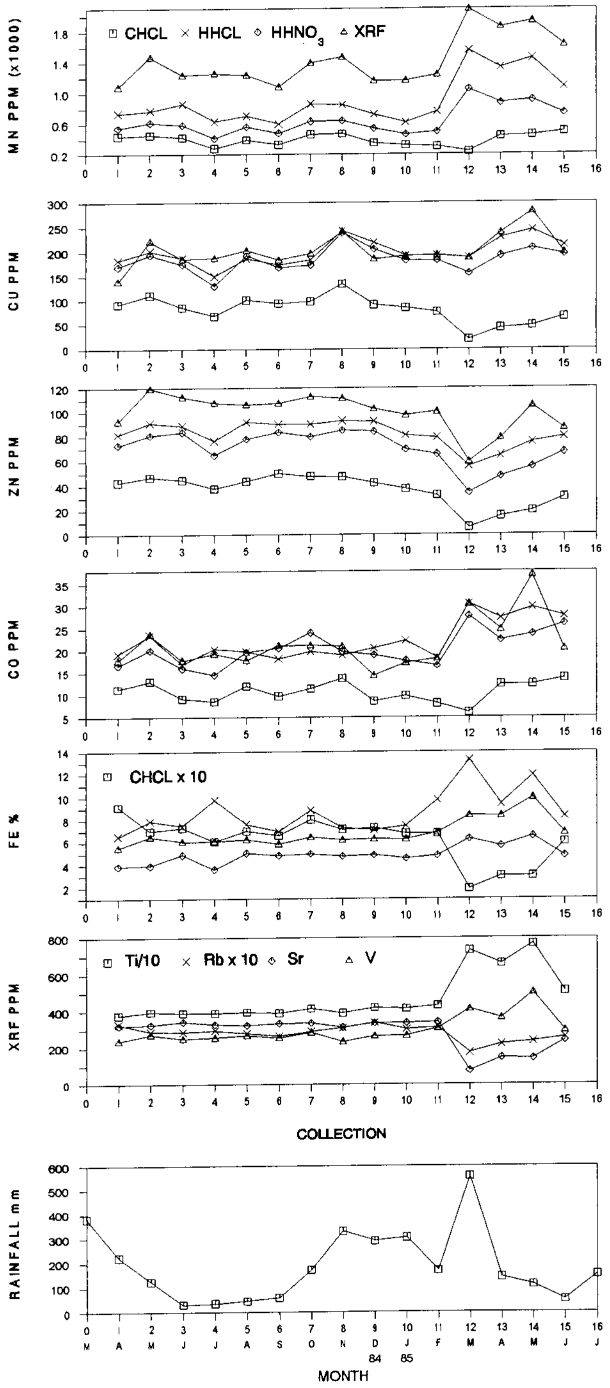
SAMPLE MEDIA

Sample media that have been used in rain forest terrains range from boulders of float, through heavy mineral concentrates, fine fraction sediments and water to mosses.

Stream sediments

The most commonly used medium in tropical terrains is the fine fraction of stream sediments. The <177 μm portion is most commonly used, although the <150 μm fraction has also been extensively employed and the <75 μm or <63 μm fraction have been advocated by some, including Pollack and Zeegers (1983) and Watters (1983). Dahlberg (1982) found difficulty in obtaining clay size material in Surinam, however, and where sufficient of this fraction was available it was frequently contaminated by organic matter or clay particles from stream bank soils. In rugged, mountainous terrain with fast flowing streams, it may be particularly difficult to obtain sufficient fine-grained material by grab sampling. It may be necessary to collect at least 500 g of sediment to produce sufficient <177 μm material for chemical analysis. In Papua New Guinea, sand bars, boulders and dead tree trunks have been found to be useful traps for silt size sediment. Because of the steep gradients, rapid flow and high daily changes in rainfall, the Papuan streams tend to be affected by incorporation of bank material so that sampling must be as far from the banks as possible (Jones, 1973). The problem becomes particularly acute if the analytical method employed requires a relatively large amount of material. XRF, for example, typically requires ca 10–15 g. Wet sieving on site to ensure collection of adequate material cannot normally be used in tropical terrains as much of the fine sediment floats off in suspension. On the other hand, sampling at stream margins was advocated by most participants at the Workshop on Geochemical Exploration in Tropical Rain Forests, held in Manaus, Brazil, in 1985 because the active sediment in the centre of drainage channels tends to be enriched in quartz and low in clays and other fine particles, whereas material deposited along stream margins and banks during flooding is locally much finer and gives better anomaly contrast.

Where mechanical dispersion is dominant and the rate of erosion exceeds that of oxidation, a coarser size fraction than the <177 μm material traditionally used in areas of intense chemical weathering may give better contrast,


MN PPM (x1000)
CHCL
HHCL
HHNO$_3$
XRF
CU PPM
ZN PPM
CO PPM
FE %
CHCL x 10
XRF PPM
Ti/10
Rb x 10
Sr
V
COLLECTION
RAINFALL mm
M A M J J A S O N D J F M A M J J
84 85
MONTH

although dispersion trains may be shorter (Coope, 1973). This might be expected to be particularly true for elements held in resistate minerals, such as Sn, which almost always reflects the cassiterite content of stream sediments. Sampattavanija (1963), however, working in peninsular Thailand, found an erratic distribution of Sn between <177 μm and <830 >177 μm sediment, and Foo (1970) reports that in Malaysia Sn in <177 μm sediment is much higher than in the <830 μm sediment fraction in both barren and mineralized granite areas. Fletcher et al. (1987) note that stream sediment dispersion patterns are very erratic for elements such as Sn, Au, and W, which normally occur in resistate heavy minerals. In areas of steep topography in peninsular Malaysia, the dispersion of cassiterite from aplites and pegmatites in granite is strongly influenced by local hydraulic conditions that result in erratic downstream decay patterns for size fractions from 590 to 55 μm (Fig. 10-9). Differences between Sn concentrations at high-energy and low-energy sites decrease from coarse to fine size fractions. Interpretation of Sn dispersion patterns in stream sediments can be aided by: (1) use of pathfinder elements (As, Cu, Pb, Zn) that are not dispersed as heavy minerals (Fig. 10-10); and (2) plotting hydraulic equivalent concentration values of Sn. Fletcher et al. (1987) also conclude that the <75 μm fraction might be effective for low density regional reconnaissance surveys.

Size fraction analysis of sediments from streams draining Au mineralization in forest covered, rugged terrain in North Sulawesi showed that the finer fraction (<90 μm) produced higher and more reliable Au results (Carlile et al., 1990). Sediment was wet sieved to <250 μm in the field, sun dried and then sieved into <250 >177, <177 >90 and <90 μm fractions which were pulverised to <90 μm prior to analysis. Gold was determined in all fractions and Ag, Cu, Pb, Zn in the <177 >90 μm fraction. Copper and Ag were used to discriminate between anomalies derived from different categories of Au mineralization. These procedures were used for a relatively high density sampling phase (1 sample per km^2); bulk-leachable gold analysis of large stream sediment samples would be appropriate for initial low-density sampling (Carlile et al., 1990). Similar procedures were used in Sumatra and Irian Jaya by Andrews et al. (1991).

In areas of moderate topographic relief in peninsular Malaysia, the <177 μm fraction of stream sediments adequately identifies minor vein quartz and greisen cassiterite mineralization. However, strong sediment anomalies are not always traceable to strong soil and bedrock anomalies due to the 10 to 20

Fig. 10-8. Variation in stream sediment chemistry with time and rainfall at a site on Guadalcanal, Solomon Islands, showing different analytical methods. Rainfall figures are for Honiara, the nearest meteorological station to the study area. The key to analytical method for Mn refers also to Co, Zn, Fe and Cu. (Reprinted from Applied Geochemistry, Vol. 6, Ridgway and Midobatu, Temporal variations in the trace element content of stream sediments: an example from a tropical rain forest regime, Solomon Islands, pp. 185–193, 1991, with kind permission from Pergamon Press Ltd., Headington Hill Hall, Oxford OX3 0BW, UK.)

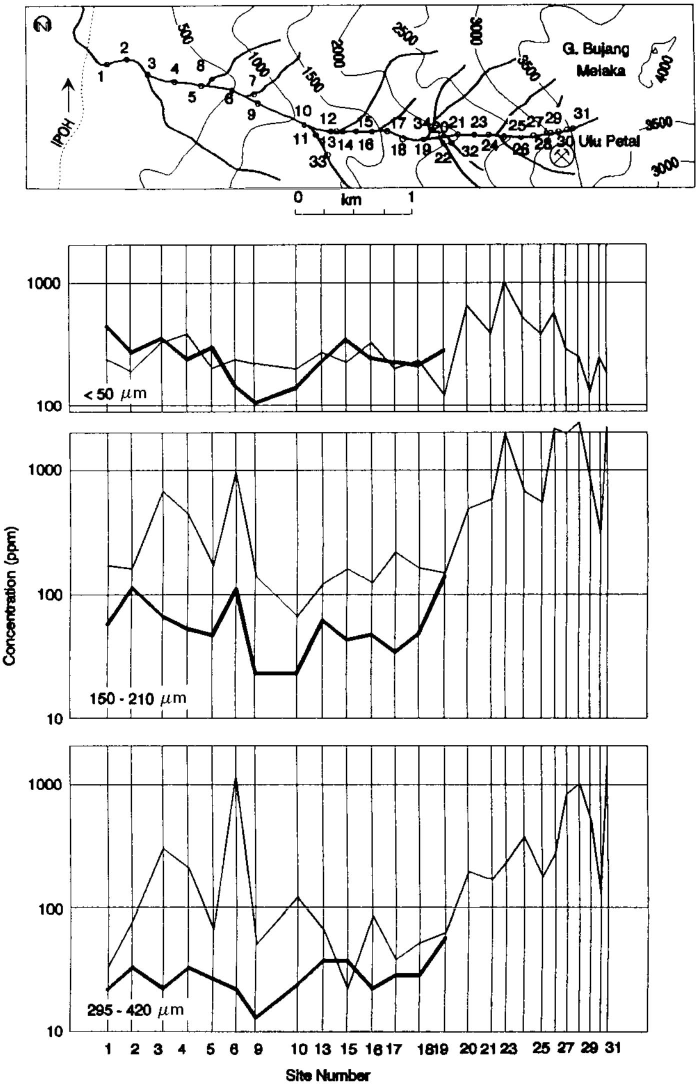


Fig. 10-9. Distribution of Sn, in different sediment size fractions from high (thin line) and low (thick line) energy environments in the Sungei Petal, Malaysia. Size fractions are shown in the bottom left-hand corner of each graph. Site numbers correspond to numbered sample locations along the Sungei Petal (modified after Fletcher et al., 1987).

times enrichment of Sn in stream sediments caused by the winnowing of light minerals in the drainage channels (Sirinawin et al., 1987).

Although careful choice of the most useful size fraction is advocated by most geochemists, there are instances where the geochemical response is essentially the same no matter which fraction is used. Lord (1978) shows that at the Frieda

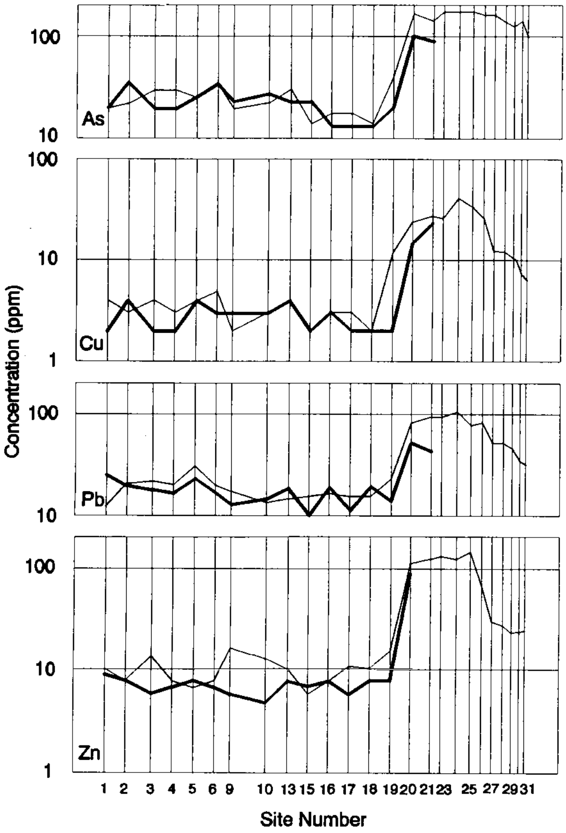


Fig. 10-10. Distribution of As, Cu, Pb and Zn in <177 μm fraction of stream sediments from high (thin line) and low (thick line) energy environments at sites along the Sungei Petal, Malaysia. Site numbers correspond to numbered sample locations along the Sungei Petal as shown in Fig. 10-9 (modified after Fletcher et al., 1987).

River Cu prospect in Papua New Guinea, "total" and cxCu in the size fractions <150 μm, <177 >150 μm, <250 >177 μm, <390 >250 μm, <830 >390 μm and >830 μm are essentially the same, although Pb and Zn show slightly higher values in the finer fractions.

Float material

Visual and chemical analysis of float has proved very useful in exploration work in the more rugged rain forest areas. In the Frieda River catchment, mineralized float with >200 ppm Cu is strongly anomalous at the mouth of an 18 km^2 basin and the anomaly persists to the mouth of a 350 km^2 basin (Lord, 1978). Page et al. (1978) have pointed out the value of examining float in exploration in Indonesia.

Heavy mineral concentrates

Exploration for resistate minerals using heavy mineral concentrates has been widely employed in the more rugged rain forest areas. Techniques range from simple panning in the field to screening out of the coarsest material on site and the subsequent separation of concentrates in the laboratory. Details of the various techniques are described in Chapter 6 of this volume, and only a few examples are given here. One of the chief advantages of heavy minerals over other stream sediment sample media in the tropical rain forest environment is the resistance to weathering of many varieties, which leads to increased anomaly contrast at greater distances from mineral deposits, thus allowing lower density sampling. They are generally of little use for the direct detection of sulphides, which are quickly oxidised in this environment, although in Venezuela goethite pseudomorphs after pyrite are found in heavy mineral concentrates (Pasquali and Lopez, 1982). Where steep gradients give rise to mechanical rather than chemical dispersion, primary sulphides have been recorded in heavy mineral concentrates; for example, by Jones (1973) from Papua New Guinea and Recchi (1982) from Panama.

The southeast Asian tin province is largely covered by tropical rain forest and much of the exploration for cassiterite has depended on the use of heavy minerals. Heavy minerals associated with cassiterite were used by Gocht et al. (1978), who recommend screening to 5 mm in the field followed by further screening to 2 mm in the laboratory and separation using tetrabromoethane. Magnetic separation and finally analysis by XRF or electron microprobe are advocated in order to examine zircon, monazite and garnet fractions which can help distinguish tin-bearing granites and indicate whether mineralization is disseminated or pegmatitic.

Heavy mineral concentrates are also used in exploration for uranium and other metals, and Watters (1983) cites a number of examples from Sri Lanka, Australia and Indonesia. In Sumatra, Indonesia, Cu, Pb and Zn anomalies occur 100 km downstream of known deposits of Au and Ag. Both heavy mineral and conventional fine-fraction samples identified a small uranium deposit in Kalimantan, Indonesia, but the heavy mineral separates appeared to show a more extensive anomaly (Fig. 10-11). The U is thought to be held in secondary Fe/Mn oxide particles (Watters, 1983). Tooms (1987) found that in Surinam, gold mineralized zones crossed by a number of streams are generally outlined by both sample types. However, results at individual sites are often discrepant, so that where much gold is recovered in the pan only background quantities are found by analysis of the fine fraction, and vice versa. Although anomalies in concentrates and fine fraction samples sometimes broadly coincide, Watters (1983) describes a number of instances where each media outlines different anomalies. Similar discrepancies between <177 μm and pan concentrate samples have been noted by Chu et al. (1982) and Lee et al. (1982) in Malaysia and by Dunkley (1986; see below) in Solomon Islands.

Combined morphological examination and chemical analysis of transported

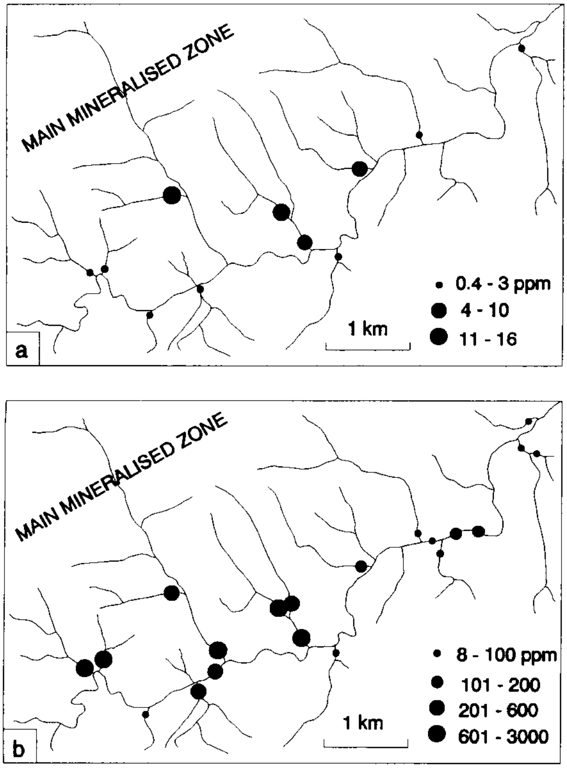


Fig. 10-11. Uranium in (a) reconnaissance stream sediments (<177 μm); and (b) follow-up heavy mineral separates, Central Kalimantan, Indonesia (modified after Watters, 1983).

gold grains from heavy mineral concentrates can provide valuable information to gold exploration programmes (Grant et al., 1991). Fineness is a better indicator than gold morphology in discriminating between the contribution of single and multiple gold sources to a sample although morphology is an effective tool in identifying proximity to source. In tropical rain forest areas where the chemical mobility of gold is high, morphological and chemical studies may aid in determining whether the gold grains are of primary or secondary origin and whether they have undergone significant transport. Morphological and microprobe examination would be carried out only on anomalous samples identified by geochemical analysis or due to the presence of visible gold. Grant et al. (1991) recommend that gold grains should be concentrated by refined techniques such as wet gravity tabling and heavy liquid separation in order to ensure the retention of fine gold.

Carlile et al. (1990) recommended field panning of five standard dishes of <2 mm sediment to produce a 500 g concentrate that was separated into <177 μm and >177 μm fractions prior to grinding of the nonmagnetic fractions to <90 μm and analysis for Au, Ag, Cu, Pb and Zn. Gold values in the <177 μm fraction were higher and more repeatable than for the >177 μm fraction and coincided with anomalies in stream sediments. In a gold exploration project in southwest Colombia, gold grains in the >125 μm size fractions were separated and weighed whilst Au in the <125 μm fraction was determined by AAS (Appleton and Greally, 1990). The results were combined to give the total Au concentration in g/m^3. Electron microprobe analyses of separated gold grains were used to investigate the genesis and source of the alluvial gold.

In general, conducting heavy mineral surveys in conjunction with conventional fine-fraction sampling is strongly recommended (Watters, 1983; Appleton and Greally, 1990; Carlile et al., 1990; Watters et al., 1991). Magnusson (1983) advocates a combination of heavy mineral and composite root samples (see below).

Stream water

Hydrogeochemistry has been little used in the rain forest environment, but has been shown to be useful for particularly soluble cations and for anions such as sulphate and arsenate. Grimbert (1963) describes a survey for uranium in Gabon and concludes that water sampling is useful provided that each drainage basin is sampled separately and in the shortest possible time, so that the same weather conditions prevail throughout. In the dry season the uranium content of streams draining known uranium-bearing areas was similar to that of streams from barren areas. The most favourable time for sampling was in the middle of the rainy season. Anomalies in water did not extend further than 1 km from the deposit. Govett and Brown (1968) conclude that stream waters are of little value in prospecting for porphyry copper deposits in the Santo Nino area of the Philippines, although Cu content in the waters increases with decreasing pH and thus measurement of pH is important as an aid to the interpretation of Cu concentrations in sediment. More positive results are reported from Puerto Rico, where Miller et al. (1982) found sulphate to be a pathfinder for pyrite mineralization and dissolved copper useful in distinguishing barren pyrite from pyrite associated with copper deposits. Zinc, fluoride and pH are also important pathfinders for porphyry copper mineralization. According to Learned et al. (1985), dispersion trains for Cu in water are shorter than those in stream sediments (Fig. 10-6) in the Rio Tanama porphyry copper district, Puerto Rico. Chu et al. (1984) report anomalous values of up to 8 ppb U in unfiltered stream water samples from the vicinity of a U stream sediment anomaly in Malaysia, but note that field-filtered acidified waters from the area show subdued, although still anomalous, values.

Aquatic plants

In an experimental study in Indonesia, Magnusson (1983) found that composite root samples taken from plants growing along the drainage systems were an effective exploration medium and better than <200 μm fraction stream sedi-

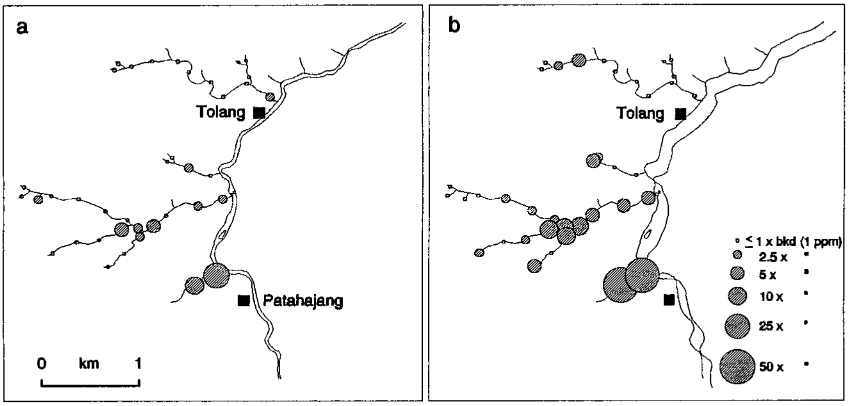


Fig. 10-12. Comparison of dispersion of Mo in (a) <200 μm fraction stream sediment; and (b) roots of plants growing along drainage channels in the Mandagang–Kotanopan area of Sumatra (modified after Magnusson, 1983).

ments (Fig. 10-12). A combination of composite root and heavy mineral samples provided an integrated approach to exploration in an area of Cu, Pb, Zn, Mo and Sn mineralizations. Aquatic mosses also give good anomaly contrast, but are not sufficiently abundant in the rain forest environment.

PRACTICAL PROBLEMS RELATED TO THE TROPICAL RAIN FOREST ENVIRONMENT

High rainfall, temperatures and humidity, together with dense forest and occasionally impenetrable undergrowth, make many rain forested areas difficult to access for geochemical surveys, particularly where the terrain is mountainous. Streams and rivers may be the only means of access — by boat or on foot — so that drainage sediment sampling coupled with boulder tracing and examination of rare rock outcrops is the most cost effective means of exploration.

If small boats or canoes are used to gain access to densely forested areas, the time of year when the survey is carried out is important. In tropical rain forested areas with seasonally variable rainfall and a dry season, such as in eastern Bolivia (Appleton and Llanos, 1985), sampling and observation of rock exposures is more effective towards the end of the dry season. However, the water level in smaller rivers is then too low to allow access by boat, so that sampling has to be carried out immediately after the main rainy season when the water level is high. Following drainage channels by foot, especially in mountainous regions such as Papua New Guinea, can be impossible immediately after heavy rainfall.

Jones (1973) comments on some of the problems associated with the use of helicopters for transporting sampling personnel during drainage surveys. Because of the high forest cover and lack of natural landing sites, the use of helicopters is often precluded (Page et al., 1978), although helicopter support for a major regional survey in Gabon was considered indispensable (Barthelemy et al., 1987).

Topographic maps do not exist for many rain forested areas, and drainage maps must be prepared using air photographs or satellite imagery. A major problem in thick forest is sample location, especially where drainage channels meander. Tape and compass and similar survey methods (Bonis, 1982) are frequently used, although some groups use cut lines and collect samples where the lines cross drainage channels (Zeegers, 1979). Due to the dense undergrowth that often occurs along drainage courses in rain forest, it is often more efficient to use cut lines as the undergrowth in the interfluvial areas is often fairly open and relatively easy to traverse. Nevertheless, devastation of large tracts of forest by tropical cyclones sometimes makes access by sampling parties extremely difficult.

Because of the difficulties of communication, sample analysis is sometimes performed in a field laboratory so that anomalies can be followed up immediately, avoiding the expense of organising an additional field expedition (Singh, 1971). Although this is practical for the determination of cxCu, for example, it is not feasible for multielement surveys or when high sensitivity analyses are necessary.

Widely-used statistical methods of data interpretation for regional surveys often require grouping of sample populations according to source rock type. However, in many tropical rain forest areas of subdued relief and few rock exposures, recognition of rock type can be impractical and alternative statistical groupings should be adopted (Dahlberg, 1982).

In some areas it may be almost impossible to achieve a regular sample distribution and statistical techniques may be required to assist with the interpretation of geochemical patterns and identification of anomalous areas. In Sumatra, for example, Page and Young (1981) used anomaly density adjusted maps, which successfully identified known and new areas of Cr, Cu and Pb mineralization.

Although it is acknowledged that stream sediment geochemistry is a highly appropriate exploration method in inaccessible mountainous tropical forested areas, there is some dispute as to whether the technique is equally appropriate for areas with mature topography (Tooms, 1987). For a regional geochemical reconnaissance survey of an area of 6000 km^2 in French Guyana, Zeegers (1979) recommended soil sampling on a grid with lines 2 km apart and samples every 500 m, plus stream sediment sample collection where cut-lines cross drainage channels. Zeegers (1979) concluded that where deep weathering occurs, as indicated by high Fe and Al in soils, it is necessary to pay detailed attention to very weak anomalies as these could be significant. The Loulo gold deposit in southwest Mali (Domanget et al., 1987) was discovered by soil sampling on a 1600 × 500 m grid in an area with very subdued topography and a poorly developed drainage pattern, such that stream sediment sampling was considered inappropriate.

Practical advice for geochemical survey parties operating in the logistically difficult, inhospitable and sometimes dangerous rain forest is contained in two guides by Berrangé (1975) and Chapman (1982).

CASE HISTORIES

Within tropical rain forest terrain, drainage geochemistry has been widely used in projects ranging from regional reconnaissance surveys to detailed investigations. Space does not permit a full examination of the many case histories in the literature and no attempt is made here to provide a comprehensive bibliography of exploration in tropical rain forest regions; the reader is referred to the bibliographies produced by the Association of Exploration Geochemists (Hawkes, 1982, 1985) for more complete coverage, and to citations elsewhere in this chapter.

Porphyry copper deposits

By far the most conspicuous successes have been in the location of porphyry copper deposits. A reconnaissance stream sediment survey in Sabah (Malaysia), conducted by the United Nations between 1961 and 1965 led to the discovery of the Mamut porphyry copper deposit and United Nations surveys in Panama, between 1965 and 1968, resulted in the location of the Petaquilla and Botija deposits (Lepeltier, 1971). Two porphyry copper districts in North Sulawesi were discovered using drainage geochemistry in 1971 (Lowder and Dow, 1978) and the Mocoa deposit in southwestern Colombia was discovered by a joint U.N.–INGEOMINAS survey carried out between 1973 and 1976 (Sillitoe et al., 1984). In Papua New Guinea stream sediment geochemistry played an important part in several discoveries including Panguna (Bougainville) (D.H. Mackenzie quoted in Joyce, 1984), Ok Tedi (Jones, 1973), Frieda River (Lord, 1978) and Yandera (Fleming and Neale, 1979). The Waisoi and Waivaka prospects in the Namosi area of Viti Levu, Fiji, were also initially located by stream sediment geochemistry (Leggo, 1977). The applicability of stream sediment techniques in the Philippines has been demonstrated by Coope and Webb (1963) and Govett and Hale (1967) amongst others.

The fine fraction of the stream sediment (normally the <177 μm fraction) is most commonly used and analytical data obtained via either cold extractable or hot acid attacks have been shown to be effective (Coope and Webb, 1963; Govett and Hale, 1967). The length of dispersion trains from porphyry coppers is often long and deposits can be detected with very low sample densities. Govett and Hale (1967) report the detection of an anomalous cxCu dispersion train extending 16 km from mineralization at Santo Nino in the Philippines. On Cebu, Coope and Webb (1963) found that significant dispersion trains ranged in length from 300 m to more than 1600 m for "total" Cu, but were much shorter for cxCu. Conversely, in Papua New Guinea, Drez (1987), and in

Puerto Rico, Learned et al. (1985) found that cxCu provided the best contrast and greatest dispersion. Jones (1973) reports that the Ok Tedi deposit in Papua New Guinea is detectable by stream sediment geochemistry over 40 km from the deposit, with values in <177 μm material in excess of 200 ppm Cu compared with a background of 10–30 ppm. Anomalous dispersion trains in North Sulawesi, with values of 500–1000 ppm Cu above a background of 100 ppm, extend for up to 3 km downstream of mineralization (Lowder and Dow, 1978).

Jones (1973) describes reconnaissance exploration in Papua New Guinea. The initial exploration, designed to collect at least one sample per 25 km^2, was by helicopter, landing at the junctions of major streams and where possible in the headwater regions of each drainage basin. Float was examined and a stream sediment sample taken at each site. If the float showed no sign of mineralization or the analysis of the sediment was not anomalous, the particular drainage system was considered unprospective. Prospective systems were then subjected to more detailed sampling and a number of porphyry copper deposits and Pb and Zn anomalies related to skarn type mineralization were discovered.

In Fiji a stream sediment survey, in which <177 μm material was collected at a density of 2.4 samples per km^2, successfully defined two Cu prospects, but failed to locate a third because barren material from alluvial flats upstream masked any anomalous sediment from the mineralization (Fig. 10-13; Leggo, 1977).

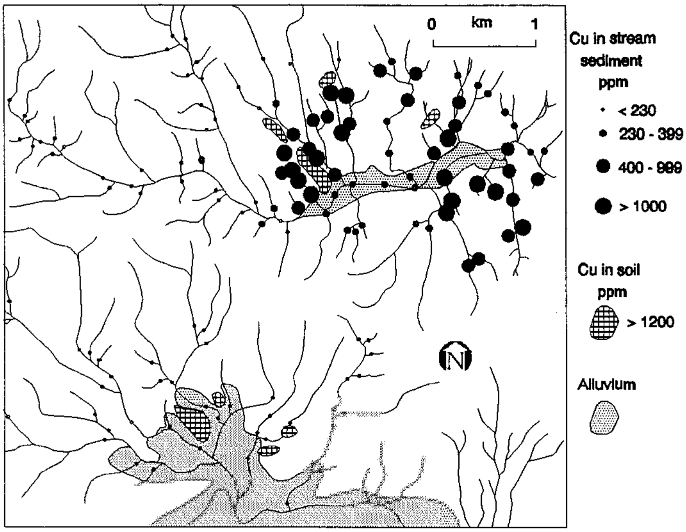


Fig. 10-13. Contrasting dispersion of Cu from two Cu prospects in the Namosi district of Fiji, showing the influence of alluvium in subduing anomalous values in the south-west sector (modified after Leggo, 1977).

Gold mineralization

Reconnaissance prospecting, largely by visual estimation of gold grains in panned concentrates from active sediments and the sediment/bedrock interface, detected vein quartz gold mineralization grading 10 g/t Au in Surinam and disseminated auriferous zones grading 2 g/t Au in lateritized metavolcanics in Liberia (Tooms, 1987). Barthelemy et al. (1987) describe a regional mineral exploration survey covering 64,000 km^2 in Gabon which included stream sediment sampling at 2–3 samples per km^2, and analysis of the <125 μm fraction for Au. Gold mineralization in hydrothermally altered ultrabasic rocks was identified from one stream sediment sample having 100 ppb Au and three heavy mineral concentrates with visible gold (Barthelemy et al., 1987; Zeegers and Leduc, 1991). Stream sediment surveys that revealed significant Cu anomalies aided the discovery of the Salobo Cu–Au and Bahia Au–Cu deposits in the Carajas region of Brazil (Meyer and Goncalez, 1982; Andrade et al., 1991). Subsequent investigations revealed that two <177 μm stream sediment samples in each of the areas contained elevated Au concentrations (167–2900 ppb). More detailed surveys are required to define the utility of the sampling medium in subdued lateritic terrain.

Background concentrations of Au in stream waters characterise the deeply weathered low-relief environment at Bahia, Brazil, whereas in the higher relief of the Salobo area significant Au concentrations occur in some surface waters (Andrade et al., 1991).

The Kelian disseminated epithermal Au deposit located in low rolling hills in Kalimantan, Indonesia was discovered during follow-up of alluvial gold occurrences within the Kelian River using stream sediment, pan concentrate, rock float and outcrop sampling. Positive indicators of mineralization were cinnabar and abundant gold in pan concentrates collected in the main stream up to 16 km downstream from the prospect and also in tributaries draining the prospect area. The extreme length of the dispersion train may be due to remobilisation of gold from fossil placers along the main stream. Tributaries yielded anomalously high Au, Ag, As, Pb and Zn concentrations in stream sediments (Van Leeuwen et al., 1990).

Gold, Te, Zn and Cu anomalies in the <177 μm fraction of stream sediments and Cu, Ag, Au and Zn anomalies in heavy-mineral concentrates are associated with the Rois Malk epithermal precious metal vein mineralization on Babelthuap Island, in the Palau intra-oceanic arc, western Pacific (Rytuba and Miller, 1990). Chalcopyrite, galena, sphalerite and gold grains identified by conventional optical techniques are also guides to precious- and base-metal mineralization. On the Gagil Tamil and Maap Islands of the Yap arc, quartz veins and quartz-cemented breccias containing up to 3.7 ppm Au were detected by Au and Te anomalies in <177 μm stream sediments and by Cu and chalcopyrite in heavy mineral concentrates (Rytuba and Miller, 1990). The gold mineralization was also clearly identified by anomalies of 10 to 100 ppb Au and from 100 to 2100 ppb Te in sediment from the mangrove coast and swamp surrounding these islands.

A regional exploration technique involving fractional analyses of gold in stream sediments and pan concentrates was used to detect Au–Cu porphyries, Au and base-metal bearing breccias, and Au in both high- and low-sulphidation epithermal systems in the rugged terrain of North Sulawesi, Indonesia (Carlile et al., 1990). Gold in the finer size fractions produced the strongest and most reliable anomalies. Strong coherent Au, Ag and Cu anomalies characterise the Au-bearing hydrothermal breccias and discriminate them from epithermal mineralization. The western part of the area is characterised by highly anomalous gold in both pan concentrates and stream sediments together with highly anomalous Ag and Cu in stream sediments (Fig. 10-14). Well-exposed hydrothermal breccias containing 2–4 g/tonne Au and 1–2% Cu were discovered at Bulagidun as a result of follow-up of stream sediment anomalies. Dispersion trains extend for 5 to 10 km. No anomalous float or exposures have been located to explain Au, Cu and Ag anomalies in the eastern part of the area.

In areas of mountainous terrain where mechanical dispersion is more pronounced, gold dispersion trains tend to be more extensive and gold levels higher than in areas of subdued relief. Middleton and Campbell (1979) discovered that the Coco Mina epithermal gold–silver deposit in northeastern Nicaragua produced a <177 μm stream sediment anomaly for Au with Au values of >400 ppb extending some 3 km from the mineralization (Fig. 10-15). This Au anomaly is more extensive than the Zn anomaly from the same source.

Watters et al. (1991) showed that analysis of both stream sediments and panned concentrates is desirable for rapid reconnaissance exploration for Au related to intermediate hypabyssal intrusives, volcanics and structural zones in Central Kalimantan. Gold was the best indicator of Au prospects with the occasional exception of Pb and more rarely Cu.

Gold in heavy mineral concentrates and As, Cu, Fe, Mn and Zn in the <177 μm sediment fraction were used in a gold exploration project in the mountainous to gently undulating terrain of southwest Colombia (Appleton and Greally, 1990). Positive correlation between Au in the <125 μm fraction of heavy mineral concentrates and Cu in stream sediment, together with the absence of a significant correlation between Au and As and other geological and gold chemistry data, indicated a mesothermal or skarn source for the primary gold which had been transported for 20–25 km in Quaternary mud-flows prior to dispersion into drainage sediments.

Pathfinder elements are often useful in gold exploration in tropical rain forest regions. Lasserre et al. (1989) show how regional stream sediment, soil and heavy mineral multielement data, used in combination indicate numerous Au mineralizations in southern French Guyana. Zones with high Au potential are identified on the basis of concentrations of K_2O, Ba, B, V and Au, together with heavy mineral indicators such as tourmaline. In regional geochemical surveys of Choiseul and the New Georgia Group of the Solomon Islands, the <177 μm fraction of stream sediments reflects known epithermal gold mineralization chiefly on the basis of Cu, Pb and Zn anomalies (Dunkley, 1986). Dispersion trains are short, less than 1 km from an anomaly peak of over 1000

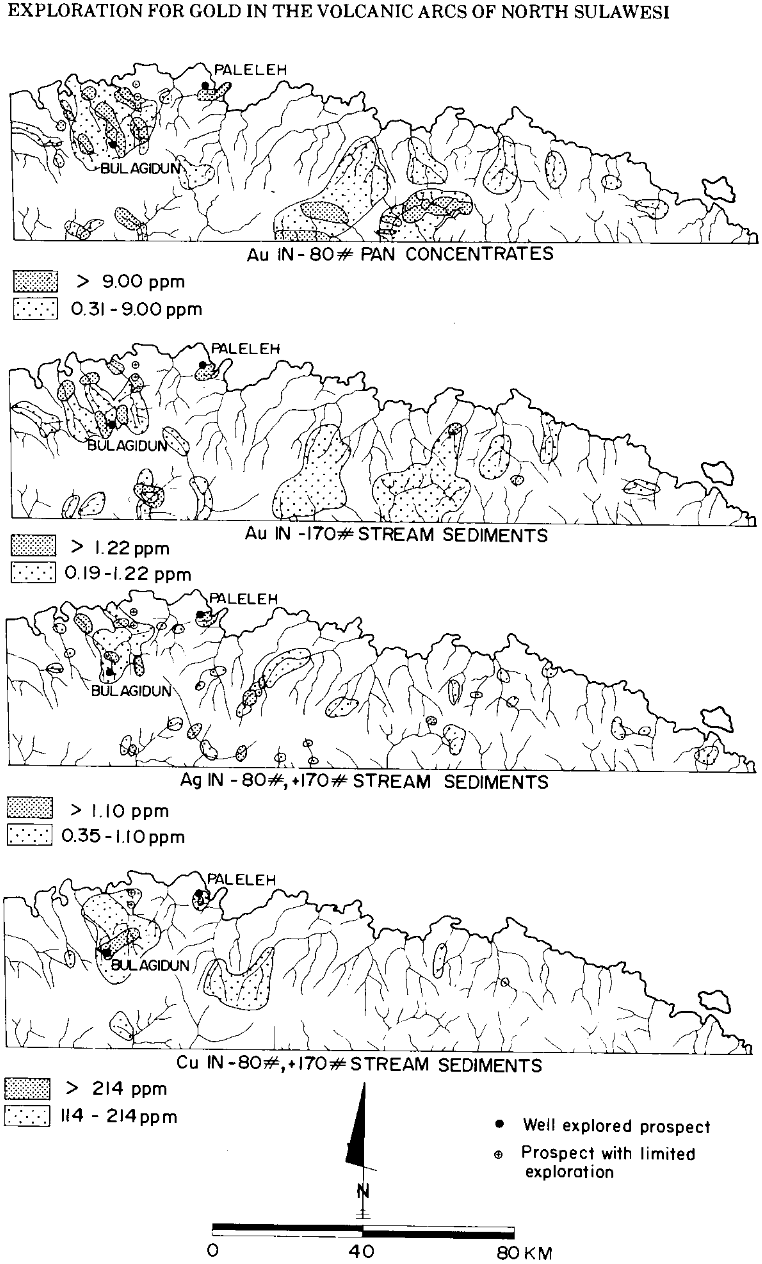


Fig. 10-14. Drainage geochemistry maps for an area in north Sulawesi (from Carlile et al., 1990).

ppm Cu with a background of 81 ppm and threshold of 129 ppm (P.N. Dunkley, pers. commun., 1986), and although follow-up sampling did produce a number of small and sporadic gold anomalies in the <177 μm fraction the technique was

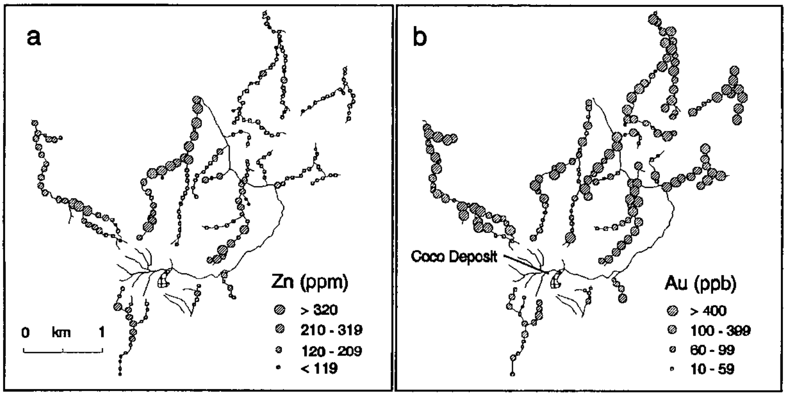


Fig. 10-15. Dispersion of (a) zinc; and (b) gold in stream sediments, Coco Mina epithermal deposit (shaded), northeast Nicaragua (modified after Middleton and Campbell, 1979).

not considered adequate for gold exploration. Panning, however, revealed free gold in stream sediments at localities where no geochemical anomalies occur, suggesting that surveys for gold mineralization should include analysis of heavy mineral concentrates (Dunkley, 1986). Secondary dispersion from alteration zones indicative of epithermal precious metal mineralization in the Philippines (Celenk et al., 1987) is highly variable with only a few samples giving Au and Ag values above detection limits. Epithermal alteration zones are outlined by secondary dispersion patterns of variable intensity by most of the pathfinder elements (Cu, Pb, Zn, Mo, Cd, Se, Mn,Te, As, Tl, Sb, Bi, and Hg). Arsenic has a particularly long dispersion train while Tl dispersion is restricted to acid leached zones and Sb, Bi and Hg tend to be generally restricted to the area of mineralization.

Other types of mineralization

Page et al. (1978); Hamidsyah and Clarke (1982); and Stephenson et al. (1982) describe a stream sediment survey over a large area of northern Sumatra in which geochemical anomalies were traced to various types of mineralization, including primary tungsten and tin. The sample interval was designed to be 4 km along drainage channels, but often this was not achieved due to the terrain and logistical difficulties. Samples were wet sieved to <1 mm in the field and the <200 >100 μm fraction milled to ensure homogeneity before analysis. Dispersion trains were generally short, 5 km being an average upper limit, and although geochemical anomalies could normally be related to mineralization, known mineralization was not always accompanied by a positive geochemical response. The importance of observation of float and in-situ geology is emphasised. Young and Johari (1978) point out that the Tangse Cu–Mo prospect in northern Sumatra gives rise to a very low level stream sediment anomaly which might have been ignored had the regional geology not been known. A blanket of alluvium (probably from an old lake which formed after the drainage system had been blocked by a landslide) inhibits erosion by all but the smaller streams and any anomalies are rapidly diluted once they meet the major rivers. Values of over 2000 ppm Cu and 12–160 ppm Mo in second order streams are reduced to 64 ppm and near zero respectively in the fourth order stream into which they flow (Page et al., 1978).

Regional geochemical surveys in central peninsular Malaysia showed that, in the <177 μm fraction of stream sediment samples collected at between 1.2 and 1.8 samples per km^2, Co, Cu, Pb, Zn, Ni, Mo, Mn and Fe were effective in locating sulphide mineralization. Scoop sampling was found to give better anomaly contrast and less sampling error than wet sieving on site to <350 μm. A heavy mineral pan concentrate survey at a density of 1 sample per 10 km^2, undertaken at the same time, was also effective, although dispersion patterns of the more mobile elements Co, Cu, Mo and Zn, were not recognized in this medium (Chu et al., 1982; Lee et al., 1982).

In Brazil, the discovery of the Salobo stratiform copper deposit was aided by the geochemistry of the <177 μm fraction of stream sediment sampled at 500 m intervals up drainage channels, which produced one anomalous sample with 2700 ppm Cu above a threshold of only 15 ppm (Meyer and Goncalez, 1982). In the Amazon region of Brazil, as in Guyana (Zeegers, 1979), both residual soil and drainage samples usually are collected at the reconnaissance stage (Mazzucchelli, 1986).

Pollack and Zeegers (1983) report that an area of Cu mineralization in the Upper Nickerie region of Surinam gave stream sediment dispersion trains of only a few hundred metres in length. The geochemical response was strongly diluted by large amounts of barren quartz and the best anomaly contrast occurred in the <63 and >1000 μm fractions. In the same region, Dahlberg (1982) found sample densities of between 1 and 2 per km^2 necessary to confirm soil anomalies of 243–448 ppm Cu and 291–884 ppm Ni respectively. Dispersion trains again were short with a maximum of 1300 m.

In northern Venezuela a geochemical stream sediment survey located barite deposits in the rain forested covered areas of the Coast Cordillera. The 125–65 μm fraction gave the best response (Rodriguez, 1985).

Stream sediment and pan concentrate sampling during the preliminary evaluation of the Maicuru alkaline–ultramafic–carbonatite complex, northern Brazil indicated the presence of P-, Nb- and REE-bearing minerals (Costa et al., 1991). Follow-up soil sampling and drilling identified phosphatic laterite containing up to 37% P_2O_5, 20% REE_2O_3 and 30% TiO_2.

EVALUATION OF THE EXPLORATION RECORD AND TOPICS FOR FUTURE RESEARCH

Standard techniques of drainage geochemistry generally perform well in areas of tropical forest. The most significant exploration successes for drainage geochemistry have been the discoveries of porphyry copper deposits in Panama, Papua New Guinea and Puerto Rico, all of which occur in areas of steep terrain, where the combination of large target size, and active chemical and mechanical weathering provide almost optimum conditions for drainage geochemistry. Although various mineral occurrences have been located using drainage geochemistry in tropical rain forest areas of more subdued topography, none have proved economically viable.

The selection of optimum size fractions for work in tropical rain forested areas, however, have not been satisfactorily resolved. Although investigations such as those of Magnusson (1983) and Pollack and Zeegers (1983) provide useful guidelines, incomplete presentation of data or failure to collect a complete range of sample types means that further research is required.

The recommendations for future research of an International Workshop on Geochemical Exploration in Tropical Rain Forests (1985) included: further size fraction investigations in different topographic terrains and for different types of mineral deposit; and for gold exploration, detailed comparisons of chemical analysis of the fine fraction of stream sediments, panning and visual grain counting, and chemical analysis of heavy mineral concentrates. Seasonal variability of stream sediments and the reproducibility of replicate samples requires investigation in rain forested areas of mature topography. Hydrogeochemistry has been used to a very limited degree in tropical rain forests. Further investigations are needed, especially of the dispersion of sulphate and arsenate anions, which may be more widely dispersed than other cations as they may be less susceptible to adsorption. Drainage biogeochemistry has been studied to a limited degree (Magnusson, 1983) and its apparent potential for mobile elements suggests that further investigations should be carried out. An additional problem requiring study is to determine why secondary oxides of manganese exert more control of mobile elements than those of iron in certain circumstances, while in others the reverse situation occurs; investigation of this is related to determining the significance of coatings of these oxides as a control on and a mechanism for dispersion in tropical rain forested areas.

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Chapter 11

DRAINAGE GEOCHEMISTRY IN ARID REGIONS

R.H. MAZZUCCHELLI

INTRODUCTION

Arid regions occupy a significant proportion of the Earth's surface and include many of the world's major mineral provinces, such as those in south-western USA/northern Mexico, southern Africa, northern Chile and all but the eastern margin of Australia. Extensive arid regions also occur in many developing countries, e.g., in north Africa, where the discovery and exploitation of mineral resources is one of the main options available for stimulating economic activity and improving living standards. Hence, mineral exploration is of major importance in arid regions where, despite the rarity of surface water, drainage geochemistry can nevertheless play an important part. The climatic and geomorphological characteristics of arid regions do, however, require the development and application of special methods.

For the purposes of this chapter, a region is defined as arid when long term moisture loss due to evaporation and transpiration exceeds precipitation. Generally, these are areas where rainfall is less than 250 mm per year, and irregular in occurrence. In Australia, however, although the accepted boundary of the arid zone closely follows the 250 mm isohyet, many localities in the tropical north-west receive more than 500 mm of rainfall but are still regarded as semi-arid (Fig. 11-3). This chapter is concerned mainly with arid regions of the lower and middle latitudes (Fig. 11-1), where high temperatures increase evaporation and hence the degree of aridity.

The geological environments represented in arid regions cover a broad spectrum and a correspondingly wide variety of minerals and ore deposit types (Table 11-I).

Exploration in arid regions is by no means limited to the types of ore deposits previously discovered, but is frequently based on conceptual models and therefore covers a wide range of deposit types.

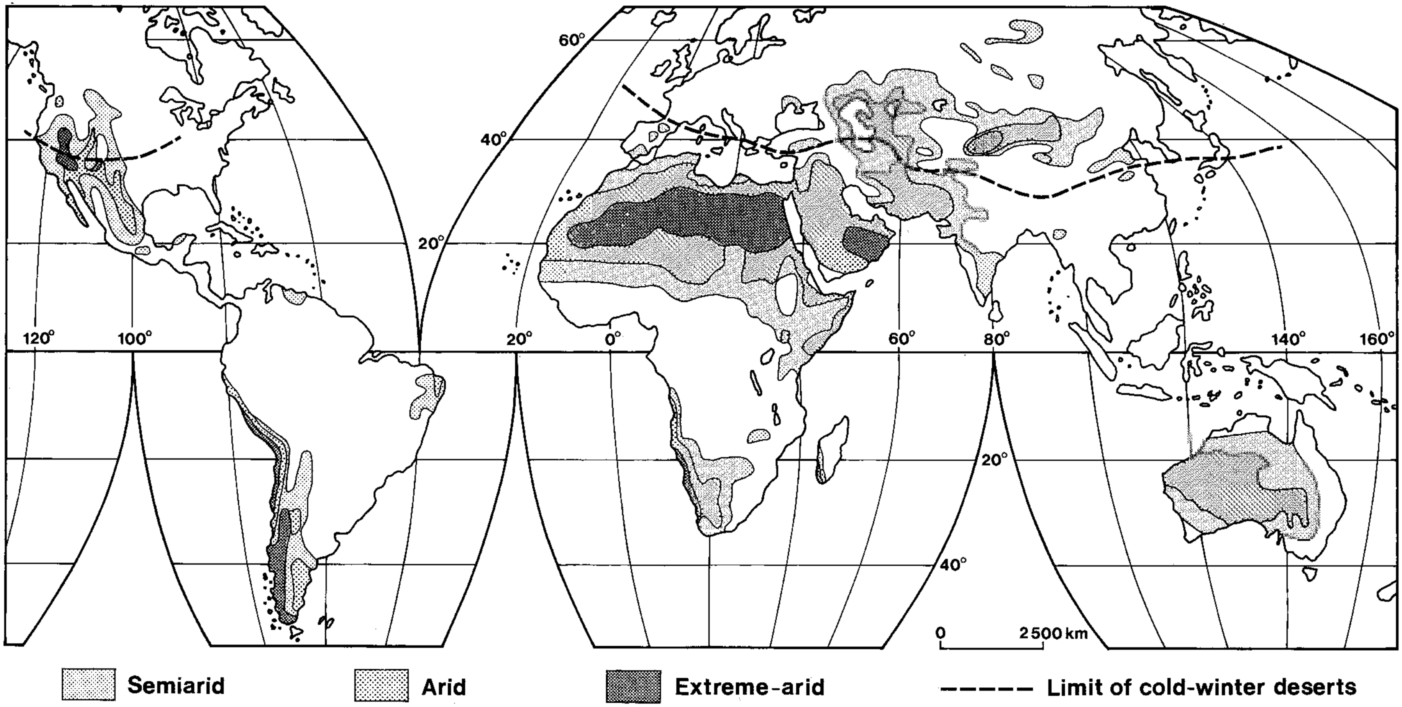


Fig. 11-1. World distribution of dry climates (reproduced by permission of UNESCO from Review of Research on Arid Zone Hydrology, Arid Zone Programme 1, by P. Meigs ©UNESCO 1953).

TABLE 11-I

Important examples of mineralization in arid regions

Geological environment	Deposit type	Examples
Archaean shield	Volcanic associated vein and shear zone gold	Kalgoorlie, Norseman (Australia)
	Magmatic nickel, copper, platinum group elements	Kambalda, Agnew (Australia); Pikwe-Selebi (Botswana)
	Volcanic associated massive sulphides	Golden Grove, Teutonic Bore, (Australia); Prieska (South Africa); Jerome (USA)
Proterozoic platform sediments	Sediment-hosted sulphide, barite	Aggeneys, Gamsberg (South Africa); Tsumeb, Otjihase (Namibia); Mt. Isa, McArthur River, Broken Hill, (Australia)
	Clastic sediment-hosted gold	Telfer (Australia)
	Vein and disseminated uranium	Rossing (Namibia); Kintyre (Australia)
Phanerozoic fold belts	Porphyry-related copper–gold–molybdenum and related veins and skarns	Chuquicamata, El Teniente, El Indio (Chile); Twin Buttes, Mission, Morenci (USA); La Caridad (Mexico);
	Clastic sediment-hosted gold	Cortez, Carlin, Pinson (USA)
Phanerozoic platform sediments	Sediment-hosted sulphide–barite	Dzhezkazgan (Kazakhstan); Cobar, Elura (Australia); Boleo (Mexico); Nacimiento (USA)
	Uranium in terrestrial sediments	Yeelirrie, Beverley (Australia); Colorado Plateau, Grants (USA); Langer Heinrick (Namibia)
Various	Tin–tungsten–tantalum veins, pegmatites, lodes and related placers	Mill City (USA); Kibara (Namibia)

THEORETICAL CONSIDERATIONS

Desert types

Desert environments can be classified into two major morpho-structural types: shield (or platform) deserts; and mountain-and-basin deserts.

The shield deserts, which characterize large areas of Africa, Arabia, Australia and India, typically comprise broad plains and tablelands separated by lowland basins. Areas of elevated topography are restricted in area so that drainage systems are often poorly developed and erosion is limited. The preservation of extensive remnants of earlier, more humid weathering cycles is common and internal drainage, where the products of erosion are deposited and accumulate in playa lake systems (or sabkhas) are also a common feature of shield deserts. Many shield deserts owe their arid climate to the zonal distribution of anti-cyclonic belts between 10° and 30° north and south of the equator.

The mountain-and-basin deserts, typified by the Basin and Range Province of the southwestern USA, are dominated by the juxtaposition of mountains and plains as a result of vertical tectonism. Aridity in such areas is often directly related to the rain shadow effect of the mountain ranges. In contrast to the shield deserts there are marked disparities in the local climates in such regions, with significant precipitation in the form of rain or snow on the higher ground, which is often sufficient to support an extensive drainage network. Major gravel outwash fans are formed at the junction between mountain and plain, while more diffuse, less organized drainage continues to deposit fine sediments in the inter-montane basins. As in the case of shield deserts, the terminal point of the drainage system is commonly a system of playa lakes where surface waters quickly evaporate. Windblown sand or loess deposits are common features of both types of desert, although major dune fields occupy only a small proportion of most deserts, e.g., approximately 2% in North America and 15% of the Sahara Desert (Mabbutt, 1977).

Weathering processes

In arid environments physical weathering processes are often regarded as being more effective than those of a chemical nature due to the scarcity of water, which is essential for chemical weathering. Nevertheless, sufficient water is present even in the most extreme arid conditions for significant chemical weathering to occur over periods of geological time (El Shazly et al., 1977). Certainly physical processes are more important in areas of high relief, where the slow rate of chemical weathering is usually outpaced by mechanical erosion. Chemical weathering is most conspicuous in the vicinity of playa lakes, where groundwater occurs close to the surface. It seems probable, however (Thornber, 1992), that similar processes operate in the capillary fringe above the water table, which lies at progressively greater depth with increasing distance from playa lakes. The dominant chemical weathering processes involve oxidation, the effects of which are most important in relation to the different ionic species of iron, manganese and sulphur.

Groundwaters in desert environments are commonly alkaline and therefore less reactive than those of temperate climates which generally contain significant concentrations of organic acids and CO_2. However, exceptionally low pH levels have also been documented in groundwater seepages and playa lake environments in southwestern Australia. Mann (1984a) attributes the development of such low pH to the "ferrolysis" process, which is thought to operate within the capillary fringe of the groundwater table in soil profiles, where oxidation of ferrous iron occurs according to the reaction:

$$2Fe^{2+} + 3H_2O + \tfrac{1}{2}O_2 \longrightarrow 2FeOOH + 4H^+.$$

The local development of low pH zones within the weathering profile may be important in mobilizing metals of interest in geochemical exploration such as gold (Mann, 1984a). In the vicinity of pyrite-bearing mineralization, the ferrous ion may be derived, at least in part, by the oxidation of pyrite at deeper levels:

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+.$$

The iron and manganese oxides produced by such oxidation reactions are removed from the surface by leaching in more humid environments but are retained in the surface environment of arid regions and impart a distinctive reddish brown colour to the landscape. Apart from the presence of oxides as discrete particles in soils and stream sediments, exposed cobbles and rocks are commonly coated by a crust of desert varnish of predominantly iron and manganese oxides, as a result of repeated wetting with saline waters and subsequent evaporation. As in other climatic regimes, these oxides play an important role in trace element dispersion. The generally alkaline conditions and ineffective leaching promote the development and retention of swelling clay minerals such as montmorillonite. Silica is also mobilized allowing its later concentration in siliceous crusts (Litchfield and Mabbutt, 1962).

Many shield deserts are characterized by deep weathering zones, up to 80 m not being uncommon. It is now generally recognized that such deep weathering is often a residual effect from an earlier, more humid climatic regime, which has been preserved as a result of the combination of low relief and change to an arid climate. The protective role of indurated lateritic horizons also plays a part in preserving the products of earlier humid climatic episodes after the onset of arid conditions. Although deep weathering may not be directly related to the present climate, its products are involved in contemporary geochemical dispersion processes and must be considered in the design of geochemical drainage surveys. Indeed Matheis and Kuester (1985) advocate selective sampling of palaeo-dispersion patterns in wadi drainage channels as a means of enhancing otherwise subtle anomalies.

Ineffective leaching of the soluble products of the chemical weathering which does take place results in the accumulation of sulphates, chlorides and carbonates, which promote further rock decomposition through the physico-chemical process known as exsudation (Jutson, 1918). The first step involves the penetration of saline moisture into joints, cracks and pore spaces in the rocks. Subsequent expansion due to hydration of rock-forming minerals or the crystallisation of salts exerts sufficient physical stress to bring about the disintegration of the rocks. Exsudation is probably the most potent process of physical weathering in arid environments, and is particularly evident at soil-rock interfaces, leading to the formation of undercut and pedestal rocks and other features often mistakenly attributed to abrasion by windborne sand particles. A particular feature of areas subjected to exsudation is the disintegration of rocks into mineral aggregates, the minerals themselves showing little or no evidence of weathering. However, the resulting increase in surface area exposed to chemical attack further accelerates the decomposition process on pediments.

Erosion processes

In general, the efficiency of various agents of erosion tends to be increased in arid regions due to lack, to a greater or lesser extent, of moisture and surface vegetation, which could bind the weathered mantle together. On the other hand protective "crusts", such as laterite, silcrete and surface lag gravels, tend to retard erosion in shield desert areas. Another factor limiting erosion, particularly in shield deserts, is the lack of relief. In many situations, there is only a very small difference in elevation (tens of metres) between the actively eroding "uplands" and the aggrading lowlands in which the products of erosion are deposited.

Water transport, despite its relative scarcity, is of great importance in erosion in deserts. In fact, the transportation of rock and soil detritus by sheet-wash on a hill slope of given attitude can be seen to be at a maximum (Fig. 11-2) in areas with a semi-arid to arid climate (Mabbutt, 1977).

During episodes of rain fall, however brief and infrequent, rain splash, sheet flow, stream flow and flow within chain-lake systems often display much greater intensity than the corresponding events in humid areas and transport the products of rock weathering from high to lower elevations.

The effects of wind erosion are also more obvious in arid environments than in humid areas. Evidence for the ability of wind to transport large quantities of unconsolidated material is most convincing in large sandy deserts. However, even in comparatively well vegetated deserts, evidence of wind erosion is usually widespread, particularly near playa lakes. Over periods of geological time the cumulative effect of even localized air turbulence, such as small thermal whirlwinds, results in the re-distribution of considerable amounts of detritus.

Erosional processes in desert environments operate within a dynamic system

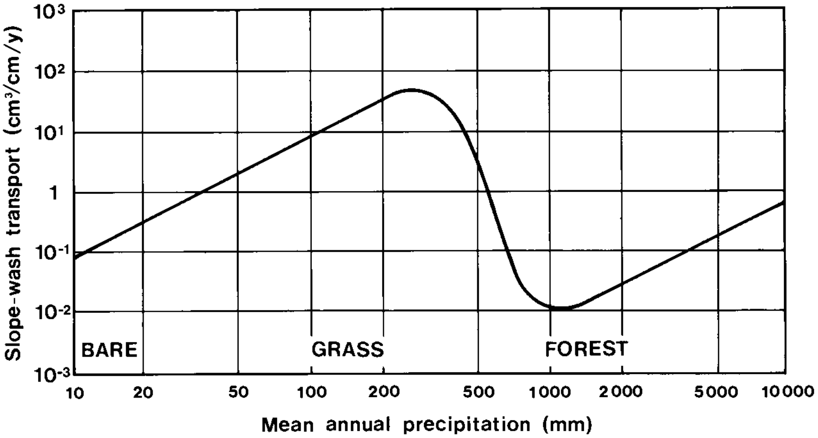


Fig. 11-2. Relationship between slope-wash dispersion and annual precipitation (reproduced with permission from Mabbutt, 1977).

in which the products of weathering are accumulated and recirculated. Drainage processes deliver soil and rock detritus from the uplands to playa lakes, which typically form the terminal points of drainage systems. Here, the fine sediments are deposited while salts, which include the soluble products of rock weathering, crystallise on the lake surface through evaporation of the saline groundwater underflow. On dessication of the playa surface, both fine clastic and precipitated material may be redistributed over the land surface by wind and subsequently by the drainage system, thus repeating a cycle which tends to homogenize surface materials, leading eventually to a reduction in geochemical contrast.

Drainage dispersion processes

Drainage dispersion in arid regions differs from comparable processes in more humid terrains in several respects that are important with regard to geochemical exploration. Firstly, the short duration and often torrential nature of flow events are not conducive to chemical equilibrium between water and sediments. Hence, for most practical purposes, drainage dispersion processes must be regarded as being entirely mechanical. Moreover, the paucity of vegetation in catchment basins combined with the erosion of stream banks leads to increased turbidity and thus enhances the carrying capacity of the discharge. Suspended loads representing 0.5 to 1.2 volume % of the discharge are common and loads of up to 40 volume % are known (Mabbutt, 1977). The density of fluid and rate of flow thus enable very large clasts to be transported over considerable distances.

A second distinctive characteristic of drainage systems in arid regions is their degree of disorganisation, as indicated by breaks in the continuity of channels and the prevalence of braided channel zones. This is particularly common in pediment zones, where the combination of high suspended load, decreasing gradient and finite supply of water from each discrete rainfall event leads to large scale deposition of sediment. Channels are repeatedly choked, further reducing in the gradient so that each new flow event must carve a new channel through the previously-deposited alluvial deposits. Individual drainage channels may thus dissipate into distributaries and, in extreme cases, extensive alluvial plains, from which they may or may not re-form into a single well-defined channel before discharging into playa lakes. The "disconnected" nature of arid region drainage partly forms the basis for Mabbutt's (1973) classification of the drainage systems in Australia (Fig. 11-3) and has important implications for drainage geochemistry.

Another factor that complicates drainage dispersion in arid regions is the localized and erratic distribution of precipitation events. It is not uncommon for major drainage systems to flow in response to a thunderstorm affecting only a small portion of the total catchment. Clearly the composition of the active sediments deposited after such an event will tend to reflect the geology of the area receiving rainfall rather than the average for the whole catchment. This phenomenon, combined with the other factors mentioned above, might be

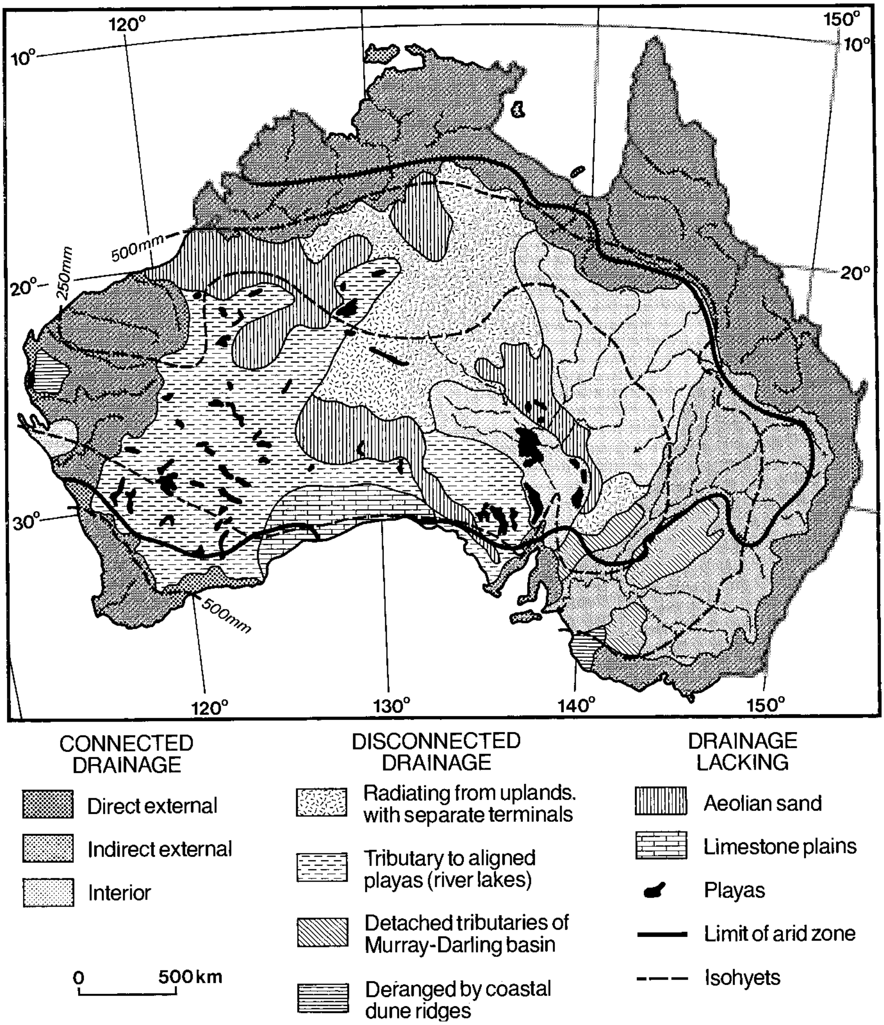


Fig. 11-3. Classification of surface drainage systems in Australia, showing relationship to precipitation and the arid zone (reproduced with permission from Mabbutt, 1977).

expected to lead to a variable and complex relationship between the geochemical character of drainage sediments and their provenance, compared to the more stable drainage processes operative in humid regions. Lack of the homogenizing effect of sediment–water interactions may be particularly significant in arid environments.

Despite these problems, deposition and sorting of sediments during stream flow events in arid regions take place according to normal hydraulic principles. The character of the sediment load changes over the length of the system, from poorly sorted soil and rock debris in the upland sections, through relatively well-sorted gravel and coarse sand in the mid-sections to fine sand, silt and ultimately clay in the playa lakes. Variations occur in response to local conditions in the stream bed, such as deposition of relatively fine clastic particles downstream from obstructions and on the aggrading margins of meanders, and concentration of heavy minerals in natural trap-sites.

The materials that constitute stream sediments in arid regions warrant some consideration. In actively eroding upland areas, these will include a relatively high proportion of fresh rock and mineral fragments. In areas of more subdued relief, however, the sediments are dominated by a few stable primary minerals, principally quartz, and secondary minerals such as clays and sesquioxides. In the extreme case of low relief, such as a shield desert with preserved remnants of an earlier deep weathering regime, the material contributed to the drainage is already strongly leached. The initial anomaly contrast in the stream sediments is therefore relatively low, and may be further decreased by the mixing of barren windblown material with sediments of local origin, as well as the inevitable dilution from barren catchments downstream. Anomalous drainage dispersion trains under such conditions can be subtle and short-lived, and appropriate measures are needed to optimise response. Ore-derived material in the drainage system may be represented by resistant primary minerals (e.g., native Au, wolframite, cassiterite, columbite or beryl) or secondary minerals, such as malachite, anglesite, carnotite or, most importantly, metal-rich ferruginous gossan fragments. The secondary minerals and ferruginous materials are, for the most part, quite friable and, with the abrasion that occurs during stream transport, are commonly reduced to silt-sized particles (Lovering and McCarthy, 1978).

Some practical implications of these factors are discussed in the following sections, which deal first with stream sediment surveys, and later review briefly the use of lake sediments in arid regions.

STREAM SEDIMENT SURVEYS IN ARID REGIONS

Practical considerations

There is no universally applicable set of geochemical survey parameters that can be adopted to optimise the results of stream sediment surveys in arid regions. Useful results have been reported for a wide range of sample types, sampling densities and analytical methods chosen to meet different objectives.

Sample type

Opinions differ widely on the fraction of stream sediments most suitable for stream sediment surveys in arid regions. The problem of dilution of stream sediments by aeolian material is widely recognised. Alternative methods proposed to minimise this problem include sieving samples and discarding, as far as possible, the barren aeolian component, as well as the use of more advanced techniques that involve the preparation of heavy mineral or magnetic concentrates.

Different approaches based on sieving fall into three main categories: those aimed at eliminating the very fine fractions; those intended to screen out the middle or sand-sized fractions; and those which are biased towards analysis of the finer fractions where aeolian dilution is not a problem.

Zeegers et al. (1985) present evidence from orientation surveys carried out in Saudi Arabia, Yemen and Oman of the presence of dilutant aeolian phases dominated by carbonates in the fine (<63 μm) fractions and quartz in the 63–250 μm fraction of stream sediments and they recommend sampling of the >250 μm fraction. Griffitts and Cooley (1978b) also point to the exotic character of the <75 μm fraction in exploration for Be in the Sheeprock Mountains, Utah, and recommend the use of the >75 μm fraction.

Bugrov and Shalaby (1975) advocate the use of either coarse (250–1000 μm) or very fine fractions (<75 μm) of wadi sediments in order to eliminate the dilutant effect of windblown sand which predominates in the mid-fractions of the sediment in the Eastern Desert of Egypt. In the same area, El Shazly et al. (1977) failed to detect anomalies associated with known Ni–Cu mineralization and only limited dispersion of Be and Li from ancient emerald mines using the <2000 μm fraction of wadi alluvium. It seems likely that the anomalies were suppressed by inclusion of the barren 75–250 μm fraction. On the other hand, Soliman (1981, 1982) reported satisfactory results for Cu, Sn, Nb and Au using the <1000 μm fraction similar to that used by Bugrov and Shalaby (1975) in the discovery of Ni–Cu mineralization at Gabbro Akarem, because aeolian dilution was not considered significant in that locality.

Other reports of the successful use of specific coarse fractions of stream sediments include exploration for U in Syria (Hale and Jubeli, 1985), Pb and Zn in South Australia (Muller and Donovan, 1971; Moeskops and White, 1980a, b), Pb in New South Wales (Dunlop et al., 1983), U, Mo and Bi in Saudi Arabia (Theobald et al., 1977) and W in Saudi Arabia (Salpeteur, 1985).

Muller and Donovan (1971) found in the willemite province at Beltana, South Australia, that anomaly contrast was highest in the coarse fraction (420–841 μm) but that anomalous dispersion trains persist further in the finer fractions. This bimodal distribution is probably more common than is apparent from the literature. Although Bugrov and Shalaby (1975) and Zeegers et al. (1985) both attribute the predominance of quartz in the middle size fraction of sediment to its introduction by aeolian agencies, it is probable, by analogy with the mineralogical composition of different size fractions in arid region soils (Mazzucchelli, 1978) that the same distribution also occurs in areas where aeolian deposition is insignificant.

Comparable results were reported by Garnett and Rea (1985) from a comprehensive orientation study over the Otjihase Cu deposit in Namibia. High contrast anomalies were documented by sampling both the 1000–2000 μm and the <75 μm size fractions of sediment samples; however, although the dispersion train is of similar length in each case, the latter fraction shows a more systematic decline in contrast with distance from the source. The results of hand-picked (<2 mm) gossan fragments show particularly high contrast values, but the dispersion train is erratic.

Another investigation involving selective hand-picking of very coarse size fraction material from stream sediments is described by Erickson et al. (1966), who found that selective sampling of veined and altered cobbles from major drainage channels in Nevada provided a better general indication of the presence of potential mineralization than the more conventional <200 μm fraction.

A great number of investigations in arid regions have achieved satisfactory results using the fine fractions of stream sediments. Table 11-II indicates the diversity of ore deposits and environments for which this has proved to be the case. In situations where an anomalous response can be obtained

TABLE 11-II

Stream sediment investigations using fine fraction samples

Elements	Area	Size fraction (μm)	Source
Cu,Pb,Zn,U,Mo,As	Rayen, Iran	<70 or <200	Beeson (1985)
U,Th,Cu,Pb,Zn	Sarkhanlu, Iran	<70 or <200	Beeson (1985)
Cu,Zn,U,Mo,As,Pb	Richtersveld, S Africa	<70 or <200	Beeson (1985)
Cu,Pb,Zn	Aggeneys, S Africa	<70 or <200	Beeson (1985)
Cu,Pb,Zn	Gamsberg, S Africa	<70 or <200	McLaurin (1978); Beeson (1985)
U,Mo	Karoo, S Africa	<70	Beeson (1985)
Cu,Pb,Zn,U,Mo	Dechan, Iran	<70	Beeson (1985)
cxCu	Eastern Desert, Egypt	<75	Bugrov and Shalaby (1975)
Au,As	Red Sea Hills, Sudan	<200	Fletcher (1985)
Cu,Pb,Zn	Otjihase, Namibia	<75	Garnett and Rea (1985)
Ni,Cu,Pb,Zn,Co	Halls Creek Province, Western Australia	<175	Halligan and Harris (1980a, b)
Cu,Mo,Pb,Zn,Ag	Safford District, Arizona	<200	Horsnail (1978)
Cu,Mo	Pima District, Arizona	<200	Lovstrom and Horsnail (1978)
cxCu,Cu	Musgrave Block, Western Australia	<75	Mazzucchelli (1980)
Zn,Cu,Pb	Mt. Isa Belt, Queensland	<175	Nisbet and Joyce (1980)
U,Cu	McArthur Basin Northern Territory	<180	Rossiter (1980a)
Zn,Pb	Adelaide Geosyncline, South Australia	<175	Moeskops and White (1980a, b)

using fine fractions, Beeson (1985) has pointed out significant advantages in selecting the <75 μm (minus 200-mesh) fraction in preference to the more traditional <200 μm (minus 80-mesh) fraction. These include the homogeneity of the background population, and hence confidence in the assessment of anomaly threshold, enhanced concentration levels,improved anomaly contrast and longer dispersion trains.

Beeson's results probably reflect the tendency for barren quartz to be concentrated in the 75–200 μm fraction sediments, as is the case in soils (Mazzucchelli, 1978). Another advantage of the fine fractions are better sampling statistics and lower costs: provided that sediments are dry and can be sieved on site, as is usually the case in arid environments, no further laboratory preparation of samples in necessary.

Several investigators have opted to sample a broad range of size fractions in order to accommodate varying or complex distributions for different elements. Examples include the use of the <590 μm fraction in the Sonoran Desert of Mexico (Overstreet and Marsh, 1981), the <710 μm fraction in Cu exploration in the Mt Isa Belt, Queensland (Rossiter, 1980b) and the examples already cited from the Eastern Desert of Egypt (Bugrov, 1974; Bugrov and Shalaby, 1975; and El Shazly et al., 1977).

Many authors report useful results from the analysis of the heavy mineral fraction from stream sediments (Overstreet and Day, 1985). Chapter 6 of this book provides a detailed account of this method of sampling and only brief reference to case histories which specifically relate to arid regions is made here. Bugrov and Shalaby (1975) and Theobald et al. (1977) point out that this technique eliminates the variable dilution effect of windblown sand and is particularly helpful in exploration for ore forming elements Sn, W, Mo, Bi, Ta, Nb and Zr, which are generally held in detrital minerals. In the case of base metals originally contained in sulphides, the secondary minerals in arid regions frequently include metal-enriched limonite of high specific gravity (Zeegers et al., 1985). These phases may be concentrated in the heavy mineral fraction, enhancing anomaly contrast and increasing the lengths of anomalous dispersion trains, thereby permitting lower sampling densities in reconnaissance surveys. This method has been used successfully for gold exploration in Sudan (Fletcher, 1985), base and precious metal exploration in the Sonoran Desert, Mexico (Overstreet and Marsh, 1981), exploration for rare metals in Egypt (Bugrov, 1974), and orientation studies for base metal exploration in Namibia (Garnett and Rea, 1985).

The method used to concentrate the heavy minerals can be critical. Both Overstreet and Marsh (1981) and Zeegers et al. (1985) describe to the possible loss of fine grained heavy minerals during panning or jigging. This can be particularly significant in surveys for precious metals such as gold, where the presence or absence of one or two particles distinguishes anomalies from background. Alternative techniques, including the use of heavy liquids to separate the heavy mineral fraction, ultrasonic concentrates (Huff, 1971) or the substitution of selective chemical extractions for physical concentration processes (Alminas and Mosier, 1976), have been suggested.

Problems in enhancing anomaly contrast by concentrating heavy minerals may be caused by natural accumulations of heavy detrital minerals from both background rocks and mineralization in natural trap sites in drainage channels. Magnetic separation is commonly necessary to eliminate such dilution by magnetite and ilmenite (Overstreet and Marsh, 1981), although in some cases magnetite itself contains anomalous levels of metals and shows extensive anomalous dispersion trains (McLaurin, 1978; Overstreet and Day, 1985). It has also been shown that magnetite of igneous or metamorphic origin may adsorb metal ions in the secondary environment, and thus become a useful concentrator of metals related to mineralization (Overstreet and Marsh, 1981). Overstreet and Day (1985) suggest that dessication and dehydration of hydrous oxides in soils and wadi sediments, leading to the development of high magnetic susceptibilities, may be much more common than has been recognized to date. Such material, when derived from the vicinity of a weathering ore deposit, could clearly give strongly anomalous indications if concentrated by magnetic means from the products of subsequent dispersion.

Sampling density

Typical geochemical reconnaissance sampling densities for stream sediment surveys in arid terrains range from one sample per km^2 to one sample per 10 km^2. However, very low densities (down to one sample per 75 km^2) have yielded useful information on the geochemical framework of the Arabian Shield (Theobald and Thompson, 1959) whereas in areas of dense drainage, such as the East Kimberley and Pilbara regions of Western Australia (Fig. 11-12), sample densities of 15–20 samples per km^2 can be achieved, allowing the precise delineation of anomalous areas and thus minimising the amount of follow-up soil or rock sampling required.

Hawkes (1976a) has shown that the strength of a stream sediment anomaly bears a constant relationship to the ratio between catchment size and area of anomalous source throughout a range of climatic conditions regardless of sampling density. This relationship provides the basis for very low density surveys carried out by some workers. Usually the sampling, analytical and interpretation techniques need to be optimized in order to detect subtle but significant variations due to mineralization when low sample densities are used. Reconnaissance work by the US Geological Survey in the Sonoran Desert of Mexico employed a sampling density of one non-magnetic heavy mineral concentrate per 24 km^2. In higher density follow-up surveys, levels of metals such as Pb were so high in concentrates that anomalies could only be resolved with recourse to unconcentrated sediment (Overstreet and Marsh, 1981). Other case histories in which significant dispersion trains permit low density reconnaissance surveys are listed in Table 11-III.

Several authors have documented extremely limited (often less than 1 km) dispersion trains associated with known mineralization, which limit the use of widely spaced stream sediment sampling for regional geochemical reconnaissance (El Shazly et al., 1977; Mazzucchelli, 1980; Rossiter, 1980a, b; Salpeteur,

TABLE 11-III

Examples of anomalous dispersion trains in stream sediments, arid regions

Elements	Area	Length of anomalous dispersion train (km)	Source
Cu,Ni	Eastern Desert, Egypt	1.5–2.0	Bugrov and Shalaby (1975)
Zn	Adelaide Geosyncline	2–3	Muller and Donovan (1971)
Au,As	Red Sea Hills, Sudan	5 (<250 μm) 5 (HMC)	Fletcher (1985)
Cu,Pb,Zn	Otjihase, Namibia	approx. 1.5	Garnett and Rea (1985)
Ni,Cu	Halls Creek Province, Western Australia	approx. 5	Halligan and Harris (1980a, b)
Cu	Rosemont, Arizona	26	Hawkes (1976a)
Cu	Safford, Arizona	10	Horsnail (1978)
Cu	Pima, Arizona	approx. 12	Lovstrom and Horsnail (1978)
Pb,Zn	Gamsberg, S Africa	approx. 16	McLaurin (1978)
Zn	Mt. Isa Block, Queensland	2.5	Nisbet and Joyce (1980)
U,Cu	McArthur Basin, Northern Territory	2–4	Rossiter (1980a, b)
Ag	Jabali, Yemen	5	Zeegers et al. (1985)

1985; Zeegers et al., 1985). However, in at least one case the brevity of the dispersion train can be attributed to the very limited areal extent of the mineralization exposed to dispersion agencies (Mazzucchelli, 1980).

The representativity of drainage sediment samples in arid regions is important. If coarse fraction or heavy mineral concentrate sampling is adopted, a larger sample may be required (1–20 kg) than in the case of samples based on collection of the fine fraction of sediment, where as little as 100 g can suffice. Multiple or composite samples should be collected over braided stream channels.

Disconnected drainage poses a more serious problem, as drainage geochemistry rarely provides a comprehensive map of the bedrock geology and mineralization in such areas. Additional exploration techniques might also be needed to complete the coverage of areas where residual material is mantled by alluvium or windblown deposits.

Analysis

Methods of analysis used in drainage geochemistry in arid regions cover the full spectrum of conventional analytical techniques. In methods involving sample dissolution, "total" metal is usually determined. However, partial or selective extraction methods have been advocated to detect subtle anomalies otherwise subdued by dilution problems. For example, orientation studies for an exploration programme for stratiform copper deposits in the Warburton Range area of central Australia (Mazzucchelli, 1980) indicate inadequate contrast over the only known occurrences of mineralization, with "total" Cu values of 20–80 ppm with a threshold of about 50 ppm. A colorimetric cold extraction method indicated background levels for cxCU were from 0.6 to 2 ppm with contrast up to sixfold. Determination of cxCu on the <75 μm fraction showed adequate contrast and concentration levels consistently above the analytical detection limit. The choice of cold extraction methods was also compatible with the remote location of the search area, which required simple low cost equipment suitable for use in a field laboratory. Bugrov (1974) reports similar enhancement of contrast with cold extraction determinations on the <75 μm fraction of wadi sediments in the Eastern Desert of Egypt, compared with spectrographic analysis on the coarse fraction of the sediments. This author, together with Garnett and Rea (1985), attributes the strong dispersion trains shown by cold extraction analysis on the fine fractions to be evidence of active chemical dispersion, but this is not necessarily the case. The increased proportion of cold extractable metal in fine fraction material derived from mineralized areas could be caused by the increased surface area exposed to acid attack and the weak nature of metal bonding associated with fine iron oxide and clay mineral particles. Another possibility is that the particles acquired their metal-rich character by chemical dispersion processes during a previous humid weathering episode, prior to being dispersed mechanically under the present arid regime. Alternatively, the fine particles may result from abrasion of coarser friable gossan fragments as a result of mechanical dispersion under the existing arid conditions. Regardless of the nature of dispersion, cold extraction techniques are effective in enhancing contrast because they are able to extract selectively metal related to mineralization. The US Geological Survey found that in areas of Zn–Pb–Cu mineralization in Grant and Luna Counties, New Mexico (Watts et al., 1978b), data obtained from the <175 μm fraction of stream sediments using the hot oxalic acid leach method of Alminas and Mosier (1976) essentially mirrored the distribution patterns for Cu, Pb and Zn obtained by analysis on the non-magnetic fraction of panned concentrates. It appears that the oxalic acid extracts both powdery limonite and its associated metals as well as some of the coarse gossan fragments recovered in the heavy mineral concentrates. The oxalic acid leach technique may thus have some advantages over panning in that it extracts ore-forming elements from the powdery varieties of limonite, which may be lost during panning. The method can be made portable, with the advantages in arid areas of eliminating the need for large quantities of water to produce panned concentrates.

Case histories

Porphyry copper–molybdenum deposits

Porphyry copper deposits usually provide a clear geochemical response in the local drainage and this is true in arid terrain. Hawkes (1976a) demonstrates

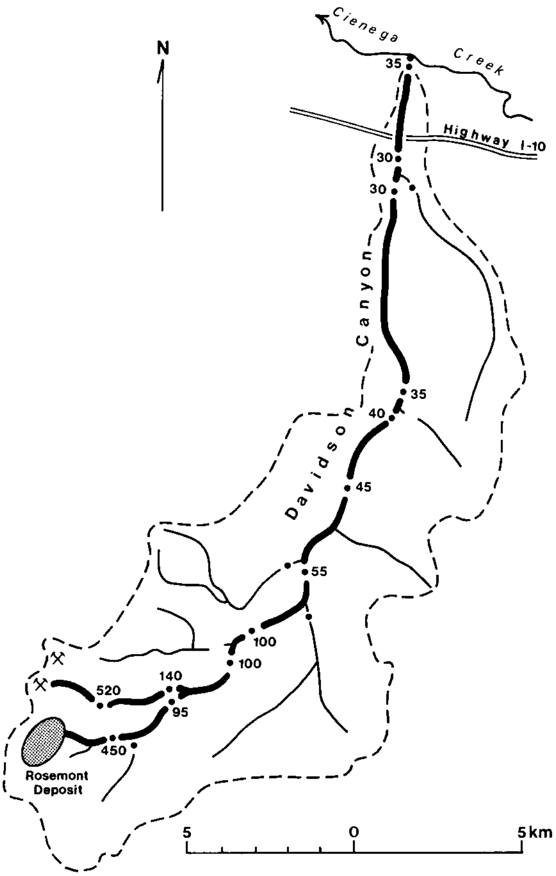


Fig. 11-4. Distribution of Cu in stream sediment samples draining from the Rosemont porphyry copper deposit, Arizona (modified after Hawkes, 1976a).

the remarkably consistent downstream dilution behaviour of Cu over a distance of 26 km below the Rosemont deposit in Arizona (Fig. 11-4). Hawkes relates the metal content of stream sediments in this drainage system to the area of catchment represented at each site and the exposed area and grade of the mineralized source, and shows that the tenor of the source mineralization estimated from each stream sediment sampling site varies within narrow limits. This example challenges the commonly held view that stream sediment anomalies in arid regions are subject to erratic high and low values.

Investigations by US Geological Survey over a major zoned hydrothermal mineralization system associated with rhyolitic intrusions in the Sonoran Desert, Mexico, showed that the results obtained using different sample media differed depending on the scale of observation (Overstreet and Marsh, 1981). At a reconnaissance scale of 1 sample per 24 km^2, stream sediment anomalies related to concentrations of Pb and Ba in certain rock-forming silicates (e.g., feldspars) could not be distinguished from those derived from significant barite occurrences. However, analytical data from the non-magnetic fraction of heavy mineral concentrates (separated at 0.6 Å on a magnetic separator), presented at 1 : 250,000 scale, revealed linear patterns of anomalies thought to define regional structural controls on the distribution of hydrothermal systems. Coarse detrital grains of secondary ore minerals accounted for the most anomalous metals, which included Sb, Ba, Pb, Cu and Mo. Concentration levels of some metals such as Pb, for which more than 50% of samples contained $>1\%$, were so high in heavy mineral concentrates that a different technique was required to resolve anomaly sources. The use of unconcentrated sediment (<590 μm) revealed an arcuate pattern of concentric anomalies at 1 : 50,000 scale, suggesting a zoned hydrothermal system; linear patterns emerging at 1 : 10,000 scale apparently reflect local structural controls on metal distribution within the major zones of the hydrothermal system.

Lovstrom and Horsnail (1978) studied the distribution of Cu in stream sediments over 700 km^2 of the Pima mining district in Arizona, which contains approximately 1.5 billion tonnes of porphyry copper ore with an average grade of 0.5% Cu (Fig. 11-5). The Cu content of the <200 μm fraction of 60 stream sediment samples revealed that anomalous values extend from four to more than 12 km downstream from the four known porphyry deposits in the area. Dispersion is probably enhanced by pollution from active mining operations at Sierrita-Esperanza, Twin Buttes and Mission-Pima but not at the San Xavier North deposit, which was still being developed at the time of sampling. A similar study over essentially undeveloped mineralization in the Safford District, Arizona, by Horsnail (1978) produced comparable results to those in the Pima District (Fig. 11-6). The geochemical expression of porphyry copper mineralization in stream sediments in this environment clearly depends on a combination of parameters such as deposit size and grade and the degree of concealment by superficial deposits, as well as the effects of contamination.

Stratiform and stratabound base metal sulphide deposits

This diverse group of deposits includes both sediment and volcanic-hosted massive sulphides. Deposit size and degree of exposure to weathering and erosion are highly variable and consequently so are the results of drainage geochemistry case histories.

The Gamsberg Zn orebody, in northwestern Cape Province, South Africa, provides an illustration of a strong extensive drainage anomaly associated with a major stratiform deposit (McLaurin, 1978). The deposit consists of 145 million tonnes grading 7% Zn and 0.5% Pb in highly folded metasediments. It is drained by a single stream which was sampled at twelve locations over a total distance of 26.8 km from the deposit. Figure 11-7 shows the downstream dispersion pattern for Zn in three size fractions of samples taken at different depths in the active sediment. Apart from a tendency for values to be slightly higher in the surface samples nearest to the orebody, there is little difference in the response from the different depths of sampling. Both anomalous and background values

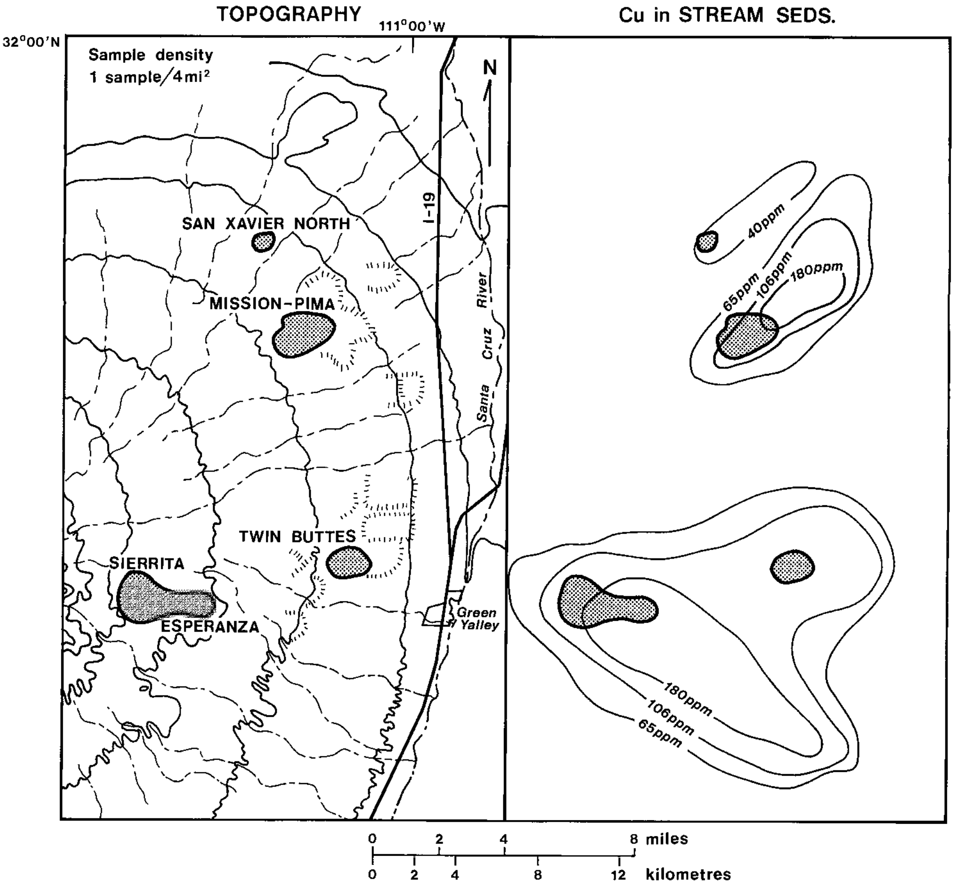


Fig. 11-5. Stream sediment anomalies for Cu (<200 μm fraction) in the Pima Mining District, Arizona (from Lovstrom and Horsnail, 1978).

increase with decreasing grain size fraction, and the length of the anomalous dispersion train appears to increase with decreasing grain particle size, from 8 km for the coarser fraction, to 14 km for the <200 μm fraction, and to 16 km in the case of the <75 μm fraction. Both effects probably relate to dilution by barren siliceous material in the coarser fraction.

The distributions of Zn and Pb in the magnetite fraction of the stream sediments also show very high contrast anomalies (Fig. 11-8), and a dispersion train of at least 14 km in length. Zinc has probably been incorporated into the lattice of magnetite within the ore zone during post-mineralization metamorphism. Magnetite concentrates are readily separated from stream sediments with a hand magnet, and their use as a sample medium reduces the effects of downstream dilution shown by the sediment.

Although Zeegers et al. (1985) note long dispersion trains of Ag in the

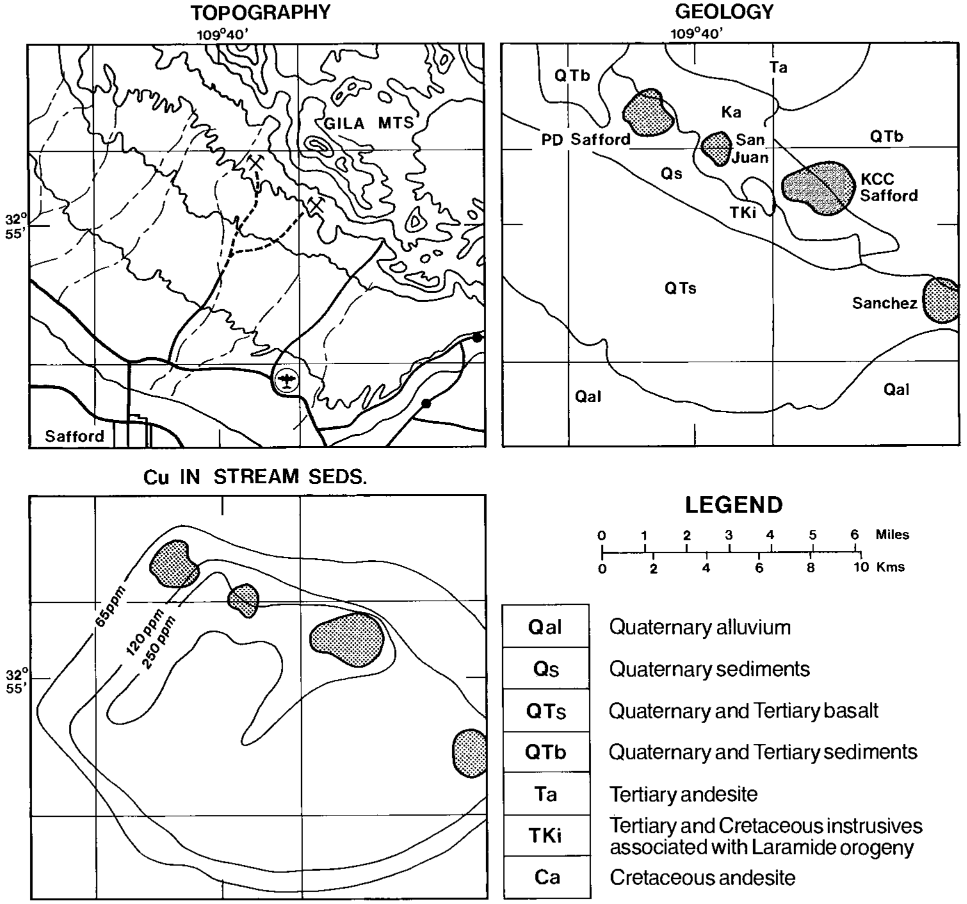


Fig. 11-6. Stream sediment anomalies for Cu (<200 μm fraction) in the Safford Mining District, Arizona (from Horsnail, 1978).

sediments in Wadi Majnah, which drains the Jabali carbonate-hosted Pb–Zn–Ag deposit in the Yemen Arab Republic (Fig. 11-9), extremely short dispersion trains are more common in arid regions of the Middle East. At the Al Washi prospect in Oman (Fig. 11-10), dispersion of Cu in the <125 μm fraction of stream sediments from a large sub-circular Cu gossan, 300 m in diameter, decreases to background within 1 km due largely to dilution of the fine fractions of wadi sediments by aeolian material (Zeegers et al., 1985).

Results for Zn from the Marramunga area, in the Squirrel Hills of Queensland, Australia, conform more closely to the Gamsberg model (Nisbet and Joyce, 1980). An occurrence 1.8 million tonnes with an average grade of 4.4% Zn gives rise to a dispersion train extending 2.5 km downstream, with a maximum value of 340 ppm Zn in <175 μm stream sediments (Fig. 11-11).

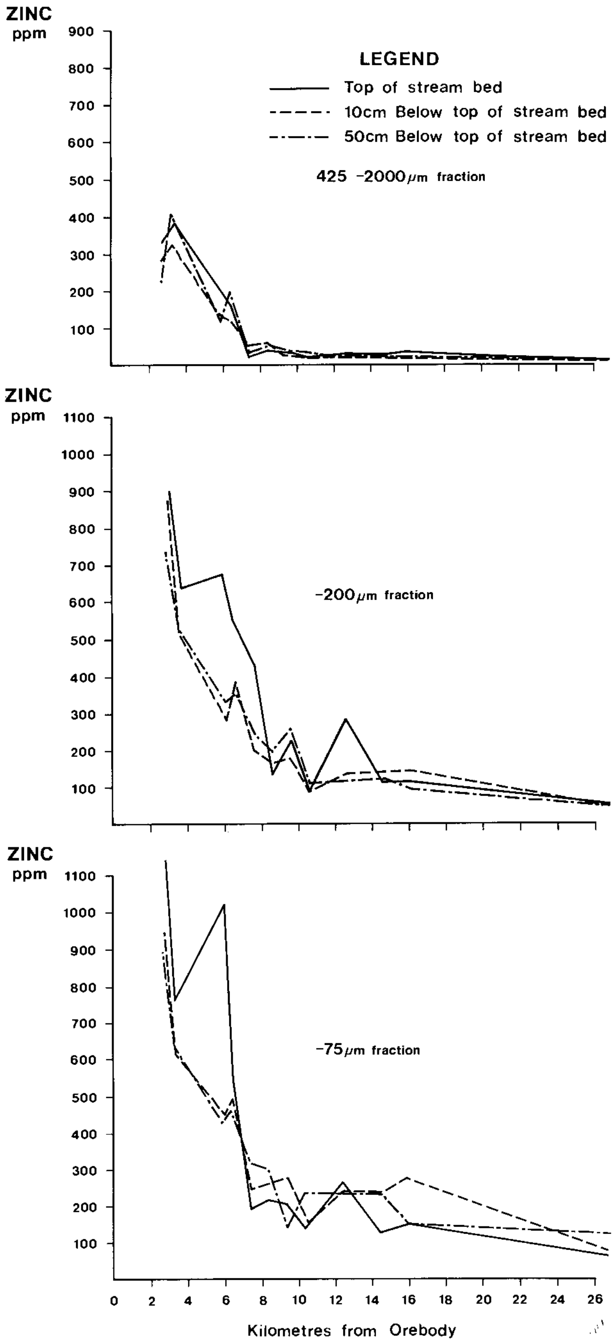


Fig. 11-7. Downstream dispersion of Zn in different size fractions of stream sediments, Gamsberg, South Africa (compiled from data from McLaurin, 1978).

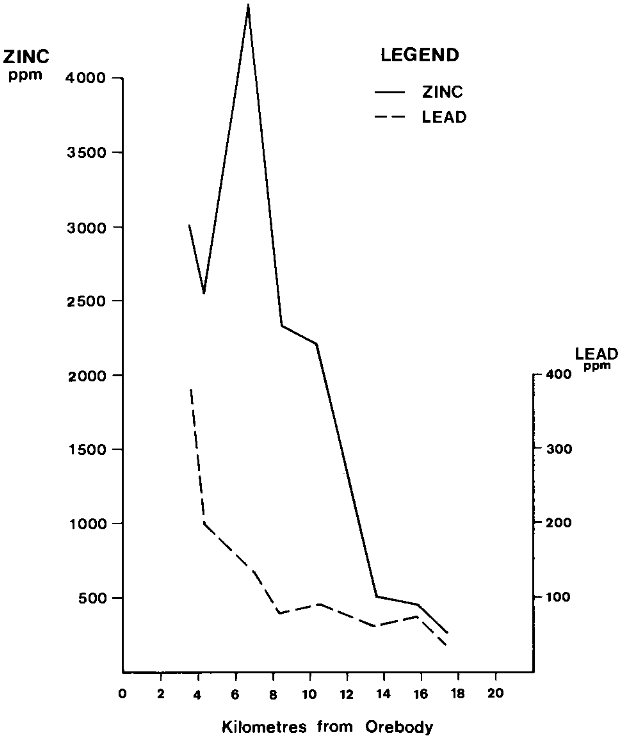


Fig. 11-8. Distribution of Pb and Zn in magnetite from stream sediments, Gamsberg, South Africa (from McLaurin, 1978).

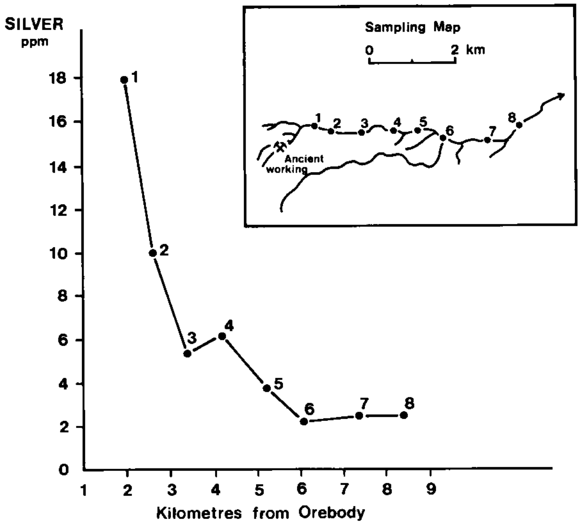


Fig. 11-9. Dispersion of Ag in the <125 μm fraction of wadi sediment draining the Jabali Pb–Zn–Ag deposit, Yemen Arab Republic (reproduced with permission from Zeegers et al., 1985).

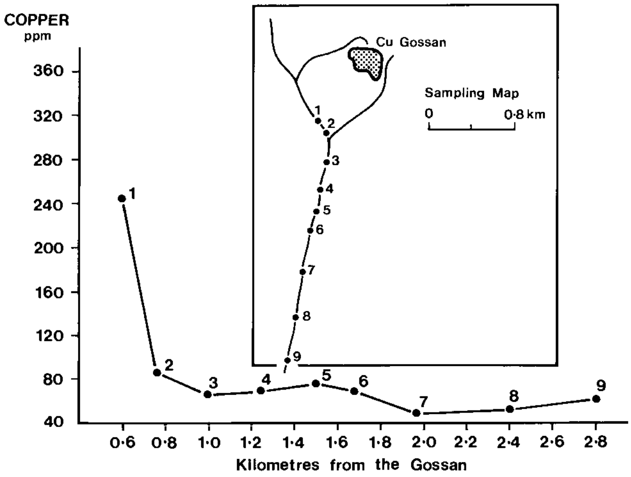


Fig. 11-10. Dispersion of Cu in the <125 μm fraction of wadi sediments draining the Al Washi prospect, Sultanate of Oman (reproduced with permission from Zeegers et al., 1985).

TABLE 11-IV

Relative anomaly constrast rankings for different size fractions of stream sediments near base metal mineralization, Pilbara Region, Western Australia

Size fraction (μm)	cxCu	Cu
2000	3.5	6.1
420–2000	5.8	5.2
200– 420	6.5	5.2
125– 200	9.9	6.1
75– 125	8.9	4.5
<75	9.3	5.9
<200	9.4	5.5

Orientation suites of stream sediment samples collected from seven widely separated occurrences of volcanic-associated massive sulphides in the Pilbara region of Western Australia provide data on the relationship between different size fractions and chemical extractions of different severities. Each sample was sieved into six size fractions which were analyzed for Cu by atomic absorption spectrophotometry using both cold extraction (dilute acetic and hydrochloric acid mixture) and hot acid decomposition (nitric–perchloric acid mixture). Mean background values were calculated for each area and contrast values computed for each size fraction of the individual anomalous samples. Arbitrary points from 1 to 12 possible size fraction/analytical combinations. The points for all anomalous samples were then averaged and the results, summarized in Table 11-IV show that, in general, anomaly contrast is higher for cxCu than "total" Cu, particularly in the finer size fractions.

Similar treatment for other elements showed a strong bias of the best

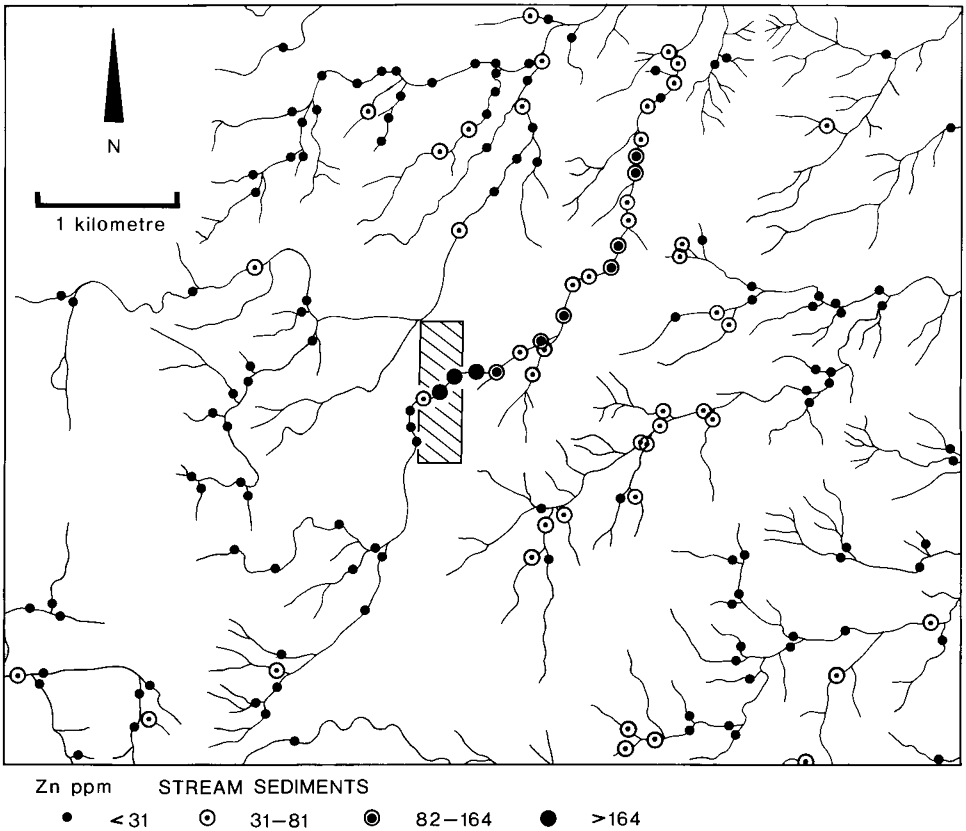


Fig. 11-11. Distribution of Zn in <175 μm fraction of stream sediments, Marramunga Area, Squirrel Hills, Queensland; shaded area indicates location of zinc sulphide deposit (from Nisbet and Joyce, 1980).

anomaly contrasts towards the 420–2000 μm fraction for "total" Pb, Zn, Co and Hg; contrast for "total" Cu also peaked in the 420–1000 μm fraction for one of the study areas. Following this study, analysis the <200 μm fraction for cxCu and the 420–2000 μm fraction for "total" base metals was adopted in routine exploration. The results of this approach in the Whim Creek-Mons Cupri area are shown in Fig. 11-12.

Strong anomalies are evident for all elements, the best response being for Pb, which exhibits dispersion trains 1.5 to 2.5 km in length. The cxCu anomaly associated with the Whim Creek deposit is better defined and stronger in contrast than the corresponding "total" Cu anomaly, even though the anomalous dispersion train is not significantly longer.

In summary, base metal responses in drainage sediments are highly sensitive to dilution by windblown material. This problem is most acute in the Middle East, particularly in areas of carbonate rocks. It may be compounded by the relative scarcity of vegetation, which appears to stabilise the landscape against

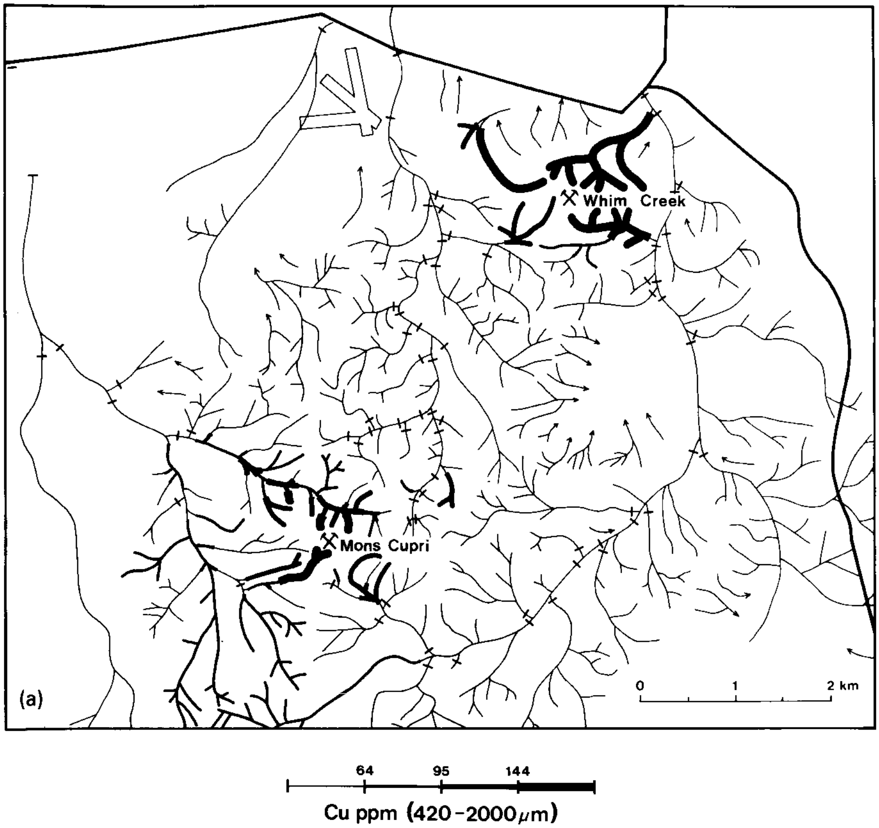


Fig. 11-12. (a) Distribution of Cu in stream sediments in the Whim Creek-Mons Cupri area, Pilbara Region, Western Australia.

wind erosion in the arid regions of South Africa and Australia. Where such dilution occurs, use of the coarse fractions or heavy mineral concentrates may be essential to enhance the anomalous expression of mineralization. The use of selective extraction techniques may also enhance response, particularly in the fine fraction, whilst the magnetic fraction may be useful when magnetite forms part of the ore mineral assemblage. Sophisticated data interpretation techniques may also have application in enhancing anomalous response in difficult areas.

Magmatic nickel-copper deposits

The discovery of significant Ni-Cu-Co sulphides in a differentiated gabbro-peridotite complex at Gabbro Akarem in the Eastern Desert of Egypt, is attributed in part to the application of drainage geochemistry within an integrated exploration programme. Bugrov and Shalaby (1975) sampled the <1000 µm fraction of wadi sediments at intervals of 250–500 m and analyzed these spectrographically for 12 elements. Interpretation was based on the sum of Ni

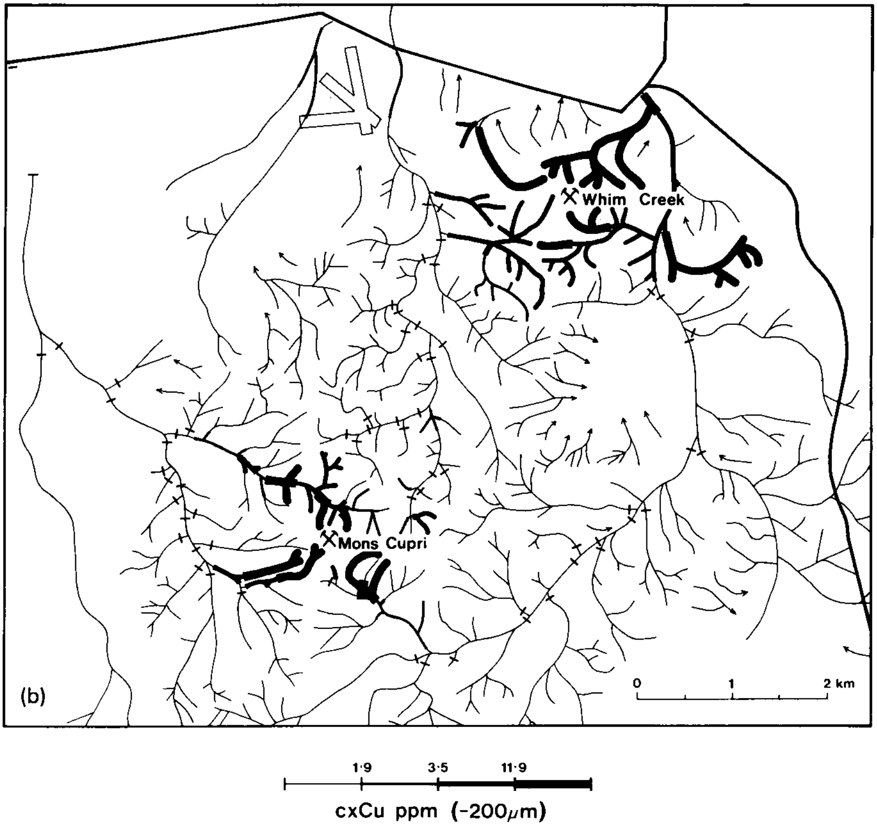


Fig. 11-12. (b) Distribution of cxCu in stream sediments in the Whim Creek-Mons Cupri area, Pilbara Region, Western Australia.

+ Cu concentrations using a threshold value of 60 ppm (Ni + Cu). Anomalous values up to 1300 ppm were recorded and dispersion trains 1.5 to 2 km in length were traced to gossans developed over Ni–Cu sulphide mineralization.

The Bow River Ni–Cu sulphide occurrence in the Halls Creek Province in the far north of Western Australia was located during follow up of anomalous values for Cu (75–100 ppm), Ni (35–60 ppm) and cxCu (5–10 ppm) in <175 μm fraction stream sediments (Fig. 11-13). The role of cxCu, extracted in this instance with an ammonium citrate–hydroxylamine hydrochloride mixture, was regarded as critical in discriminating the response related to mineralization from that derived from the mafic-ultramafic host-rocks within the generally felsic country rocks.

Gold mineralization

Exploration for gold using drainage geochemistry in arid terrains usually involves the determination not only of Au concentrations but also those of As or other elements as pathfinders for Au (e.g., Mazzucchelli, 1965; Halligan

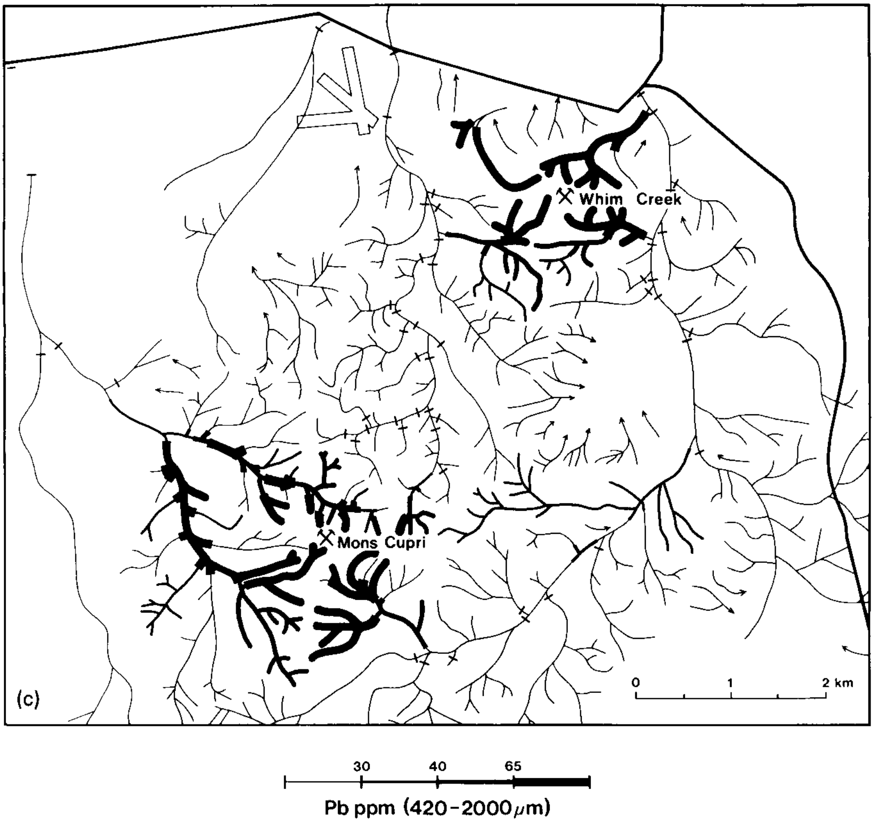


Fig. 11-12. (c) Distribution of Pb in stream sediments in the Whim Creek-Mons Cupri area, Pilbara Region, Western Australia.

and Harris, 1980a). In common with base metals, optimum contrast for As is obtained either in the coarse (Zeegers et al., 1985) or fine fractions (Halligan and Harris, 1980a; Beeson, 1985) of stream sediments.

Fletcher (1985), reporting an orientation drainage geochemical survey around the Oyo deposit in the Red Sea Hills of Sudan, shows that Au and As in two different size fractions and heavy mineral concentrates indicate strong and erratic responses over 500–1000 m immediately down-drainage from mineralization, with weaker responses up to 5 km downstream (Fig. 11-14). The <250 μm fraction yields a long and more consistent anomalous train than to the 250–1200 μm fraction. The highest anomaly contrast is shown by the heavy mineral concentrates, suggesting the suitability of this medium in low density regional reconnaissance. The heavy mineral concentrates circumvent the problem of aeolian dilution of the fine fraction encountered in many drainage channels.

However, in the Yilgarn Block of Western Australia, some problems have

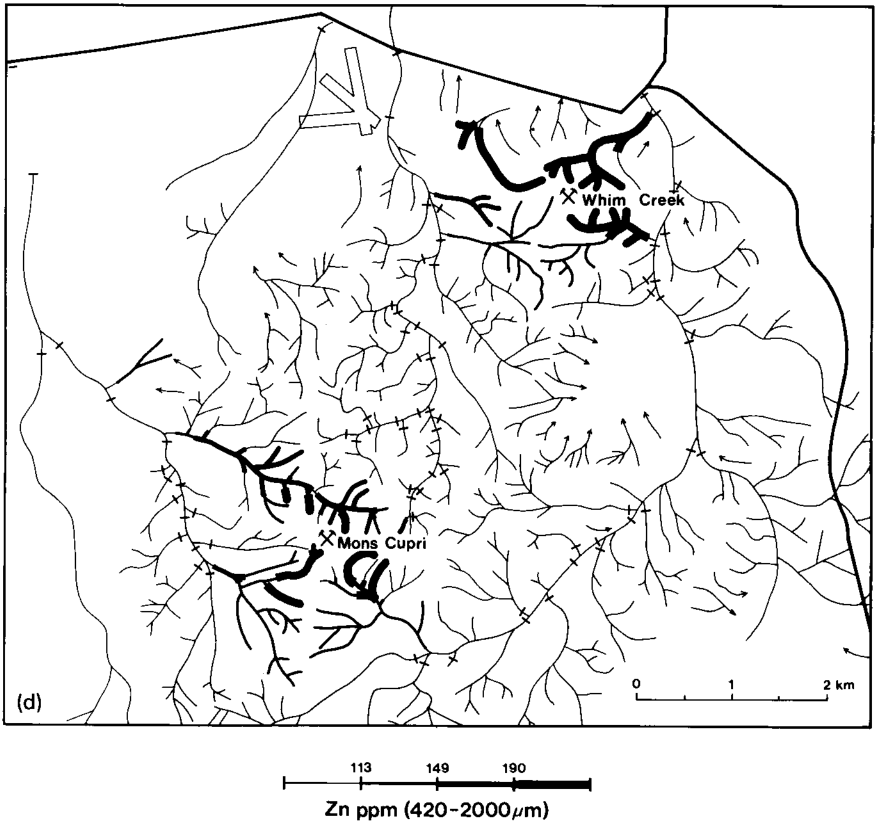


Fig. 11-12. (d) Distribution of Zn in stream sediments in the Whim Creek-Mons Cupri area, Pilbara Region, Western Australia.

been encountered in the use of heavy mineral concentrates as a geochemical sampling medium for gold. Figure 11-15 shows the distribution of Au in heavy mineral concentrates from detailed sampling of drainage around a small Archaean gold deposit in the Norseman district. There are extreme variations in concentration levels over short distances, an inconsistent spatial relationship between the highest values and known mineralization and anomalous soils, and relatively short dispersion trains. These dispersion pattern characteristics arise because trap-site efficiency is at least as important in determining the abundance of Au in heavy mineral concentrates as proximity to, and the size and grade of the source mineralization. In general, Au abundance in drainage sediments can be significantly higher in areas of strongly dissected topography than in low relief plains, leading to problems in the interpretation of surveys covering large areas. Further problems may arise because sampling is usually biased towards coarse particulate gold, fine and adsorbed gold being lost in most of the methods available for preparation of concentrates. Mann (1984a)

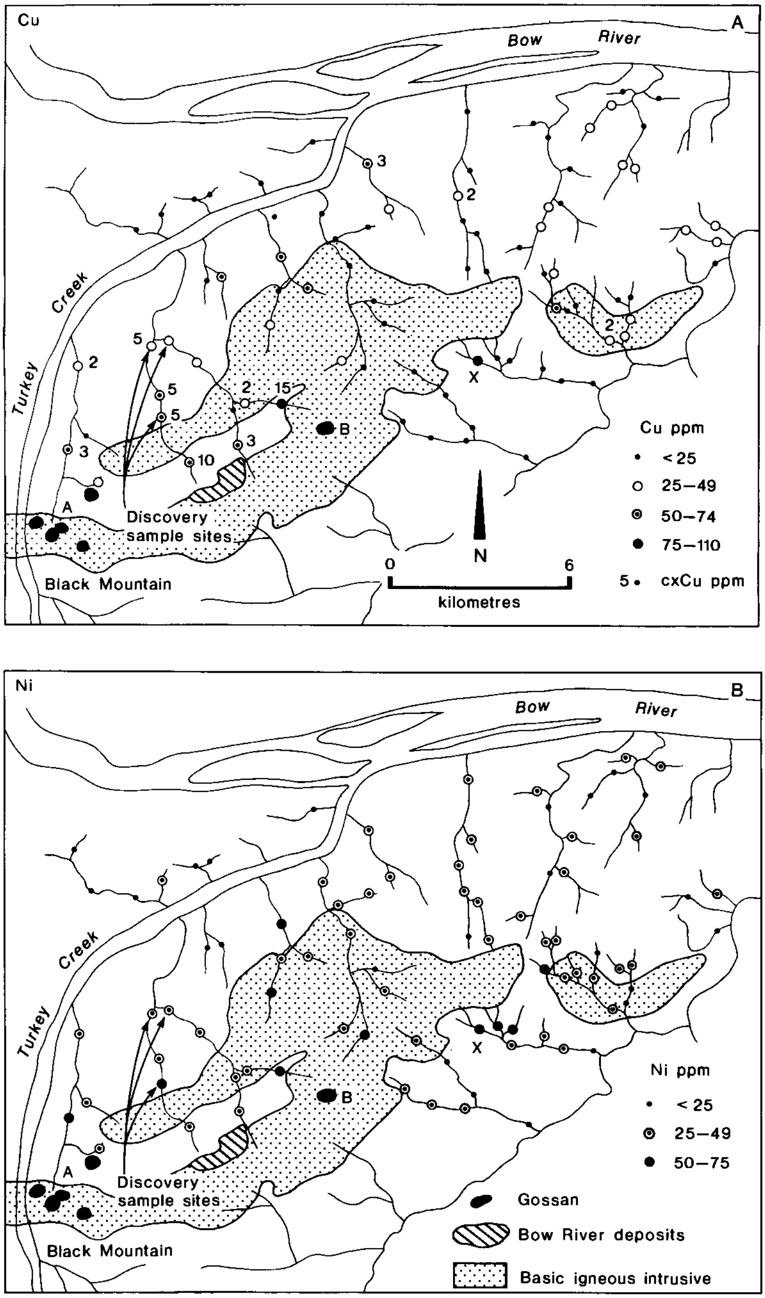


Fig. 11-13. Distribution of (a) Cu, cxCu; and (b) Ni shown by detailed stream sediment (<175 μm fraction) geochemistry, Bow River, Halls Creek Province, Western Australia (from Halligan and Harris, 1980a, b).

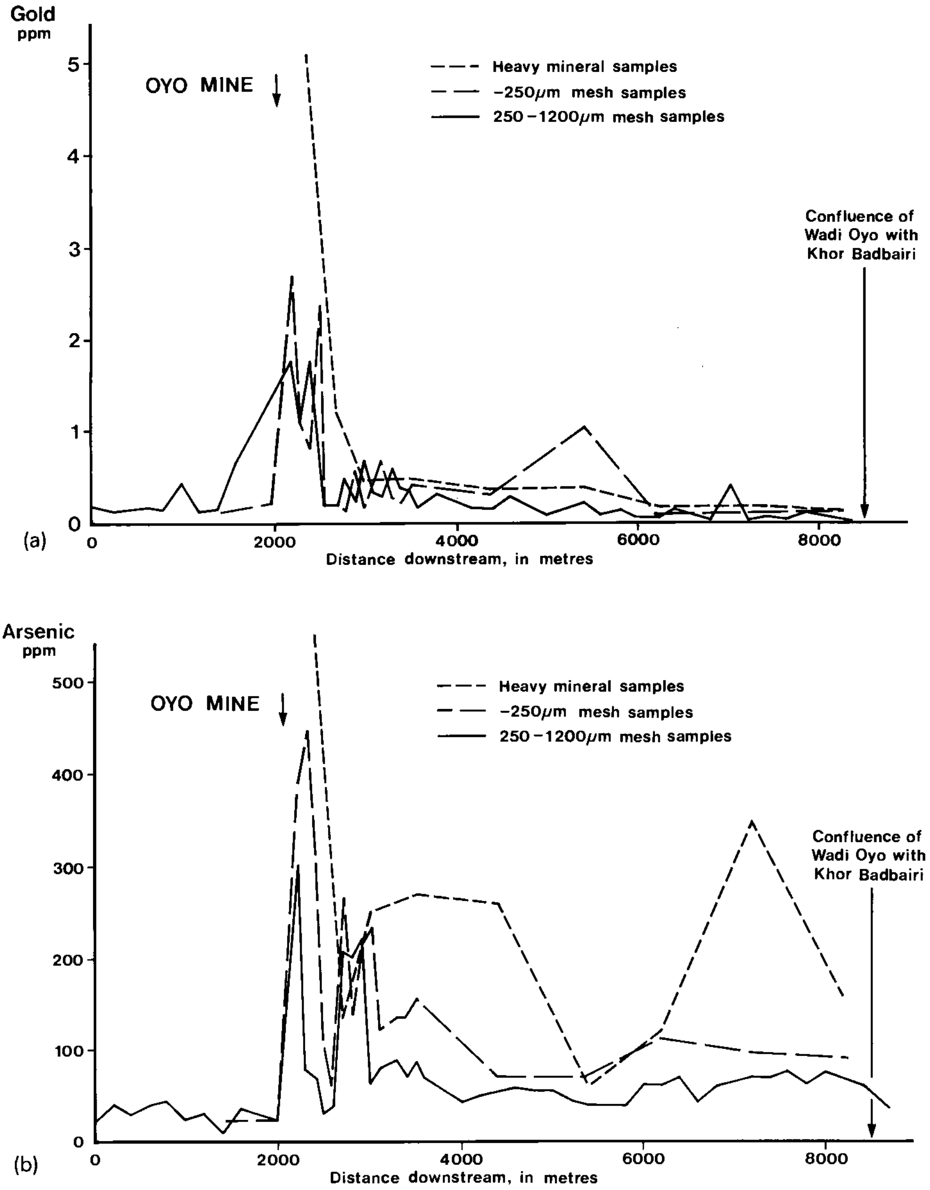


Fig. 11-14. (a) Gold; and (b) arsenic values in stream sediment samples along Wadi Oyo, Red Sea Hills, Sudan (reproduced with permission from Fletcher, 1985).

has shown that secondary gold developed in the lateritic profiles of the Western Plateau of Australia is characteristically very fine-grained (<10 μm) and is often associated with friable iron oxide minerals. This gold could constitute an important component of the gold present in drainage in deeply weathered areas.

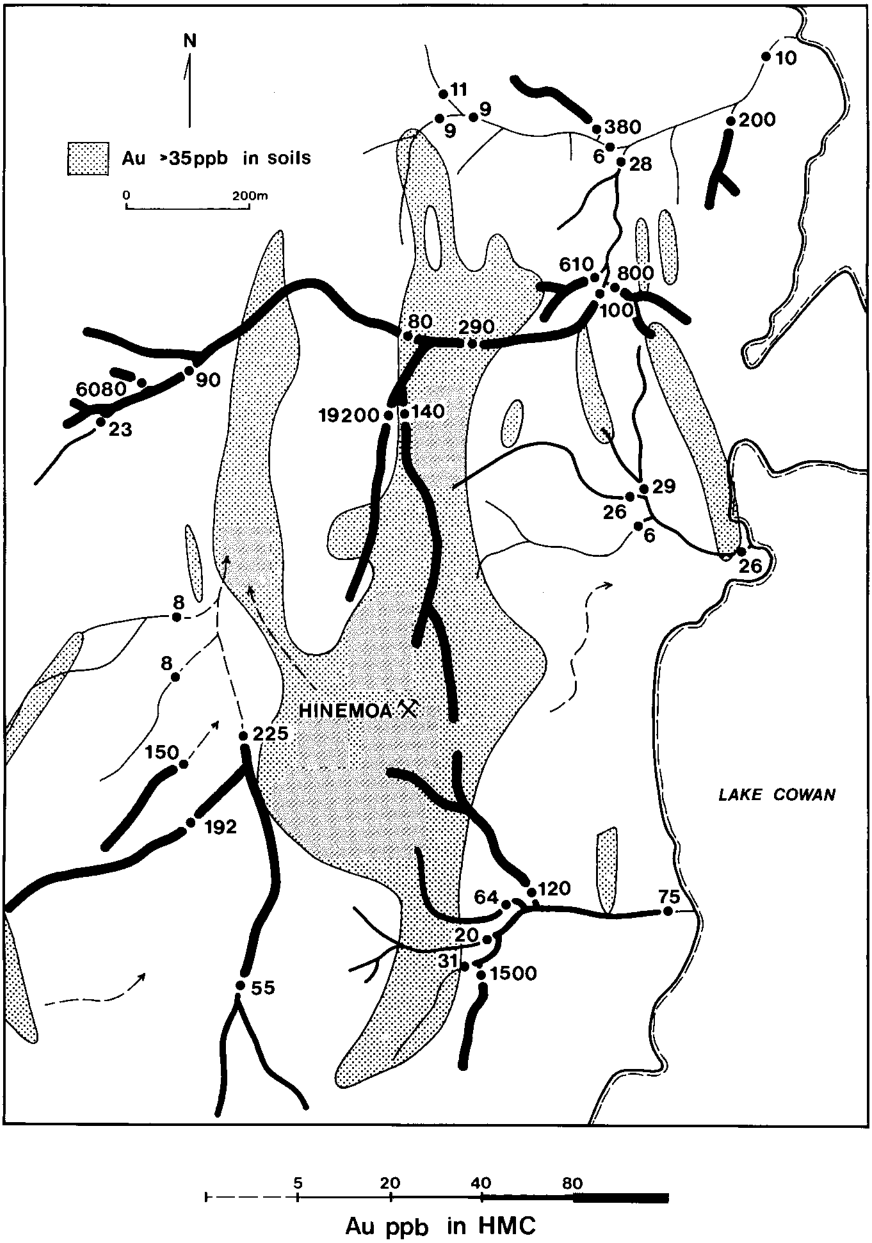


Fig. 11-15. Distribution of Au (ppb) in heavy mineral concentrates from stream sediments, Norseman area, Western Australia.

Alternative techniques to the collection of heavy mineral concentrates or the determination of pathfinder elements in drainage surveys for gold mineralization include analysis of specific sieve fractions for gold at ppb levels, and the "bulk leach extractable gold" (BLEG) method. Figure 11-16 provides a comparison of drainage dispersion patterns for Au in heavy mineral concentrates, by BLEG and in the <75 μm fraction of stream sediments, in the vicinity of the Badgebup gold deposit, some 300 km southeast of Perth (Mazzucchelli, 1987).

All three methods indicate the presence of mineralization over distances of at least 3 km. Gold in heavy mineral concentrates displays a positive gradient towards the most significant deposit, at Jinka's Hill, but the mineralization at Clegg's is poorly reflected. The BLEG results in the southern channel indicate an apparent decrease in Au concentration as the Jinka's Hill mineralization is approached whilst the value in the northern channel is at the threshold level of 0.2 ppb. The BLEG results are clearly affected by sediment composition, the sediments of the northern channel being dominated by coarse quartz sand, whereas those of the southern channel, where higher results were obtained, are of silty composition. Gold in the <75 μm fraction, for which a threshold of 5 ppb applies, displays a regular dispersion train at least 4 km downstream from the mineralization at Jinka's Hill and also suggests another anomaly at the eastern extremity of the northern channel.

In general, heavy mineral concentrate results for gold in drainage sediments of arid terrain give high contrast but erratic anomalies with poor reproducibility due to the "nugget" effect. The resulting data should be regarded at best as semi-quantitative.

The BLEG technique, although widely used in Australia, also has defects. First, it makes no allowance for dilution by variable quantities of windblown

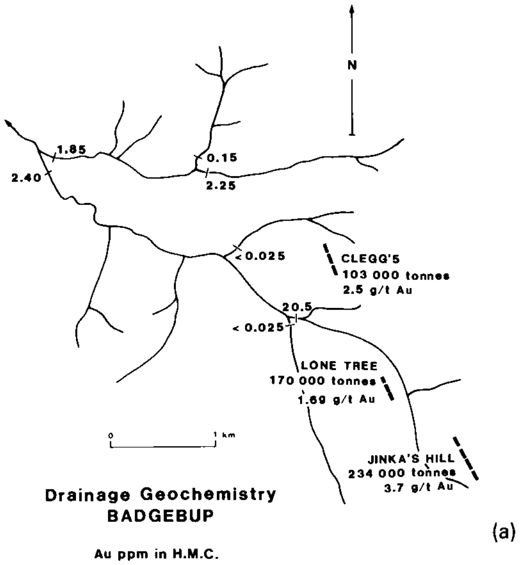


Fig. 11-16. Dispersion of gold in drainage associated with mineralization at Badgebup, Western Australia: (a) heavy mineral concentrates.

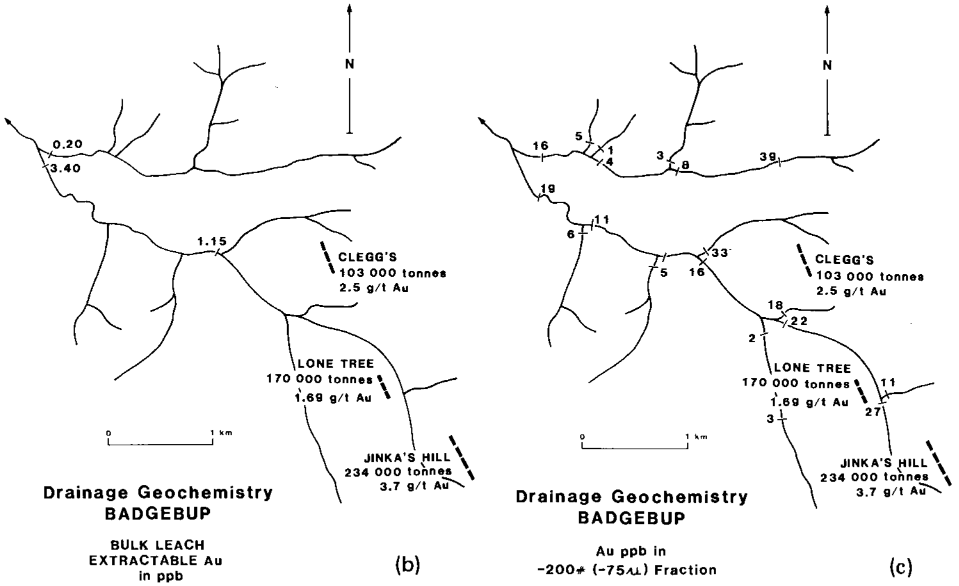


Fig. 11-16. Dispersion of gold in drainage associated with mineralization at Badgebup, Western Australia: (b) BLEG; (c) 75 μm fraction.

loess or barren quartz, which are features of the drainage systems of arid terrain. Second, the chemistry of the cyanide extraction is sensitive to variations in clay mineralogy and organic matter. These two factors could be responsible for variations in response unrelated to the presence or absence of mineralization, such as highly variable background levels ranging from 0.1 to 5 ppb gold found in different areas. The BLEG leach is only partial for coarse gold particles and gold intimately associated with certain sesquioxides. The BLEG method thus suppresses the "nugget" effect to the extent that any coarse gold present in the sample is only partially attacked. The method is effective for fine gold, but it might be argued that any fine gold which is present can be more conveniently evaluated by direct analysis of fine fraction samples.

Use of the finest practicable size fraction (usually the <75 μm fraction) may alleviate some of the problems inherent in the other methods. First, the nugget effect is substantially reduced by excluding coarse particles of gold from the sample taken for analysis. Second, dispersion patterns of fine gold are more likely to lead to the discovery of deposits which escaped the attention of earlier prospectors. Fine gold particles are less influenced by hydraulic factors due to the decrease in the ratio of weight to surface area (Saxby and Fletcher, 1986). This makes sampling error less critical, conventional sampling of silty material being effective. One disadvantage of this approach, however, is the substantial sample needed (often 2 kg or so) to yield sufficient <75 μm material for analysis.

Uranium mineralization

Although much exploration for uranium relies on radiometric techniques, several investigations in arid regions have indicated that anomalies related to mineralization can be readily detected in stream sediments. Beeson (1985) shows that in several areas of Iran and South Africa, the U response in stream sediments is optimized by analyzing the <70 μm fraction rather than the <200 μm fraction. In an example from Dechan (Fig. 11-17), both the contrast and length of anomalous dispersion is better for the <70 μm fraction. Rossiter (1980a) also found the U response well developed in the <180 μm fraction of stream sediments in the Northern Territory, Australia. However, an orientation survey by Hale and Jubeli (1985) showed that the U content of the 250–500 μm fraction of wadi sediments in Syria, provided the best dispersion trains from minor occurrences of carnotite and related minerals.

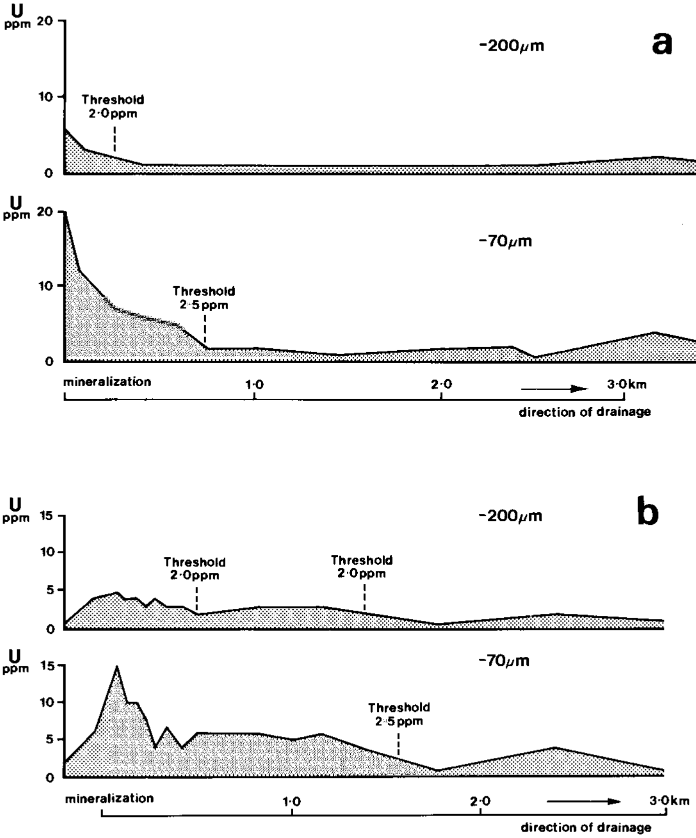


Fig. 11-17. Dispersion of uranium in two streams (A and B) draining mineralization, Dechan, northwest Iran (from Beeson, 1985).

PLAYA LAKE GEOCHEMISTRY SURVEYS

Playa lake sediments might be expected to exhibit both clastic dispersion patterns related to the surface drainage network, and hydromorphic patterns reflecting the geochemical character of groundwater entering the lake. In both cases there is potential for the development of anomalous patterns reflecting the presence of mineralization in the adjoining catchments. To date, however, their exploration significance has received very little attention.

Mazzucchelli (1965) demonstrates that arsenical gold mineralization in a small catchment adjacent to Lake Dundas, in the Norseman district of Western Australia, gives rise to a fan-shaped As anomaly with dimensions of 300 by 200 m in the <200 μm fraction of playa lake sediments. Values greater than 21 ppm As occur close to the input margins of streams draining the mineralized area, whilst a halo of weakly anomalous values extends asymmetrically in the direction of flow within the lake system.

Killigrew (1971) carried out a more comprehensive study in Western Australia, examining the mineralogy, particle size distribution and trace element geochemistry at 43 input sites, representing a variety of catchments, in Lakes Lefroy, Cowan and Dundas. The correlation between catchment lithology and geochemistry is obvious in the case of Ni (Table 11-V). The more nickeliferous sediments were found to contain significant amounts of talc, dispersed mechanically from weathered outcrops of ultramafic rocks. There is no obvious spatial relationship between Ni abundances in sediments and known Ni sulphide mineralization, but Cu : Ni ratios generally exceed 0.25 in sediments from known mineralized areas. In general the playa lake dispersion patterns conform to a deltaic distribution focused on the input point of the drainage channel, more or less modified at the outer fringes by further dispersion of fine sediment within the playa lake core.

Mehrtens (1978) found a general spatial relationship between metal values in alkali-salt flats in Nevada and Utah and areas of mineralization, although no direct relationship could be established. Black shale was considered the likely source of anomalies. Of the elements determined (Cu, Pb, Zn, Mo, Au, Ba, Sr, As and U), Mo showed most strongly anomalous concentrations. In follow-up investigations, a flume of groundwater with anomalous concentrations of Mo

TABLE 11-V

Average nickel values in playa input sediments in relation to catchment lithology (from Killigrew, 1971)

Lithology	Nickel (ppm)
Granite	8, 15, 20
Granite/Basics	31, 61, 61
Basics	44, 55, 63, 81, 82
Basic/Ultramafic	100, 106, 125, 136, 139, 143, 166, 176, 183, 184
Ultramafic	277, 377, 490, 1683

was traced up the hydraulic gradient from the anomalous sediments over a distance of 32 km. The increase in the Mo concentration in surface sediments of the salt flat is marked by a corresponding decrease in the Mo content of groundwater, supporting the belief that the sediment anomaly is developed by evaporation from the groundwater.

These few reports confirm the efficacy of playa lake geochemistry, with anomalies related to mineralization in the adjacent catchments developed by both mechanical dispersion through the surface drainage network and hydrogeochemical dispersion in the groundwater. Playa lake sediments appear to have a wider role to play in geochemical reconnaissance surveys in arid regions, in much the same way as lake sediment geochemistry has become important in the exploration of many glaciated areas (see Chapter 7).

SUMMARY AND CONCLUSIONS

Drainage geochemistry is generally applicable in mineral exploration in arid regions, but some modifications to procedures may be required to overcome problems inherent in such environments.

The disconnected nature of drainage systems and the concealment of large areas by alluvial gravels, silts and aeolian sands limit the areas which can be effectively covered using drainage surveys. Where one or more of these problems exist, alternative exploration methods must be adopted to supplement the data obtained from drainage geochemistry.

In general, case histories do not support the frequently expressed view that trace element distribution in arid region drainage is more erratic than in humid regions. Where this occurs, however, measures such as the collection of composite samples from several separate sites at each sampling station, increasing the sample size and decreasing the average grain size of the material collected should improve the data obtained.

Diminished anomaly contrast, due to dilution by barren aeolian material or deeply leached materials is the most widely recognized problem in arid terrain. The simplest solutions to this problem involve the use of specific sieve fractions to eliminate the barren component of the sample prior to analysis. The 75–500 μm size range is commonly dominated by barren siliceous material, a large proportion of which can be of exotic origin in areas where aeolian transport is important. Thus fine <200 μm or coarse (>400 μm) fractions are commonly sampled, although in some areas, the <75 μm fraction too is largely of aeolian origin and cannot be used.

Alternative techniques for enhancement of anomaly contrast include the recovery and analysis of heavy mineral or magnetic concentrates or the use of selective extraction techniques on a suitable size fraction of the sediment. The last technique appears to be particularly appropriate in arid regions, when designed to extract metal associated with secondary iron oxides.

The sampling and analysis of playa lake sediments appears to have application in drainage geochemistry in arid regions, potentially assisting in the detection of both exposed mineralization and deposits concealed by superficial deposits. Further research is required into the mechanisms of metal dispersion from mineralization into the playa lake environment and subsequent metal re-distribution.

Drainage Geochemistry
edited by M. Hale and J.A. Plant
Handbook of Exploration Geochemistry, Vol. 6 (G.J.S. Govett, Editor)

Chapter 12

DRAINAGE GEOCHEMISTRY IN YOUNG FOLDED MOUNTAIN BELTS

E. WILHELM and D. ARTIGNAN

CHARACTERISTICS OF YOUNG FOLDED MOUNTAIN BELTS

The great young mountain belts were formed during successive Alpine orogenic episodes, which started in the Mesozoic and culminated in the Cenozoic between approximately 100 and 20 Ma ago. They resulted from folding of sedimentary strata or the tectonic remobilization of basement rocks that were variably intruded by igneous rocks, and are found on all continents except Australia. Alpine fold belts include the two circum-Pacific domain that stretches from North Africa via the Alps to the Himalayas, and which are shown schematically in Fig. 12-1. These belts tend to be characterized by dissected relief, rapid rates of mechanical erosion and short contact times between rock and groundwater.

Despite their similarities, the different mountain belts show great diversity because of climatic factors and their different geological and mineralogical environments. The last two are not randomly distributed, but depend upon the overall geotectonic setting and palaeo-climatological factors.

Geotectonic settings

The tectonic forces that create folded mountain belts fall into two major categories: those that are caused by crustal-plate collision, and those that derive from crustal-plate subduction.

Crustal-plate collision, which can be of the continent–continent or continent–island arc type, causes folding and thrusting, and in some cases the obduction of slices of continental or oceanic crust. The Eurasian Alpine domain provides the best of such settings, caused by the collision of Africa against Europe which gave rise to the Alps, the collision of Arabia against Asia that created the Turkish and Persian mountains belts, and that of India against Asia which caused the uplift of the Tibetan mountain chains.

At greater distances from collision zones, intracontinental mountain chains may be formed such as the Himalayas sensu stricto and the Pyrenees Mountains.

The subduction of oceanic crustal plates below each other or below a conti-

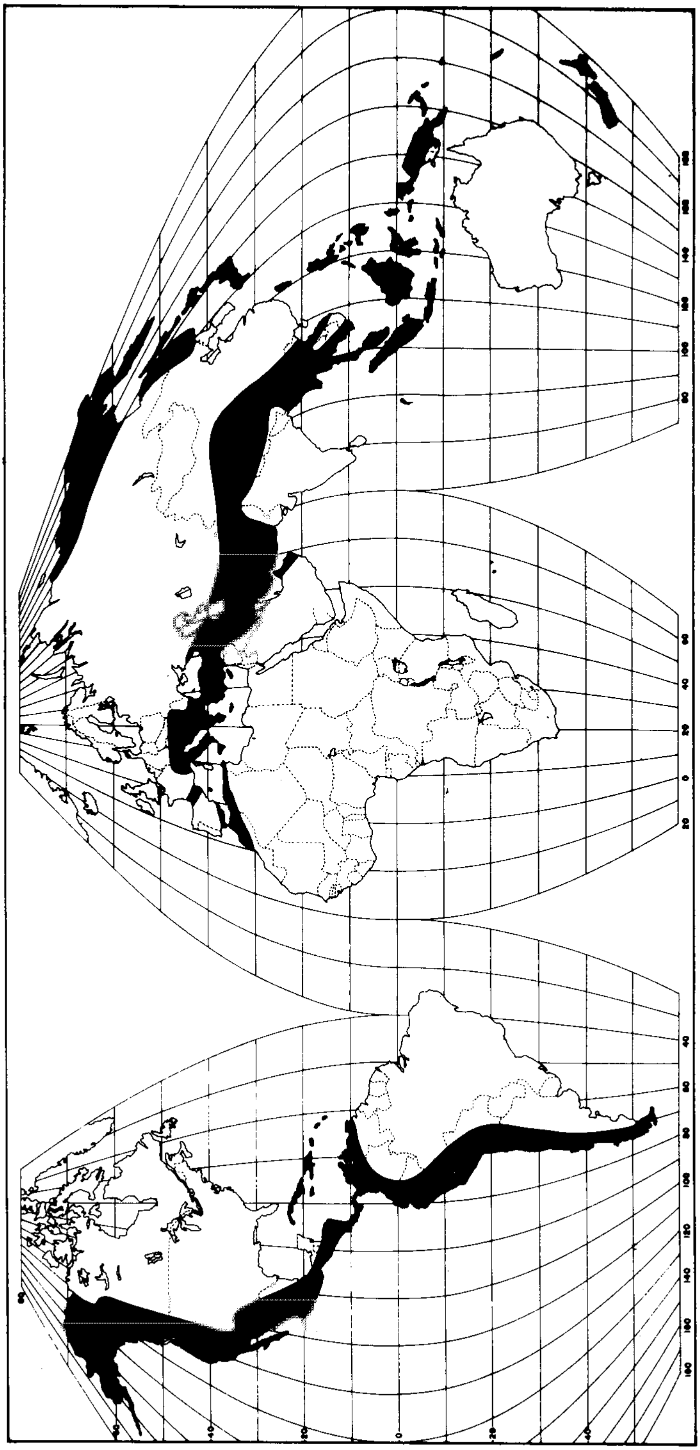


Fig. 12-1. World-wide distribution of young folded mountains.

nental margin is usually accompanied by abundant volcanism. Two major relief types characterize subduction:

(1) the Cordilleran type on the edge of a continental plate, for which the model type is the American Rocky Mountains and Andes domains that stretches over almost 20,000 km along the western edge of the American plates;

(2) the island-arc type, which is essentially volcanic and of which the Japanese islands and Antilles are among the best-known examples.

Collision and subduction not only cause folding, thrusting and the intense fracturing that favours fluid migration, but are also at the root of differentiated volcanic and intrusive activity, which can affect sedimentary cover formations and reactivate basement crystalline rock. The plutons and volcanics stocks that are emplaced during orogenic history, commonly play an important role in the control and distribution of metalliferous mineralization.

The mountain chains that border the great rift zones, such as those along the East African lakes, complete the geotectonic scheme. These are formed by tectonic doming or uplift of the dominantly volcanic rocks which accumulate in such rift zones; they are not associated with major folding or thrusting and therefore fall outside the definition of young folded mountain belts.

Economic geology setting

Mountain belts host a great variety of mineralization types as they include fragments of obducted oceanic crust, reactivated basement, and thrust or folded cover rocks, all of which can be affected by volcanic or intrusive activity. Nevertheless, they preferentially contain certain types of mineralization (Mitchell and Garson, 1981), such as epigenetic Sn, W and Sb mineralization linked to magmatic intrusions, and particularly dioritic intrusions above subduction zones associated with porphyritic-type mineralization and massive sulphides typical of volcanic-island-arc settings. Collision zones are commonly characterized by ophiolitic complexes, which can host copper, gold, chromite and platinum-group metals deposits. Intense fracturing and geothermal anomalies promote hydrothermal circulation, and favour the emplacement of epithermal mineralization such as Pb, Zn, F, Ba, Au and Ag veins and stockworks.

The most valuable types of mineralization are those linked with subduction zones in cordilleras and island arcs. If one then considers the geographical distribution of such metallic mineral deposits along, for instance, the Pacific coast of North and South America, it is obvious that massive sulphides are preferentially located on the seaward side and the porphyry types further inland (Routhier, 1980). Thus, the presence and thickness of continental crust seem to play an important role, both in the quantitative and qualitative sense. At the other end of the spectrum, continent–continent areas seem to hold the least metallogenic mineralization.

Climatic controls

As young mountain belts extend between 70°N and 50°S, they lie in all major climatic zones of the earth (Fig. 12-2). The specific climatic characteristics of each mountain area are, however, blurred by the major role played by relief, which not only causes lower temperature as a result of altitude, but also presents a barrier to precipitation. This leads to a narrow vertical and horizontal imbrication of climatic zones within mountain chains. For example, mountain glaciers lie in equatorial New Guinea, and sub-desert regions are found on the eastern slopes of the Rocky Mountains in North America. The interaction of azonal factors, such as altitude and relief, and general climatic constraints is, however, insufficient to explain the morphology of mountain regions. Past climatic history, in particular Quaternary glaciation because of its geographical extent (Flint, 1971), plays a very important role. Glaciation has shaped many of the major morphological features of northern and temperate mountain areas.

Figure 12-3 shows the maximum extent of Quaternary glaciation, 18,000 years B.P. (smaller glaciers are not shown because of scale considerations). This glaciation caused active mechanical erosion and deposition of this material in moraines, which limit the use of exploration geochemistry due to their widespread blanketing of the substratum.

FACTORS INFLUENCING MORPHOLOGY AND DISPERSION IN YOUNG MOUNTAIN AREAS

In high mountain areas, the supergene alteration processes that control secondary dispersion of metals around primary mineralization and govern the choice of geochemical exploration techniques, are fundamentally different from those of adjacent climatic zones. A single climatic classification cannot be used for geochemical exploration in such regions, which are generally characterized by increasing aridity with increasing altitude, modifying the morphological, soil-genetic, and physiographic conditions of the environment. Supergene alteration processes fall into two main classes: "azonal" factors that directly contribute to the specific morphological conditions of high mountain areas; and "zonal", mainly climatic, factors that either accentuate or attenuate "azonal" effects.

Azonal factors

The principal azonal factors include altitude, precipitation, relief, exposure and wind.

Altitude

Altitude is generally the dominant control on the morphological and geological characteristics of mountain chains, and its effects are usually more

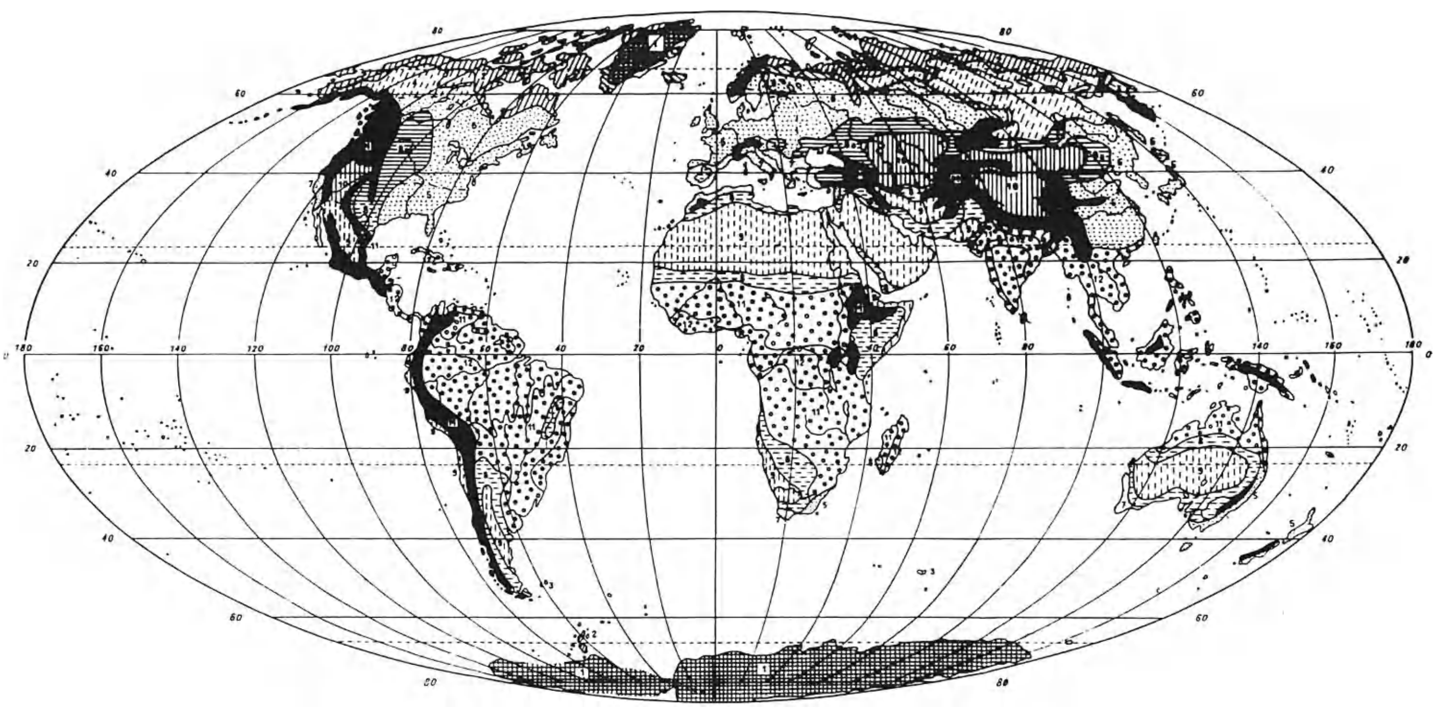


Fig. 12-2. World major morphoclimatic regions (reproduced with permission from Tricart and Cailleux, 1965). 1 = Polar climate; 2, 3 = Tundra climate with/without permafrost; 4 = Rainy climate with severe winters: forest and Quaternary permafrost; 5, 6 = Rainy climate of medium latitudes: forest with/without warm winters; 7 = Mediterranean warm humid climate; 8, 8a = Steppe or semi-arid climate with/without cold winters; 9, 10 = Arid climate: desert and degraded steppe (warm dry/cool dry); 11, 12 = Rainy climate with no winter: tropical savannah/tropical rain forest; 13 = Mountain regions with azonal organization of climate depending on altitude.

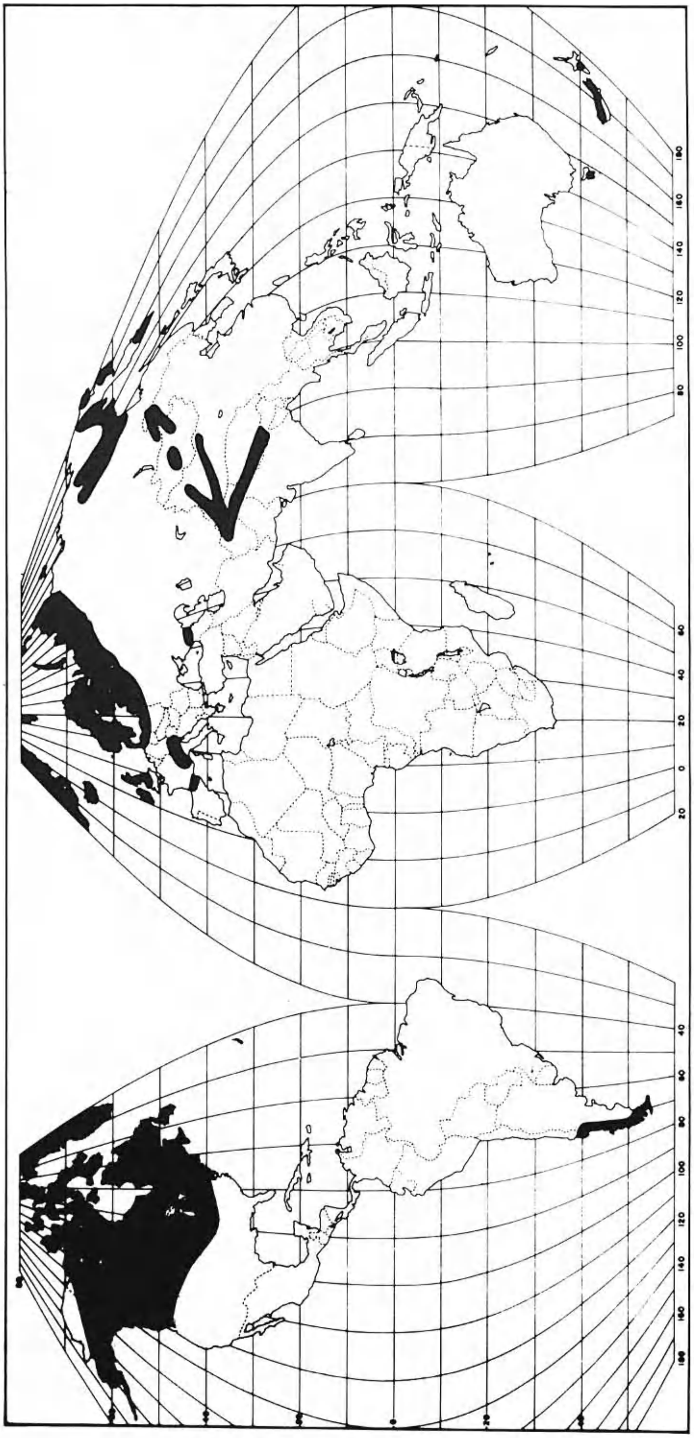


Fig. 12-3. Sketch map showing maximum extent of former glaciers (very small areas not shown).

significant than those of geographical or climatic location. Higher altitudes correspond to lower temperatures.

In the Alps, the average temperature drops by 0.6°C for every 100 m. Hence, snow and ice persist at high altitudes, and various vegetation levels occur that become less diverse with increasing altitude, before terminating in scree slopes below escarpments, snow and ice. At this elevation, high mountains tend to acquire the characteristics of glacial relief in northern latitudes. The denuded areas are subject to frost action, especially where snow cover is seasonal, and freezing and thawing of water in cracks is a major cause of mechanical weathering.

In the Canadian Cordillera, average temperatures are more sensitive to elevation change than to latitude; tundra extends from the Arctic Coastal Plain at sea level to elevations above 2000 m near the 49th parallel.

Each level is characterized by a specific type of soil development, which is generally very active on average and becomes progressively less developed with increasing altitude. Soil development is strongly influenced by the other azonal factors as well as by the climatic environment.

Precipitation

Areas of high relief disturb atmospheric circulation and precipitation as a result of their barrier effect. Rainfall is not only a function of altitude, but also of physiography, nearness to sea, and latitude. Slopes exposed to the prevailing wind are likely to be wetter than lee slopes.

Precipitation also varies as a function of altitude; on sufficiently high mountains there is usually a level with more abundant precipitation and greater cloud cover, which develops because of the decreasing moisture-saturation level of air with increasing altitude. Thus, in each climatic zone there is a zone of optimal condensation, which corresponds to the altitude where saturation is reached for the average water-vapour content generated from adjacent plains (Tricart and Cailleux, 1965). Generally speaking, this pluviometric optimum is at lower altitude as the climate becomes more humid, which explains the rare development of glaciers in subtropical and tropical high-altitude areas where rainfall is scarce.

Rainfall varies widely and is greatly influenced by topography, as is illustrated by the Canadian Cordillera where it attains a maximum of 250–500 cm per year over the coastal mountains and reaches a minimum of below 50 cm per year over the semi-arid southern plateau. In the case of soils, heavy rains favour leaching and the development of podzols, but in dry interior areas brunisols and more developed brown soils predominate (Bradshaw, 1975).

In desert areas with low precipitation, many of the higher ranges receive sufficient moisture from winter storms and summer thundershowers to support relatively dense forests along their crests, although the intramontane basins will have only sparse vegetation (Lovering and McCarthy, 1978).

Precipitation variations also occur in tropical areas. For instance, on the Western Cordillera of northern Peru, which has a temperate to cold climate, the western (Pacific) slope is almost dry and precipitation generally increases northwards and eastwards, where the main rivers maintain a perennial flow (Baldock, 1977), and vegetation varies from shrub to thick mountain and subtropical forest.

Relief

In high mountain areas, regardless of the climatic zone, erosion is highly active in areas with steep relief, due to the abundance and erosive strength of surface water. The great amounts of water that derive from thunderstorms or tropical rainfall as well as melting snow, acquire a considerable erosional energy and shape a characteristic morphology, with a high density of drainage channels that have strong currents. Such torrential erosion causes vigorous dissection and the development of canyons with steep walls, which are filled with heterogeneous material, mechanically transported as blocks and scree without apparent sorting. The fine size fractions, which could provide geochemical samples, are usually carried away in torrential streams to accumulate on the first breaks in slope as enormous alluvial cones. These normally represent a far too large catchment area to be of use as a geochemical sample medium.

The exploration geochemist, in order to take advantage of this intense mechanical dispersion, should thus sample the less diluted and more representative material found in traps above such alluvial cones. However, this poses operational difficulties. The relief itself is a major obstacle to access as a result of the absence or low density of roads and motorable tracks, necessitating the use of helicopters, horses and, in some cases, walking. Sampling costs are thus increased, prompting low-density sampling to be carried out. Such operational considerations are important, as they have a direct influence on the geochemical techniques that can be employed.

Exposure

Exposure can vary considerably from one climatic zone to the next, not only as a result of slope orientation, but also because of cloud development that blocks sunlight and can disturb atmospheric circulation, which is generally more irregular in the tropics than in temperate areas. For example, in the Venezuelan Andes the east and southeast facing slopes receive the first sunlight, which subsequently melts the nocturnal snowfall. Northwest and west facing slopes, however, receive very little sunlight, because heavy cloud cover usually develops over the mountains during the morning; this renders such slopes humid and maintains their perennial high-altitude snow and ice cover (Tricart and Cailleux, 1965). These differences are at the root of specific erosion and weathering mechanisms, which need to be taken in account in exploration geochemistry.

Wind

Wind is important in the development of temperature inversions that are commonly observed between valley floors and the slopes and crests of high mountains. Wind also removes snow from exposed slopes and thus increases the exposure of rocks to frost-weathering. Furthermore, wind impedes the development of vegetation on crests and other highly exposed areas.

Zonal factors

Zonal factors are mostly climatic. Climatic zones include glacial and periglacial, temperate, arid to semi-arid, and tropical ones.

Glacial and periglacial zones

The weathering evolution of mountain areas in high latitudes is directly controlled by the climatic history as far back as the Ice Ages. Since the end of the Cenozoic, several glaciations have affected the morphology and soil development of mountain areas. Glaciers carve and sculpt the landscape, scour valleys to form fjords and lakes, and commonly leave thick deposits, ranging from tills to fine silt, which form most of the present cover of mountain regions in such climatic zones.

At high altitude these mountain areas are extremely cold and consist of vast denuded rock faces. Organisms are scarce and their action insignificant. Shaping of the landforms, except for tectonic deformation and glacial scouring, is directly controlled by meteoric factors, with incessant frost action, solifluxion and wind blasting. At lower altitudes and in the periglacial zone, the mountain tundra domain occurs, soil appears, plants counteract the mechanical solifluxion processes, and organic matter accumulates as peat. This environment holds some, albeit limited, possibilities for hydromorphic dispersion.

Temperate zones

Mountain areas in middle latitudes have much in common with those in high latitudes. According to their altitude and the resulting vertical climatic zonation, they are subject to the same periglacial processes. Glaciation during the Quaternary was much more widespread than today, so that the effects of glaciation are widespread even in the temperate zone. At present, glaciers deposit major moraines capable of damming valleys. The resulting deposits affect the use of exploration geochemistry over wide areas.

At moderate elevations, the streams from periglacial mountain zones, fed by precipitation and meltwater, are mostly torrential; their erosive power increases the steepness of slopes, promotes mechanical erosion processes, and generally forms scree and landslides. These mechanisms are influenced by the overall exposure, diurnal temperature variations and the development of soil that acts as an insulating layer.

Arid and semi-arid zones

Mountains in desert or semi-desert areas are like "islands with rugged relief in an ocean of gravel" (Callahan, 1977). Steep mountain chains, which are commonly long and narrow with a predominance of bare outcrops, are juxtaposed with vast arid basins and flats filled with alluvium, which can be tens of kilometres wide. Such intramontane basins usually are remnants of palaeo-weathering during humid periods when rainfall was high. Much of the alluvium now covering broad desert valleys is a veneer of pediment gravel that gradually slopes from mountain fronts to the edges of deep basins, which can contain hundreds of metres of Tertiary and Quaternary sediments. Such areas are virtually inaccessible to exploration geochemistry because of the allochthonous cover sediments.

Mountain chains in these regions have a narrow forested zone that gives way to shrubs and grasses at higher altitudes. They are dissected by canyons with perennial streams that disappear in arid intramontane basins. The great diurnal and seasonal soil-temperature variations, combined with insignificant cloud cover, cause strong mechanical weathering of the rock, which usually is covered with stones and scree. Frost action is highly efficient, because snow that normally acts as an insulator is rare in these low latitudes.

Numerous tributary drainage channels, steep and choked with fallen rock, feed the major canyons. These can provide representative sediment samples although the sediment trapped in them may be removed by torrential rainfall. Here, the most recently river-transported silt should be collected.

In these climatic zones, aeolian contamination of samples may be important. Its impact is usually minimal in areas of steep topography, but fine aeolian material tends to concentrate downstream, particularly near breaks in slope, which are otherwise the best sites for geochemical sampling.

Tropical zones

In tropical zones at low to moderate altitudes, mountains are characterized by intense ferralitic weathering caused by abundant rainfall, up to several metres a year, and relatively high temperatures, averaging more than 20°C with little seasonal fluctuation. The typical soil profile consists of a yellow, unconsolidated saprolite horizon with kaolin and quartz, locally overlain by indurated residual laterite which commonly contains stone lines, and underlying saprolitic rock with preserved original structures. Such areas are covered by dense tropical rain forest, which impedes access and geological mapping. The depth of surficial weathering and the oxidation zone is highly variable, ranging from a few metres to as much as 300 m in areas of deep fracturing (Leggo, 1977). This depends, however, on the rate of erosion, which usually overtakes chemical weathering when the relief gets steeper; in such cases, the soil profile generally is truncated and the drainage, which cuts directly into the substratum, accentuates mechanical dispersion.

With increasing elevation the lower ambient temperature leads to a differentiated vegetation, ranging from reduced forest to a type of semi-desert steppe where precipitation is so low that vegetation growth is stunted. Generally, there is little snowfall in the tropics, so that soil is directly exposed to intense climatic changes, including strong diurnal temperature variations.

Chemical weathering is hardly active in the high tropical mountains, where periglacial-type frost action breaks up the rock into blocks and gravel, favouring mechanical dispersion processes.

GEOCHEMICAL DISPERSION TRAINS IN DIFFERENT CLIMATIC ZONES

The major morphological and soil characteristics of mountain areas tend to be related to their steep topography, which causes strong, predominantly mechanical, erosion. Although this type of dispersion is central to the efficacy of drainage geochemistry in such regions, other regional environmental criteria, particularly climatic factors, must be taken into account as well.

Glacial and periglacial climatic zones

Several case histories of geochemical dispersion around porphyry copper deposits in glacial and periglacial zones have been described by Bradshaw (1975), but relatively little is known of other types of mineral deposits in such areas. The major handicap in using geochemistry in such areas lies in the possible presence of allochthonous glacial cover. Three surficial covers can be distinguished: areas with residual soil unaffected by glaciation; areas covered by till of local derivation; and areas with a clearly allochthonous cover.

Areas with residual soil not affected by glaciation

Such areas either have strong relief or a dry arctic climate, which impeded the development of glaciers. Soil-forming processes are slow and soils are poorly developed; these conditions are unfavourable for the formation of surface geochemical halos associated with mineralization. In general, halos that developed directly over mineralization are subject to lateral displacement, which can be considerable depending upon the degree of slope. In the latter case, the geochemical response from drainage sampling is good, and dispersion trains are extensive, being essentially detrital. The length of trains depends upon the dilution of detritus from the orebody by barren rock.

In the case of porphyry copper deposits, which have a large primary aureole, the dispersion trains are usually several kilometres long. The Casino deposit in the Yukon (Canada) shows well-developed stream-sediment anomalies over about 12 km (Archer and Main, 1971). The Stikine deposit in British Columbia (Barr, 1966) provides another good example of the effectiveness of stream-sediment geochemistry.

On the other hand, no discernable geochemical expression is found in streams draining the Williams Creek porphyry Cu–Mo deposit in the Yukon (Horsnail and Elliott, 1971). This is explained by the low pyrite content of the primary ore and/or the low groundwater level, both factors that are unfavourable for hydromorphic dispersion.

In the case of smaller high-grade deposits such as vein or massive sulphide orebodies, the dispersion halos are usually smaller and generally not more than a few kilometres in size, for example, around the Pb–Ag–Zn vein mineralization in the Keno Hill area, Yukon Territory (Fig. 12-4) (Boyle and Gleeson, 1972).

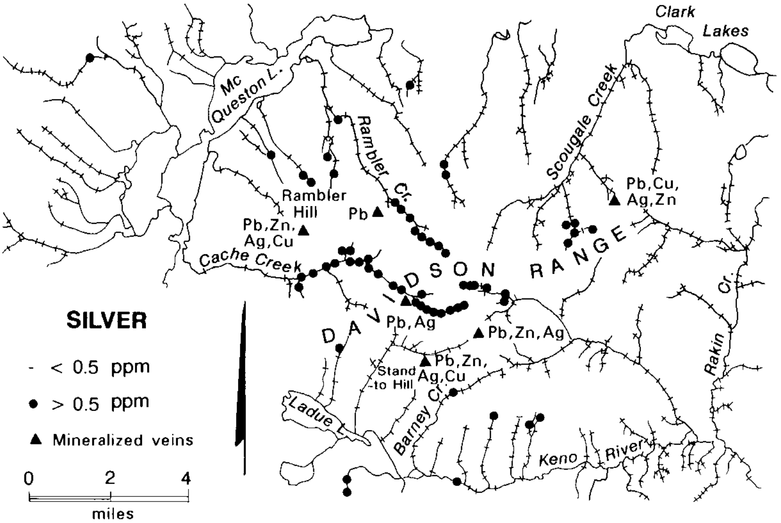


Fig. 12-4. Distribution of total silver in the minus 80-mesh fraction of stream sediments, Keno Hill area (reproduced from Boyle and Gleeson, 1972, with permission of the Minister of Supply and Services Canada, 1993).

Areas covered by locally derived till

Here, studies of the dispersion trains of distinctive types of rock or ore fragments show that, in general, the transport distance of clasts is limited; this is particularly the case for fine material from till, although boulders are commonly transported over greater distances.

For the purposes of exploration geochemistry, glacial deposits in areas with steep slopes can be considered as residual, since their displacement is usually less than 100 m. Farther downslope, glacial transport is generally more significant, and post-glacial creep may further increase dispersion.

Elsewhere, regional drainage geochemical patterns are similar to those observed in areas of residual soil cover, but metal concentrations are usually lower, as erosion affects till more than bedrock, leading to a greater dilution by unmineralized material; the stream sediment dispersion trains that characterize such environments are thus weaker. In the case of the Huckleberry porphyry copper deposit in British Columbia, which lies in an area of relatively subdued relief on the fringe of an alpine area (Sutherland-Brown, 1974), Cu anomalies in seepage samples have significantly higher metal contents than those in sediment samples, due to the strong development of a hydromorphic component superimposed on the detrital anomaly (Fig. 12-5).

Other western Canadian porphyry copper deposits that show a good geochemical response in stream sediments or water is found at Boss Mountain (Soregaroli, 1975a), Brenda (Soregaroli, 1975b), Chutanli (Mehrtens et al., 1973) and Sam Goosly (Sutherland-Brown, 1975).

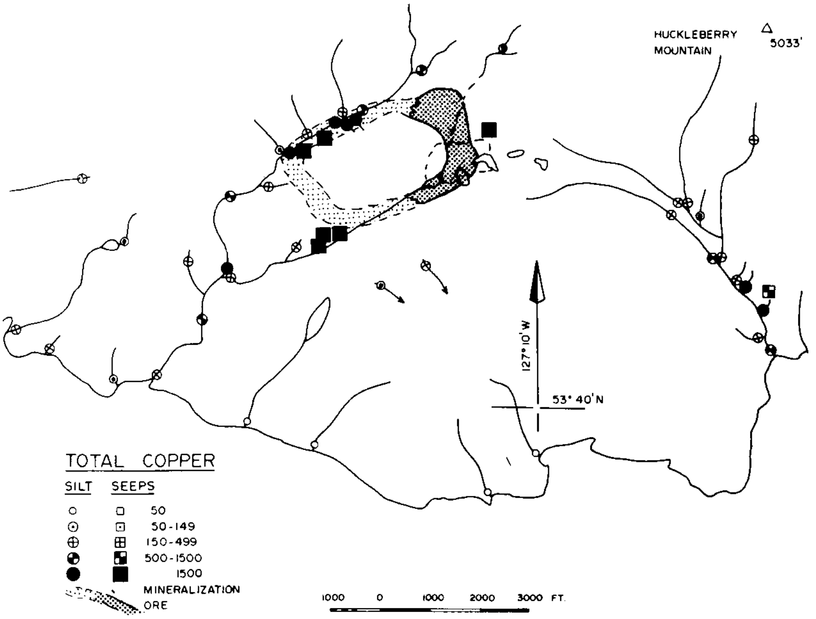


Fig. 12-5. Copper in stream sediments and seepages, Huckleberry, British Columbia (reproduced from Sutherland-Brown, 1974, with permission from the Canadian Institute of Mining Metallurgy and Petroleum).

Areas with allochthonous cover of distant origin

In such areas, surface anomalies related to buried or concealed mineralization may be absent or confined to anomalies of hydromorphic origin. Such "seepage" anomalies, which are closely controlled by topography and the drainage system, can develop at breaks in slope, or may be displaced towards the bottom of slope. Hence, they commonly have a distant origin that is difficult to pinpoint by surface sampling alone. If the cover is thick and its constituents are neither fine-grained nor porous, it is unlikely that such seepage anomalies will occur. Examples of such negative results are numerous: for instance, no significant anomaly could be found by sampling a meltwater river below the Toby Pb–Zn–Ba mine in British Columbia (Sleath et al., 1982) because of the extensive deposition of allochthonous glacier-derived silt in the river.

Levinson and Carter (1979) carried out one of the few recent studies on the use of geochemical methods in such areas at Babine Lake, British Columbia, where several porphyry copper deposits occur, and found that:

(1) dispersion is approximately 80% mechanical, so that a "total" analytical method should be used;

(2) glaciolacustrine silt and clay contain the highest levels of partial extractable metals;

(3) hydromorphic dispersion of metals is primarily through groundwater beneath till;

TABLE 12-I

Summary of length and strength of anomalies over different deposits

Name (reference) Sub-outcrop size (m) of mineralization Metals present	Overburden type	Extraction and element	Sediments	
			maximum dispersion length (km)	contrast
Porphyry-type mineralization				
Casino (Archer and Main, 1971)	residual	tot Cu	13	6
1800 × 750 m		tot Mo	0.8	17
Cu, Mo		tot Au	0	2
		tot Ag	0.5	3.5
Gibraltar (Bradshaw et al., 1974)	glacial till	tot Cu	3.2	3
5 separates zones		tot Mo	3.2	2
Sheslay (Coope, 1966)	mainly residual	tot Cu		
Size unknown		tot Mo		
Cu, Mo		exHM		
Huckleberry (Sutherland-Brown, 1975)	glacial till	tot Cu	2.8	50
Diameter 1000 m with low centre		tot Mot	2.8	100
		tot Zn	2.8	5
Maloney Creek (Horsnail, 1978)	residual plus volcanic ash	tot Cu	3.2	20
Size unknown		tot Mo	3.2	10
Cu, Mo				
Boss Mountain main zone (Soregaroli, 1975a)	glacial till	tot Mo	9.6	100
150 × 45 m		tot Cu		
Mo				
Dansey-Rayfield R. (Hoffman and Fletcher, 1972)	glacial till	tot Cu	16	
Size unknown				
Cu				
Vein-type mineralization				
Stand-to Hill, Zahn Hill, Keno Hill areas (Boyle and Gleeson, 1972)	residual on hilltop, glaciofluvial in valleys	tot Pb	3.2	44
0.6×?		tot Zn	15?	15
Multiple veins of Pb, Zn, Ag, Cu		tot Ag	1.6	2
		tot Cu	6.4	10
		tot B	15?	20
		tot As		
Mt. Haldane region, Keno Hill area (Gleeson, 1965)	residual on hilltop, glaciofluvial in valleys	tot Pb	6.4	35
0.6×?		tot Zn	6.4	8
Veins of Pb, Zn, Ag and As		tot Ag	0.8	15
		tot Cu	0.8	15
		tot Ba	6.4	20
		tot As	6.4	900

TABLE 12-I (*continued*)

Name (reference) Sub-outcrop size (m) of mineralization Metals present	Overburden type	Extraction and element	Sediments	
			maximum dispersion length (km)	contrast
Massive-sulphide-type mineralization				
Sam Goosly (Sutherland-Brown, 1975)	thin till	tot Cu	3?	14
1200 × 120 m		tot Zn	3?	2.5
Ag, Cu, (Zn)		tot Ag	3.2	75
		tot Mo	3?	2.5
		tot F		

(4) mechanically-dispersed sulphides can be identified in till up to about 1.5 km down-ice from deposits;

(5) in regions such as Central British Columbia, areas with mineral potential should not be eliminated from further work solely on the basis of negative or inconclusive geochemical data.

In conclusion, the various examples cited above from glacial and periglacial environments form a set of models that interfinger under field conditions, and are influenced by local morphological and soil conditions. These can either amplify or attenuate the geochemical signal from a particular mineral deposit. Additional factors that may affect dispersion include exposure of mountain slopes to the sun; in the northern hemisphere geochemical dispersion is stronger in drainage on south-facing slopes, which are less subjected to permafrost and thus develop more evolved soil profiles, than on north-facing slopes (Horsnail, 1975a). Other factors, such as the amount of silty material available in stream beds for sampling, or the relative abundance of iron sulphides associated with mineral deposits, which controls the pH of circulating solutions and thereby the migration of metal ions (Horsnail, 1975a), can also influence the intensity of dispersion. There is thus a relatively large amount of variation in strength and extent of dispersion around mineral deposits in the Canadian Cordillera, as illustrated in Table 12-I.

Temperate climatic zones

In view of the strong preponderance of detrital dispersion over hydromorphic migration in mountain areas located in a temperate climatic zone, one of the most suitable geochemical exploration approaches has proved to be panning of alluvial sediment with subsequent mineralogical examination of the concentrates. This procedure led to the discovery of the Mittersill stratiform scheelite deposit in Austria (Maucher, 1977). Another example is given by exploration for Pb–Zn mineralization in the eastern Italian Alps, using geochemical analysis of stream sediments in tandem with optical determination of heavy minerals

(Brondi and Polizzano, 1976). The latter technique was more successful than the first, in view of the widely-spaced sampling grid of 1 sample per 10 km^2. Exploration carried out for uranium in Austria (Smith et al., 1976b), for scheelite in eastern Tyrol (Hausberger et al., 1982) and the French Pyrenees (Cachau and Prouhet, 1971), for gold in alpine Bald mountain (Taisaev and Plyusnin, 1984) and for Cu–W occurrences in Nepal (Kaphle, 1982) showed the effectiveness of stream-sediment analysis, panning and hydrogeochemical techniques in a mountain areas of medium elevation that are relatively unaffected by glaciation. Panning and hydrogeochemistry carried out with a large sample spacing (1 sample per 2 to 10 km^2) allowed rapid outlining of areas of interest; stream-sediment geochemistry, with a closer sample spacing (between 1 and 5 samples per km^2) was especially suitable for target identification.

Cagatay (1977) worked out a detailed methodology for geochemical exploration based on drainage sampling for massive sulphides in the eastern Black Sea region of Turkey. Drainage in this area has a well-developed dendritic pattern. The headwaters of stream networks are in high mountains, and as streams approach the sea they deposit their load in wide stream beds. Stream-sediment sampling at a density of one sample per km^2 defined well-developed dispersion trains several kilometres long for Cu and Zn, and to a lesser extent for Pb and Ag. Stability of the hydromorphic anomalies was, however, severely affected by flooding, which meant that reliable anomalies are restricted to the smallest tributaries. The presence of sulphide mineralization is also indicated by pH values less than 4 to 5 in spring and stream waters.

None of the foregoing examples deals with geochemical exploration in moraine-covered areas. Interpretation of data from such environments requires a thorough knowledge of palaeo-glacier movements, which can be illustrated by recent geochemical exploration by BRGM in the French Alps. Detailed stream-sediment sampling based on a density of 3 samples per km^2 led to recognition of two regional Pb–Ag anomalies (Fig. 12-6). The northeastern "B" anomaly reflects Pb–Zn–Ag veins on slightly higher ground, but the southwestern "A" anomaly derives from mineralized boulders that were first transported to the southwest by Quaternary palaeo-glaciers and then incorporated in allochthonous slope deposits up to 50 m thick, which formed when the ice melted.

Arid to semi-arid climatic zones

Lovering and McCarthy (1978) provided an excellent synthesis of conceptual models for exploration geochemistry in the Basin and Range Province of southwestern North America, although relatively few data are available on regional drainage geochemistry. If the topography is steep and residual soils or colluvial material are present, geochemical dispersion trains are well developed as long downstream dilution by sediments from unmineralized areas does not mask the anomalies. Anomaly trains comprise mainly fine-ground particles of ore minerals and gossans, derived by strong mechanical weathering and abrasion. Most examples of regional drainage geochemistry deal with exploration for porphyry

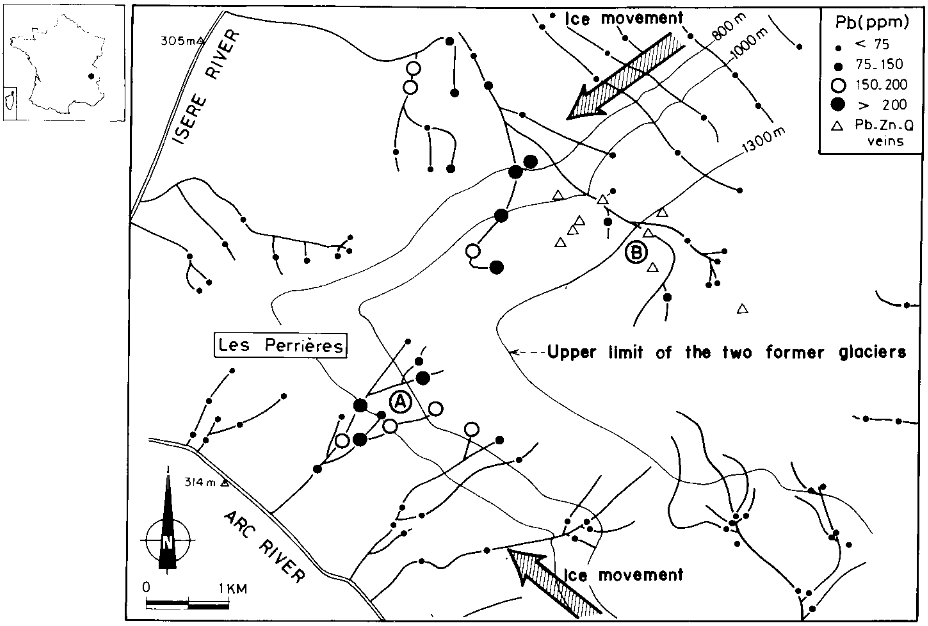


Fig. 12-6. Les Perrières prospect (French Alps): distribution of lead in stream sediments.

copper deposits. Significant Cu and Mo anomalies and slightly less strong Pb, Zn and Ag anomalies, are observed up to 32 km below many porphyry copper deposits, such as Copper Creek in Arizona (Ullmer, 1978), Caridad in Mexico (Coolbaugh, 1979), and Pima and Rosemont in Arizona (Lovstrom, 1978; Lovstrom and Horsnail, 1978). Table 12-II summarizes the major dispersion characteristics of metals in the Basin and Range Province.

Information on other types of deposits is much less readily available. Dispersion trains for the Aguachile fluorspar/beryllium deposit in northern Mexico were reported by Griffitts and Cooley (1978a) to be several kilometres long (Fig. 12-7). At least one example can be cited from another geographical setting, the Wadi al Wariah massive-sulphide mineralization in ophiolites of the Oman Mountains (Fig. 12-8; unpublished BRGM data). Anomalous copper concentrations exist in the stream near the deposit but not in the stream sediments of the main river. The dispersion is mainly detrital, and is more readily identified in the heavy-mineral fraction, obtained by heavy-liquid separation, or in coarser size fractions that contain no aeolian sand component to depress geochemical anomalies.

Tropical climate zones

Examples of regional stream-sediment geochemistry in tropical high mountain areas are mainly concerned with porphyry copper exploration in the Andes

TABLE 12-II

Summary of some characteristics of geochemical exploration case histories in the Basin and Range province (modified after Lovering and McCarthy, 1978)

Name and location of area (reference in parentheses)	Ore elements and type of deposit	Sample material	Tracer elements	Size of anomaly	Comments
Aguachile, North Coahuila, Mexico (Griffitts and Cooley, 1978a)	Be, fluorspar replacement	Minus 200-mesh stream-sediment	Be, Mn, Mo, Ti, V, Y, Zr	600 m downstream	
Copper Creek, Pinal county, Arizona (Ullmer, 1978)	Cu, Mo; stockworks	Mesquite twigs	Mo	10 km downstream at mouth of stream	Isolated anomaly at mouth of stream draining mineralize area. High Sn zone surrounds Mo anomaly
Eastern Santa Rita quadrangle, Grant county New Mexico (Watts et al., 1978a)	Cu–Mo, Pb–Zn Ag; disseminated, vein and replacement	Stream-sediment	Cu, Fe, Mn	$16\ km^2$ maximum	Several anomalies in area
		Heavy-mineral concentrate	Mo, Pb, Sn, Zn, Ag		
Helvetia district, Pima county, Arizona (Drewes, 1973)	Cu, Ag, Pb, Zn; vein, metasomatic and disseminated	Minus 80-mesh stream-sediment	Cu	–5 km in stream sediment	Ag, Cu, Pb, Zn in mineralized rock give good anomalies near ore
		Mineralized rock	Cu, Ag, Pb, Zn		
La Caridad Mine, Sonora, Mexico (Coolbaugh, 1979)	Cu; disseminated	Minus 60-mesh stream-sediment	Mo, Cu, Zn, Ag, W	32 km downstream	Mo gave longest anomaly dispersion trains in all three sample media
		Mesquite and oak leaves		22 km downstream	
		Heavy-mineral concentrates		22 km downstream	

Pima district, Pima county, Arizona (Lovstrom, 1978)	Cu, Mo; disseminated	Minus 80-mesh stream-sediment	Cu, Mo	10 km downstream	Interpretation of anomalies complicated by contamination
		Mesquite twigs	Cu, Mo		
Rosemont deposit, Pima county, Arizona (Lovstrom and Horsnail, 1978)	Cu; contact metasomatic and disseminated	Minus 80-mesh stream-sediment	Cu, Mo, Pb, Zn, Ag	8 km downstream	
		Mesquite twigs	Cu, Mo, Pb, Zn, Ag	6 km downstream	
Safford district, Graham county, Arizona (Horsnail, 1978)	Cu; vein and disseminated	Minus 80-mesh stream-sediment	Cu, Mo, Pb, Zn, Ag	approx. 200 km^2	
		Mesquite twigs	Mo		
San Manual district, Pinal county, Arizona (Lovering et al., 1950)	Cu; disseminated	Minus 80-mesh soil and alluvium; various desert plants; groundwater	Cu, Pb, Zn	−2 km in alluvium	Anomalies in soil over ore zone; Cu anomalies in leaves of creosote bush, palo verde and oak over ore
Sheeprock Mountains, Tooele county, Utah (Griffitts and Cooley, 1978b)	Be; disseminated	Rock, stream-sediment	Be, Sn, Zr	approx. 2.5 km^2	Co, Mn and Cr

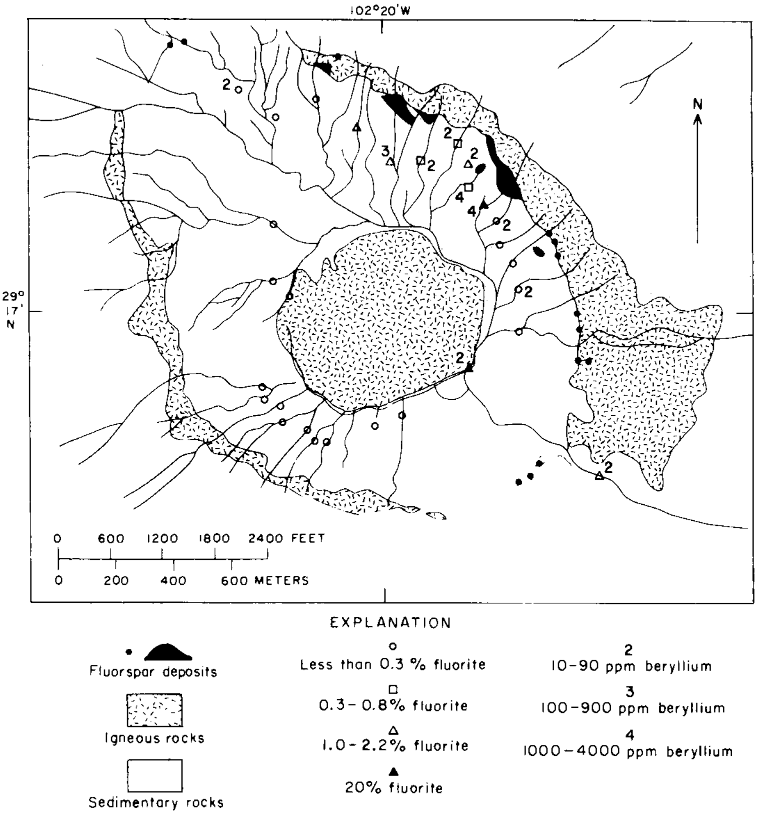
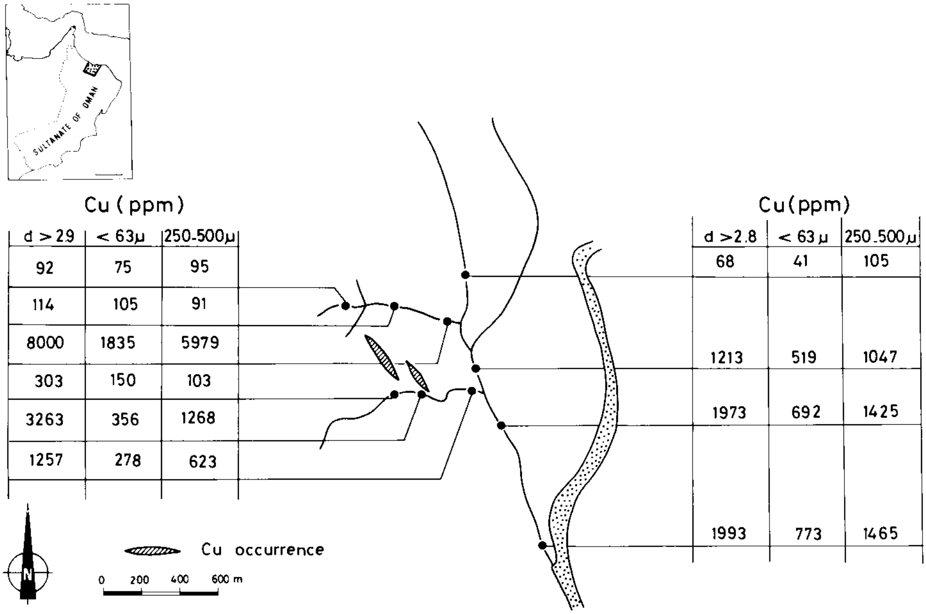


Fig. 12-7. Sketch map of Aguachile beryllium-fluorspar deposits, showing sample localities and concentration ranges of fluorite and Be in the minus 200-mesh stream sediment (from Griffitts and Cooley, 1978a).

(South America) and the southwest Pacific. Govett and Hale (1967) and Coope (1973) reported dispersion trains that extend as far as 20 km from porphyry copper source in areas of high relief in humid tropical areas. Other examples are drawn from successful exploration campaigns on Sabah (Cooper et al., 1965), Cebu (Hawkes and Webb, 1962) and Bougainville (MacNamara, 1968).

A useful example is provided by the orientation survey, described by Baldock (1977), at the Michiguillay porphyry copper deposit in northern Peru, which comprised sampling at 100 to 200 m intervals along the main drainage channels around the orebody. The distribution of high levels of copper and, to a lesser extent, molybdenum in the minus 80 mesh fraction of stream-sediment samples (determined with hot and cold extraction techniques) was erratic, but geochemical dispersion below the deposit was recognizable for more than 8 km (Fig. 12-9), despite the predominance of limestone. Resampling of various streams around the prospect at different periods during one year, showed that seasonal variations are small when compared with overall data variability, including sampling and analytical errors. The results indicated that sampling was



Cu (ppm)

d > 2.9	< 63µ	250-500µ
92	75	95
114	105	91
8000	1835	5979
303	150	103
3263	356	1268
1257	278	623

Cu(ppm)

d >2.8	< 63µ	250-500µ
68	41	105
1213	519	1047
1973	692	1425
1993	773	1465

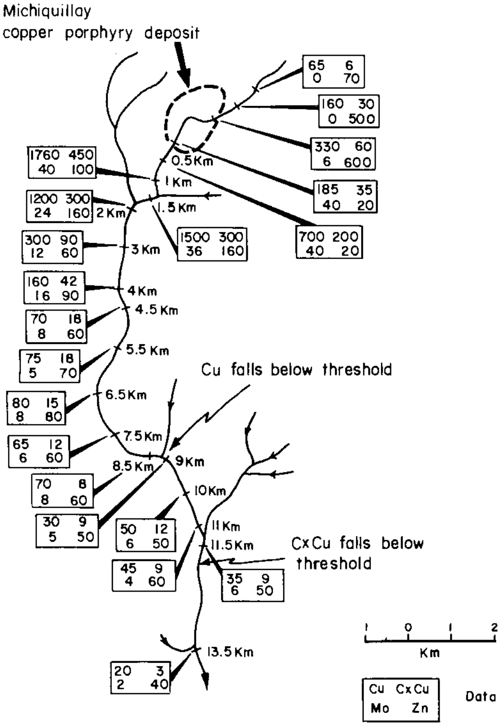
Fig. 12-8. Sultanate of Oman (Wadi al Wariah copper prospect): Cu contents of different size fractions.

most successful if restricted to the longer second-order channels, and to third-, fourth- and the upper parts of fifth-order channels. Following this orientation work, the average sampling density adopted for the regional survey was 1 sample per 10 km^2, increased to 1 sample per 5 or 8 km^2 in areas underlain by carbonate, which provides alkaline water and tends to reduce copper solubility, thereby shortening anomalous dispersion trains.

Leggo (1977) described a stream-sediment survey in Fiji, based on a sampling density of 2.4 samples per km^2 in tropical-forest-covered mountains. This led to the discovery of several large, low-grade copper-sulphide systems. Copper and molybdenum values are strongly anomalous over 3 km in the Waidoi Creek system (Fig. 12-10), but not in the adjacent Wainabama system covered by recent volcanic material that dilutes stream sediments and attenuates geochemical anomalies.

In north Sulawesi, Indonesia, porphyry copper deposits were discovered by stream-sediment geochemistry, which identified Cu anomalies of 500 to 1000 ppm compared to background values of 100 ppm and with downstream dispersion of more than 3 km (Lowder and Dow, 1978). Sevillano and Fernando (1981) described trains of a similar length around the Basay deposits in the Philippines.

The discovery of polymetallic skarn-type mineralization in Kalimantan, Indonesia, by a combined team of the Geological Survey of Indonesia and BRGM, provides one of the few case histories of a discovery of mineralization other than porphyry copper by drainage sampling in tropical-rain-forest mountains. In this



Within and at lower (downstream) end of deposit: Cu > 2T, CxCu > 4T
Max values at 1-2.5 Km below end of deposit : Cu > 16T, Cx Cu > 32T
at 2.5-4 Km " " " " Cu > 2T, Cx Cu > 4T
at 4 - 8.5 Km " " " " Cu ⩾ T , Cx Cu > 2T
at 8.5-11.5 Km " " " " Cu < T , but CxCu > T
at 4 Km Mo 2T; from 4.5 - 11.5 Km : Mo ⩽ T
For 0.5 Km above limit of Cu deposit : Zn > 2T

Fig. 12-9. Orientation survey at Michiquillay copper porphyry: threshold (*T*), upper limit of local background values (redrawn with permission from Baldock, 1977).

area of particularly high mountains, prospected from sea level to altitudes of 2500 m, the steep mountain sides are drained by torrential streams that are mostly perpendicular to the contours. The warm climate and the annual rainfall of about 4 m maintain an exceptional humidity and allow the development of very dense forest. Regional exploration with an average density of one stream-sediment sample per 6 km^2 led to the discovery of an anomalous polymetallic zone around a Pb, Zn, Ag, Sn and Cu deposit, with dispersion trains of several kilometres length as shown in Fig. 12-11 for Pb and Zn. Table 12-III shows the mean values of anomalous samples and background for all five elements. The patterns were confirmed by panning concentrates, which were rich in cassiterite. The stream-sediment anomalies are thus directly linked to primary mineralization and are only slightly attenuated, compared to anomalies in other tropical areas that are more subject to ferralitic weathering.

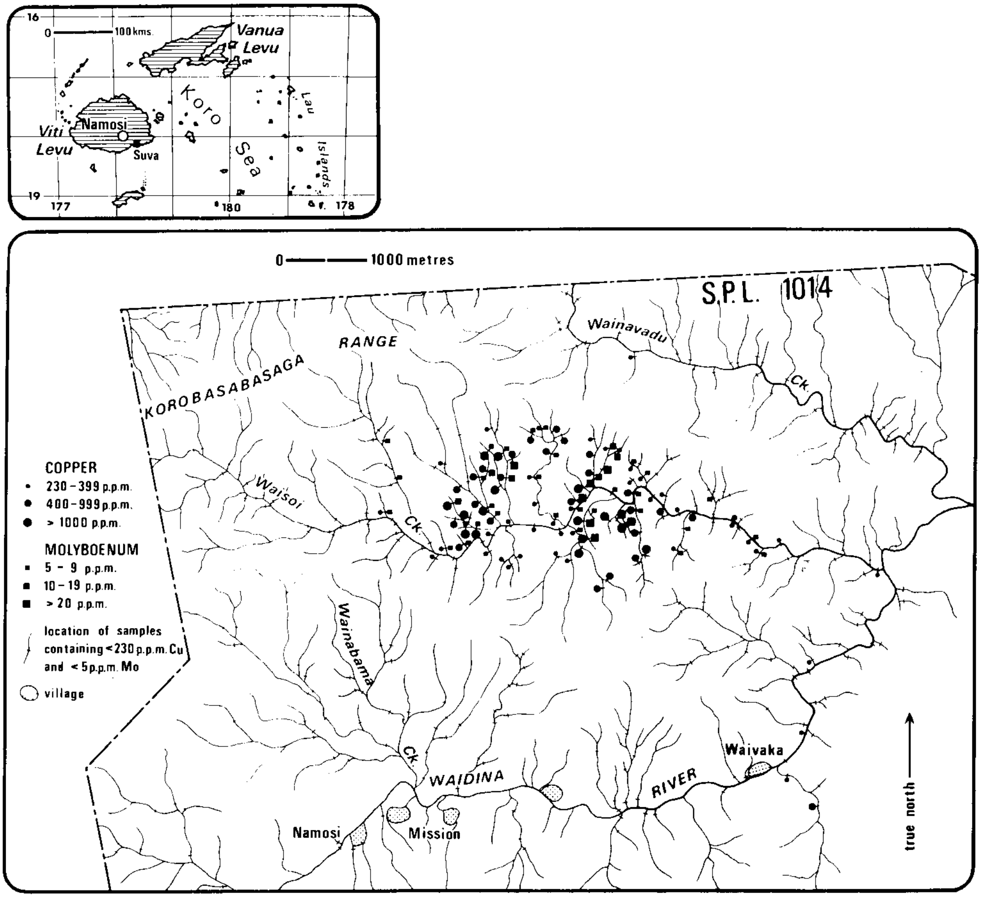


Fig. 12-10. Stream sediment Cu and Mo values for the Waisoi and Wainabama prospects (from Leggo, 1977).

TABLE 12-III

Comparison of anomalous and background stream-sediment values over polymetallic skarn-type mineralization in Kalimantan (Indonesia)

	Analytical range	Anomalous mean (47 samples)	Background (7143 samples)
Pb	37 -1593	305	4
Zn	122 -3279	324	74
Cu	24 -1557	146	30
Sn	1 - 527	16	1
Ag	0.1- 14.1	0.7	0.1

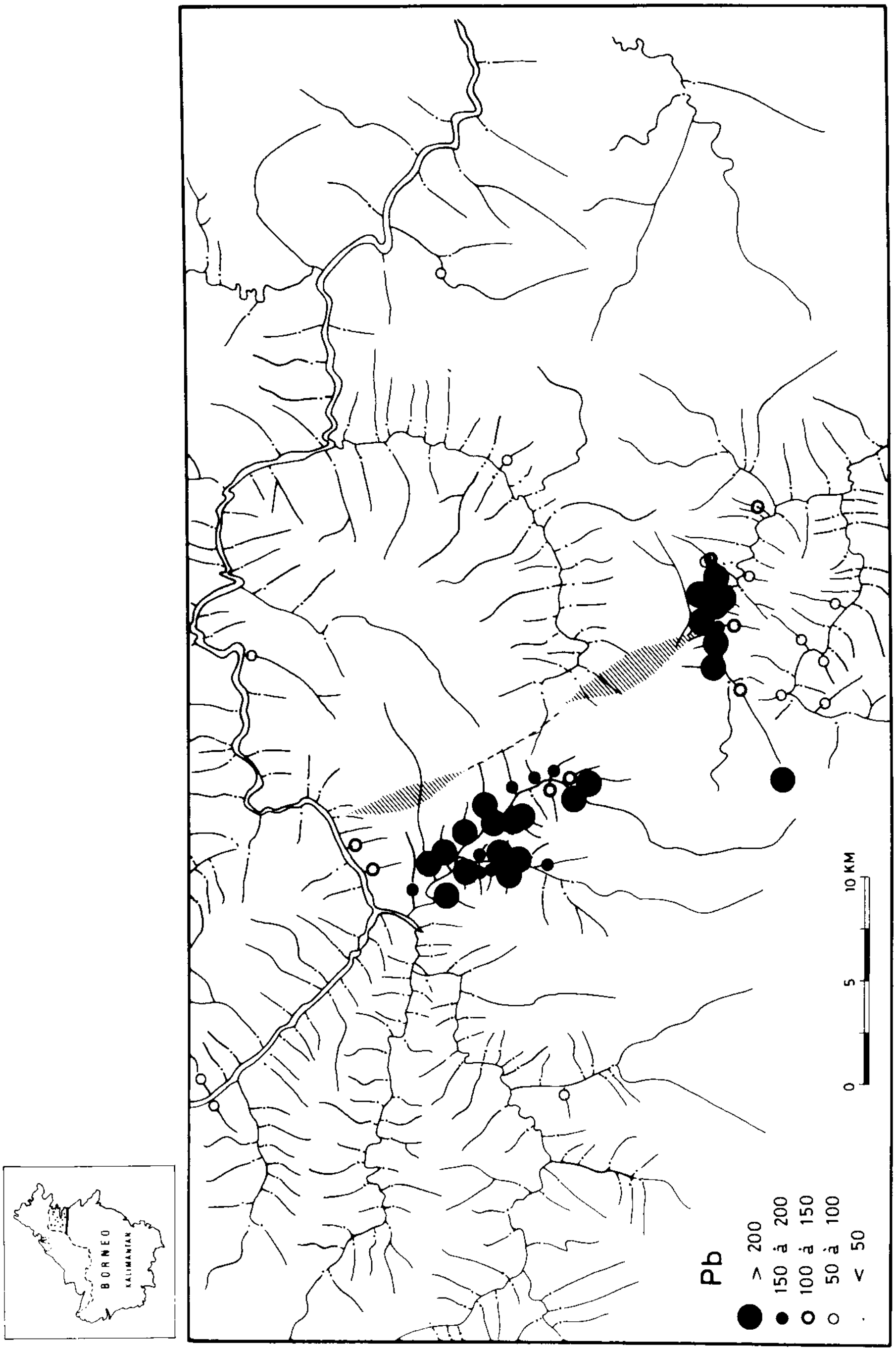


Fig. 12-11. Regional geochemical Pb anomalies around a skarnoid mineralization in Kalimantan, Indonesia.

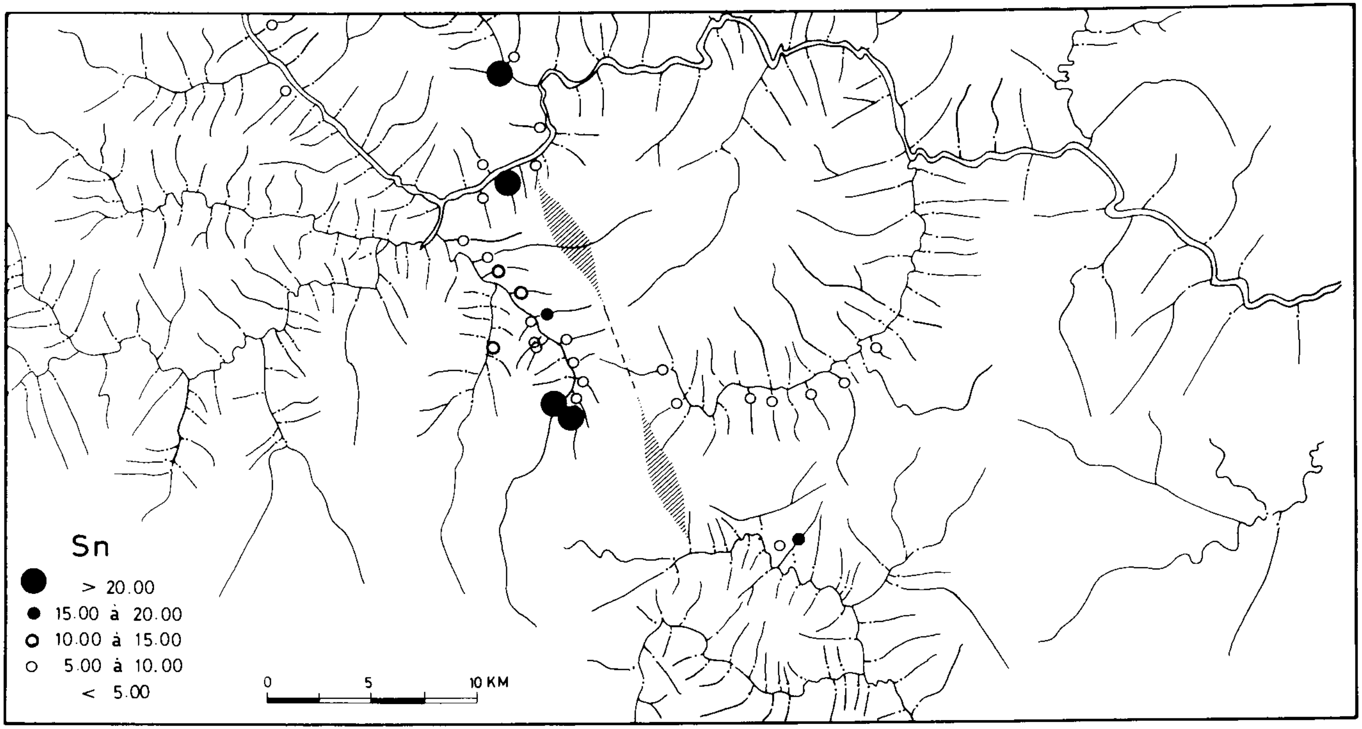


Fig. 12-11. Regional geochemical Sn anomalies around a skarnoid mineralization in Kalimantan, Indonesia.

RECOMMENDATIONS FOR GEOCHEMICAL EXPLORATION IN HIGH MOUNTAIN AREAS

In high young mountain areas, geochemical exploration based on drainage sampling is usually more effective than in peneplain areas due to the following factors:

(1) the high density of drainage systems;

(2) the deeply incised drainage systems, which cut deep into bedrock;

(3) the constant renewal of freshly eroded material in the drainage;

(4) the sediment-carrying power of streams, which produce long dispersion trains in the drainage system;

(5) the generally easy correlation on slopes between a mineralized source and its anomaly.

The most important of the many problems that can affect geochemical exploration in high mountains, reducing or even obliterating geochemical anomalies, is the presence of allochthonous cover, whether of glacial, aeolian or volcanic origin. Another problem is the absence or scant occurrence of fine-grained material, which is commonly the case in areas of high relief, where stream gradients are steep.

However, geochemical-drainage samples in these areas are not confined to alluvial material, but can be water and even vegetation. The following sections consider the various sample media and methods.

Sampling in coarse alluvial material

It is possible to sample coarse fragments of altered or mineralized rocks, gossan material, vein fillings and fracture coatings, at the mouths of streams where they leave the mountains. Obviously, this provides useful indications of mineralization in the upstream drainage basins. A refinement of the method is the removal of coatings of iron and manganese oxides on stream pebbles and cobbles, which can be analysed for metallic ions that are carried in solution and are selectively adsorbed by these coatings. Under certain conditions, such coatings may provide better anomaly patterns than fine-grained sediments, as demonstrated by Huff (1971). Horsnail (1975) noted that downstream from the Maloney Creek porphyry copper deposit in Yukon Territory, considerable solution of metallic cations caused precipitation of manganese and iron hydroxide crusts on boulders in the drainage. Such coatings are also common in desert areas and were, for instance, used in exploration for porphyry copper deposits in the southwestern USA, as reported by Chaffee (1975), Watts et al. (1978a), and Filipek and Theobald (1981).

Qualitative determinations in these sample media can be carried out in the field by means of reagent tests that provide a first indication of the presence of oxidation products, which usually are difficult to recognize mineralogically. Such procedures, which are used to complement more systematic geochemical analyses, are especially recommended in a carbonate-rock environment.

Sampling in stream sediments

Type of dispersion

Stream sediments are the most commonly used sample medium for reconnaissance geochemical exploration in almost all mountain areas. In steep areas, where rocks occur as (sub-)outcrop, anomalous metallic dispersion trains are mostly formed by sulphides or primary oxides, which can form a large part of detrital heavy minerals in the silt fraction of stream sediments. In areas farther downstream, or in less steep terrain where chemical weathering processes are developed, oxidation may transform part or all of the primary sulphides into stable secondary minerals or soluble ions, some of which may be adsorbed by secondary iron and manganese oxides and hydroxides (Wilhelm et al., 1979).

Float from mineralized outcrops is commonly rather soft and friable, and the violent abrasion to which such float is subjected during flash floods rapidly reduces it to silt-size particles, which are carried and dispersed down-stream. Anomaly trains thus mainly consist of finely-ground particles of mineralized rock.

The contribution of hydromorphic dispersion is most readily detected in localized areas below breaks in slope, but this contribution is normally subordinate to that of the detrital component. The hydromorphic component is detected in the field by seepage sampling when a glacial cover is present (as illustrated in Fig. 12-5), and in the laboratory by applying selective chemical attacks to sediment samples in order preferentially to dissolve the iron and manganese oxi-hydroxides and associated trace elements. This type of approach is complementary to the direct analysis of pebble coatings and has been used particularly in arid and semi-arid climatic zones (Overstreet and Marsh, 1981).

Sampling density and type

Sampling of silt-sized stream-sediment fractions is particularly effective for reconnaissance surveys in which samples are collected from small tributary streams with catchment areas of not more than a few square kilometres. Downstream dilution occurs where other tributaries drain unmineralized areas, and their sediments can completely mask the anomalous geochemical signal. Hence, a relatively high sampling density should be used, although this depends on the size and nature of the target. Porphyry copper deposits with large primary halos tend to give large dispersion trains and can be detected with relatively low sample densities, whereas high-grade veins and massive sulphides, by virtue of their smaller size, require greater sampling density. The average stream-sediment sampling density should be about one sample per km^2, adjusted to the type of target, and the shape and hydraulic energy of the drainage system. The choice of a sampling site, which is of primary importance in mountain areas, should consider the surface area of upstream basins in order to achieve optimum coverage; accessibility of the site is also important, since it directly affects the cost of the survey.

Sampling of active recent stream sediment is recommended; in certain drainage channels much of the fine fraction may have been washed out, although it is usually possible to find some sediment between blocks, close to the banks, or trapped by roots.

Grain size to be sampled

Traditionally, the <80 mesh (<180 μm) grain-size fraction is analysed (French geochemists also use a <125 μm cut-off, but the comparative results differ insufficiently to recommend one or the other fraction). Such a fraction is well suited to the mostly detrital dispersion patterns found in high mountains. In the case of aeolian contamination, dilution can be minimized by analysing a slightly larger size fraction, for instance, the 250–500 μm fraction as recommended by Griffitts and Alminas (1968) in New Mexico. Certain refractory ore minerals, such as chromite, cassiterite, columbite, tantalite, scheelite, thorite, monazite, beryl, and fragments of gold-bearing quartz, are preferentially concentrated in sand; in this case, the coarse fraction contains larger anomalies than do the fine fractions. Use of such coarse material necessitates the grinding of all samples before analysis.

Sampling of alluvial concentrates

To increase the sensitivity of a sediment sample, the light fraction, which normally is unmineralized and thus acts as a dilutant, can be removed by panning. The method is generally used in exploration for mineralization that weathers to produce resistant heavy minerals, such as gold, tin, tungsten and certain rare-earth-element phases. The technique is also useful for base metals, because primary sulphides and their principal oxidation products can be recovered by careful panning.

This panning technique has been widely used in Alaska and in other arctic mountainous areas (Overstreet et al., 1975, 1978; Pan et al., 1980), in British Columbia (Barakso and Tegart, 1982) and in temperate climatic zones (Watts et al., 1978a; Hausberger et al., 1982; Xie and Zheng, 1983). However, little information is available from tropical regions.

The technique most commonly used is based on gravimetric concentration by means of a pan, which recovers only relatively large heavy-mineral grains. In high mountain areas, where mineral particles usually are abraded, it is commonly necessary to use more advanced techniques, such as a riffle table or heavy-liquid separation, to recover the heavy minerals of fine grain size (see also Fig. 12-8).

The relatively high sensitivity of heavy-mineral concentrate samples usually allows a wider sample spacing than is possible with stream-sediment sampling, as concentrates can be obtained from lower-order drainage channels. Moreover, anomaly trains in stream sediments can generally be traced much farther from their source by using heavy-mineral concentrates than when using fine sediment samples, particularly where ore elements occur in resistant minerals, or when aeolian contamination is present.

On the other hand, the technique can suffer from less reproducibility, as material constituting the fine fraction is variably removed from the samples. Also, interpretation of analytical results is usually more difficult than for the results from the fine fraction of stream sediments, as they are highly dependant upon conditions of deposition at individual samples sites, a factor difficult to control. Finally this technique is mostly used in mountainous tropical climatic zones.

Hydrogeochemical sampling

Miller (1979) summarized the factors to be considered in hydrogeochemical exploration. Water is chemically most reactive and maximum trace-element anomaly contrast is obtained in areas of moderate relief and rainfall; an increase of either of these parameters tends to decrease contrasts, because of dilution by unmineralized water, and because the time of contact between primary minerals and water is short and does not allow complete chemical reactions. Springs and first-order streams are probably the best sample media, and the best time for sampling usually is after spring run-off, when streams have returned to normal flow, or during autumn or winter when flow decreases. In general, streams and springs in tropical areas do not provide favourable sample media for hydrogeochemical exploration.

The use of this technique in the mountainous areas of the Williams Creek copper prospect in the Yukon was discussed by Horsnail and Elliott (1971), and by Mehrtens et al. (1973) for the Chutanli molybdenum deposit in British Columbia. Taisaev and Plyusnin (1984) showed how hydrogeochemical techniques can be used in gold exploration in an Alpine mountain area. In arid areas, spring-water sampling has been used in Arizona (Trost and Trautwein, 1975) and Afghanistan (Kolotov et al., 1982). Good results were obtained using water sampling for uranium exploration in Austria (Smith et al., 1977).

CONCLUSIONS

Compared with other types of physiographic regions, most young folded mountain areas are subjected to strong meteorological action, reflecting their topography, altitude and climate effects. These facts result in intense erosion related to high levels of precipitation, and diurnal and seasonal temperature variations that cause frost action and heat spalling.

The rock debris produced, which is of highly variable grain size, is carried away in the drainage system and dispersed mostly mechanically over large distances under the influence of considerable hydraulic energy.

The vertical climatic zonation, which results from decreasing temperature with increasing altitude and variations in precipitation, cannot be considered as a simple extra-zonal extension of climates that exist in colder lowland regions of other latitudes. Indeed, numerous peculiarities of mountains belts influence processes of rock alteration, soil formation and run-off. The detection of geochemical dispersion patterns of minerals and elements in drainage systems thus necessitates an approach that is not based on climatological principles alone.

Generally, the mountain environment is particularly suitable for the use of regional geochemical exploration techniques based on sampling of erosion products. Extensive secondary dispersion halos allow a wider sample spacing than would be possible in areas with a gentler topography, but the cost saving is generally off-set by the higher cost of getting to the sample sites. To be representative, sampling sites should lie downstream of first-order or, at most, second-order drainage channels, whose upstream catchment basin should be less than 5 to 10 km^2 to reduce dilution by unmineralized sediment.

For the purposes of exploration geochemistry, two types of terrain can be distinguished.

(1) High mountain areas with steep topography, where rock is directly exposed to erosion, and especially abrasion. Here, sampling of fine stream sediment and/or heavy-mineral concentrate in the first-order drainage network and near breaks-in-slope is recommended. Heavy-mineral concentrates allow a lower sampling density than stream sediments, but precaution is required to retain the finest grain-size fractions.

(2) Mountain areas of moderate elevation with a less steep topography, and plateau areas where deep oxidation and soil formation are developed. Here mechanical dispersion, although remaining important, can locally be accompanied by hydromorphic dispersion of metallic ions. The resulting geochemical halos, although of poor contrast, can be detected by collecting materials that adsorb metal ions, such as iron and manganese oxides and hydroxides, and sediments enriched in organic matter. When allochthonous cover material is present, which in mountain areas is usually of glacial origin or is formed by vast piedmont fans, the only geochemical exploration method lies in defining hydromorphic anomalies by sampling spring waters or seepages at the base of slopes.

Overall, it is recommended that several types of sample media should be collected in order to obtain maximum information from each sampling programme, particularly as in mountain areas the travelling to and from sample sites commonly is the most expensive part of geochemical exploration. Ideally, direct observational prospecting techniques, using reagent tests on outcrops and stream boulders, should be combined with stream-sediment sampling at the base of first-order streams that drain catchment areas of no more than 10 km^2, and with the collecting of heavy-mineral concentrates at larger sample intervals in the drainage farther downstream. Hydrogeochemistry can be used in areas of thick allochthonous cover.

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Chapter 13

DRAINAGE GEOCHEMISTRY IN CONTAMINATED TERRAINS

D.C. COOPER and I. THORNTON

INTRODUCTION

The application of geochemical surveys, based on the systematic sampling and analysis of surface and subsurface waters and drainage sediment, to metalliferous mineral exploration has been comprehensively discussed in previous chapters. However, except in the most remote or unpopulated areas, the influence of human activity on the chemical nature of the surface environment has led to varying degrees of contamination. This contamination of soils, waters and sediments has long been of concern to those prospecting for metals in the more heavily affected areas, as it is frequently difficult to distinguish metal concentrations derived from untapped mineralisation, old mines and other anthropogenic sources (e.g., Williams, 1955; Webb, 1958a; Hawkes and Webb, 1962). The problem has become more acute in recent years as larger areas become affected by higher levels of pollution and there are increasing socio-economic pressures in some countries to explore for new deposits in existing mining fields.

Geochemical atlases, initially compiled in the United Kingdom but now available for many parts of the world, show metal anomalies that may reflect natural variations or pollution arising from past or present industrial activity, urban development or agricultural practice. Locally it may be very difficult to distinguish between these sources of metals and, commonly, the artificial sources mask or modify dispersion patterns arising from mineralisation. However, the multi-purpose geochemical survey is now firmly accepted as a basis for geochemical mapping and the resulting information on the regional distribution of metals from both natural and anthropogenic sources has obvious applications in agriculture, pollution studies and health, as well as the more traditional role of mineral exploration (Webb, 1964; Thornton and Webb, 1974). To maximise the usefulness of the geochemical data for these purposes it is important to be able to distinguish variation caused by natural and artificial sources. However, in contrast to the burgeoning literature concerned with the environmental impact of pollution, the problems that contamination brings to the interpretation of drainage geochemical surveys for mineral exploration purposes have received little attention from exploration geochemists except for studies of dispersion downstream of metalliferous mine workings.

It may be assumed that national differences between the uses of metals and disposal of wastes over a long period will influence the background ranges of metal concentrations in soils and drainage sediments. For example, concentrations of lead in agricultural soils in the United States of America (median 11 ppm) appear lower than in Britain (median 37 ppm; Holmgren et al., 1983; Archer and Hodgson, 1987). A statistical examination of soil data from England and Wales (Davies, 1983a) indicates that the normal lead content of surface soil (0–15 cm) lies between 15 and 106 ppm. The relatively high values in Britain probably indicate a widespread low level contamination arising from more than two centuries of largely uncontrolled industrial and mining activity. As stream sediment is derived in part from the erosion of topsoil it is to be expected that background values of lead in drainage sediments will reflect to a degree those in the soils, and that differences for some elements due to pollution will occur between the two countries. However, it is on a more local scale that contamination generates drainage anomalies of sufficient magnitude and contrast to provide major problems for the exploration geochemist, and it is on these anomalies that the following chapter concentrates.

Affected terrains

There are few, if any, areas of the world not affected by some degree of metal pollution. In Greenland snow accumulation registers the long distance dispersal of lead pollution since 800 B.C., with Arctic snow containing ten times the amount of lead as that in Antarctica, reflecting the greater use of lead in the northern compared with the southern hemisphere (Murozumi et al., 1969).

However, the main areas affected are those parts of the world with a long history of mining, urbanisation and other human activities associated with metal inputs to the environment, including intensive farming, motorised transport and power generation. Consequently, Europe, North America and Japan contain the most widespread contaminated terrains. For example, Goto (1973) reported 33 areas in Japan polluted with cadmium, in Colorado 450 miles of surface streams are affected by mine tailings (Wentz, 1974), and in Britain about 25% of river courses are polluted (Department of the Environment, 1971, 1978). More recently industrialised and urbanised areas across the world, such as parts of Central and South America, Taiwan, Indonesia, Thailand, the Philippines, Papua New Guinea and Australia, are constantly adding to the list of contaminated terrains (Förstner and Wittmann, 1981), as are rural areas practising intensive agriculture (Richardson, 1991).

Historical controls on pollution

The earliest forms of drainage pollution were associated with metal mining and smelting. Lead pollution of the atmosphere dates from about 4500 years ago when smelting lead sulphide ores and cupellation of silver were developed in south-west Asia (Settle and Patterson, 1980). There is evidence of metal working in the Mediterranean area (e.g., Cyprus) over a similar period and from pre-Roman times in central and northern Europe. Copper has also been used in the Americas for a similar period. The explosion in contamination, however, dates from the onset of the industrial revolution in the seventeenth and eighteenth centuries in Europe and a little later in North America. The brass foundry at Gusum in Sweden dates from 1661 and smelting in South Wales from 1717 (Hutchinson, 1979) whilst Lake Eyrie sediment cores indicate mercury pollution from 1835. The use of copper as a fungicide dates from about 1800 when Bordeaux mixture was first made (Thornton, 1979), but the intensive use of fertilisers, herbicides and insecticides is largely a feature of the second half of this century. Since the industrial revolution, pollution has changed from a localised problem associated with specific towns and mining areas, through a regional-scale feature largely restricted to Europe and parts of North America, to a global multi-source problem of the late twentieth century.

Early industrial mining and smelting activities were less efficient than those of today and were rarely subject to any control with respect to the discharge of effluent: it is estimated, for example, that as much as 2% Pb was converted to aerosol in the course of smelting in the period 1750–1880. Factories and mines were frequently sited by rivers and therefore had the maximum impact on the drainage. Other factors which conspired to enhance contamination included the absence of refuse collections and proper treatment of sewage. Consequently, although industrial activity in the late twentieth century is greater than ever before, due to legislative control pollution levels in some of the long-industrialised areas of Europe and North America are reducing. Pollution inputs to the Rhine, in terms of cadmium, mercury and lead in soluble form and suspended solids, showed a pronounced decrease between 1972 and 1979 (Salomons and Förstner, 1984; Fergusson, 1990). Similarly, in England and Wales the total length of grossly polluted rivers and canals decreased from over 2000 km in 1958 to 810 km in 1980 (Royal Commission on Environmental Pollution, 1992).

Nriagu and Pacyna (1988) compiled an inventory of current global metal emissions to the atmosphere and inputs into soils and the aquatic environment, showing that nearly every industry discharges one or more metals into water or soil. It was estimated that man-induced mobilisation of trace metals into the biosphere amounts each year to about 120,000 tonnes of arsenic, 30,000 tonnes of cadmium, 2,150,000 tonnes of copper, 11,000 tonnes of mercury, 470,000 tonnes of nickel, 1,160,000 tonnes of lead and 2,340,000 tonnes of zinc. It was also estimated that, on average, anthropogenic emissions to the atmosphere of arsenic, cadmium, copper, lead, nickel and zinc exceed the inputs from natural sources. Consequently, the cumulative effects of human activities now have a major impact on the global and regional cycles of most trace elements (Nriagu, 1984; Nriagu and Pacyna, 1988).

Previous research

The effects of pollution from industrial activity have long been recognised; Borlase (1758) and Farey (1811) referred to the effects of mining and smelting on agriculture in Cornwall, and Derbyshire, respectively, but it is during the last 20 years that the volume of research and publications on all aspects of pollution have increased dramatically. Consequently, there is now a wealth of information available for many areas and metals. Reviews of individual metals include those for lead (Nriagu, 1978), zinc (Nriagu, 1980), selenium (Zingaro and Cooper, 1974), copper (Nriagu, 1979a), molybdenum (Chapell and Petersen, 1977), mercury (Nriagu, 1979b) and tin (Byrd and Andreae, 1986), whilst compilations of studies in lakes and rivers include those of Baker (1980); Förstner and Wittmann (1981); Förstner (1983); Salomons and Förstner (1984); Kelly (1988); and Hadley and Ongley (1989). Environmental scientists, who in the 1970's and early 1980's provided much information on the formation and effects of anthropogenic heavy metal concentrations, have in recent years increasingly studied the impact of organic chemicals on the environment (e.g., Richardson, 1991).

Cannon and Anderson (1971) first drew attention to the information that the geochemist can contribute to studies on environmental health where pollution has a role. Subsequently the links and applications of geochemistry to the environment, and the impact of both the natural environment and anthropogenic effects on plant, animal and human health were explored in the work and compilations of many researchers and editors (Cannon and Hopps, 1971, 1972; Jones, 1975; Thornton and Webb, 1979; Bowie and Webb, 1980; Thornton, 1983, 1986, 1988; Bowie and Thornton, 1985; Plant and Thornton, 1986). The establishment of geomedical research in Scandinavia (Låg, 1980, 1984, 1990) and the development of the new field of urban geochemistry in the United Kingdom followed (ApSimon et al., 1990; Thornton, 1990).

As environmentally-oriented research has concentrated on the effects of a relatively small range of essential and toxic metals there is most information available for elements such as As, Cd, Cu, Hg, Ni, Pb and Zn, and relatively less for others, such as Sb, Sn and Bi, which may be of equal or more interest to the exploration geochemist. Also, pollution studies have tended to focus on rivers and estuaries with less sampling of the small streams that normally form the basis of mineral exploration surveys.

The Applied Geochemistry Research Group, founded in the early 1950's (Williams, 1955), addressed the use of drainage geochemical data for environmental purposes and the discrimination of anomalies from natural and anthropogenic sources. The pioneering geochemical atlas of England and Wales (Webb et al., 1978) was one product of this work. It recognised that contamination was a major source of variation and that regional stream sediment data were able to identify regional-scale pollution related to old mining fields and aerosols from major industrial centres. No major features could be related to domestic/industrial effluent or agricultural practice, but this result was ascribed to the sampling method employed. Another product was the work of Taylor (1968), who found that in two British mining fields drainage anomalies from untapped mineralisation were concentrated in different phases from those caused by past mining and smelting activity, and that the anomalous sources could be differentiated by a combination of selective chemical extraction and simple statistical methods. Other related work included the interface between applied geochemical data, pollution and agriculture (Colbourn et al., 1975; Abrahams, 1983).

During the same period workers at the British Geological Survey, engaged on mineral exploration work across contaminated terrains on behalf of the United Kingdom's Atomic Energy Authority and Department of Trade and Industry, were developing methods for discriminating natural and anthropogenic anomalies based on the mineralogical examination of heavy mineral concentrates, the comparison of metal concentrations in different sample types collected from the same site and statistical methods (Dawson et al., 1977; Leake et al., 1978a; Cooper et al., 1982).

A perceptive study by Hosking (1971) noted that in south-west England contamination came from a multitude of sources which included metal mining, beneficiation and smelting, agriculture, other industries and domestic activities, and that each form of contamination had particular characteristics useful in identifying or avoiding it when carrying out geochemical surveys. Many other surveys in the 1970's documented the often great dispersion trains of pollution from mining and other industrial activities located in many parts of the world.

As the extent and difficulty in some areas of discriminating natural and anthropogenic anomalies became more widely recognised the use of alternative sample types or procedures to avoid contaminants was advocated. Allan and Timperley (1975) recommended that when sampling lake sediment in the Canadian Shield samples should be taken below 10 cm to avoid the effects of airborne pollutants, and Qvarfort (1977) proposed bank sampling in conjunction with active stream sediment sampling as a means of monitoring contamination in drainage. More recently the use of overbank samples has been proposed for regional geochemical surveys and the advocates of this medium point out that contamination-free samples can be obtained from layers deposited before industrial development took place (Ottesen et al., 1989).

Approach

This chapter reviews the major sources of contamination that may influence drainage geochemistry, the type of anomaly that these sources are likely to generate, and the methods that have been used to discriminate contaminated samples. A large number of references have been quoted to enable the reader to follow-up any particular area of interest in more detail. Most emphasis is placed on the effects of pollution on stream sediment, the commonest sampling medium, which acts as a sink for many metals in the aqueous environment. Relatively little attention is paid to the environmentally important area of contamination by organic chemicals because, unless they are present as organo–metallic compounds, they are unlikely to be the direct cause of metal anomalies of interest to the exploration geochemist. Natural concentrations of metals in any form are not included here as contaminants although they are sometimes described as such, particularly when they reach toxic levels (e.g., Weissburg and Zobel, 1973). Examples of such natural concentrations include deposits from metal-rich geothermal waters and terraces or glacial deposits derived from untapped mineralisation (e.g., Dunlop and Meyer, 1973).

Guidelines

Before considering the sources of contamination it is perhaps helpful to mention first several general factors which influence the extent and degree of contamination in drainage.

(i) Individual pollutants may be dispersed on a wide or localised scale from diffuse or moving sources, such as vehicles, or from essentially fixed point sources, such as factories or power stations.

(ii) Dispersion may be in the form of (a) atmospheric gases and particulate materials, (b) liquid effluent from factories, farms, dwellings and sewage works or (c) in situ site contamination from operational activities and the disposal of waste.

(iii) Dispersion may either result from controlled emissions, such as those from a smelter stack or effluent pipe, which are required to meet regulatory standards, or uncontrolled, accidental or fugitive emissions and spillages which are difficult to quantify but whose impact may be great.

(iv) Pollutants may enter streams and rivers directly from airfall, tipping and discharges, via groundwater or surface run-off, and by erosion of contaminated soil or waste.

(v) High water discharge and erosion rates lower the degree of contamination. Floods flush out pollutants which build up in periods of low flow.

(vi) Catchments most at risk from pollution are those in lowland areas where agriculture is usually most intense, most urban centres are sited, and streams have a low gradient.

(vii) Most metals are transported in streams and rivers in particulate form, for example Gibbs (1977) concluded from a study of the Yukon and Amazon rivers that less than 3% of the transition metals were associated with dissolved species.

(viii) Generally, the more contaminated the drainage the higher the proportion of metal likely to be present in dissolved form (Fergusson, 1990), particularly near to outfalls of urban and industrial waste water and acid mine water.

(ix) Sediments are effective sinks for particulate and dissolved metals during fluvial dispersal.

MAJOR SOURCES OF CONTAMINATION AND THEIR IMPACT ON DRAINAGE SAMPLES

The sources of pollutants affecting contaminated and derelict land have been reviewed recently by Bridges (1987) and Cairney (1987) and may act as a guide to those activities or materials significantly affecting the concentrations of metals and other chemicals in the surface environment, including drainage.

Potential sources of contamination on an element by element basis are summarised in Table 13-I and the major sources of contamination and their effect on metal concentrations in drainage samples are reviewed below.

Urban development

Construction and demolition of buildings

The building of housing, offices and industrial premises together with the installation of services and roadways involves major disturbance to the land surface, frequent soil removal and relocation, the introduction of numerous materials and the tipping of wastes. The majority of building materials are relatively inert, though demolition of older buildings and industrial premises may lead to contamination of soils with heavy metals (including lead from paint), gypsum and asbestos, and streams from tipping and leaching of these materials. Services, such as electricity supply, are the potential source of a range of metals including zinc from galvanised steel and copper.

Household activities

Cultivation of lawns, flower beds and gardens is often accompanied by over application of fertilisers, soil ameliorants such as lime, and pesticides. Soil pH values in vegetable gardens and allotments tend to fall within the range 6.5 to 7.5 irrespective of the natural parent material, and in general are higher than found in agricultural soils. Heavy metal accumulation in household gardens is well documented (Davies, 1978; Thornton et al., 1985), lead concentrations in surface soils (0–15 cm) increasing with the age of the house. Sources of metals in garden soils include the disposal of fossil fuel residues (ash and soot) and of household refuse, bonfires, fragments of lead containing paints, the long-term application of phosphatic fertilisers, deposition of airborne particulates from vehicle emissions, the burning of fossil fuels and industrial processes. Thornton (1990) summarises data for cadmium, lead and zinc in garden soils from five cities in Britain which demonstrate the high degree of metal enrichment that commonly occurs, values in London soil reaching 2.8 ppm Cd, 4100 ppm Pb and 2182 ppm Zn. Even higher levels are recorded from towns and villages in old mining areas, where mine waste may have been used as fill and incorporated into soil. The older and more industrialised parts of urban areas are normally the most polluted. Davies and Houghton (1984), for example, demonstrated a relatively simple relationship between the Pb content of soil and distance from Birmingham city centre, and Klein (1972) found that the highest levels of a wide range of metals (Ag, Ca, Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn) were present in the surface soils of the industrial parts of the Grand Rapids urban area.

Waste disposal

Problems associated with waste disposal and management are reviewed in depth in the 11th report of the Royal Commission on Environmental Pollution

TABLE 13-I

Potential sources of contamination in drainage samples

Metal	Industry	Specific sources
Antimony	Metal mining and smelting	Waste tips, smelter emissions
	Fossil fuels	Combustion products
	Metallurgical	Alloys with lead (solder, "hard" lead)
	Electrical/electronic	Batteries
	Chemical	Flame retardents, pigments, plastics, explosives (fireworks)
	Agricultural	Fertiliser (sewage sludge)
	Urban/domestic	Refuse
Arsenic	Metal mining and smelting	Waste tips, mine waters, smelter emissions
	Fossil fuels	Waste tips, mine waters, petroleum refining, combustion products
	Metallurgical	Additives (Pb and Cu alloys)
	Chemical	Manufacture of sulphuric acid, ammonia, arsenic trioxide, fertilisers, explosives, pharmaceuticals
	Various	Wood preservatives, pigments
	Agricultural	Herbicides, insecticides
	Urban/domestic	Sewage, detergents
Barium *	Mining	Waste tips
	Various	Fillers and extenders (paints, plastics, paper, rubber), drilling mud
	Glass	Flux
	Construction	"Heavy" concrete, bricks, asphalt
Bismuth	Metal mining and smelting	Waste tips
	Metallurgical	Alloys (low melting points)
	Chemical	Pharmaceuticals, cosmetics, rubber vulcanising
	Electrical/electronic	Fuses
	Urban/domestic	Sewage, fire control instruments
Cadmium	Metal mining and smelting	Waste tips, mine waters, smelter emissions
	Fossil fuels	Petroleum refining, combustion products
	Metallurgical	Electroplating, solder and brazing materials, manufacturing of alloys, motor vehicles and aircraft
	Chemical	Plastics (stabilisers)
	Electrical/electronic	Batteries, lamps, television tubes
	Various	Pigments, dyes (ceramics, textiles, plastics, paints, inks)
	Agricultural	Fertilisers (sewage sludge, phosphates)
	Urban/domestic	Refuse, sewage, refuse incineration, laundries
Chromium	Fossil fuels	Petroleum refining, combustion products
	Metallurgical	Metal cleaning, treatment, plating, manufacture of alloys, aluminium anodising, motor vehicles and aircraft
	Leather	Tanning
	Chemical	Catalysts
	Various	Pigments, inks and dyes (textiles, glass, ceramics), paints, glues, refractory bricks, corrosion inhibitors
	Agricultural	Fertilisers (sewage sludge)
	Urban/domestic	Sewage, laundries, preservatives

TABLE 13-I (*continued*)

Metal	Industry	Specific sources
Cobalt *	Metal mining	Waste tips
	Metallurgical	Alloys
	Chemical	Catalysts
	Various	Pigments, paints, inks, enamals
	Glass	Decolouriser
Copper	Metal mining and smelting	Waste tips, mine waters, smelter emissions
	Fossil fuels	Petroleum refining, combustion products
	Metallurgical	Metal cleaning and pickling, manufacture of copper, brass and other alloys, plating, motor vehicles and aircraft
	Chemical	Dyes, explosives, copper sulphate, rayon manufacture
	Electrical/electronic	Wire
	Various	Wood preservatives
	Agricultural	Fungicides, fertilisers (lime locally, sewage sludge, additives), feedstuff additives, pig slurry
	Urban/domestic	Food processing, laundries, refuse, sewage, surface run-off, pipes, waste incineration
Fluorine	Mining	Waste tips, mine water
	Metallurgical	Aluminium and uranium refining, flux in steel production and smelting; pickling and electroplating
	Chemical	Fluorocarbons for plastics, aerosols, refrigerants and fire extinguishers
	Ceramics/glass	Flux, opacifier
	Construction	Bricks
	Agricultural	Insecticides, rodenticides, fertilisers (phosphatic)
	Urban/domestic	Preservatives, toothpaste
Gold *	Metal mining and smelting	Waste tips
	Metallurgical	Jewellery
	Electrical/electronic	Circuitry
	Urban/domestic	Dentistry
Lead	Metal mining and smelting	Waste tips, mine water, smelter emissions
	Fossil fuels	Combustion products, especially from petrol additives
	Metallurgical	Plating, alloys (including solder), corrosion inhibitors, motor vehicles
	Chemical	Explosives, manufacture of rubber products, tetraethyl lead production
	Electrical/electronic	Batteries, manufacture of television tubes, semiconductors, photosensitive devices, cable sheathing
	Glass	Additives, pigments
	Various	Pigments (ceramics, paints, textiles), ammunition
	Agricultural	Insecticides, fertilisers (lime locally, sewage sludge)
	Urban/domestic	Roofing, weights, type-metal, pipes, packaging, surface run-off, refuse, sewage, incineration products
Manganese	Metal mining and smelting	Mine drainage, waste tips
	Metallurgical	Ferromanganese and electrolytic manganese production; alloys (Al and Cu)
	Electrical/electronic	Batteries, coils
	Various	Dyes, pigments, paints, varnishes
	Agricultural	Fertilisers
	Urban/domestic	Disinfectants, matches, animal food additive, refuse

TABLE 13-I (*continued*)

Metal	Industry	Specific sources
Mercury	Metal mining and smelting	Smelter emissions
	Fossil fuels	Combustion products
	Metallurgical	Gold and silver recovery
	Chemical	Chlor-alkali and acetaldehyde plants, explosives, rubber and plastic manufacture, catalysts, pharmaceuticals, fertiliser mills
	Electrical/electronic	Batteries, electrical instruments and apparatus, lamps
	Paper and pulp	Paper mills (fungicide)
	Various	Paints (anti-fouling and mildew proofing)
	Agricultural	Fungicide, seed dressing, fertilisers (phosphatic, sewage sludge)
	Urban/domestic	Domestic waste incineration, dentistry
Molybdenum	Metal mining and smelting	Waste tips
	Metallurgical	Oil refining, combustion products
	Chemical	Catalysts, plastics, rubber
	Electrical/electronic	Alloys, corrosion inhibitors, tubes
	Various	Pigments, dyes and lubricants
	Agricultural	Fertilisers (phosphatic, additives, sewage sludge)
	Urban/domestic	Refuse
Nickel	Mining and smelting	Waste tips, smelter emissions
	Fossil fuels	Petroleum refining, combustion products
	Metallurgical	Pickling and plating, manufacture of alloys, armaments, motor vehicles, aircraft, business machines and tableware
	Various	Pigments (paints)
	Electrical/electronic	Batteries, electrical equipment
	Agricultural	Fertilisers (sewage sludge)
	Urban/domestic	Cosmetics, cleaning products, refuse, sewage
Selenium	Metal mining and smelting	Smelter emissions
	Fossil fuels	Combustion products
	Metallurgical	Copper refining by-products, alloys
	Chemical	Sulphuric acid production
	Electrical/electronic	Electrophotography (Xerox), rectifiers, photometers
	Glass	Decolouriser
	Various	Pigments (rubber, plastics, paints, inks, glass, ceramics)
	Agricultural	Insecticides, feedstuff additive, fertiliser (phosphatic-locally)
Silver	Metal mining and smelting	Waste tips, mine waters, smelter products
	Metallurgical	Jewellery and silverware, "hard" solders, alloys, electroplating, motor vehicles and aircraft
	Electrical/electronic	Contacts, batteries (especially armaments)
	Chemical	Ink formulation, catalysts, medicines
	Agricultural	Fertiliser (sewage sludge), "seeding" clouds
	Urban/domestic	Photographic products, food and beverage processing, refuse, sewage, dentistry, coinage, mirrors and reflectors

TABLE 13-I (*continued*)

Metal	Industry	Specific sources
Tin	Metal mining and smelting	Waste tips
	Metallurgical	Plating (tin plate), alloys (solder, bronze, bearing-metals, pewter), motor vehicles and aircraft
	Chemical	Plastics
	Glass and ceramics	Opacifier
	Various	Paints (anti-fouling), wood preservatives
	Agricultural	Sewage sludge, fungicide, rodenticide
	Urban/domestic	Refuse, sewage, soap, packaging
Titanium *	Metal mining	Waste tips
	Metallurgical	Aircraft, alloys
	Various	Pigment, paints
Tungsten *	Metal mining and smelting	Waste tips
	Metallurgical	Alloys (high temperature), motor and aircraft industries
	Electrical/electronic	Ignition devices, electronic tubes
	Various	Tools and abrasives, lamps, pigments
	Urban/domestic	Refuse
Uranium	Mining	Waste tips
	Fossil fuels	Waste, combustion products
	Nuclear	Effluent
	Agricultural	Fertilisers (phosphatic)
Vanadium *	Metal mining	Waste tips
	Fossil fuels	Waste tips, combustion products
	Metallurgical	Alloys (steel)
	Chemical	Catalysts
	Textiles	Mordant
Zinc	Metal mining and smelting	Waste tips, mine drainage, smelter emissions
	Fossil fuels	Petroleum refining, combustion products
	Metallurgical	Plating (galvanising), alloys (brass), motor vehicles
	Chemical	Rubber products, plastics, artificial fibres, cosmetics, pharmaceuticals
	Electrical/electronic	Batteries, lamps, television tubes, electrical equipment
	Paper/pulp	Wood pulp, newsprint and paper production, photosensitive paper
	Construction	Pipes, culverts
	Various	Inorganic pigments, glues, inks, paints, wood preservatives
	Agricultural	Insecticides, fungicides, fertilisers (lime, phosphatic, sewage sludge, additives)
	Urban/domestic	Surface run-off, refuse, sewage, incineration emissions, food processing, pipes, laundries

* With the exception of metalliferous mining, anthropogenic anomalies in drainage are rarely recorded.

Compiled from many sources including Fimreite, 1970; Dean et al., 1972; Klein et al., 1974; Zingaro and Cooper 1974; Barnhart, 1978; Patterson, 1979; Wilber et al., 1980; Adriano, 1986; and Wilson, 1987.

(1985). Toxic metals are present in varying levels in domestic and industrial wastes, which are often mixed, resulting in isolated pockets of hazardous substances including phenols, organo–tin compounds, cyanides and asbestos. In the United Kingdom some 90% of refuse is now disposed of in landfill sites from which there is usually little loss of metals into neighbouring soils and watercourses, though leachates may contain other more soluble constituents, be extremely acidic and contaminate groundwater. A study on Long Island, USA, concluded that anomalous metal levels in groundwater are localised and related to point sources, whereas nitrate and organic chemicals have penetrated deep within the aquifers (Kimmel, 1984). Chemical data for sanitary landfill leachates in the USA are summarised by Cartwright (1984), who also lists municipal and industrial sources of groundwater pollution. Land disposal of solid wastes is the groundwater contamination source of most current concern and disposed substances in old unregulated sites are often susceptible to leaching into groundwater.

The other 10% of refuse in Britain is processed in municipal incinerators from which it has been estimated that as much as 6 tonnes of cadmium and 115 tonnes of lead per year are discharged into the atmosphere (Wadge and Hutton, 1987). However, in a study around a north London incinerator which processes 4×10^5 tonnes of waste a year there was little evidence of extensive cadmium and lead pollution downwind, though surface soils within 0.2 km of the stack were enriched 12-fold in cadmium and two-fold in lead compared with nearby areas (Hutton et al., 1988). In the United States municipal incineration has been identified as a major source of mercury emission (Glass et al., 1990).

Waste water from urban areas can include a variety of sources including sewage effluent, industrial waste and surface run-off water. Some of these sources, such as industrial waste, can and are controlled, but others, such as surface run-off, may be less well regulated. Consequently the metal content of urban waste water can be extremely variable. Waste waters from a whole range of non-industrial urban activities, such as food processing, laundries and breweries, often contain high concentrations of metals. For example, Angino et al. (1970) drew attention to the presence of arsenic in common household detergents and Klein et al. (1974) reported that waste water from many urban activities contained high levels of metals. The list included laundry discharges containing 1220 μg/l Cr, 1700 μg/l Cu and 1750 μg/l Zn and a range of food processing industries discharging water with in excess of 1000 μg/l Cu and Zn. Storm run-off waters from towns contain high levels of lead, significant quantities of zinc, copper and locally other metals (e.g., Chow, 1978; Wilber et al., 1980). Sewage sludge may contain high levels of many metals and is frequently disposed of on agricultural land (see section *Agriculture and forestry*).

Effect on drainage samples

Built-up areas give rise to a wide range of drainage anomalies in all the sample media commonly used by the exploration geochemist. Household and industrial sources are often in close proximity and the wastes are frequently mixed. Unofficial tipping of material into streams and the erosion of made ground containing domestic/industrial debris gives rise to strong anomalies downstream of most villages and towns. Experience in Britain has shown that even a single dwelling can generate large metal anomalies in small streams due to the dumping of domestic refuse over a number of years. Panned concentrate anomalies are characterised by the presence of high levels of tin, usually accompanied by lead, and often by copper, antimony and zinc anomalies. Cadmium and mercury anomalies may also be present but were not determined routinely in these studies. Typical causes of these anomalies are lead glass, lead batteries, tin cans, galvanised iron, solder and copper wire from electrical goods (e.g., Cooper et al., 1982, 1991). Fine fractions of stream sediment and waters may also be anomalous depending on the nature of the dumped material and stream conditions.

Fine fractions of stream sediment, particularly the organic component, may be enriched in Ag, As, Cd, Cr, Cu, Hg, Pb, Sn and Zn (e.g., Salminen, 1976; Galloway in Christensen et al., 1978; Byrd and Andreae, 1986; Schebak et al., 1991) due to the presence of metals in untreated or partially treated sewage and waste water, but high concentrations of metals solely from urban run-off may be, perhaps surprisingly, limited to one or two metals, notably Pb and Zn, Cu, Cd or Hg (Christensen et al., 1978; Fergusson, 1990). Vanadium, Co and Ni may be enriched in areas subject to petroliferous pollution (Ramondetta and Harris, 1978). Landfill sites may also be a source of heavy metals in sediments. Mantei and Foster (1991) reported Ag, Cd, Cu, Pb and Zn emitted by one site and Ag, Ba and Cd by another with the metals held in carbonate and hydrous oxide phases in the sediment. In an earlier study Mantei and Coonrod (1989) reported stream contamination from a sanitary landfill site in Missouri where, unusually, in one of the affected streams the levels of the contaminant metals (Ag, Cu and Zn) did not decrease noticeably downstream.

Transport

Common features

Sources of stream contamination associated with roads, railways, canals and airfields include spillage, fly tipping, the frequent use of mine waste as hardcore and the constructional materials themselves, particularly galvanised iron in bridges over streams. Emissions from coal and petroleum products affect land downwind of the sources.

Roads and motor vehicles

Nearly all the lead in the air in the United Kingdom comes from the exhaust gases of petrol engines (Royal Commission on Environmental Pollution, 1983). In 1981 some 9700 tonnes of lead were used in petrol of which about 75% was released to the atmosphere. It has been estimated that about 10% of emitted lead is deposited within 100 m of the road and that the remainder can be

TABLE 13-II

The lead content of soil at three distances from typical main roads (calculated from data in W.H. Smith, 1976)

Distance from road	Number of samples	Geometric mean (μg/g)	95% probability range (μg/g)
<10 m	20	192	18–2017
15 m	6	161	50– 511
>30 m	17	53	14– 203

transported over considerable distances (Little and Wiffen, 1978; Chamberlain et al., 1979). It is now widely accepted that the settling out of lead-rich aerosols derived from the exhaust fumes of cars results in contaminated surface soils and this is demonstrated by the data in Table 13-II calculated from W.H. Smith (1976). The effect of long distance transport is illustrated by Berrow et al. (1987) who concluded that a major portion of the lead in organic-rich topsoils in south and central Scotland came from atmospheric sources. Although the lead content of petrol has been drastically reduced in many countries, resulting no doubt in a reduction in the deposition of airborne lead in soil, it must be stressed that lead in soil is virtually immobile and that therefore the existing contamination is in all essence a permanent phenomenon and that concentrations of lead resulting from many years of deposition will remain, and in many areas continue to build up.

Although Pb derived from atmospheric sources is strongly fixed in organic rich topsoil, reducing its effect on drainage samples, particulates deposited on roads are often carried directly into streams via culverts by storm run-off waters. These run-off waters and sediments are enriched in lead, zinc and, in some cases, other metals (Ellis and Revitt, 1979; Pope et al., 1979; Wilber et al., 1980). Road dusts may contain very high levels of lead, for example dusts in Birmingham, England, measured between 1972 and 1975 gave a median value of 950 μg/g (Archer and Barratt, 1976). These levels have since decreased substantially (Davies et al., 1987). Predictably, the first flush of run-off water following rain is the richest in metals (Harrison and Wilson, 1985). The distribution of metals between suspended matter and water is dependent on a number of factors including flow regime and pH. The practice of salting roads to prevent icing may effect the speciation of metals in run-off water and drainage seasonally. Although relatively rare, spillage and washings from lorries and tankers following road accidents can cause severe local contamination of watercourses receiving run-off water from the road where the accident occurred (Royal Commission on Environmental Pollution, 1992).

Mine waste is often used in the construction of roads and tracks within economic trucking distance of mining fields (see section *Field observation and mapping*). As the waste is often used as hardcore and fill, its presence may not be obvious at surface. However, at some places in south-west England its presence beneath the tarmac topcoat can be detected using a scintillometer due to the presence of uranium minerals in the waste.

Other transport

Large areas of railway land including tracks, sidings, workshops and marshalling yards may have scrap metal, oil and debris from rolling stock in the soil, even after the land has been reclaimed for other uses. Canal and dock areas may have similar debris as well as accumulations of dredged materials comprising organic-rich sludge and sometimes heavy metals resulting from spillage of cargo and motor fuel and paint. The presence of organic tin compounds, used in anti-fouling paints, is a particular feature of harbours and estuaries (Byrd and Andreae, 1986; Schebak et al., 1991). Airfields, which often attract industrial development nearby, may be the centre of particularly heavy contamination (Klein, 1972).

Effect on drainage samples

Fly-tipping and spillage, particularly from bridges across streams and rivers, makes roads the locus of a wide range of drainage sample anomalies generated by domestic and industrial waste. For example Cooper et al. (1985) record groupings of tin in panned concentrate anomalies following major roads across rural areas, despite the sampling having taken place upstream of the roads (Fig. 13-1). In this case the anomalies were caused by heavy detrital phases, derived principally from the partial breakdown of dumped refuse containing metalliferous items such as tin cans and electrical goods.

Metals from oil, petrol or coal burning emissions, along with a proportion of the metals from other sources described, are concentrated in the fine fraction of stream sediment, absorbed onto clays, hydrous oxides or organic matter. Harrison and Wilson (1985) note that the speciation characteristics of small streams cutting or running close to highways may be dominated by input from highway run-off water. Other specific sources of anomalies in water and fine sediment samples locally include leaching of mineralised hardcore and corrosion of galvanised structures. Levinson (1980), for example, records zinc anomalies in stream sediment below road and rail bridges in British Columbia attributed to metals dissolved from structural parts of bridges and culverts. Lead and zinc anomalies are the most common in fine sediment contaminated by roads, but a wide range of other metals may be enriched locally as a result of spillage and tipping.

Airborne pollutants from transport coupled with the other principal sources of air pollution have a significant regional effect on the concentration of lead and some other metals in organic rich topsoil. For example, As, Cd, Pb and Sb levels in undisturbed humus topsoil in south Norway are many times higher than in the north, and the northward decrease is attributed to the lessening impact of air pollution from the industrial areas of Europe (Page and Steinnes, 1990). A similar pattern was recorded for lead in Scotland (Berrow et al., 1987). In the Norwegian study it was noted that the metal enrichment in the south was

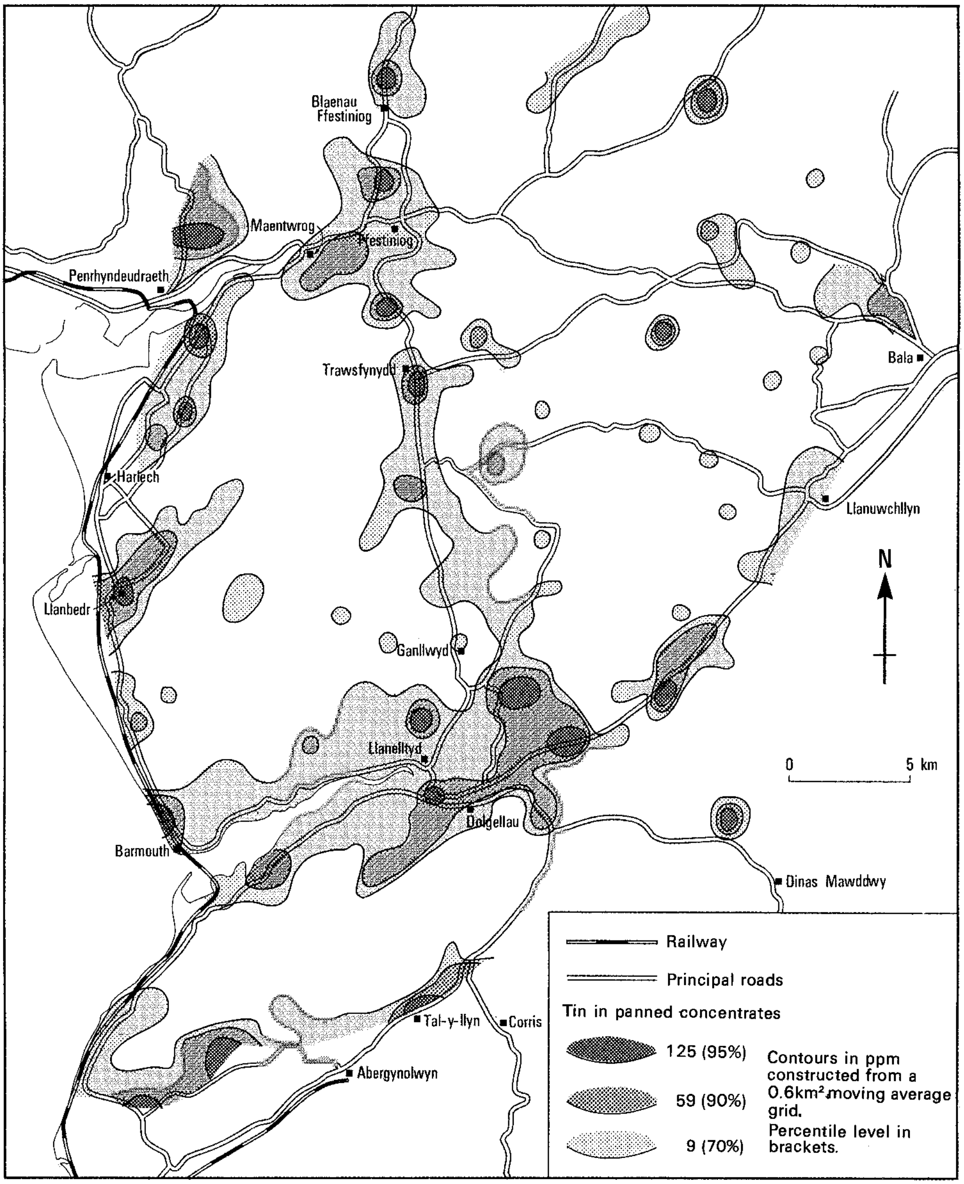

Fig. 13-1. The relationship between the tin content of panned concentrates and principal roads, villages and towns in the Harlech Dome area of Wales (compiled from Cooper et al., 1985).

not detected in disturbed soils, due to dilution of deposited metals by mixing with the underlying mineral soil and the range of natural variation in those soils. It is therefore unlikely that airborne pollutants from transport or other sources will generate significant metal anomalies in drainage samples in areas remote from source, though some broadscale changes in background levels may occur.

Metalliferous mining and smelting

Sources

In many areas the oldest and most extensive sources of metal pollution are related to the history of metalliferous mining. For example, in Britain it has been estimated that in excess of 4000 km^2 of agricultural land and many urban areas in England and Wales are contaminated with one or more metals due to the very extensive historical mining and smelting activities (Thornton, 1980; Thornton and Abrahams, 1984). Metal contamination of soils may be considerable, with as much as 1% or more of lead recorded in surface garden soils in a Derbyshire village (Barltrop et al., 1975).

The environmental impact of mining and smelting have been the subject of detailed studies in many countries. These have been reviewed by, amongst others, Down and Stocks (1977), Davies (1983b), and Kelly (1988). The principal sources of metal pollution from mines and associated plant are water, solid wastes and airborne products. Water from the mine, concentrators and tailings ponds frequently enters the drainage. The waters are often highly acidic and, besides high concentrations of metals in solution, usually carry metal-rich particulate matter. They may also contain a wide range of inorganic and organic chemicals as a result of spillage or poorly controlled use. These chemicals may include oils, fuel, blasting agents, hydraulic fluids and mineral processing reagents such as cresols, xanthates, cyanides, dithiophosphates, lime and acids (used as frothers, collectors, depressants, flocculants, pH modifiers, etc). Solid waste, including dumped constructional and mining materials and redundant equipment, as well as broken rocks and ore, frequently finds its way into the drainage. Lime compounds may be added to the drainage to reduce acidity, resulting in calcium sulphate flocculant as well as hydrous oxide precipitates. Metal-rich clasts come in all grain sizes from the erosion of dumps and old tailings ponds, run-off from concentrate storage piles and spillage from transportation lines. Airborne pollutants come from machinery and metal-rich particulates blown off storage piles, transport lines and crushers. A very wide range of metals may be involved, depending on source. Förstner and Wittmann (1981) summarise work that reports more than 100 fold enrichment of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn, and at least traces of Ag, Al, Au, B, Ba, Ca, Hg, K, Li, Mg, Na, P, Ti, Th, U, V, Zr and Pt Group metals in waste water from the Witwatersrand mines. In situ leach mining for uranium represents a special case in which there is generally less surface disturbance and pollution than is associated with a conventional mine, but considerable potential for groundwater contamination (Charbeneau, 1984). The discharge of effluent from modern mines is normally strictly controlled and the efficiency of modern mineral processing methods results in old and abandoned mines being the principal sources of pollution.

Oxidation and leaching of sulphide minerals released during mining, producing acid metal-rich waters and precipitates, are the principal source of groundwater contamination from metalliferous mining. Many such mines are underground workings which can create a direct link between the land surface and aquifer, whilst dewatering of mines can change the groundwater flow-field, possibly triggering new contamination sources.

Metal smelters, both primary and secondary, result in contamination of the land surface and drainage through stack and fugitive emissions, dissolved species in liquid effluent, the dumping or erosion of particulate slag and the transport and spillage of metal concentrates. Atmospheric emissions may be very large but depend on the technology employed in the plant, ore composition and the air pollution control system. Pacyna (1986), in summarising emission factors from primary and secondary non-ferrous metal production processes from a number of plants, demonstrates this variability. Soil contamination arising from airborne dispersion around smelters has been studied at several locations. Generally, contaminated ground describes an ellipsoid, with the long axis aligned with the direction of the prevailing wind. In typical cases contamination is most severe within 3 km of the smelter, decreasing exponentially until background levels are reached at 10–15 km (Davies, 1980, 1983b). Elevated levels of Ag, As, Cd, Cu, Hg, Ni, Pb, Sb, Se and Zn have been recorded within these areas (e.g., Little and Martin, 1972; Wixson and Jennett, 1975; Ragaini et al., 1977; Temple et al., 1977; Chan and Lusis, 1986). Depending on the type of smelter, other metals and metalloids, such as Bi, F, Mo, Sn, Tl and W may also be enriched, but these have not been determined in many investigations. Fluorine is a particular hazard associated with aluminium smelters. Legislation has reduced the emission of toxic metals from smelters in most countries and, generally, the older and larger the smelting operation the greater the probable contamination.

Effect on drainage samples

Mining and smelting can generate metal anomalies in all types on geochemical drainage samples. The dispersion of metals downstream of metalliferous mineral workings has been the subject of more studies than any other form of drainage contamination. The impact on drainage is commonly great because of the historic practice of siting mines close to streams. Data are available for a large number of sites, particularly in Europe and North America; Förstner and Wittmann (1981) and Kelly (1988) review briefly examples from many parts of the world. Some areas that have been the subject of wide-ranging studies, covering topics such as speciation, seasonal variation, grain size effects and reclamation, include central Wales (Grimshaw et al., 1976; Wolfenden and Lewin, 1977, 1978; Bradley and Lewin, 1982; Lewin and Macklin, 1987; Fuge et al., 1991), south-west England (Hosking, 1971; Aston et al., 1974; Merefield, 1974; Thornton, 1980; Purves, 1981; Yim, 1981; Byrd and Andreae, 1986), Clark Fork River, Montana, (Moore et al., 1989; Axtmann and Luoma, 1991) and Coeur D'Alene, Idaho (Galbraith et al., 1972; Mink et al., 1972; Reece

TABLE 13-III

Background metal concentrations in stream sediment and panned concentrates from four drainage surveys in Wales compared with the maximum values in samples contaminated by base-metal and manganese mining

Element	Stream sediment (<0.15 μm)		Panned concentrate (<2 mm)	
	Pristine (unmineralised)	Contaminated by mining	Pristine (unmineralised)	Contaminated by mining
As	<2 - 45	2000	2 - 22	9600
Ba	13 - 950	3420	27 - 830	138,000
Co	<10 - 100	426		
Cr	<10 - 100	277		
Cu	<3 - 45	4000	<6 - 60	4500
Fe (%)	1.0- 8.5	29.4	0.29- 13.0	26.8
Mn	130 -5500	148,000	55 -2600	64,800
Mo	<1 - 5	41		
Ni	4 - 110	652	<5 - 67	240
Pb	<5 - 110	6300	<13 - 125	22,000
Sn	<5	15	<9	1200
Zn	<5 - 200	3100	15 - 305	9900

Values in ppm except for Fe (%).

Values outside of the ranges quoted for unmineralised catchments occur in sediments where strong hydrous oxide precipitates are developed and in both sample types where the catchment consists of a single metalliferous lithology.

Higher values of Ba, Cr, Mo and Sn in sediment and Ni, Pb and Sn in panned concentrates were recorded from other sources.

Data from Cooper et al. (1982, 1984, 1985) and Cameron et al. (1984).

et al., 1978; Wai et al., 1980; Mok and Wai, 1990). Typically the range of anomalous metals is much greater than those extracted for profit, partly due to the upgrading of gangue minerals such as pyrite and arsenopyrite in the waste and partly due to the introduction of additional metals, such as mercury at old gold mining sites, during extraction and refining processes. Table 13-III indicates the magnitude of anomalies in both stream sediment and panned stream sediment samples that can be expected downstream of base metal and manganese mining. Close to source anomalies may be more than 100 fold the local background, particularly in heavy mineral concentrates. The high values of tin recorded in the dispersion trains are not derived from the mineralisation but from human activities associated with mining. Concentrations of other metals listed may also be enriched by these activities, notably by the corrosion of dumped machinery.

The highest concentrations of metals are generated by the dumping or erosion of mine waste products, but regional-scale stream sediment anomalies may be produced by airborne pollutants from major smelters, for example downwind of the Avonmouth smelter near Bristol in south-west England (Fig. 13-2) and the Swansea smelters in west Wales (Webb et al., 1978). Near the nickel refinery at Nikel, close to the Norway–Russia border, only the organic

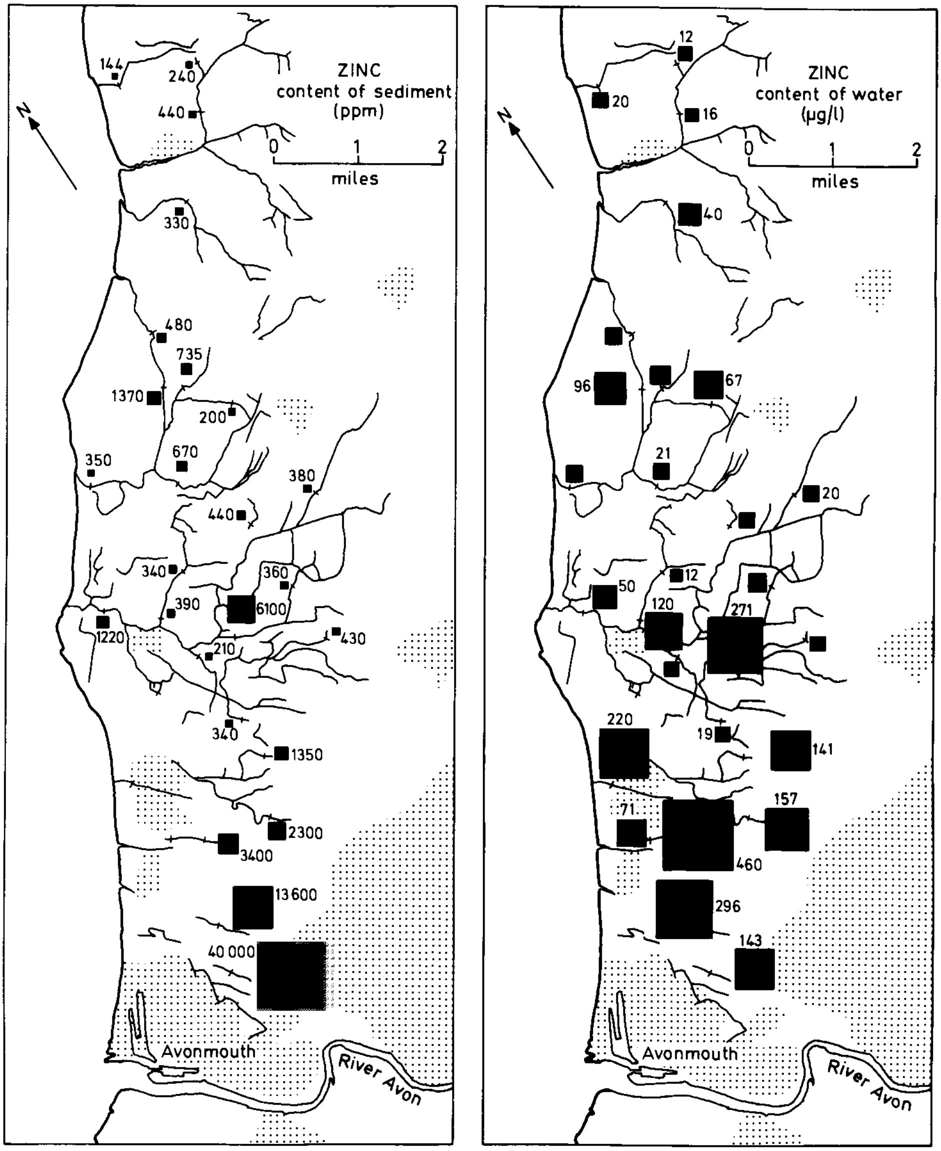

Fig. 13-2. The zinc content of stream sediment and water samples collected from streams northeast of Avonmouth, England.

fraction of the sediment contains highly anomalous levels of nickel (Bölviken et al., 1986) and in some areas airborne pollutants from smelting operations may have little impact on drainage samples due to retention of the metals in the soil. Fauth et al. (1985) recorded only slightly elevated lead concentrations in stream sediments or waters around the Nordenham lead smelting works, despite the presence of high levels of lead in soils, and Olsen and Brookins (1984) found that uranium levels in water and sediment samples in a study area were not affected by upwind uranium milling operations at Ambrosia Lake, New Mexico.

Large metal anomalies in water frequently come from the outflow of acid mine waters, principally generated by the oxidation of pyrite, from the mine itself, spoil heaps or slimes dams. Many examples are briefly reviewed by Förstner (1981b) and Kelly (1988) summarises the chemical processes and the effects on the biota. High levels of copper, lead and zinc are the most frequently recorded. Highly anomalous levels usually only persist for short distances in stream water due to the absorption of metals onto clays or organic matter and the precipitation of hydrous oxide phases, following dilution, microbial oxidation and consequent changes in Eh and pH as the minewater equilibriates with the surface environment (e.g., Chapman et al., 1983; Kelly, 1988; Walton and Johnson, 1992). The critical pH value is about 4.3, in more acid conditions Fe (III) ions are soluble, but as the pH rises above this level the classic orange-brown hydrous iron oxide precipitates form. In a complex series of reactions other metals also precipitate as the pH rises (e.g., Al at about 5.2) and/or are scavenged and absorbed by the hydrous iron oxide precipitates. Acid mine water anomalies are minimised in areas such as the south-east Missouri lead belt where streamwater is relatively basic and has a high carbonate content (Jennet and Foil, 1979). In contrast, in areas such as Central Wales where the rocks are carbonate poor and the soils acid, long dispersion trains in water are recorded. Here, in the River Rheidol, over 100 μg/l Zn was recorded in water 16 km downstream of the acid water influx (Fuge et al., 1991). A similar situation is reported from West Squaw Creek, California, where streams cross igneous rocks of low neutralising capability. In this stream, despite dilution with an almost equal volume of unpolluted water, Al, Cu, Mn and Zn remained in solution (Filipek et al., 1987). Placer mining may produce few metal anomalies in water (filtered) whilst producing long sediment and suspended matter trains. Where placer-mined gold is associated with other metalliferous minerals these are largely present in the particulate fraction (Kelly, 1988).

High metal values in the near-surface layers of lake sediments are often caused by mining and smelting operations in the vicinity. Besides the input from contaminated drainage and the direct discharge of effluent or tailings, airborne particulate matter may form a significant input. A particularly well documented example of lake pollution is that arising from the nickel smelting and mining operations in the Sudbury area of Canada (Allan, 1974; Allan and Timperley, 1975).

In stream sediment metals may be present as sulphides or other natural or artificial detrital phases in a wide range of grain sizes, absorbed onto or co-precipitated with hydrous oxide phases and bound to organic matter. The distribution of metals in precipitated hydrous oxide phases has received particular attention, with the results highly dependent on local conditions (e.g., Carpenter et al., 1975; Carpenter and Hayes, 1978; Filipek et al., 1981; Robinson, 1981; Laxen, 1984; Johnson, 1986). Anomalous levels may persist

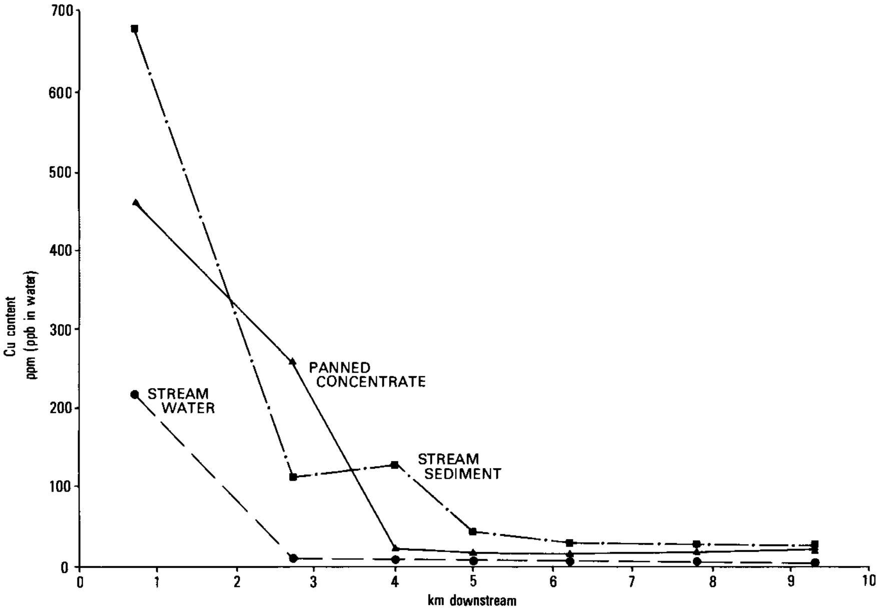

Fig. 13-3. Downstream dispersion of copper in the Afon Wygyr from Parys Mountain in three different types of geochemical exploration sample media (compiled from Cooper et al., 1982).

for great distances downstream of source, sometimes for more than 100 km (e.g., Norris et al., 1981; Axtmann and Luoma, 1991). Decrease in metal values downstream normally approximates to a simple decay model of negative linear exponential or power form, but in ephemeral streams in semi-arid environments this relationship may break down (Macklin, 1992). A study of base metal dispersion trains downstream of the Parys Mountain mine in Wales indicated that anomalies for copper, lead and zinc in stream water had the shortest dispersion trains, and that sediment anomalies for the same metals persisted for greater distances than those in panned concentrates, which were largely dependent on the dispersion distance of detrital sulphide grains prior to breakdown (Fig. 13-3).

Rehabilitated land, now in agricultural use but formerly the site of metalliferous mining, may generate very large anomalies in soil and stream sediment. Thornton (1988) reported that four stream sediment sites draining such an area around Shipham in south-west England contained >90 ppm Cd. Nearby soils contained more than 1% Pb and Zn and 100 ppm Cd. Agricultural land on floodplains many miles from the site of historical metalliferous mining may also be contaminated. Macklin and Dowsett (1989) reported, for example, that in August 1986 extensive sheets of fine gravel containing high levels of cadmium, lead and zinc were deposited across riverside agricultural land along more than 80 km of the Tyne valley in northern England. Erosion of such sediments by first order streams cutting the floodplain may give rise to substantial stream sediment anomalies whose source is not immediately obvious as they are so remote from the mining field.

Extraction and combustion of fossil fuels

Extraction

Old coal mines, frequently with railway sidings, leave a legacy of waste materials including coal and coal dust which present a fire hazard. Modern, closely controlled surface and underground workings are less damaging. The main sources of drainage pollution from coal-working are separation and cleaning plants, stock storage and spoil disposal sites, transport lines and the mines themselves. Studies, predominantly in the USA, on the environmental impact of these activities were reviewed by Olen (1981). Almost half the coal mined in the United States is cleaned, leading to particle-rich waste water which may be enriched in metals such as As, Cd, Mo, Pb, Se and Zn (Kagey and Wixson, 1983), but closed circuit coal cleaning and preparation plants have now obviated the need for direct discharge to water courses. Strip-mining can damage particularly large areas; a total of nearly 800,000 acres has been disturbed in the Appalachians area of the United States alone (Barnhisel and Massey, 1969). In some areas drainage from coal mines and leachates and run-off from coal and waste piles may be acid due to the oxidation of sulphides, with pH levels as low as 2.2 recorded in acid mine water, which may contain high levels of Cu, Fe, Mn, Ni, Zn and appreciable amounts of other heavy metals, such as As and Pb, in solution (e.g., Barnhisel and Massey, 1969; Kagey and Wixson, 1983; Roy et al., 1984b). Such effluents often lead to the downstream deposition of dense ferric hydrous oxide precipitates which may contain enhanced levels of absorbed metals. Significant stream pollution can also occur in areas where acidity is not a problem (El-Ashry, 1979). Drainage contamination may be extensive; it was estimated that in 1970 over 10,000 miles of streams in Appalachia were significantly degraded by coal mining related pollution. Groundwater may be contaminated by acid mine water or effluents and leachates from surface activities (Woodward and Selby, 1981). Such contamination is often the result of long term processes, the Royal Commission on Environmental Pollution (1992) reporting that between 1907 and 1974 chloride-rich water pumped from a coal mine in south-east England soaked, via a collection lagoon, into the chalk aquifer, contaminating 27 km^2.

Like coal, oil shales may contain high levels of several metals and metalloids and production processes may promote the concentration and release of these to the environment. The composition of oil shales, extraction processes and environmental impact of such processes is described in many papers including symposium compilations (e.g., Petersen, 1981; Gary, 1984). Oil shale is often looked upon as a recently developed source of hydrocarbons but in some countries, such as France, Germany and Scotland, extraction dates back to the mid-nineteenth century when environmental controls were few. The most persistent industry was probably that of Scotland where extraction lasted from

1850 until 1962 (Cook, 1981). The major types and origins of waterborne pollutants that may be associated with oil shale facilities are listed by Nowacki (1981). These include suspended solids from dust and erosion, oil and grease, dissolved gases, inorganic and organic species from mine waters, retorting processes, and leachates from raw and spent shale piles. The spent shale that remains after retorting is alkaline and contains higher levels of many elements compared with the raw shale (e.g., Wilding and Zachara, 1981). Principal potential contaminants include B, F, Li and Mo in leachates, As in solid waste and Hg in the gaseous effluent (Chapell, 1979).

Drilling and extraction of oil can lead to groundwater contamination, particularly as these activities may create a direct link between the aquifer and land surface. Leakage from wells, spillages and mismanaged direct injection of liquids to aid extraction are some of the potential sources (e.g., Reichard et al., 1990).

Power stations

Sites of disused and demolished power stations will give rise to contamination from (a) coal dumping and storage, (b) pulverised fuel ash, (c) areas of unknown history which may contain dumped materials with toxic or combustible properties and (d) sites of demolished buildings with possible asbestos residues, heavy metals, combustible residues, oil spillages, PCB's from transformers and capacitors and waste electrical equipment.

Combustion products

When coal or lignite is burnt in power stations the combustion products are gases, fly-ash and bottom ash. The composition of the combustion products will depend on a number of factors including composition of the fuel, the combustion process, working practice, fly-ash control system and the surrounding environment. Due to regulatory control and scientific advances modern plants generally release the least pollutants (e.g., Mulchi et al., 1990). Air pollution from coal fired plants includes dust, oxides of sulphur and nitrogen, polynuclear aromatics, ozone, carbon dioxide, radionuclides, B, Cr, F, Hg, S, Se and V (Kagey and Wixson, 1983). Emission factors for 16 trace elements resulting from different types of coal and combustion process are given by Pacyna (1986). Similarly with oil, trace elements in combustion products depend on the source of the oil and the combustion and cleaning processes. In general the heavier the oil the more metal present. Some crudes contain high levels of Hg (to 30 ppm), Ni (to 345 ppm) and V (to 1400 ppm) (Pacyna, 1986) and, in general, vanadium emissions from oil-fired plants are an order of magnitude higher than those from coal-fired stations (Husain et al., 1984; Husain, 1986). Metals emitted into the atmosphere are carried varying distances depending on the metal-bearing phases and wind velocity. The smallest particles (<1 μm) are not significantly affected by gravity, and wind turbulence and smoke plume temperature are important controls on their dispersion (Davies, 1983b). Significant metal enrichment in soil and vegetation is typically restricted to within about 3 km of the source (e.g., Cannon and Swanson, 1975) with the dispersion pattern influenced by the prevailing wind direction. Metals which may be enriched in the soils around coal-burning plants include Ag, Cd, Co, Cr, Cu, Fe, Hg, Ni, Ti and Zn (Klein and Russell, 1973). Aerosols carrying combustion products from the burning of fossil fuels can be detected at great distances from source, and their chemical composition may enable the source to be identified (Olmez and Gorden, 1985; Husain, 1986; Kitto et al., 1992).

Some ash is dispersed in the atmosphere, the remainder is collected, sometimes as a slurry in settling ponds, and either dumped at infill sites or spread on land. The utilisation and disposal of fly-ash and other residues was reviewed by Adriano et al. (1980). Element concentrations in ash vary with particle size; chalcophile and volatile elements are concentrated in the finer fractions (e.g., Davison et al., 1974; Campbell et al., 1978). Elements concentrated in fly-ash relative to coal may include As, B, Be, Ba, Cd, Co, Cu, Cr, F, Fe, Hg, In, Mn, Mo, Ni, Pb, Sb, Se, Te, U, W, V and Zn (Cannon and Swanson, 1975; Roy et al., 1981; Adriano, 1986). The range of metal concentrations recorded in ash from a wide range of sources is listed in Table 13-IV. The data are not normally distributed and for most of the metals listed the most commonly recorded (modal) levels are well below the mid points of the ranges quoted. In slurry form the ash, particularly when fresh, may be acid or strongly alkaline (pH range 3.3–12) and leachates under certain conditions contain As, B, Cd, Co, Cr, Cu, Mn, Ni, Se, V and Zn (Chu et al., 1979; Roy et al., 1981, 1984a; Kagey and Wixson,

TABLE 13-IV

Metal concentrations in chemical fertilisers, agricultural lime and limestone, farm manure and slurry, sewage sludge and fly-ash

Element	Chemical fertilisers	Lime/limestone	Manure/slurry	Sewage sludge	Fly-ash
As	2 - 120	0.1 - 25	0.6 - 25	1.1- 230	2 -3000
B	5 - 115	<1 - 20	0.3 - 24	4 - 1000	10 - 618
Ba		<10 - 600	54 -305	150 - 4000	110 -7000
Cd	0.05- 10	0.04- 0.1	0.1 - 0.8	<1 - 1500	0.3- 85
Co	1 - 13	0.4 - 20	0.3 - 24	1 - 260	5 - 520
Cr	3 - 245	<10 - 15	1.1 - 56	8 -40,000	10 -1000
Cu	1 - 300	<0.3 - 160	2 -675	50 - 8000	14 -2800
Mn	40 -2000	20 -4500	30 -969	32 - 3900	58 -3000
Mo	0.1 - 60	<0.1 - 15	0.05- 49	1 - 40	6 - 160
Ni	<5 - 38	<2 - 50	2.1 - 30	6 - 5300	2 -1000
Pb	2 - 225	<5 - 200	1.1 - 27	13 - 3000	3 -5000
Se	<0.5 - 25	0.08- 0.1	0.3 - 2.4	1 - 10	0.2- 134
Sn			2 - 7.4	40 - 700	0.8- 300
V	2 -1600	<1 - 100	3 - 43	10 - 400	10 -1200
Zn	1 -1450	<1 - 500	15 -566	72 -16,400	10 -3500

Values in ppm.
Some exceptionally high levels from individual sources omitted.
Principal sources: Berrow and Webber (1972); Capar et al. (1978); Bouska (1981); Roy et al. (1981); Mattigod and Page (1983); Adriano (1986); and Alloway (1990).

1983). A comparison of metal concentrations in uncontaminated soil and fly-ash indicates that the disposal of fly-ash on land, which can be used to provide plant nutrients and reduce acidity, may give rise to a wide range of metal anomalies (Klein and Russell, 1973; Adriano et al., 1980; Mattigod and Page, 1983). The practice of burning refuse-derived fuel with coal in some power plants does not appear to greatly increase the range and magnitude of element concentrations in the ash (Norton et al., 1988), whilst desulphurisation sludge, largely comprising calcium sulphate, unreacted calcium oxide and coal ash is less likely to be a source of metal anomalies than fly-ash.

Effect on drainage samples

Coal or lignite mining and associated waste tips can produce stream sediment anomalies characterised by a wide range of metalliferous enrichments which may include As, Cd, Co, Cu, Fe, Mn, Mo, Ni, V and Zn (e.g., Hood et al., 1984; Roy et al., 1984b). The precise metal enrichments will depend on the source of pollution. In common with metalliferous mines, acid water, directly from the mine or from coal slurry or cleaning waste water, is a common source of anomalies. Anomalies in water normally decrease rapidly downstream of source, partly due to dilution and partly due to the formation of iron-rich precipitates as the pH rises (e.g., Rasmussen and Sand-Jensen, 1979; Kelly, 1988). Other metals precipitate with or are scavenged and absorbed by these hydrous ferric oxide precipitates which may then appear as fine fraction stream sediment anomalies. Where the effects of acid mine water and hydrous oxide precipitation are not excessive, the signature generated in stream sediment may be very similar to that produced by metalliferous dark shales, but metals such as tin may also be enriched, particularly in heavy mineral concentrates, due to associated industrial activity (Cooper et al., 1991). Similar anomalies can be expected from the mining of oil shales. The retorting of oil shales may produce waste water enriched in metals, including arsenic and selenium (Dale and Fardy, 1984; Patterson et al., 1987, 1988), whilst spent shale leachates may contain high levels of fluorine, lithium and molybdenum (Wilding and Zachara, 1981). Leachates from ash deposits, or direct incorporation of ash into stream sediment by erosion of dumps or spillage, are potential sources of a wide range of metal anomalies in geochemical drainage samples and groundwater (e.g., Gay and Davis, 1987).

The effect of airborne pollutants from fossil fuel combustion alone on metal concentrations in stream sediments appears to be relatively small. This is no doubt in part due to the fixing of metals in soil (Fauth et al., 1985). Regional-scale raising of background levels may occur but in many cases the effects noted have multiple sources in urban areas. "Sore thumb" anomalies are unlikely to be produced unless enhanced by an additional factor, such as the erosion of waste. Smelters produce a much greater effect (e.g., Webb et al., 1978; Chan and Lusis, 1986) and road transport is now the most important single source of lead in aerosols (see section *Roads and motor vehicles*).

Manufacturing industries

These are many and varied and the pollutants that can be produced are as varied as industry itself. Generally the older the industry the more likely it is to have produced substantial contamination of nearby drainage. The range of heavy metals found in twelve groups of major manufacturing industries is illustrated by Dean et al. (1972) and hazardous materials contained in waste water from 15 groups of industrial processes are summarised by Barnhart (1978). Patterson (1979) lists sources of metal-containing waste water from major industrial sources on an element by element basis. These summaries show that many industries may be the source of polymetallic anomalies but a few, such as leather tanning, are associated with only one or two metals.

Chemical and gas works and oil refineries

These are all associated with a wide range of chemicals, some of which may be dispersed in the air whilst others contaminate the site or enter surface drainage and groundwater. Potential pollutants from chemical works include a wide range of acid and alkaline substances and metals such as Cd, Cr, Cu, Hg, Pb, Sn and Zn; in particular, chlor-alkali plants are associated with mercury pollution in rivers (Wood, 1972; Förstner and Wittmann, 1981). Agricultural chemicals and fertiliser plants may be associated with a very wide range of pollutants, whilst waste waters from explosive plants may contain As, Cu, Hg and Pb (Barnhart, 1978). Oil refineries and oil products are potential sources of As, Cd, Co, Cr, Cu, Mo, Ni, Pb, V and Zn concentrations (Dean et al., 1972; Ramondetta and Harris, 1978) whilst petroleum cracking catalysts and their products have been traced as the source of light rare earth element anomalies in sediments off southern California (Olmez et al., 1991). Old gas works may be contaminated with coal and coal residues, spent iron oxides, cyanides, sulphates and organic compounds associated with tars. Water pollution from these sources is recorded long after the closure of the works (Royal Commission on Environmental Pollution, 1992).

Metallurgical industries

This group includes steelworks, foundries, electro-plating and finishing works, car and aircraft manufacturing plants. Almost all metals may be present in anomalous amounts depending on the specific function of the plant. There are numerous occurrences of polluted streams and rivers from these sources, a well documented example describes the high levels of Fe, Mn, Pb and Zn discharged into the Tees estuary from a steelworks in north-east England (Prater, 1975). The cleaning and etching of bare metal surfaces in a wide range of metal finishing and plating processes is a major source of contaminants in drainage systems; high levels of Cd, Cr, Cu, Ni and Zn may be produced (Förstner and Wittmann, 1981). Predictably, battery manufacture may generate waste streams rich in Cd, Ni (Bower et al., 1978), Hg, Pb, Sb and Zn (Barnhart, 1978; Purchase and Fergusson, 1986).

The storage, processing, recycling and disposal of scrap materials results in site contamination and soils will often contain a range of toxic substances. Heavy metals, waste oil, PCB's and other organic and inorganic substances may be present.

Other industries

Paint and dyestuff industries use a wide range of pigments and raw materials and Barnhart (1978) lists Cd, Cr, Cu, Hg, Pb and Se in the waste streams. Electrical and electronic industries may produce waste containing Cd, Cu, Pb, Se and Zn (Asami, 1974; Patterson, 1979). Cadmium, Pb, Sn and Zn are employed in the manufacture of synthetic rubber and/or plastics as stabilisers and pigments. The leather and textile industries use chromates and dichromates, resulting in effluent which is a major source of chromium enrichment in sediments (e.g., Förstner and Muller, 1973). The glass industry also uses chromium as well as lead. The pulp and paper industries are well known as a source of mercury pollution in sediments, several examples from Sweden and North America are cited by Förstner and Wittmann (1981). The photographic industry is the principal consumer of silver compounds and photographic processing activities are the main source of silver in waste water effluent and some solid wastes (e.g., Metal Bulletin, 1992). Some industries, for example cement and brickworks, are rarely the source of metal anomalies in streams (e.g., Brumsack, 1977).

Industrial sources may contaminate groundwater via a number of pathways (Lawrence and Foster, 1991). Most directly, liquid wastes from industrial processes sometimes enter the groundwater system via wells (Reichard et al., 1990). In many cases the recorded pollution is caused by organic chemicals which will not raise directly the levels of metals of interest to the exploration geochemist. Examples include the three specific cases of groundwater contaminated by organic chemicals related to the pharmaceutical, food and sawmill industries in Finland described by Nysten (1991).

Effect on drainage samples

The impact of industrial pollutants on stream and lake sediments has been reviewed by several authors (Förstner and Wittmann, 1981; Salomons and Förstner, 1984; Fergusson, 1990) who cite many examples and individual studies from North America, Europe and south-east Asia. These studies show that extremely large anomalies may be produced in the water and fine sediment of streams and rivers close to industrial effluent discharge pipes. For example, Förstner and Muller (1973) reported up to 6400 ppm Cr, 38 ppm Hg, 1200 ppm Pb, 1600 ppm Cu, 340 ppm Co and 3290 ppm Zn in the clay fraction of sediments taken from tributaries to the Rhine, and Vivian and Massie (1977) recorded up to 916 ppm Cu, 3109 ppm Ni, 70 ppm Cd and 10,596 ppm Zn in <2 mm sediment from the River Tawe, South Wales. In general, the smaller the stream in relation to the volume and concentration of the discharge the greater the impact. Tipping, corrosion, spillage and erosion of made ground are responsible for coarse detritus which will have a great impact on panned concentrate samples. Fragments of a wide variety of metals and alloys, constructional materials and glass are the commonest contaminants in these samples. Anomalous levels of Ag, As, Cd, Co, Cr, Cu, Hg, Ni, Pb, Sb, Sn, V and Zn may be generated, depending on the precise sources and form of contamination. In many cases the contaminant metals will be present in different species from those of natural origin, allowing them to be discriminated by chemical, mineralogical or statistical methods (see below).

Due to spatial proximity, drainage anomalies from urban/domestic and industrial sources are frequently mixed, waste from several sources reaching natural drainage through a single outfall pipe. Dispersion trains from urban/industrial conurbations may be very long, persisting for great distances down major rivers to their estuaries, which are also usually heavily polluted; the Rhine is a prime example (e.g., Förstner and Muller, 1973; Förstner and Wittmann, 1981).

Agriculture and forestry

Farmland and managed forestry constitute the major land-use within many drainage systems. The impact of these activities on freshwater resources in the United Kingdom has been reviewed recently (Royal Commission on Environmental Pollution, 1992). In this account attention will be restricted largely to the use of substances containing metals commonly determined during geochemical exploration surveys.

Fertilisers

Chemical fertilisers commonly applied to agricultural land may contain sufficient quantities of one or more metals to generate anomalies locally. Although considerable variation between N, P and K fertilisers is reported, in most cases metal concentrations are well below the mid point of the ranges quoted in Table 13-IV. On occasion, however, metal concentrations above the upper limit in the table are found (e.g., Thornton, 1979; Mattigod and Page, 1983), as well as high levels of uranium, fluorine and rare earth elements (Levinson, 1980; Vandelannoote et al., 1984). The application of lime to agricultural land to correct soil acidity has been common agricultural practice for long periods. Most lime and limestone contains low levels of metals, but if mineralised source rocks are used then the content of several metals, particularly barium, copper, lead and zinc, may greatly exceed the levels indicated in Table 13-IV (Hosking, 1971; Thornton, 1979; Levinson, 1980).

Sewage sludge, used as a fertiliser and soil conditioner, may contain a wide range of metals, sometimes in highly anomalous concentrations (Table 13-IV). The metal content is extremely variable, depending on source. A general observation is that as urbanisation and industrialisation increase in an area, so does the metal content of the sewage sludge (Adriano, 1986). Concentrations are generally higher in sewage sludge than manure, livestock wastes or chemical fertilisers (Table 13-IV). In addition to the metals listed in Table 13-IV, Ag (5–150 ppm) and Bi (<12–100 ppm) levels may also be much higher than normally found in soils (Berrow and Webber, 1972).

Specific chemicals may be added to the ground to correct deficiencies and promote growth of plants and livestock. Zinc is added to fertilisers to promote potato growth in particular and copper, commonly as CuO, $CuSO_4$ or $Cu(OH)_2$, is added to promote the growth of a wide range of crops and correct deficiencies in animals, in places caused by excess molybdenum (Gupta, 1979; Thornton, 1979).

Repeated application of fertilisers can lead to the build-up of substantial anomalies of a wide range of metals in the soil and in a few cases may be compounded unintentionally by, for example, spreading lime (containing lead) to adjust the pH after application of sewage sludge. Recognition of the potential hazards arising from the build up of heavy metals in soil has led to the placing of limitations on the application of sewage sludge by setting maximum levels for metal concentrations in soils amended with this material. These include mandatory levels for EU soils of 3 ppm Cd, 100 ppm Cu and Pb, 50 ppm Ni and 300 ppm Zn (Alloway, 1990).

Although, depending on circumstances, added metals may be effectively fixed in the soil, they may also be transported into the surface drainage and groundwater. For example, studies of uranium in phosphatic fertilisers have shown that it is retained in the plough layer of arable soils in England and New Zealand (Rothbaum et al., 1979), but in other areas it is deemed to be the cause of uranium anomalies in streamwater (Spalding and Sackett, 1972; Michie and Cooper, 1979). There is concern from the results of predictive modelling studies that the long term (40 year) application of phosphatic fertilisers could result in significant groundwater pollution by cadmium and selenium and, perhaps, other metals including molybdenum and uranium (Bignoli and Sabbioni, 1981).

Coniferous afforestation may increase the acidity of soil and water. This is most likely to occur in upland areas where the deposition of acid pollutants is high and the buffering capacity of the soils is low (Royal Commission on Environmental Pollution, 1992). Frequently increasing acidity may lead to higher concentrations of metals such as copper in water, though this will be in part dependent upon the metal-rich phases in the soil. Fertilisers and soil conditioners are increasingly used in managed forestry, sometimes to counteract these effects, and Dawson et al. (1977) reported the presence of phosphatic rock and basic slag particles in panned concentrates collected from streams during a mineral exploration survey in forested areas of southern Scotland.

Feed stuffs and slurry

Feed stuffs are unlikely to enter the drainage directly in substantial quantities unless spilt, but in rural areas slurries from livestock units and yard washings frequently enter streams and rivers in an untreated state. Analyses of cattle manure and poultry wastes indicate enrichment of most inorganic elements in the wastes compared with feeds (Capar et al., 1978). Metal concentrations in manures and slurry suggest that only copper, molybdenum and zinc may be present at levels likely to produce drainage anomalies of concern to the exploration geochemist (Table 13-IV). Pig slurries are the most likely source of anomalies, as they may contain highly anomalous levels of copper and sometimes zinc due to the presence of these metals in pig fattening rations, and slurries containing up to 1990 ppm Cu have been reported (Thornton, 1979). In Portugal, Bicudo and Madureira (1991) estimated that only 12.5% of piggery units have effluent treatment systems and that as a result critical pollution may arise locally.

Pesticides, fungicides and herbicides

Inorganic agricultural sprays are mainly derivatives of As, Cu, Hg, Mn, Pb, Se, Sn and Zn. Although the compounds applied have evolved with time, in many cases chemicals containing the same metal have been applied to agricultural areas for more than 50 years. In recent years the use of inorganic pesticides has decreased (Bowen, 1979) but, historically, copper compounds in particular have been applied in large quantities. Bordeaux mixture (copper sulphate plus slaked lime) has been widely applied to control numerous disorders including downy mildew in viniculture, potato blight and leaf spot in sugar beet. As a result copper concentrations of over 1500 ppm have been reported from top soils in orchards (Hirst et al., 1961). Inorganic and organic mercury compounds have been used as seed dressings and foliage sprays. This practice, now banned, gave rise to particularly high levels of mercury in the bulb fields and associated drainage ditches (up to 223 ppm Hg in sediment) of Holland and the United Kingdom (Moriarty and French, 1977; Bowen, 1979). Arsenical herbicides are used in weed control programmes (Isensee et al., 1973) and lead arsenical sprays in orchards, whilst sodium arsenate has been sprayed directly into lakes to control weeds. Organo–tin compounds have been used extensively in wood preservatives and as fungicides, selenium compounds as insecticides and dietary supplements, and thallium in pesticides/rodenticides (Jones et al., 1990; Neal, 1990). Until they were banned in the UK in 1987 organo–tin compounds were also used on fish-farms to prevent algal growth on nets; since then copper compounds have been used for the same purpose by some units.

Irrigation

Changes to the drainage system resulting from irrigation schemes in forest and agricultural land can generate anomalous metal concentrations by acceleration of naturally occurring leaching, evaporation and flushing processes. For example, in California large fertile alluvial fans containing high concentrations of mobile oxidised selenium phases have been cut by extensive tile drainage irrigation systems which have enhanced the mobilisation of selenium into surface and groundwater (White, 1987).

Effect on drainage samples

In general, a relatively restricted range of metal anomalies (As, Cd, Cu, F, Hg, Pb, Se, Sn, U, Zn) might arise directly from intense agricultural practice and, in most cases, these will occur in stream sediment and water samples rather than panned concentrates. Anomalies from some sources, such as pesticides and fertilisers, may show seasonal variation, particularly in surface waters.

Experiments have shown that the movement of some organic pesticides from agricultural fields to receiving waters can take only a few hours following rainfall (Royal Commission on Environmental Pollution, 1992). Because of its extensive use over long periods in sprays, copper anomalies are most common. Notable amongst these are the high levels of copper in stream sediment and water reported on a regional scale from hop and wine growing areas of Germany, for example at Hallertau, north of Munich, and south-west of Frankfurt (R. Hindel, pers. commun., 1992). Elevated uranium and fluoride concentrations in stream waters caused by phosphatic fertiliser application are also recorded from Germany (Fauth et al., 1985) whilst high lead values in Ontario have been attributed to lead compounds used to spray orchards (Fortesque and Terasmae, 1975). Organic chemicals, used increasingly during the last twenty years in sprays, may accumulate in stream sediment (e.g., Heinisch and Klein, 1991) but, except in the cases where these are organo–metallic compounds, they are unlikely to give rise to anomalous levels of parameters measured routinely by exploration geochemists. Slurries are often washed directly into streams and any metal enrichments in them are likely to be registered in sediment or water samples. Alther (1975), for example, concluded that Ca, Cu, K, Mg, Na and Zn levels were significantly increased in stream sediment contaminated by waste from a pig farm in Ontario.

Due to the lack of refuse collections in many rural areas, dumping of waste into streams near farms was at one time common, and this source gives rise to a wide range of metal anomalies in rural areas of Britain.

Intensive agriculture can give rise to the pervasive enrichment of metals in groundwater. A review of groundwater contamination in the USA indicated that in dominantly rural States agriculture was the major source of groundwater contamination (Pye and Kelley, 1984). The contamination of both surface and groundwaters from natural and artificial sources may be promoted by irrigation systems.

Other sources of drainage contamination

Military and other defense establishments can be the source of a wide range of surface drainage and groundwater contaminants as a result of dumping, leakage or spillage. A well documented example, principally involving the contamination of groundwater by chemicals, is the Rocky Mountains Arsenal, Colorado (Konikow and Thompson, 1984). Military training and storage areas which contain a wide range of metal debris can produce strong metal anomalies particularly in panned concentrates. Copper, Pb, Sn, Zn and, possibly, Mo and Ni anomalies in rural areas of Britain have been attributed to this source (Gallagher et al., 1977; Cameron et al., 1984; Cooper et al., 1985). Crashed aircraft have also been found to be responsible for isolated metal anomalies (Leake et al., 1978b; Levinson, 1980).

The seeding of clouds with silver iodide crystals to induce precipitation has resulted in perplexing silver anomalies, and is responsible for high silver values in some recent lake sediments (Levinson, 1980). Another unusual form of contamination comes from the disposal of pot-ale, a liquid waste from the production of malt whisky, in some Scottish fields (Reith et al., 1979). This waste causes copper anomalies in the fields and is probably also the source of high (up to 200 ppm) copper in stream sediment values reported from near whisky distilleries in the Spey Valley, north-east Scotland (British Geological Survey, 1991).

Generally emissions from nuclear installations are well controlled but the catastrophic accident at Chernobyl produced widespread contamination of soils and rivers. The accident gave a relatively easily measured illustration of the widespread rapid dispersion that can occur in the atmosphere (e.g., ApSimon et al., 1988). High levels of Cs^{137} were recorded in suspended sediment hundreds of miles from the scene of the accident and accumulations of Chernobyl-derived radionuclides have been recorded in floodplain and channel sediments at similar distances (e.g., Walling et al., 1989).

Long dispersion trains of radionuclides have been recorded in streams and rivers below some nuclear facilities. The best documented examples come from long established plants in the United States, notably in the Columbia River below the Hanford Reservation (e.g., Haushild, 1980; Beasley and Jennings, 1984), below the Savannah River Plant (Goldberg et al., 1979) and in White Oak Creek and the Clinch River downstream of the Oak Ridge Laboratory (Pickering 1970; Cerling and Spalding, 1982). The radionuclides are frequently attached to clay minerals in the fine fractions of the sediment.

A relatively new source of pollution can arise from geothermal power stations which, by spillage or leakage, can generate or enhance natural anomalies already present from the exhalation of metal-rich geothermal waters. Some of these waters are effectively ore-forming fluids which may carry high concentrations of several metals including B, Ba, Fe, Mn, Pb and Zn (Mattigod and Page, 1983).

IDENTIFICATION AND DISCRIMINATION OF CONTAMINATED SAMPLES

In exploration geochemistry the objective in most cases is to identify dispersion patterns derived from hitherto unrecognised ore deposits. Consequently a survey method must be adopted that maximises the response from the potential target and eliminates or minimises other sources of variation, including that from any contamination. However, in many cases a contaminant in drainage samples may be present in similar or identical phases to that coming from the target sought, making differentiation particularly difficult. Contaminants in drainage may exist as discrete particulate phases, absorbed onto clays, precipitates (hydrous oxides, carbonates, phosphates and sulphides) or organic matter, or dissolved in water. Metals from untapped mineralisation may also be present in all these phases but, depending on the sources, the proportions may differ and these differences have been used in attempts to distinguish the sources. Metals derived from human activities may also be present in distinctive phases, resulting in different ratios and associations of metals compared with those from natural sources, and these differences often provide powerful evidence of source. However, the single most distinguishing feature of contaminants in geological terms are their age: they are all recent additions to drainage systems.

A number of methods have been used to exploit the features outlined above in distinguishing drainage anomalies from natural and artificial sources and these are reviewed below. Most of the individual methods do not give a definitive answer and several may be employed in a single survey to maximise discrimination. Each contaminated area is likely to differ in sources and intensity of contaminants, each of which may generate a particular geochemical signature. Orientation surveys, aimed at determining the most advantageous conditions to allow the objectives of the survey to be fulfilled are, therefore, a necessary prerequisite to any geochemical drainage survey in a contaminated terrain.

Remote sensing

Satellite and aircraft borne sensors provide a powerful means of identifying sources of contamination at the planning stage of a survey; Barrett and Curtis (1982) briefly review the potential. By applying image processing and statistical techniques, such as band ratioing, edge enhancement, contrast stretching and principal components analysis, images from a range of different sensors can be used to locate industry and different types of land use (e.g., Van Genderen et al., 1983; Khorram et al., 1991). In a study of the Swansea Valley, Coulson and Bridges (1984) found that they could use multi-spectral scanner data to map contaminated and other land surfaces, discriminate various classes of metalliferous waste, notably residues from copper, zinc and iron smelting, and identify a vegetated surface underlain by contaminated material. The effect of air and water-borne pollutants on vegetation can be detected and the spread of pollution in drainage from factories and more widespread urban/domestic sources can often be seen. For example, Measures (1984) demonstrated the use of airborne fluorosensors to monitor the effluent from the pulp and paper industry, and Lind and Glass (1980) used Landsat images to show the dispersion of taconite tailings following discharge into Lake Superior.

Remotely sensed data has also been widely used to try and locate mineralised areas, either directly from the presence of altered and mineralised rocks, or indirectly through the effect of metal enrichments on vegetation (e.g., Collier et al., 1986; Cole, 1988; Hussey, 1988; Bierwirth, 1990). Consequently remotely sensed data cannot only be used to predict where metal anomalies are likely to be derived from artificial sources, but also where they may be related to untapped mineralisation.

Field observation and mapping

In carrying out geochemical surveys of contaminated terrains it is important to note or map actual and possible sources of contamination in the vicinity and upstream of sample sites. Many forms of contamination will not be obvious, particularly those from agricultural (sprays, fertilisers) and airborne sources. In some agricultural areas clues, such as discarded containers and empty fertiliser bags, may give an indication that sprays or fertilisers have been applied, whilst in others farm records may provide more definite information. Some contaminants, such as recently tipped domestic refuse, will be very obvious, but it must be remembered that a freshly discarded empty can will not produce a stream sediment anomaly; it is only an indication that tipping takes place. It is the long-discarded decomposed container, broken into small fragments, or its contents, or associated garbage, that is most likely to generate a drainage anomaly.

Areas containing old mineral workings are a particular problem and maps to show the precise location of the workings, haulage ways, tips, mills and smelters, as well as a knowledge of the minerals extracted, can greatly aid the selection of drainage sample sites and subsequent data interpretation (e.g., Heetveld and Pretti, 1975). The transportation of mine waste for use as land-fill, hardcore and other constructional purposes is a particular problem within economic transportation distance of any mining area. The field sampler should pay particular attention to this source as road construction often takes place close to streams and has been responsible for many spurious drainage anomalies. A typical example, reported by Cooper et al. (1985), consists of a prominent copper anomaly in both sediment and heavy mineral concentrate samples taken from a stream in the Harlech Dome, Wales. The source proved to be hardcore in the base of a road running by the stream which had come from a quarry within the mineralised zone of the Coed y Brenin porphyry copper deposit a few miles away. Another example is provided by the lead and zinc anomalies (up to 1900 ppm) in stream sediments collected from a 50 km^2 area of forest east of Koblenz, Germany. These anomalies have been caused by the use of spoil from former lead–zinc mines about 20 km away as hardcore in nearly all the forest roads (R. Hindel, pers. commun., 1992).

It is often possible to apply information obtained during the early or orientation stages of a geochemical drainage survey to the later stages of the same survey. For example, if it is recognised at an early stage of a survey that mineralised hardcore is present in roads or tracks of a particular age, or has been used by a particular contractor, then drainage sampling sites for the later stages can be adjusted accordingly.

Sampling

Sample location

Because the outstanding feature of pollution is that, in geological terms, it is a relatively recent event and normally effects the surface layers of soils and sediments, sampling undisturbed (fixed) sediment at depth can be a simple means of avoiding contaminated material. Numerous studies of heavy metal pollution in lake sediments have been carried out (Förstner and Wittmann, 1981; Fergusson, 1990). Some of these determined the distribution of metals in dated cored profiles and were thereby able to demonstrate the build up of metal concentrations in the upper layers of the sediment due to contamination. In most cases it is only the uppermost 10 cm of North American lake sediment that is affected (e.g., Thomas, 1972; Allan and Timperley, 1975) but in some cases, where sedimentation has been more rapid, pollution started earlier, or there has been disturbance or migration within the sediment pile, deeper sediment may be affected. For example, at Lake Windermere in the United Kingdom there is evidence that sediment from c. 1400 A.D., now at a depth of 0.50 m, is enriched in mercury (Aston et al., 1973). In most cases lake sediment samples collected below 0.50 m are free of contaminants (Warren, 1981).

Overbank (or river-plain) sediment can offer the same advantage as lake sediment in that fixed sediment deposited prior to the onset of pollution can be sampled (Ottesen et al., 1989). This sampling medium is most appropriate for low density regional surveys and is therefore of limited use for detailed mineral exploration purposes but, where applicable, it can provide a means of collecting a sample free of contamination from areas which are often heavily polluted. However, Lewin and Macklin (1987) found that in overbank sediments from the River Rheidol in Wales contaminated by lead–zinc mining operations, there was no straightforward relationship between zinc concentration and apparent age of sediment, and Ridgway and Macklin (1990) concluded that at some localities it may not be possible to provide a complete succession from pristine, pre-anthropogenic material, through to present day sediment. Therefore, because of scouring, reworking and metal movement within the floodplain sediment pile, metal distribution may be complex, so profile-related sampling at carefully selected sites is required to ensure the collection of material free of contamination (Lewin and Macklin, 1987; Macklin and Dowsett, 1989; Marron, 1989).

Where active stream sediment is sampled in areas where contamination is not pervasive, careful selection of sample sites can minimise the effects of point source contamination. Where other considerations permit, samples should be taken at least 100 m upstream of the identified sources.

Seasonal variation

The concentration of contaminants, particularly in water samples, often shows seasonal variation. This may be caused by a number of factors but is normally dominated by variations in stream-flow and in the discharge of contaminants (e.g., Grimshaw et al., 1976; Rasmussen and Sand-Jensen, 1979; Bird, 1987). Increased stream flow may reduce metal concentrations in stream sediment (e.g., Geesey et al., 1984) as well as waters, but in many cases seasonal variations in flow will affect metal concentrations from natural and contaminant sources to a similar degree, and therefore will be of little help for discriminating between the sources, particularly as the seasonal variation in the metal content of stream sediment is usually relatively small compared with that from other sources (Barr and Hawkes, 1963; Howarth and Lowenstein, 1971; Chork, 1977; Bölviken et al., 1979). Exceptions may occur where the contaminant input is seasonal, where appreciable natural variations occur and, particularly when metals from natural and contaminant sources are held and transported in contrasting phases, although the situation may be complicated by the movement of metals in different phases during low flow and storm conditions (Wixson, 1978). Carey (1979) indicates that this may occur in a Tennessee river where a large volume of coal, ranging in size from fine sand to coarse gravel, is transported as bedload during run-off events but at other times stream sediment transport is dominated by suspended silt and clay. Data from a river in south-west England (Fig. 13-4) illustrates the appreciable seasonal variation recorded in some areas and how, by choice of sampling period and sample type, the signature from the mineralised (polluted) source may be maximised or minimised with respect to the unmineralised background.

The most obvious sources of seasonal pollutants are agricultural and it is predictable that seasonal variation from these sources will be most evident in water samples. Appreciable temporal variation in drainage samples is recorded in tropical and sub-tropical terrains (e.g., Govett, 1960; Ridgway and Dunkley, 1988; Ridgway and Midobatu, 1991), suggesting that agricultural areas in such terrains may offer the greatest scope for using seasonal differences to minimise the effects of contaminants.

To use seasonal variation effects successfully careful area by area orientation studies are required because, although principles such as storm dilution effects are universal, metal concentrations may be affected in detail by many other factors which are not always predictable from a desk study.

Grain size

Metals in a stream sediment from natural and anthropogenic sources may be concentrated in different phases with contrasting grain size distributions. Metal concentrations generally increase in the finer fractions of stream sediment, and the silt and clay fractions normally comprise the major carriers of both natural and anthropogenic metals as these fractions contain a high proportion of organic matter, precipitates and clays, whereas coarser fractions contain a large amount of detrital quartz. Consequently, a fine (<63 μm) fraction of the sediment is often recommended for pollution studies (e.g., Förstner, 1983); mineral exploration surveys commonly employ a coarser cutoff (e.g., <150 μm; Plant, 1971). A typical example of the effect of pollution is given by Förstner and Wittmann (1981) who compare analyses of zinc and nickel in different size fractions of sediment from Lake Constance (relatively uncontaminated) and the Lower Rhine (highly contaminated). The Lower Rhine sample is enriched in both zinc and nickel in all size fractions but the enrichment of zinc is greater, particularly in the fine fractions. On occasion, however, contaminant metals may be present in relatively coarse particulate form, giving rise to a greater contrast between natural and anthropogenic sources in the coarser than the finer fractions. For example, Salomons and Förstner (1984) report and illustrate data from Wilber and Hunter (1979) which shows a marked increase in metal

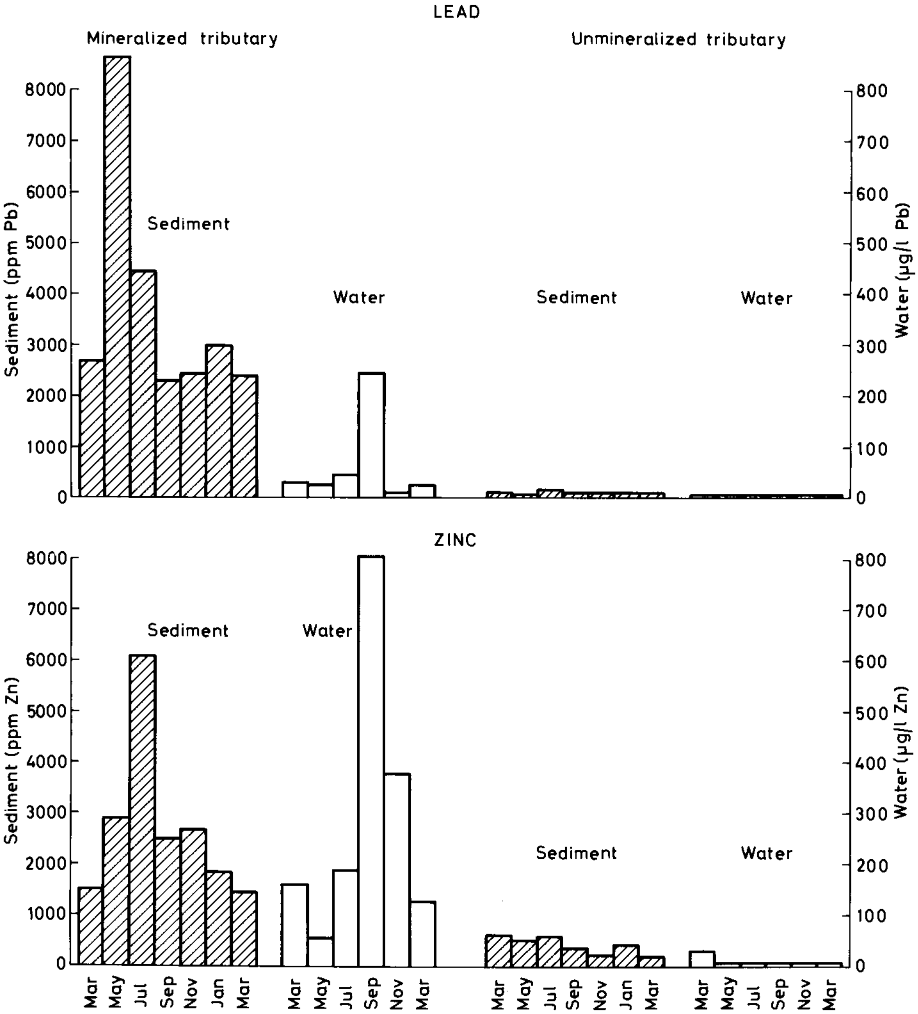

Fig. 13-4. The bi-monthly variation in lead and zinc content of sediment and water samples taken from mineralised and unmineralised tributaries to the river Gannel, Cornwall.

(Cd, Cr, Cu, Fe, Ni, Pb and Zn) concentrations in the medium and coarse sand fractions downstream of an urbanised area on the Saddle River, New Jersey. Although there are also increases in the clay and silt fractions, which contain higher concentrations of metals than the coarse fractions, the contrast between samples collected above and below the urban area is considerably greater in the coarse fraction, allowing the conclusion to be reached in this area that the coarser sediment fractions best reflect the impact of urbanisation. Metalliferous mining and smelting operations may also produce atypical metal distributions in different size fractions of stream sediment (e.g., Leake et al., 1978b; Dossis and Warren, 1980; Warren, 1981; Moriarty et al., 1982; Moore et al., 1989). These studies show that often the metal concentrations in the coarser fractions of contaminated samples increase relatively more than in the fines due to the presence of crushed ore particles.

It may therefore be possible in some areas to minimise or maximise the impact of contamination by careful selection of stream sediment size fractions. Salomons and Förstner (1984) concluded that the fine sand fraction (approximately 20–200 μm) may be particularly useful for the differentiation of natural and pollutant metal transport, but orientation studies would be needed to determine the optimum fraction for an individual area and any effects of dispersion distance from source on the grain size signature.

Sample type

Some types of drainage sample are effectively size fractions: a float (suspended sediment) sample is composed largely of clay and fine silt size material; a stream sediment is normally sieved to exclude material coarser than a predetermined size; and, depending on method of collection, a heavy mineral concentrate is often largely composed of sand size grains. Therefore a consequence of the relative concentration of urban contaminants from at least some areas in the coarser sediment fractions is the impact that it has on panned concentrate analyses. Panned concentrates made from the <2 mm fraction of the sediment often record large anomalies for metals (Cu, Pb, Sn, Zn) derived from urban/domestic sources. At the opposite extreme, several studies have demonstrated the concentration of pollutants in the finest phases, suggesting that float or other very fine fraction sediment samples will give particularly strong pollution signatures (e.g., Biksham et al., 1991).

Comparison between the metal content of two sample types collected from the same site can provide particularly valuable information on the distribution of metals and where natural and contaminant metals are present in different phases may enable the two to be distinguished. For example, Geer and Closs (1983) were able to use a fine (<170 mesh) fraction of stream sediment and bromoform extracts from panned concentrates to distinguish two types of mineralisation and contamination from past mining activity in an area of Idaho. When held in contrasting phases the downstream dispersion patterns of natural and contaminant metals may also differ, and the patterns may be particularly distinctive when data for more than one sample type are available. For example, acid mine drainage from a worked sulphide deposit may initially produce large anomalies in streamwater to be replaced downstream by large anomalies in the fine sediment, as the water becomes more alkaline and hydrous oxides precipitate, while panned concentrates often produce very large anomalies from detrital wastes which decrease exponentially downstream. In contrast, untapped natural sulphide mineralisation will generally produce more subdued anomalies in one or more of these sample types depending on style and location with respect to drainage.

Biological (plant and animal) samples have been suggested as a means of monitoring contamination in streams and rivers as they can provide an integrated record of pollution over a period of time and therefore have potential for recording effectively intermittent pollution events (Kelly, 1988). This property may reduce their effectiveness for discrimination purposes, but in some instances, depending on the speciation of the natural and contaminant phases and the response of the organism in terms of uptake and loss, they may be worth consideration.

Analytical: partial and sequential extraction methods

Metals may be present in streams in a number of phases including detrital particles from the erosion of rocks and contaminant sources, organic matter and inorganic precipitates, principally hydrous iron and manganese oxides, carbonates and sulphides, as well as dissolved in the water. Metals may be bound within the solid phases or held to their surfaces. Metals from natural and contaminant sources may be present in different phases or distributed amongst the same phases in different proportions and held on or within these phases by different mechanisms (e.g., Shuman et al., 1978; Warren, 1981). The potential for metals derived from natural and contaminant sources to be present in different species offers a means of discriminating between the sources by using selective dissolution reagents followed by determination of the metal content of the extract. A single reagent may be chosen to extract elements from certain phases (partial extraction) or a series of reagents of increasing strength applied in succession to gain information on the distribution of metals between most or all of the phases present (sequential extraction). A typical sequential scheme will endeavour to differentiate metals held in (i) exchangeable sites, (ii) organic matter, (iii) carbonates, (iv) reducible phases (hydrous iron and manganese oxides), (v) sulphides and (vi) silicates. Many partial and sequential extraction schemes have been developed for use in geochemical prospecting (e.g., Gatehouse et al., 1977; Peachey and Allen, 1977; Hoffman and Fletcher, 1979), reviewed by Chao (1984); Pickering (1986); and Coats et al. (1994), and/or for environmental studies (e.g., Tessier et al., 1979; Adams et al., 1980; Sposito et al., 1982), reviewed by Förstner (1983) and Fergusson (1990). The schemes for geochemical prospecting have generally been aimed at optimising the signature from mineralisation or aiding the interpretation of data by indicating the mode of occurrence of metal anomalies, whereas schemes developed for environmental purposes have often been used to simulate the availability of essential and toxic elements or their potential for remobilisation. For a variety of reasons (see Chapter 16, this volume) most extractants are not as specific or efficient as is implied in some of the schemes (Kheboian and Bauer, 1987). However, although identifying the precise species may not be possible, wide use has been made of the technique and results suggest that in specific areas it can provide a means of discriminating natural and anthropogenic anomalies.

Taylor (1968), in a study of two British lead–zinc mining fields, found that natural and contaminant anomalies in stream sediment could be distinguished by a combination of dilute HNO_3 extractable Pb/Zn ratios, total Pb/Zn ratios and correlation patterns of lead and zinc with other metals. This was possible because of (i) the preferential extraction of lead during early mining resulted in the contamination being either more lead or zinc rich than the mineralisation, (ii) the prevalence of simple oxidised forms of lead and zinc in the smelter wastes and their absence from natural anomalies and (iii) contrasting metal associations characteristic of smelting, mineralisation and other sources of variation, such as black shales and hydrous oxide precipitates. In a similar study of sediments from the River Geul, Belgium, Dijkstra et al. (1979) tested the effectiveness of a partial extraction scheme for distinguishing between zinc anomalies derived from in situ mineralisation and those caused by dispersion from smelter dumps. It was found that single extractants were ineffective, but that the differences in quantities of metal released by two of the extractants (hydroxylamine and sodium dithionite) distinguished the natural and contaminant sources. Similar studies have been carried out on soil samples (e.g., Sondag, 1981).

Contaminants from domestic, industrial and agricultural sources rarely contain metals in sulphide species, the metals from these anthropogenic sources often being transported in sorbed, precipitated and organically complexed forms (Förstner and Wittmann, 1981; Fergusson, 1990). Also it has been confirmed in several studies that the proportion of total metal present in the residual/lithic fraction is greatest in unpolluted samples (Pickering, 1986). For example, in a comparison of relatively clean and polluted sediments from the Haw River, North Carolina, it was found that in the clean sediment most chromium and antimony were carried in crystalline minerals whereas in the polluted sediment, which contained higher levels of these metals, they were largely held in oxide coatings with some increase in the organic component (Shuman et al., 1978). Metals derived from mineralisation may also be concentrated in organic matter and precipitated phases (e.g., Filipek et al., 1981), but in the cases where active erosion of metal sulphides or oxides results in these detrital phases being principal metal carriers, selective extraction, or a relatively simple sequential extraction scheme, coupled with a particular sediment sample fraction or type (e.g., heavy mineral concentrate), has potential for differentiating mineralisation anomalies from other sources.

Mineralogical

Mineralogical analysis can be used to provide detailed information on the mineral phases present in a sediment sample and their likely source. This is normally carried out by splitting the sample into a number of size fractions to which different techniques may be applied. For example, Förstner and Wittmann (1981) outlined a scheme involving the determination of the clay minerals in the finest (<2 μm) fraction, carbonate in all fractions, and heavy minerals in the fine and medium sand fraction.

A specific scheme to discriminate between natural and anthropogenic stream sediment anomalies in contaminated terrains has been used extensively by the British Geological Survey during a Mineral Reconnaissance Programme funded by the Department of Trade and Industry. The samples examined normally comprise heavy mineral concentrates, made in the field by panning about 4 kg of the <2 mm stream sediment to c. 50 g (Leake and Aucott, 1973). The method used involves the separation of the methylene iodide sink fraction of the sample into five sub-fractions according to magnetic susceptibility. Each sub-fraction is examined microscopically and, where necessary, sub-fractions or individual grains are analysed by XRF or XRD to confirm their identity (e.g., Cooper et al., 1982, 1991). A broadly similar mineralogical approach was described by Watt and Johnson (1987) for discriminating between the sources of dust particles. They showed that single particle analysis, based on scanning electron microscopy with chemical analysis by energy dispersive X-Ray spectroscopy followed by statistical analysis of the chemical and physical properties, allowed apportionment of the particles to sources such as paint, smelter emissions and automotive exhausts.

Mineralogical analysis has the major advantage of being able to identify readily multi-source anomalies. The morphology of individual grains and the total mineral assemblage in the sample also provide clues to the sources of both natural and contaminant phases. However, the method is time-consuming, requires highly-trained staff and good laboratory facilities. The technique is particularly useful in terrains containing tin mineralisation and to confirm statistical or selective extraction results.

Anthropogenic phases identified in heavy mineral concentrates by mineralogical analysis and responsible for drainage anomalies include lead shot (Pb), glass (Pb), yellow glaze (Pb), solder (Pb, Sn), "hard" lead (Pb, Sb), brass (Cu, Zn), bronze (Sn, Cu), galvanised iron (Zn), tinplate (Sn), wire (Cu, Sn, Zn) and other metallic fragments from a range of manufactured goods (Cu, Pb, Sb, Sn, Zn) (e.g., Leake et al., 1978a; Cameron et al., 1984; Cooper et al., 1991). In addition crushed phosphatic rock and basic slag particles have been identified locally (Dawson et al., 1977, 1979). Metallic fragments are the commonest contaminant in panned concentrates. Lead is also commonly present in glass fragments. Tin is often present as SnO and SnO_2, derived from glaze or tinplate; unlike naturally occurring tin oxides the contaminant phases are typically poorly crystalline and do not respond to the tinning test (Cooper et al., 1984).

The application of mineralogical analysis to aid the interpretation of panned stream sediment analyses from part of Anglesey, North Wales, is illustrated in Fig. 13-5. In this area a number of lead anomalies were recorded in panned concentrates close to the base of the Carboniferous in the vicinity of major faults, a favourable setting for lead mineralisation. Mineralogical examination indicated, however, that all the anomalies except one were solely the product of contamination. The exception contained galena as well as contaminants, indicating a dual source.

In some circumstances it is possible to distinguish natural phases derived from old mine workings from those dispersed naturally from untapped mineral-

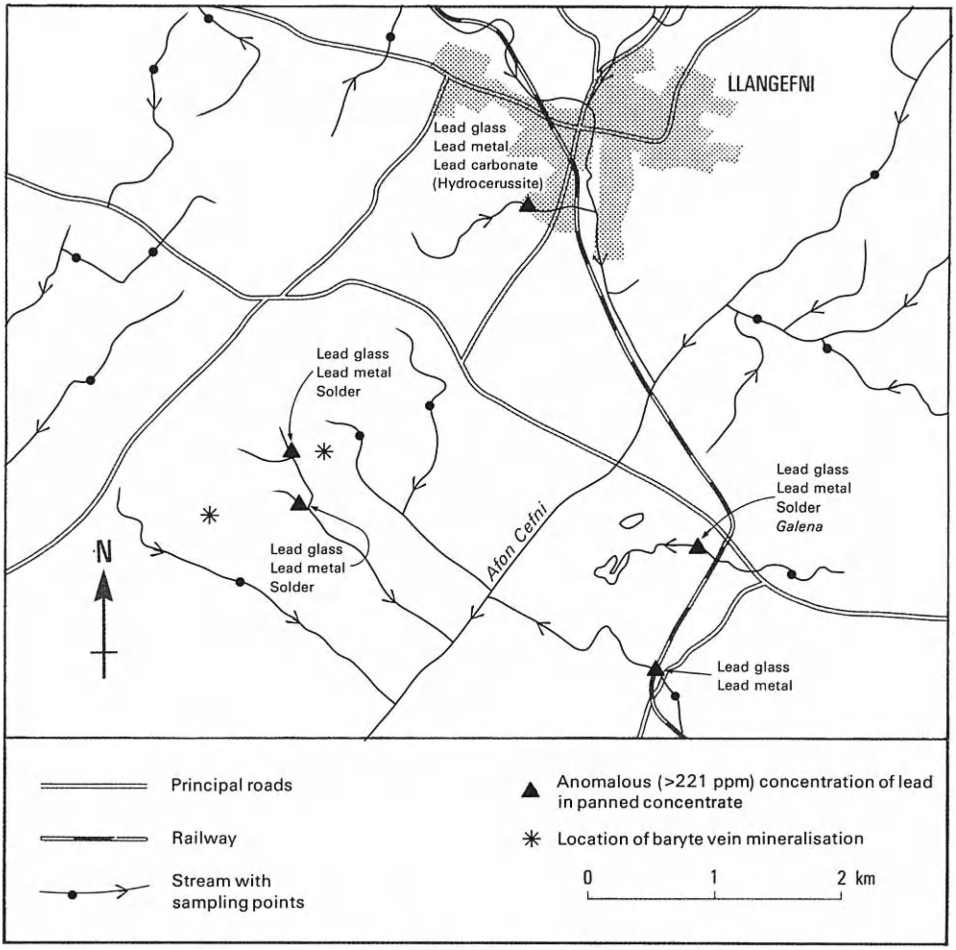

Fig. 13-5. The location of lead in panned stream sediment concentrate anomalies south of Llangefni, Anglesey, and their cause determined by mineralogical examination of the concentrates (compiled from Cooper et al., 1982).

isation. For example Leake et al. (1978b) reported that exploited mineralisation in the Talnotry area of southern Scotland generated panned concentrate dispersion trains containing a complex association of fresh sulphides, whereas previously undetected mineralisation in Penkiln Burn produced only secondary minerals of relatively fine grain size.

Statistical

Element concentrations and co-varying associations arising from natural sources often differ from those produced by human activity. Although some convergence may occur in stream sediments as a result of metals in phases from both sources being subjected to common physico-chemical processes in streams, it is often possible to detect metal signatures characteristic of the various sources and processes through the statistical analysis of geochemical data. The methods that can be used range from the simplest univariate presence/absence criteria to advanced multivariate techniques. No attempt will be made here to give details of the range of statistical methods which might be applied to the problem of discriminating variation due to contamination, but simply to review some techniques that have proved successful.

Univariate methods

These methods examine a number of values of a single variable. Perhaps the simplest method in this group is to class a sample as contaminated if it contains a higher concentration of an element than would be expected from natural sources. The threshold level may be chosen relatively arbitrarily from tables of the ranges of metals found in the lithologies comprising the survey area or from sample population analysis using cumulative frequency plots (see below). In areas of Britain believed to be free of tin mineralisation, levels of tin in stream sediment or panned concentrate samples have commonly been used in this way, with levels between 9 and 88 ppm Sn in panned concentrates taken as the level above which a sample is deemed to be contaminated (Gallagher et al., 1977; Bateson and Johnson, 1983; Bateson et al., 1983; Wadge et al., 1983). The method has the merit of simplicity but provides little information besides the probability that the sample contains contaminants. Importantly, tin-free sources of contamination escape detection.

Examination of the frequency distribution of individual element concentrations in a group of samples, commonly by the analysis of cumulative frequency curves, can lead to the identification of sample populations related to a number of sources, including contamination (e.g., Sinclair, 1976; Macklin, 1992). Identification of the sources of multiple sample populations can be assisted by the analysis of curves for the same element in different sample media collected from the same site and other data, such as that from mineralogical analysis (e.g., Chapter 16, this volume). In some cases specific populations can be related to background sources, mineralisation and contamination (e.g., Michael et al., 1973). Where populations are well defined the data plots allow the identification of contaminated samples and the range of metal concentrations which are produced by contamination. The significance and partitioning of samples into sub-populations so defined can be investigated using appropriate statistical tests.

Bivariate methods

These methods can be used to examine the relationship between two measured variables for a group of samples. The most common statistic used to measure this relationship is the correlation coefficient. There are a number of methods for determining correlation, each makes basic assumptions about the measured variables and care must be taken to choose the most appropriate (e.g., Cheeney, 1983). Correlation coefficients are easily generated by computers and this leads to the danger of misleading results if basic assumptions are not fulfilled, particularly with regard to the distribution of the variables, outlying values and values below the detection limit of the analytical method. Nevertheless useful information can be gained on elements that increase sympathetically (positive relationship) or elements that increase when others decrease (negative relationship). For example, Förstner (1981a) was able to assign positive and negative correlations between groups of elements determined on 87 lake sediment samples to a number of causes including lithology of lake catchment, amount of carbonate in the sediment and pollution.

Further examination of the relationship between two variables can be carried out by using simple scatterplots of the two variables, element ratios, or linear or quadratic regression analysis. In many sediments a wide range of metals frequently show a close correlation with aluminium due to their presence in clay minerals and chlorite (e.g., Hirst, 1962; Calvert, 1976). In a group of samples showing such a close relationship an individual sample that has a markedly different metal to aluminium ratio may be contaminated, although this should be verified by some independent means, as such variation can also be caused readily by a range of natural processes, such as the presence and local sorting of heavy minerals or changes in hydrous oxide components (Sholkovitz and Price, 1980; Windom et al., 1989). Ratios which may be particularly useful involve metals commonly associated with clay/chlorite but not precipitates or organic matter, for example Cr/Al and B/Al.

There are several examples of the use of ratios to discriminate between contaminants or between contaminants and natural sources. Taylor (1968) found that in two British metalliferous mining areas, Pb/Zn ratios were related to the source of metal anomalies when a single anomalous source was responsible. Four groups of anomalies were distinguished: (i) Pb : Zn >5 : 1, lead smelters were the probable source of metals; (ii) Pb : Zn 6 : 1–1 : 1, natural or lead smelter source; (iii) Pb : Zn 1 : 1–1 : 4, natural source probable; and (iv) Pb : Zn >1 : 4, natural (Zn mineralisation or hydromorphic concentration) or zinc smelter source. Fractionation of cadmium with respect to zinc during milling and smelting suggests that Cd/Zn ratios may also be useful for this purpose (Jennet and Foil, 1979). A further example of the use of ratios, in this case Mn/V, is to provide information on the regional source of aerosols (Husain et al., 1984). The technique relies on the much higher levels of vanadium in oil combustion products than coal combustion products. Ratios of V/Se and V/As may be useful for the same purpose (Husain, 1986) and La/V ratios can distinguish oil refinery and power plant emissions (Olmez and Gorden, 1985; Kitto et al., 1992).

Ratios of a single element in two different sample types collected at the same site can also be used in a similar manner to determine the probable sources of metals. For example, a much higher level of arsenic in a panned concentrate than a stream sediment taken from the same site suggests the presence of arsenic in a heavy phase such as arsenopyrite, whereas the reverse suggests that arsenic is held in a light phase, perhaps a hydrous oxide precipitate. Similarly, a high value of barium in a panned concentrate is nearly always caused by baryte, whereas a higher level in the sediment than the concentrate strongly suggests that barium is held in feldspar, mica or clay minerals (see Chapter 16, this volume).

Multivariate methods

These methods deal with three or more measured variables. Of the methods commonly applied to geochemical datasets (e.g., Koch and Link, 1971; Davis, 1973) cluster and factor analysis have probably been most widely used in attempts to recognise specific metal signatures caused by contamination.

Cluster analysis comprises a whole range of mathematical methods for grouping samples or elements on the basis of the similarity of measured variables. The correlation matrix is frequently used as the basis for clustering elements, and this method has been used to demonstrate differences between element variation in polluted and unpolluted lake and marine sediments (Förstner, 1983). In contrast cluster analysis based on euclidian distance was used by Tada et al. (1983) to classify Japanese rivers into differently polluted groups on the basis of the 0.5 N HCl extractable fraction of heavy metals in bottom muds. Obial and James (1973), who applied R- and Q-mode cluster analysis to the chemical analyses of −80 mesh stream sediments collected in Derbyshire, England, found that the method could be used to distinguish mineralised areas and appeared capable of distinguishing anomalies related to untapped mineralisation from those associated with old mine workings or other sources of contamination.

Factor analysis attempts to resolve a large number of variables into a much smaller number of new independent variables which account for a high proportion of the variation in the original dataset (e.g., Jöreskog et al., 1976). These new variables, or factors, can often be related to known geological sources of variation but in some cases their origin is obscure or misleading and there are theoretical objections to the use of factor analysis in geology (e.g., Temple, 1978). Despite the theoretical constraints many authors have found the method to produce useful results when used with caution on geological data and there are several instances of its use to identify variation caused by contamination. For example, factor analysis of groundwater data from New York State in which 10 factors were extracted revealed a factor dominated by copper, zinc and phosphorus that other data suggested was due to contamination (Rose et al., 1983). Factor analysis of stream sediment and panned concentrate data from three separate surveys in Scotland all revealed a factor which evidence from mineralogical and other sources indicated was related to contamination, principally from metallic detritus such as lead shot, tin cans and solder. The variables with high loadings in the contamination factor varied in detail in the three areas, but in all cases included tin and lead in sediment or concentrate, accompanied in one area by antimony in panned concentrate (Smith et al., 1978; Coats et al., 1981, 1982).

In a study of analytical data from sediment and panned concentrate samples collected from Anglesey, Wales, and contaminated locally by domestic, industrial and metalliferous mining wastes, Cooper et al. (1982) assessed the effectiveness of factor analysis for discriminating contaminated samples. This was achieved by comparing the results of a factor analysis model with information obtained from the mineralogical examination of panned concentrates. A six-factor model accounting for 73% of the total variance was generated from the correlation matrix of the drainage data following the method described by Davis (1973). Factor one is related to base metal mineralisation, principally at Parys Mountain; factor 2 to basic and ultrabasic rocks; factor 3 to baryte mineralisation; factor 4 to contamination from domestic/industrial sources; factor 5 to pH changes; and factor 6 to lithological (sandstones) variation (Fig. 13-6). To test the effectiveness of the analysis the factor scores for each of the 40 samples examined mineralogically were compared with the mineralogical data. It was found that agreement was generally good. More detailed examination revealed that in 21 out of 25 cases a high factor 4 score corresponded with the identification of particulate contaminants in a sample and in 15 out of 17 cases a high factor 3 score corresponded to the identification of baryte. The correspondence between

Factor	1	2	3	4	5	6
Loading						
+0.9	Cu_sZn_s					Zr_s
+0.8	Zn_p		Ba_s	Sn_p Pb_s	Zn_w	
+0.7	Pb_s Fe_s		Ba_p			
+0.6	Cu_p					
+0.5	Mn_s				Ni_p	
+0.4	Fe_p Mn_p		Fe_s Ti_p	Cu_p Zn_p		
-0.4		Mn_s Ni_p	Ca_p		Mn_s	
-0.5						
-0.6		Ca_p Fe_p				
-0.7						
-0.8		Ti_p Mn_p				
-0.9						
Σ % total Variance	33	44	54	61	67	73

Fig. 13-6. Factor loading graph for Anglesey drainage data (modified after Cooper et al., 1982). Subscripts denote sample media: s = stream sediment (<150 μm); p = panned concentrate; w = water.

the identification of sulphides in the panned concentrates and a high factor 1 score was less good, as some factor 1 variation was related to the presence of strong hydrous oxide precipitates downstream of metalliferous mine workings. Agreement between the methods was near-perfect for large anomalies, most discrepancies occurring in weaker anomalies. The need for a strong signature was confirmed in a further study of a less strongly mineralised and contaminated area of Wales, the Berwyn Dome (Cooper et al., 1984). Here, where the chemical signatures from contamination and mineralisation were weak, factor analysis and other statistical methods proved ineffective discriminatory tools. Other statistical methods were used on the Anglesey dataset, including cluster analysis, linear regression and simple ratios. None of these methods achieved the success rate of factor analysis in identifying contaminated samples (when compared with mineralogical data), partly because of the presence of several variables (e.g., Cu and Zn in panned concentrate) in both contamination and mineralisation and partly because high levels of tin are not present in all contaminated samples.

DIAGNOSTIC SIGNATURES OF CONTAMINANTS

Each contaminated area will produce anomalies in drainage samples which will depend on a large number of factors including the source of contamination, its history, the physico-chemical conditions operative in the drainage system and the distance from source the samples are taken. As a result anomalies caused by contaminants and any features that distinguish them from natural anomalies may vary markedly between areas. However, it is evident from the description of contaminant sources that some generalisations can be made which provide guidelines for carrying out the orientation studies that are necessary to establish the precise signatures of contaminants and mineralisation in a particular terrain.

Pollution of drainage systems via waste water from mining, industrial and urban/domestic sources is reflected in the presence of high levels of contaminant metals in solution, suspended matter and fine sediment, where the metals are associated with clays, precipitates (hydrous oxides, carbonates, phosphates, sulphides) and organic matter. Particularly large anomalies are found in some acid mine waters and in sediments below mines and some industrial sources. Förstner (1981a) records that human activities are reflected in polluted fine lake sediments by a Cd, Hg, Pb, Zn, (Cu, C) association and Hirner et al. (1990) found that organic fractions were enriched in As, B, Cd, Co, Cr, Cu, Fe, Pb and Zn. Urban and industrial areas frequently overlap and generate a common pollution signature which may involve enrichment of a very wide range of metals in the fine fractions of stream sediments. Elements noted as enriched in drainage from one or more industrial areas include Ag, As, Cd, Co, Cr, Cu, Fe, Mo, Mn, Ni, Pb, Sb, Sn, V and Zn. Those which appear to be enriched in the fine sediment of streams draining virtually all urban areas are Pb and Zn. In many cases Cd, Cr, Cu and Hg are also enriched. It is suspected that levels of some other metals, such as Ag, Sb and Sn are also often affected, but these conclusions may be biased by the incomplete range of metals determined by many investigations.

Some forms of urban contamination provide distinctive signatures in sediment. Motor vehicles cause enrichment in lead via street run-off water, whilst contamination from oil/petroleum sources can often be identified by the relatively high level of vanadium, perhaps associated with increases in cobalt, nickel or molybdenum. High levels of silver are associated with photographic processes and high levels of chromium are a feature of wastes from the leather, textile or electroplating industries. These wastes commonly give rise to elevated levels of chromium in the fine fractions of polluted stream sediments (e.g., Gephart and Long, 1981). In contrast, the natural sources of chromium sought during mineral exploration surveys are often present as coarse grained, dense resistate phases such as chromite, so in this situation there is a good chance of readily distinguishing the natural and pollutant sources by, for example, panned concentrate sampling.

Metal, coal and oil shale mining activity may produce signatures in stream sediment that are very similar to untapped mineralisation or metalliferous dark mudstones respectively. However, differences, for example in element ratios or speciation, are often present and the range of anomalous metals downstream of mine workings may be enhanced by associated human activities to include elements such as tin that are not enriched in the natural occurrences.

Less information is available on contaminant signatures in panned concentrates but work in Britain shows that domestic/urban sources of pollution produce anomalies characterised by tin and lead, often accompanied by high levels of antimony, copper, zinc or nickel. Contaminant sources, except for old mine workings, rarely produce barium anomalies in panned concentrates whereas mineralised sources do so commonly, due to the presence of baryte.

In summary, close associations of metals in any sample type which are rare in nature, such as chromium or nickel with cadmium, tin or mercury provide a strong indication of urban/industrial contamination, whereas the presence of high levels of barium with chalcophile elements such as copper, lead, antimony and zinc is a good indicator that these elements have at least in part come from a natural source.

Agricultural pollution, except where sewage sludge is a source, tends to be characterised by elevated levels of only one or two metals, notably copper or mercury in fine sediment or copper, uranium or fluoride in water. Panned concentrates would not be anomalous, but dumping from farms of domestic/metallic waste can confuse the signature by creating a wider range of anomalies, particularly in panned concentrates.

Atmospheric deposition, even where intense close to metal smelters, does not always generate drainage anomalies. Galloway et al. (1982) concluded that Ag, Cd, Cu, Pb, Sb, Se and Zn can be expected to show the greatest increases due to human activity with little or no increases in Co, Mn, Ni and Tl. Run-off, enriched in Pb and Zn, and dumping from roads is more likely to be a direct cause of drainage anomalies than the lead-rich airborne pollutants from motor vehicles, which in many cases are effectively fixed in soil. The features of airborne pollutant anomalies are that they will be concentrated in the fine fractions of sediment and give rise to broad regional-scale anomalies for metals such as Cd, Pb and Zn, depending on source.

Besides the absolute levels or association of elements in a given sample type or extract from it, element ratios can provide useful signatures to distinguish contaminants. Some examples have already been given, for example Pb/Zn (Taylor, 1968), Zn/Cd, Cr/Al and Mn/V. Other useful signatures may be generated by the ratio of a single metal between two extracts of a partial extraction scheme or two different sample types. Combinations of all these variables may be needed, particularly to discriminate worked and untapped mineralisation.

From the above discussion it is evident that in some areas additional elements may need to be analysed solely to allow determination of clear element signatures associated with pollutants and natural sources. For example tin is nearly always worth determining in contaminated terrains for this purpose and, depending on the sample media and sources of pollutants, cadmium, antimony and mercury should also be considered. Barium should often be determined for precisely the opposite reason; it is commonly associated with some styles of mineralisation but contamination rarely generates significant anomalies. In some cases consideration should also be given to determining elements which form anions, such as phosphorus and fluorine, as a means of characterising contaminants (e.g., Reddy, 1980).

CONCLUSIONS

(i) As time passes more areas are becoming affected by a significant degree of pollution which masks or modifies the dispersion of metals from natural anomalous sources. Even so called rural areas can have significantly contaminated drainage from agricultural activity or spillage and tipping from lines of communication, but in some long-industrialised areas pollution is decreasing. A feature of contaminated drainage is that, in geological terms, it is a recent phenomenon and rarely extends below 0.50 m in an undisturbed pile of lake sediment.

(ii) The main sources of pollution affecting drainage samples are solid and liquid waste from urban, industrial and mining areas and lines of communication. These sources often increase the concentrations of commonly used metals such as zinc, lead and tin 100 fold above background in drainage samples collected from near the source of contamination, and anomalies may persist in fine sediment for more than 100 km downstream of source. Agricultural sources may also provide problems in rural areas, particularly in fine sediment and water samples. Except where intense, such as downwind from smelters, airborne pollution may raise the background but does not otherwise normally interfere with drainage surveys for mineral exploration purposes. The majority of metals are concentrated in the fine fractions of natural sediments; contaminants are also often concentrated in these fractions, but at least locally coarse metal-rich contaminant detritus may also be present. Metals from both natural and contaminant sources are concentrated in, or on the surface of, organic matter, clay minerals and precipitates (hydrous oxides, carbonates, phosphates, sulphides) in the fine sediment. The partition of metals from different sources between these phases will vary between areas and even seasonally, depending on source and drainage environment. Although imperfect, selective or sequential chemical analysis methods provide a means of distinguishing these differences.

(iii) The use and effectiveness of a geochemical drainage survey for mineral exploration purposes in a contaminated terrain depends on the ability to discriminate metal concentrations from natural and anthropogenic sources. Therefore, before embarking on such a survey, orientation studies should be carried out to determine the most cost-effective method of reducing, eliminating and/or discriminating the effects of contamination and maximising the signature from the target sought.

(iv) Pollution can be avoided by sampling lake and overbank river sediment that was deposited before the onset of industrial activity in the area concerned. Care must be taken to ensure that locally pollutants have not been leached from or carried through the upper layers of sediments and deposited in the older strata.

(v) In contaminated drainage samples, anomalies due to pollution can be reduced or discriminated from those of natural origin by a number of physical, chemical, mineralogical and statistical techniques, but the effectiveness of individual methods is greatly dependent on local conditions. A combination of methods is normally most effective.

(vi) Additional elements may need to be determined when carrying out a survey in a contaminated terrain solely to determine the effect of contamination. The most useful urban/industrial indicators are those metals with low Clarke values that are used extensively in manufacturing industry (e.g., Cd, Hg, Sb, Sn and, possibly, Ag and Se). Other elements which may be useful because of their different natural and anthropogenic associations include Al, B, Cr, F, P and Pb.

(vii) Drainage surveys of contaminated terrains for mineral exploration purposes are a practical proposition, but particular care is required at the planning, sampling and interpretation stages. Consequently, a survey of a contaminated terrain will be more expensive than one of comparative size in a relatively unpolluted area.

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Chapter 14

DRAINAGE GEOCHEMISTRY IN GOLD EXPLORATION *

IAN NICHOL, MARTIN HALE and W.K. FLETCHER

INTRODUCTION

Gold, which has been the focus of much exploration over the last fifteen years due to its attractive price, has some unique properties that require the use of special techniques in the search for new deposits. The objective of this chapter is to review the application of drainage geochemistry to gold exploration. The historical background is considered first, followed by brief accounts of the geology of gold deposits, the geochemistry and sedimentology of gold. Subsequently, sample representativity and procedures for the analysis of gold and its pathfinder elements are reviewed: selected case histories which draw attention to the varying responses of different sample media are also discussed. Finally, attention is focused on aspects to be taken into account in identifying the optimum methodology for undertaking drainage surveys in the search for gold deposits.

BACKGROUND

Modern exploration geochemistry can trace its origins to 19th century and earlier prospectors who searched for both bedrock and placer deposits of gold by panning stream sediments. The method relied on the recognition of gold grains in the heavy-mineral panned concentrate and tracing the origin of the gold grains to their source. The same method is used today, although it has been extensively refined and modified.

The twenty-five year period 1955–80 witnessed the development of geochemical exploration methods suited to the search for a wide variety of deposit types in a range of surface environments. However, prior to the marked increase in the price of gold in the late 1970's, gold exploration attracted only limited interest with little or no emphasis on the development of appropriate techniques. Until this relatively recent activity earlier geochemical exploration mostly involved the detection of anomalous concentrations of pathfinder elements, such as arsenic, antimony or mercury, on account of their frequent association with

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* Manuscript of Chapter 14 first submitted in October 1988.

gold deposits, their higher concentrations, more homogeneous distribution and easier analytical determination than gold itself (R.W. Boyle, 1979b). However, the weakness of this approach lies in the fact that not all gold deposits have anomalous associations of pathfinder elements, and not all anomalous zones of pathfinder elements are associated with gold mineralization. During the late 1960's, however, more sensitive analytical techniques for gold became available with detection limits of the order of 5 ppb or less which in many cases were suitable for detecting anomalous gold concentrations in drainage sediments. The significant increase in the price of gold in the late 1970's and early 1980's coupled with the depressed prices of many other metals was accompanied by a very marked increase of interest in gold exploration. This activity was characterized by a greater emphasis on the direct determination of gold using the relatively new and highly sensitive analytical procedures, in preference to the tradition use of pathfinders.

GEOLOGY OF GOLD DEPOSITS

Gold deposits occur in a variety of geological environments. R.W. Boyle (1979b) classified them in terms of host lithology and structural control as: disseminations in igneous, volcanic and sedimentary rocks; skarns; porphyry dykes, sills and pegmatites; and veins, stockworks, lodes, sheeted zones, silicified bodies and saddle reefs in bedding plane discontinuities, shears, faults, fractures, drag folds and breccia zones. Their principal modes of genesis are hydrothermal, metamorphic and placer (Table 2-III), with those of hydrothermal origin exhibiting alteration and mineralization assemblages (Lewis, 1982) ranging from chlorite–carbonate or silicate in the case of deep seated deposits to propylitic and alunitic in epithermal deposits.

Analyses of gold grains have indicated the existence of variations in element associations not only with metallogenetic provinces (Warren and Thompson, 1944), but also with deposit type in a given area (Gay, 1963; Denisov et al., 1966; and Antweiler and Campbell, 1977). In a compilation of data on gold deposits in Ontario, Hodgson et al. (1982) classified deposits into four types according to their geological characteristics and noted considerable variations in their associated ore assemblages of galena, molybdenite, tellurides, scheelite, arsenopyrite and sphalerite, even within a given deposit type. The composition of gold grains from gold deposits of Ontario has been shown to vary according to deposit type (Guindon and Nichol, 1983). On the above basis, gold deposits present diverse targets in terms of their geological setting and mineralogical characteristics and further variations may be introduced as a result of their weathering history and present day surface environment.

In areas where a high level of geological information is available, and gold deposits are of a type characterized by minerals or elements that can be used as pathfinders then the use of pathfinders in geochemical exploration may be advantageous. On the other hand, where the base level of geological information in an area of interest is low and there is a potential diversity in the character of gold deposits and their associated minerals and element associations, there are clearly limitations to basing exploration on the determination of pathfinder elements and clear advantages in directly determining gold contents. A critical feature to be considered in exploration is the design of an appropriate programme having regard to the fact that the mode of occurrence of gold in different types of deposits varies significantly from coarse grained to micron sized gold particles so account should be taken of the size distribution of gold particles in different types of deposits.

GEOCHEMISTRY OF GOLD IN THE SURFACE ENVIRONMENT

Insofar as one of the keys to successful exploration is an understanding of the character of the gold deposit being sought, the mode of dispersion and of accumulation in a given environment, brief consideration is given to the geochemistry of gold in the low temperature or surface environment.

Traditionally the commonly held view that gold is insoluble in the surface environment and is transported mechanically has, until recently, dominated the design of exploration programmes for gold deposits. In 19th and early 20th century literature in both Australia and the United States there are several references indicating that gold can be dispersed chemically in the surface environment. For example, early miners in the California gold rush suggested that some of the gold had been concentrated by solution and reprecipitation (in Evans, 1981). The occurrence of nuggets in alluvial deposits larger than any found in bedrock deposits, together with the higher fineness (purity) of the alluvial gold, also led to the suggestion that alluvial gold formed, at least in part, by precipitation from solution. In addition, experimental data showed that gold is precipitated from dilute solutions in reducing conditions related, for example, to the presence of organic matter (Landsweert, 1869, in Evans, 1981). Furthermore, the considerable difference in many cases between the character of gold in alluvial and vein deposits as evidence for the two types having different origins, recognised by Bischoff, was described by Landsweert (1869).

In Australia the relationship between alluvial gold, gold nuggets and particulate gold in the weathered zone and gold in bedrock was, according to Mann (1984a), discussed by Brough-Smyth (1869). Gold of higher fineness in the weathered zone than associated primary gold and of crystalline nature suggestive of transport in solution and subsequent deposition from a low-temperature aqueous solution was described by Liversidge (1893). Subsequently the occurrence of gold of higher fineness and crystalline form in the weathering environment relative to primary mineralization was described from Western Australia by Simpson (1902). In relation to Western Australia, Gibb-Maitland (1919) stated "The mode of occurrence, associations, and character of this gold (gold in the weathering zone) all point to a secondary origin; this secondary gold has been deposited from solution not only in some cases in the alluvium and other superficial and residual deposits, but also in the zone of decomposition of the bedrock." Thus from the early days of geochemistry there was evidence that gold, under certain conditions, was soluble and could be dispersed chemically.

A number of investigators have cited experimental data indicating the solubility of gold in chemical solutions that may occur in the weathering environment. For example, the dissolution of Cripple Creek ore in a solution of ferric sulphate, sodium chloride and sulphuric acid and subsequent precipitation in the presence of organic matter was noted by Clarke in 1908 (Clarke, 1924). The ability of ferric salts to dissolve gold was confirmed by McCaughey (1909) but it was reported that addition of ferrous ions to these solutions inhibited the dissolution of gold. Later the dissolution of gold in, and subsequent precipitation from, sodium sulphide solutions at low temperatures was noted by Smith (1943). Based on theoretical considerations, the importance of the chloride ion, low pH and oxygen (redox potential) on the solubility of gold was described by Krauskopf (1951). Gold has been shown to be dissolved in significant quantities at low pH with sodium chloride in the presence of crushed pyrolusite in acid chloride solutions by Cloke and Kelly (1964).

Gold can occur as the monovalent or trivalent ion but gold occurs in aqueous solution mainly as a variety of complex (chlorides, bromides, iodides, cyanides, thiocyanates, thiosulphates and hydroxides) anions (Lakin et al., 1974; R.W. Boyle, 1979b). The ease of oxidation of gold to form complex anions increases in the order chloride, bromide, thiocyanate, thiosulphate, iodide and cyanide (Table 14-I); the chloride and cyanide complexes being reportedly the most important in the surface environment. Experimental data suggest that the tendency for gold to be removed from solution (either by sorption or reduction to gold metal) decreases in the order: chloride, bromide, iodide, cyanide, thiocyanate and thiosulphate (Table 14-II). In particular, the halide anion complexes are much less stable and thus less mobile than the cyanide, thiocyanate and thiosulphate complexes.

However (to quote Mann, 1984a, p. 39), "Despite the numerous field observations indicating solution migration of gold, and the numerous laboratory experiments indicating the types of solutions likely to be responsible for solu-

TABLE 14-I

Relation of gold complex to oxidation potential. From Lakin et al. (1974)

	E (volt)
Cl_4^{-1}	−1.00
Br_4^{-1}	−0.87
$(CNS)_4^{-1}$	−0.66
$(S_2O_3)_2^{-2}$	−0.65
Aul_2^{-1}	−0.50
$Au(CN)_2^{-1}$	−0.20

TABLE 14-II

Number and type of minerals which remove over 90% of gold from solutions of various complexes. From Lakin et al. (1974)

Mineral groups (No.)	Cl^{-1}	Br^{-1}	I^{-1}	CN^{-1}	CNS^{-1}	$S_2O_3{}^{-2}$
Sulphides (20)	20	19	13	3	2	2
Silicates (30)	7	7	1	–	–	–
Oxides (26)	7	5	1	–	–	1
Carbonates (5)	3	2	–	1	–	–
Other minerals (28)	10	9	6	1	–	–
Carbonaceous matter (7)	5	5	2	1	2	–
Percentage	45.6	41.2	20.2	5.3	3.5	2.6

tion migration of gold in nature, there have been few, if any, detailed attempts to link closely field observations with laboratory experimentation." The existence of gold-rich rims in nuggets and crystalline gold grains within the lateritic weathering profile of Western Australia is indicative of dissolution, transport and precipitation of gold during lateritization.

The chemical mobility of gold in the surface environment has been attributed to dissolution and precipitation from chloride, thiosulphate and organic complexes (Butt, 1989a; Table 14-III) based on work by Baker (1978), Mann (1984a, b), Webster and Mann (1984), Webster (1986), and Stoffregen (1986). Strongly acidic chloride solutions produced in lateritic profiles by ferrolysis account for the dissolution of gold and silver. High-fineness gold is subsequently reprecipitated in the mottled zone by reduction of the $AuCl_4^{-1}$ ion with Fe^{+2} whereas Ag stays in solution as $AgCl^0$. In contrast under neutral to basic, moderately oxidizing conditions, gold and silver are dissolved as the respective complex thiosulphate ions and subsequently reprecipitated as a gold–silver alloy at the water table by oxidation in the MnO_2 wad assemblage (Webster and Mann, 1984). In this situation the reprecipitated gold tends to be of low fineness.

Organic complexes may also give rise to mobilization, transport and reprecipitation of gold in the surface environment.

Additional evidence for the chemical mobility of gold during weathering, in part substantiating earlier indications, falls into different categories and relates to different parts of the world and is as follows:

(1) Differential concentration of gold in the weathering zone of mineralization: Nigeria and Tanzania (Mackay, 1944); United States (Kinkel and Lesure, 1968); Papua New Guinea (Webster and Mann, 1984); Australia (Davy and El-Ansary, 1986; Glasson et al., 1988); and Cameroon (Freyssinet et al., 1989a).

(2) Variation in the grain size of gold in the overburden or weathering profile: Mali (Bassot and Traoré, 1980; Freyssinet et al., 1989b); United States (Evans, 1981); Bolivia (Tistl, 1986); Brazil (Michel, 1987; Rao, 1987; De Oliveira and Campos, 1991); India (Nair et al., 1987); and Australia (Glasson et al., 1988).

(3) Increased fineness of gold within laterite profiles and/or chemical zoning of gold grains relative to bedrock sources: Nigeria and Tanzania (Mackay, 1944);

TABLE 14-III

Gold solution and precipitation mechanisms. From Butt (1989a)

1 *Thiosulphate complexes*

1A Pyrite oxidation: high carbonate, alkaline, mildly oxidizing
$2FeS_2 + 4CaCO_3 + 3H_2O + 3.5O_2 = 2FeO(OH) + 4Ca^{2+} + 4HCO_3^- + 2S_2O_3^{2-}$

1B Pyrite oxidation: low-moderate carbonate, mildly acid-mildly alkaline, oxidizing
$2FeS_2 + 3O_2 = 2Fe^{2+} + 2S_2O_3^{2-}$

Gold dissolution
$Au^0 + 2S_2O_3^{2-} = Au(S_2O_3)_2^{3-}$
(electrum)

Gold precipitation: oxidation, acidification
$4Au(S_2O_3)^{3-} + MnO_2 + 4H^+ = 2Au^0 + 2S_4O_6^{2-} + Mn_{2+} + 6H_2O$
(electrum)

Gold precipitation: reduction, acidification
$2Au(S_2O_3)^{3-} + 2H^+ = 2Au^+4S^0 + SO_4^{2-} + H_2O$
$Au^+ + Fe_2 + 2H_2O = Au^0 + FeO(OH) + 3H^+$
(electrum)

2 *Organic complexes*

Gold dissolution: neutral-acid, oxidizing
$Au^0 + H^+ + organicacid + O_2 = Au[humate]^{3+} + H_2O$
(electrum)

Gold precipitation: reduction
$Au[humate] + Fe_{2+} = Au^0 + organicacid + Fe^{3+}$
(fine gold)

3 *Chloride complexes*

Gold dissolution; acid, oxidizing, saline
$4Au^0 + 16Cl^- + 3O_2 + 12H^+ = 4AuCl_4^- + 6H_2O$
(electrum)

Gold precipitation: dilution, alkalinity or reduction
$AuCl_4^- + 3Fe_{2+} + 6H_2O = Au^0 + 3FeO(OH) + 4Cl^- + 9H^+$
(fine gold)

United States (Evans, 1981); Brazil (Michel, 1987; De Oliveira and Campos, 1991); and Australia (Glasson et al., 1988).

(4) Form of gold which may be present as distinct crystals, colloform textures of mobilized gold and associated iron hydroxides precipitated contemporaneously, or botryoidal gold nuggets and gold nuggets containing detrital quartz grains: West Africa (Bonnemaison, 1986); Canada (Warren, 1982); Australia (Webster and Mann, 1984; Wilson, 1984; Davy and El-Ansary, 1986; Glasson et al., 1988); Papua New Guinea (Webster and Mann, 1984); Burkina Faso (Huot et al., 1987); Niger (Gleeson and Poulin, 1989); Fiji (DiLabio et al., 1988); and Brazil (De Oliveira and Campos, 1991).

The processes operative in a given area are largely related to climate and geomorphology. Two major types of gold deposits have been suggested to form as a result of chemical mobilization, transport and accumulation in the surface environment, i.e., lateritic gold deposits and supergene gold deposits (Butt, 1989a). Such deposits are considered to have formed initially under tropical lateritic weathering conditions and to have been modified subsequently during different climatic and geomorphological conditions (Figs. 14-1 and 14-2; Butt, 1989a, b; Gray et al., 1992). During the Cretaceous to mid-Tertiary extensive areas between latitudes 35° N and 35° S were characterized by seasonally humid tropical climates; but after the mid-Tertiary the climate changed to conditions similar to the present day. Moreover, many continental landmasses (e.g., Western Australia) have been exposed to sub-aerial weathering since the Proterozoic (Ollier, 1978) which together with changing climatic conditions and uplift, has given rise to a range of weathering surfaces (Fig. 14-3; Butt, 1989b). The existence of six weathering surfaces from Lower Paleozoic to recent in age has also been noted in northern Sierra Leone (Fig. 14-4; Macfarlane et al., 1980). Hence landscapes in many parts of the world represent varying degrees of downcutting and truncation with the surface soils having been derived from significantly different parent material (Fig. 14-5; Butt and Smith, 1980). The influence this has had on the gold distribution in drainage systems requires consideration.

A considerable number of investigations have been undertaken in various parts of the world to establish the relation of alluvial gold to primary sources. These include studies of:

(1) Zoning in the composition of gold grains, mostly with gold-rich rims but in some cases silver-rich rims which have variously been related to primary or secondary deposition of gold and the leaching or deposition of silver: United States (Desborough, 1970; Desborough et al., 1970, 1971; Groen et al., 1990); Sumatra (Bowles, 1988); Sierra Leone (Davies et al., 1989).

(2) Compositions of the cores of gold grains or entire gold grains which have been attributed to heterogeneity of the primary mineralization or multiple sources: United States (Desborough, 1970; Desborough et al., 1971; Antweiler and Campbell, 1982, 1987; Mosier et al., 1989); Canada (Knight and McTaggart, 1986).

(3) Evidence of deposition from solution on the basis of the occurrence of octahedra: Canada (Warren, 1979, 1982; Giusti, 1986).

(4) Increase of fineness downstream indicative of chemical dispersion: United States (Desborough, 1970); South Africa (Hallbauer and Utter, 1977); and Sumatra (Bowles, 1988); whilst on the other hand no variation in fineness was noted in Canada by suggesting that leaching took place prior to transport (Giusti and Smith, 1984).

(5) Decrease of fineness with decreasing grain size: Canada (Giusti and Smith, 1984).

The evidence suggests that the relationship between alluvial and primary gold is complex and an understanding of local weathering processes, soil chemistry and groundwater flow patterns is essential for understanding the

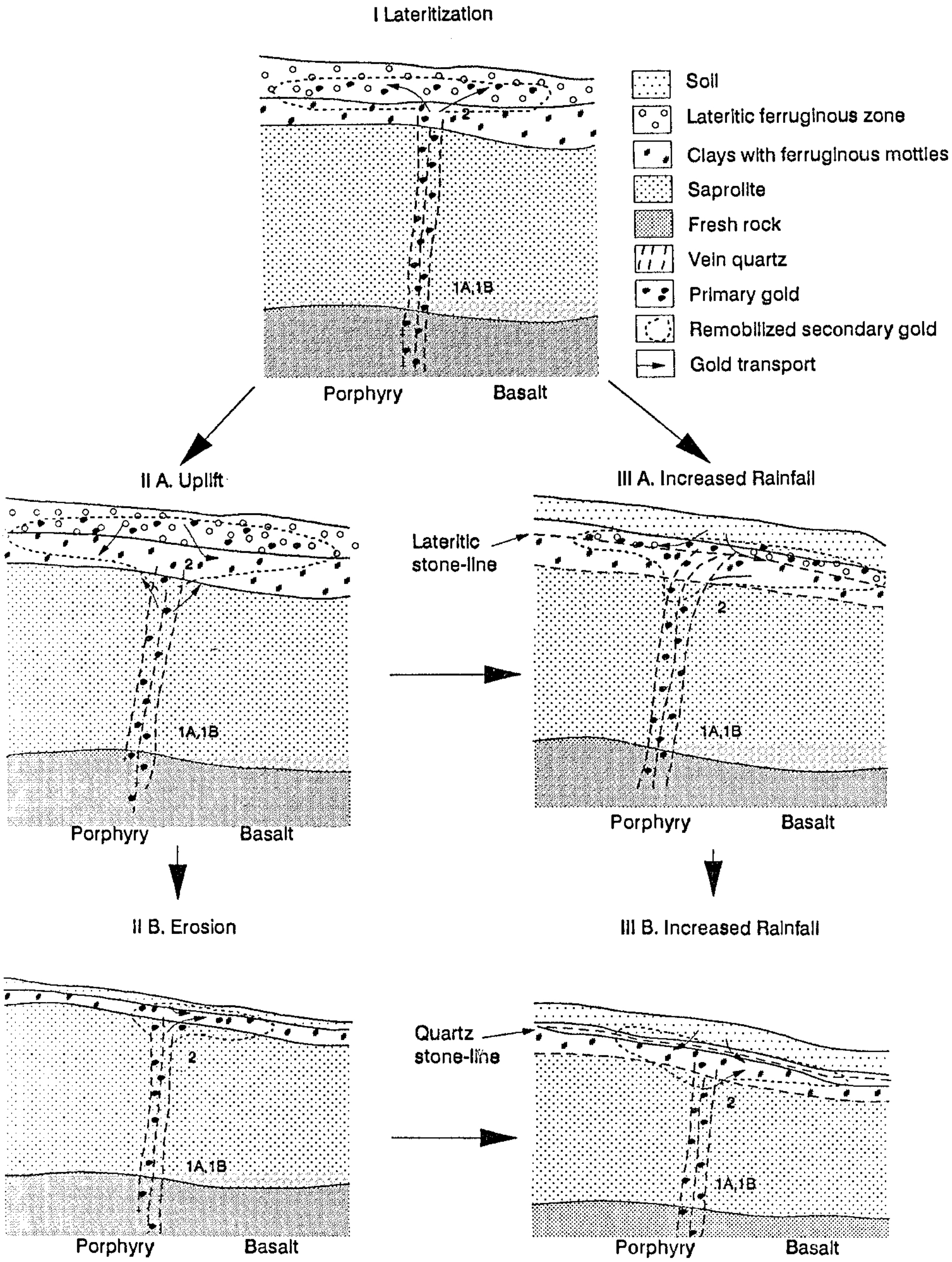


Fig. 14-1. Model illustrating the modification of gold dispersion patterns as a result of uplift and a change to a rain forest climate. Numerals refer to possible gold mobilization reactions given in Table 14-III. Reproduced with permission from Butt (1989a).

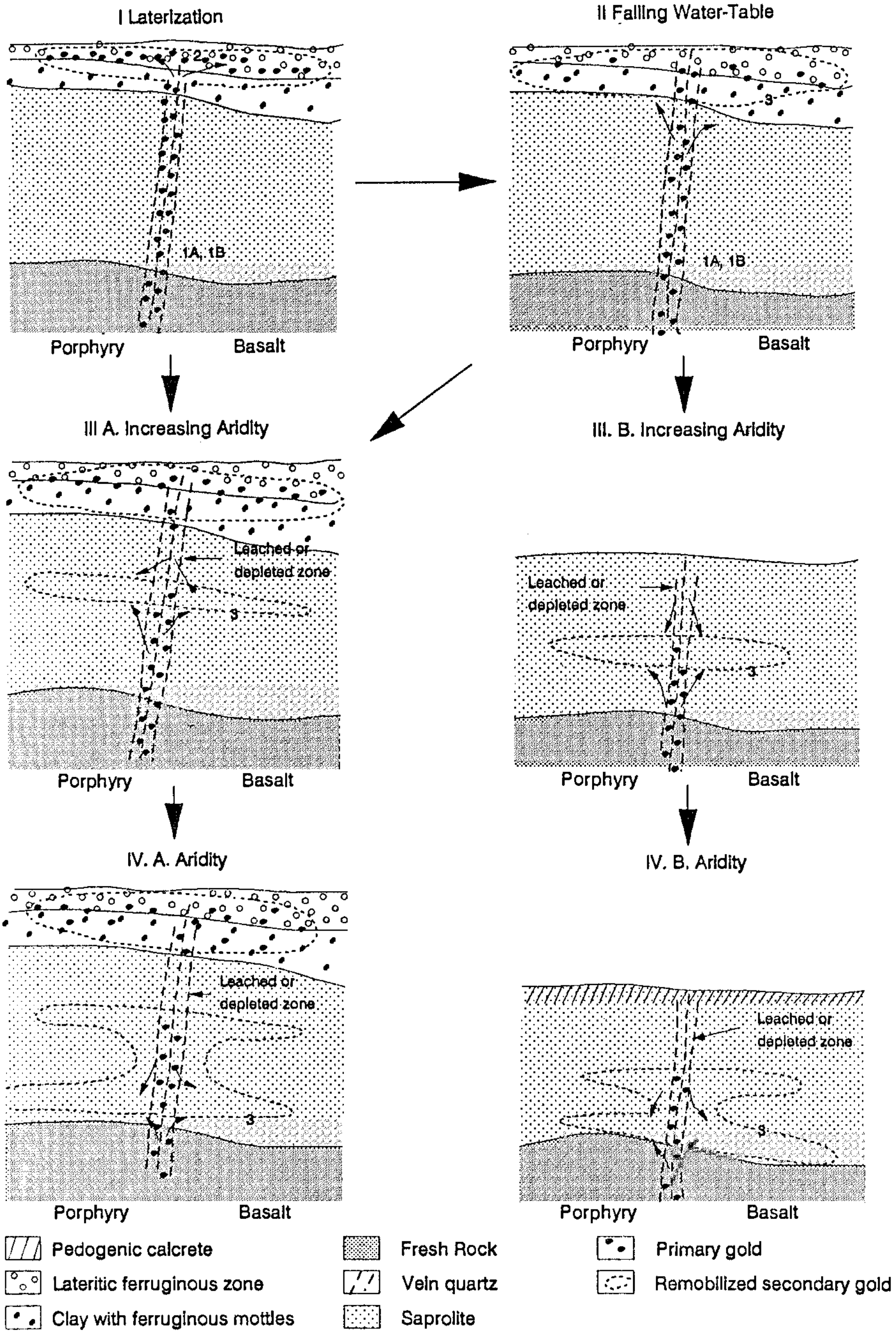


Fig. 14-2. Model illustrating the modification of gold dispersion patterns as a result of uplift and a change to an arid climate. Numerals refer to possible gold mobilization reactions given in Table 14-III. Reproduced with permission from Butt (1989a).

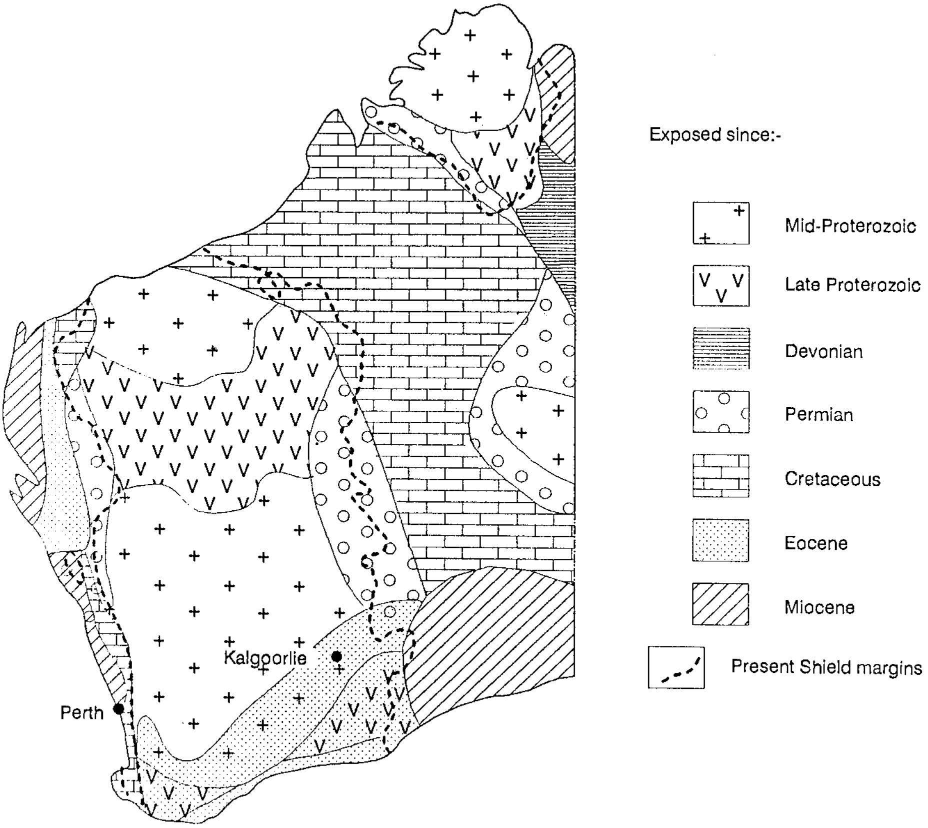


Fig. 14-3. Periods of exposure to subaerial weathering, Western Australia. Reproduced with permission from Butt (1989b), Economic Geology, Mon. 6, p. 463.

relation of alluvial gold (in effect, gold in stream sediments) and its bedrock source.

SEDIMENTOLOGY OF GOLD IN DRAINAGE SEDIMENTS

Anomalous levels of gold in drainage sediments, together with other elements dispersed in drainage sediments as major constituents of rare heavy minerals are typically erratic and difficult to verify (Fletcher and Day, 1988c, 1989) frequently because samples normally collected are too small to be representative. Even when care is taken to obtain representative samples gold concentrations can vary markedly as a result of varying hydraulic processes in the stream and the different responses of high- and low-density minerals during transport (e.g., Fletcher and Day, 1988c, 1989; Day and Fletcher, 1989). However, before considering these processes further it is necessary to briefly review the principles underlying drainage surveys.

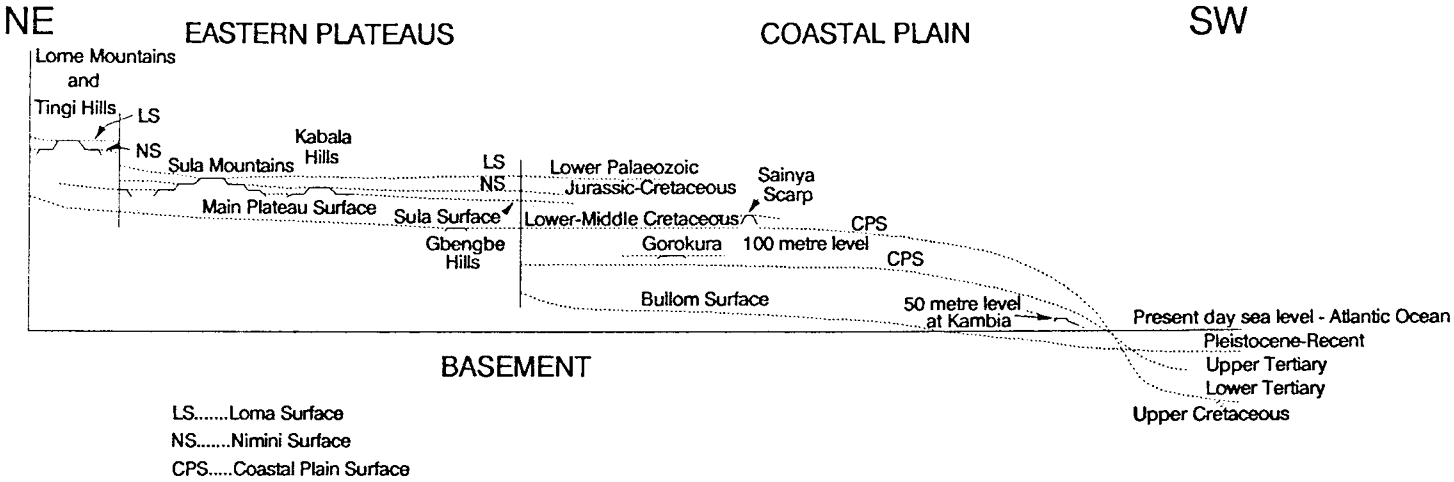


Fig. 14-4. Planation surfaces in northern Sierra Leone. Modified after Macfarlane et al. (1980).

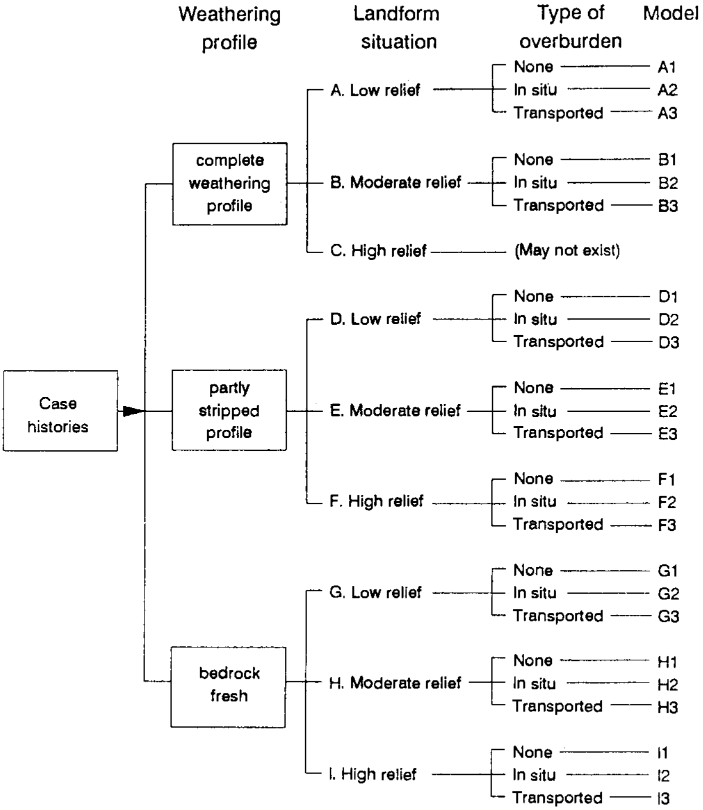


Fig. 14-5. Hierarchical classification of landform situation and models. From Butt and Smith (1980).

Stream sediments are generally assumed to be representative of the geochemistry of catchment basins upstream of sample sites. The point of maximum metal values is usually considered to be close to the source of the anomalous values and to provide the starting point for follow-up exploration.

A downstream dilution model for sediment sampling programmes was described by Hawkes (1976a) as follows:

$$\mathrm{Me_m A_m = A_a(Me_a - Me_b) + A_m Me_b},$$

where the terms are those defined in Fig. 14-6. This model, which implies a smooth exponential decay of the anomalous dispersion train downstream from the cut-off point (Fig. 14-7), is based on an assumption of: uniform rate of erosion; uniform background; no feedback between water and sediment; no sampling error; a single anomalous source; and no contamination. Moreover, within a given size fraction, the various components of the sediments must be transported at the same rate and without sorting. However, the high density of gold frequently results in a lower transport rate than for the less dense

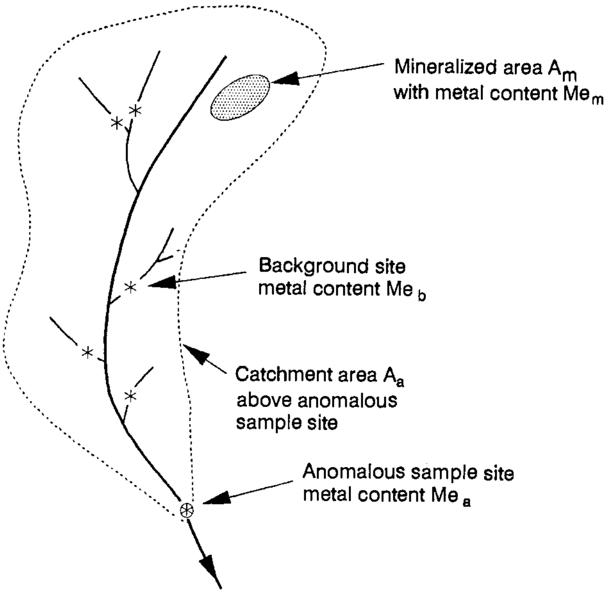


Fig. 14-6. Anomaly dilution model, definition of parameters. Modified after Hawkes (1976a).

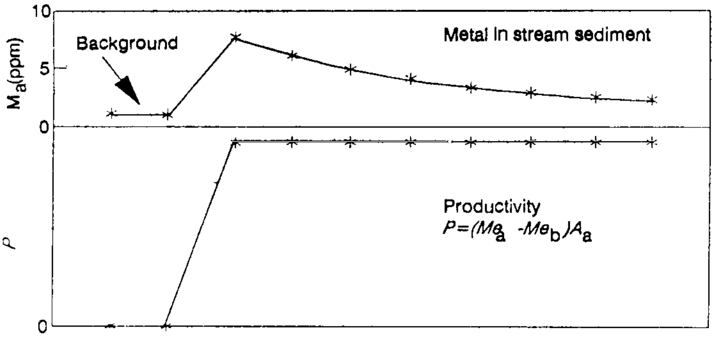


Fig. 14-7. Anomaly dilution curve and Productivity (*P*). See Fig. 14-6 for definition of parameters. Reproduced with permission from Rose et al. (1979).

minerals, so that it tends to be concentrated in depositionally favourable areas of the stream bed. From the perspective of an exploration geochemist such differential enrichments can be both an advantage (anomaly enhancement) or disadvantage insofar as the erratic nature of anomalous zones are at variance with the basic principles of traditional stream sediment dispersion patterns and thereby complicate survey design and interpretation.

Heavy-mineral placers have been classified by Slingerland (1984) according to scale along a stream's longitudinal profile namely at the bed (10^0 m), bar (10^2) and system (10^4) scales (Table 14-IV), which collectively are at variance

TABLE 14-IV

Observed sites of heavy-mineral accumulation in stream systems. Modified from Slingerland (1984)

System scale: 10^4 m	Heads of wet alluvial fans; points of abrupt valley widening; points of exit of highland rivers onto a plain.
Bar scale: 10^2 m	Concave sides of sharp bends; convex banks of meanders; heads of mid-channel bars; point bars with suction eddies; scour holes especially at tributary confluences; inner bedrock channels; bedrock riffles.
Bed scale: 10^0 m	Scoured bases of trough cross-strata sets; winnowed tops of gravel bars; tangential toes of foresets; tin ripple-form accumulations of dune stoss slopes; dune crests; dune foreset beds; plane parallel laminae; leeward side of obstacles.

with the normal downstream dilution model (Hawkes, 1976a). Heavy-mineral placers at the bed and bar scale can be considered as sources of local sampling variability. As system scale processes are a cumulative response to bed and bar scale processes acting along the longitudinal profile in conjunction with changes in stream gradient and discharge, it is useful to consider local processes first.

Accumulation of free gold particles on the bed of a stream will occur if their motion stops (deposition) or that of other minerals commences (erosion) under different conditions to that of the rest of the sediment. Processes that sort grains during sediment deposition or erosion are referred to as settling (or suspension), and entrainment sorting, respectively. Mineral grains that, despite differences in their physical properties, accumulate together on the stream bed exhibit either settling or entrainment equivalence depending on the processes involved. Settling equivalence is also sometimes known as hydraulic equivalence (Rubey, 1933; Rittenhouse, 1943). Similarly, Fletcher et al. (1992) refer to grains that, despite differences in their physical properties, have the same virtual transport velocities as exhibiting transport equivalence. They demonstrate that heavy minerals are transported at the same rate as specific larger sizes of less dense mineral grains.

The role of sorting processes in the development of stream placers has been discussed by Grigg and Rathbun (1969), Slingerland (1984), Reid and Frostick (1985), and Slingerland and Smith (1986). Settling sorting relates to the relative settling velocity of mineral grains (predicted by Stoke's equation for spheres <0.5 mm diameter) as determined by their size, shape and density. Discs or flakes of gold have settling velocities two to three times lower than gold spheres of the same mass (Table 14-V). Settling results in small particles of high density being deposited together with larger, less dense mineral grains (Fig. 14-8). Conversely, if grain size or shape result in heavy minerals having lower settling velocities than the bulk of the sediment being transported, they will tend to be transported higher in the water column and higher concentrations may be found in overbank (flood plain) deposits than in the sediments of the main channel (Slingerland, 1984). This might be particularly relevant to the behaviour of very fine flakes of "skim" gold.

TABLE 14-V

Measured settling velocities of gold particles of constant mass at various flatnesses. Modified from Walsh and Rao (1986)

Gold Mass (μg)	Shape *	Settling velocity (cm/sec)
31.0 (150 μm sphere)	1.0	9.0
	0.5	8.4
	0.1	4.1
	0.05	3.6
3.7 (75 μm sphere)	1.0	3.94
	0.5	3.68
	0.1	2.29
	0.05	1.56
1.1 (53 μm sphere)	1.0	2.29
	0.5	2.05
	0.1	1.19
0.6 (38 μm sphere)	1.0	1.35
	0.5	1.25
	0.1	0.78

* Corey Shape Factor = $C/\sqrt{ab}$ where a = long axis; b = intermediate axis; and C = short axis. n.b. A Corey Shape Factor of 1 = a spherical particle.

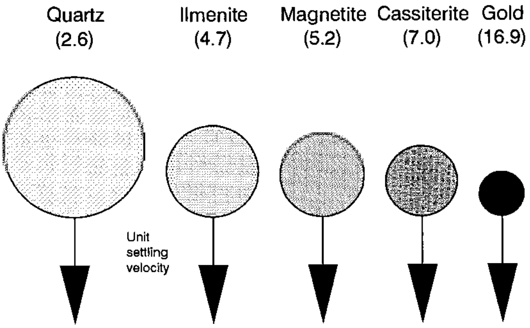


Fig. 14-8. Relative diameters of spheres of selected minerals having the same settling velocity as quartz. Modified after Reid and Frostick (1985).

Entrainment sorting is closely related to the criteria defined by Shields (1936) for the onset of grains in response to the shear stresses acting on them (Grigg and Rathbun, 1969). This threshold of motion for a grain, defined as the critical boundary shear stress, is shown for grains of gold, ilmenite and quartz in Fig. 14-9. As would be expected, denser grains are less easily entrained than less dense grains of the same size and can therefore concentrate on the bed as a lag deposit. Figure 14-10, from Ljunggren and Sundborg (1968), shows the optimum range of conditions of water velocity and grain size for this to occur. This simple entrainment model is valid only for uniformly sized grains.

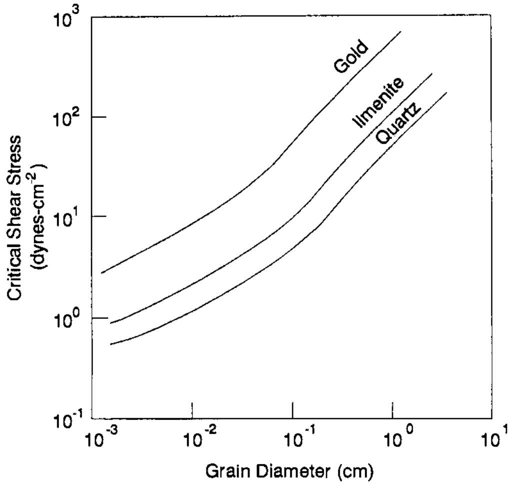


Fig. 14-9. The effect of density on the critical boundary shear stress required to initiate particle motion using densities for quartz, ilmenite, and gold of 2.65, 4.70 and 19.3 g/cm^{-3}, respectively. Modified after Slingerland and Smith (1986).

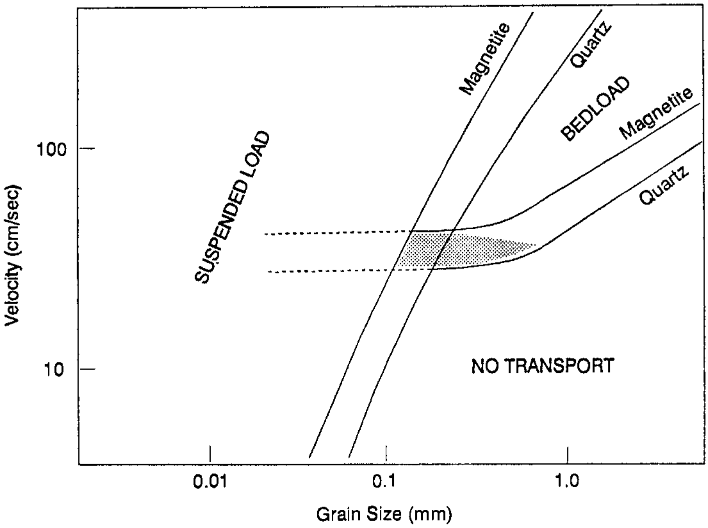


Fig. 14-10. Relation between water velocity, grain size and state of sediment movement for quartz (density 2.65 g/cm^{-3}), and magnetite (density 5.20 g/cm^{-3}). Shading indicates conditions particularly favourable to enrichment of the heavy minerals. Modified after Ljunggren and Sundborg (1968).

However, with reasonably well sorted sands it is likely that larger sand grains protruding further into the flow will be entrained more easily than the bed sediment as a whole (Reid and Frostick, 1985; Slingerland and Smith, 1986).

Entrainment thus sorts according to size as well as density and tends to narrow the size difference between light and heavy minerals that remain in the bed.

The shielding effect whereby large clasts protect smaller particles from turbulent flow is not allowed for in Fig. 14-9. Behaviour of heavy minerals is more generally predicted by transport sorting models that consider sediment transport based on: (i) physical properties of the grain — its size, shape and density; (ii) bed characteristics — particularly its roughness and ability to shield particles from full turbulent flow; and (iii) hydraulic conditions — channel width, depth, slope, flow velocity, discharge and loss of energy by friction against the beds and banks.

Many bedload transport formulae have been proposed. Probably none are capable of accurate, quantitative prediction of sediment transport rates in natural streams (Gomez and Church, 1989). However, they do provide a basis for studying the effect of varying conditions on relative transport rates of low- and high-density minerals. Slingerland (1984); Fletcher and Day (1988c, 1989); and Day and Fletcher (1991) have used the bedload transport formula of Einstein (1950) for this purpose.

Estimated rates of transport for quartz (density = 2.7 g/cm^3) and magnetite (5.2) grains moving over a cobble bed with empty voids are shown in Fig. 14-11.

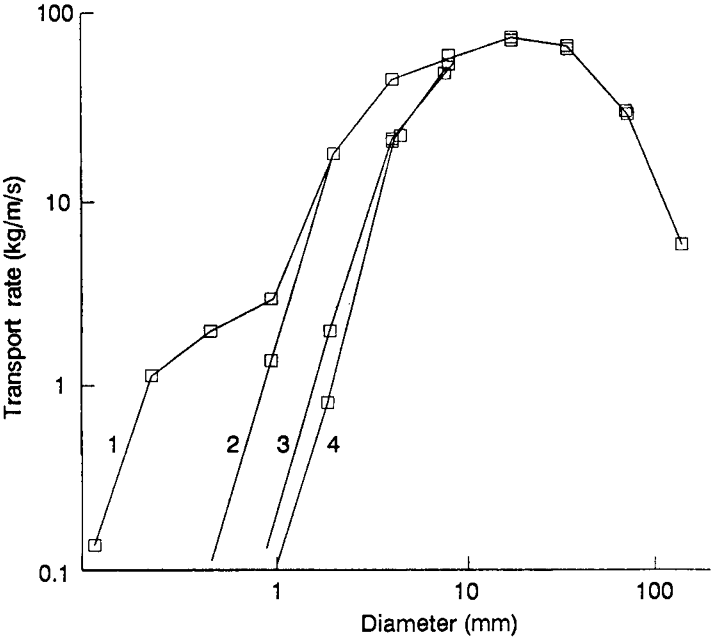


Fig. 14-11. Typical transport rates curves for quartz and magnetite moving over a gravel bed calculated using Einstein's bedload function. Curves (1) and (3) for quartz moving over gravel beds with characteristic roughness (D_{65}) of 4 and 8 mm, respectively. Curves (2) and (4) are the corresponding plots for magnetite. Modified after Day and Fletcher (1991).

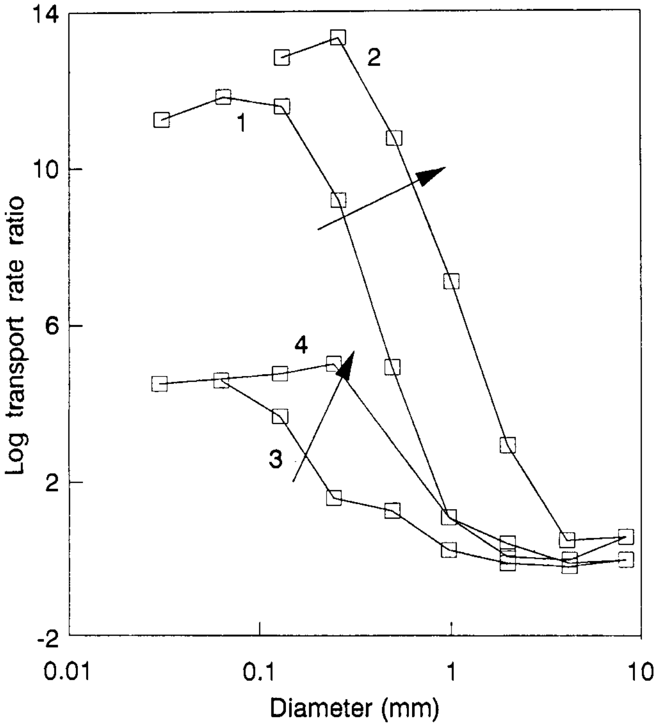


Fig. 14-12. Typical transport rate ratio curves for quartz : magnetite and quartz : gold calculated using Einstein's bedload function. Curves (1) and (2) for gold with a characteristic bed roughness (D_{65}) of 4 and 8 mm, respectively. Curves (3) and (4) the corresponding plots for magnetite. Arrows indicate direction of increasing bed roughness. Modified after Day and Fletcher (1991).

Grains close to the median diameter of the bed have the highest transport rates whereas transport rates for very fine particles are several orders of magnitude lower. In Fig. 14-12, curves similar to those of Fig. 14-11 have been ratioed to obtain log transport ratios of magnetite and gold to quartz for different bed roughness conditions. The higher the ratio, the greater the chance of quartz overpassing the bed while the heavy mineral is selectively trapped.

A high bed roughness (lines 2 and 4, Fig. 14-2) gives large transport rate ratios for sand size sediment and implies that large voids are favourable sites for the preferential accumulation of heavy minerals. Coarse gold is more likely to be trapped than fine gold, and gold, because of its density, is trapped to a much greater extent than magnetite. However, as bed roughness decreases the ability of the bed to selectively trap high-density minerals shifts towards the finer grain sizes. Thus preferential enrichment of sand sized, high-density minerals will continue as long as the surface half-voids remain empty, but will be reduced as infilling of voids decreases both bed roughness and the transport rate ratios.

Behaviour of very fine, silt-size particles requires further consideration. Most of this sediment will overpass the bed in suspension. However, as shown by the very low transport rates in Fig. 14-11, fine particles that do enter the bed are effectively immobilized whatever their density. In Einstein's bedload formula this reflects a "hiding" or shielding factor whereby small particles are protected from stream flow by larger particles. In the beds of natural streams, transport and infiltration of ultra-fine particles into the smallest passages within the bed will very effectively shield them from re-entrainment. Thus, although relative transport rates suggest the possibility of differential accumulation of very fine heavies, their low absolute transport rates mitigate against such enrichments actually developing (Fig. 14-12).

So far it has been assumed that stream channels are single, linear and unobstructed. However, natural streams flow around obstructions, meander, vary in width and have tributaries. Such changes in bed geometry can produce pressure gradients in the fluid and cause flow separation (Mosley and Schumm, 1977; Best and Brayshaw, 1985); and vortices and turbulence associated with flow separation promote winnowing of light materials and the development of heavy-mineral lag deposits at several scales (Figs. 14-13 and 14-14).

Changes in concentrations of gold along a stream's longitudinal profile will reflect a balance between downstream anomaly dilution (Hawkes, 1976a) and the cumulative effects of decreasing gradient and increasing discharge on the processes that favour accumulation of gold. Furthermore, because stream sediment surveys are often the preferred method of geochemical reconnaissance in hilly or mountainous terrains, there are likely to be large changes in stream gradient between sample sites on first order, headwater streams and third or fourth order streams sampled at lower elevations.

Calculations indicate that as the slope decreases to 1 or 2% the transport rate ratio for magnetite : quartz increases with the greatest response in the medium to coarse sand fractions (Fig. 14-15). Thus, as gradient decreases along the longitudinal profile and depending on the grain size distribution of gold

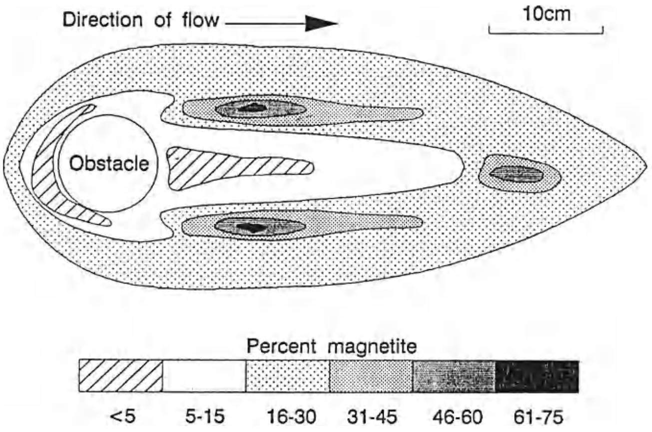


Fig. 14-13. Concentration zones of magnetite formed around an obstacle. Free stream magnetite content is 9%. Modified after Best and Brayshaw (1985).

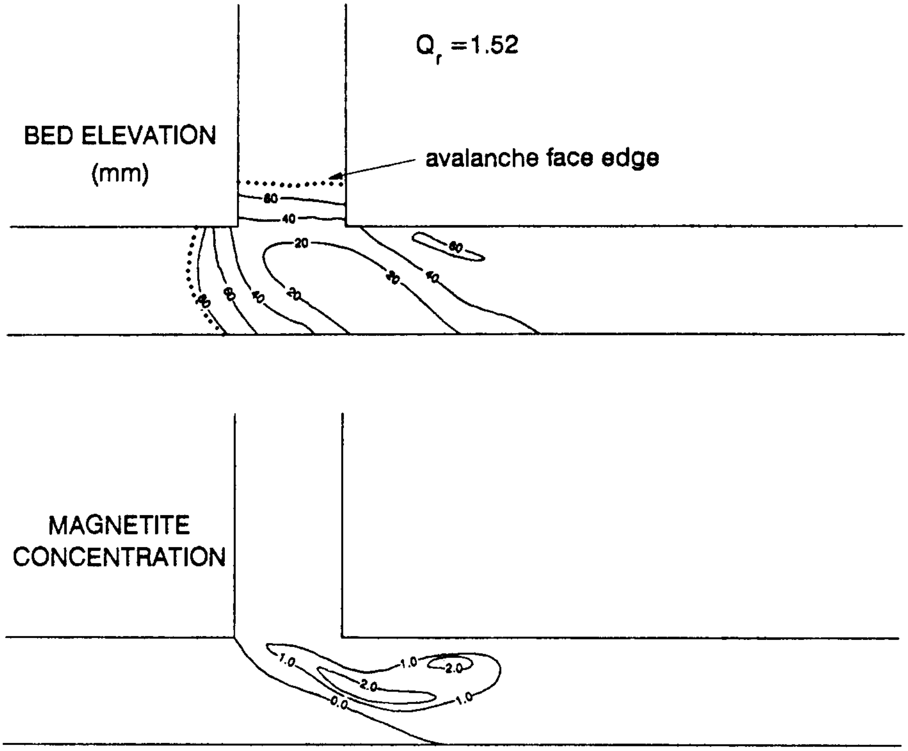


Fig. 14-14. Variations in concentrations of magnetite (%) at a channel confluence. Modified after Best and Brayshaw (1985).

and lighter minerals, a zone may be reached where conditions are particularly favourable for the preferential accumulation of gold and other heavy minerals. Placer gold deposits displaced downstream from their bedrock source are a well-known manifestation of this situation. This distribution pattern clearly diverges from the classical downstream dilution model for geochemical anomalies.

To summarize, it is apparent that local (bed and bar) scale variations of gold concentrations in streams are complex and poorly understood. Nevertheless, it is to be expected that coarse gold will in general preferentially accumulate in areas of high bed roughness or where flow separation increases turbulence. In these locations accumulation (sorting) efficiency will decrease with decreasing size of gold particles. Entrainment lag deposits can also develop on more uniformly sized, sandy beaches and overbank deposits could become enriched in particles of "skim" gold.

With regard to field observations the lore of placer miners for finding gold paystreaks in bar head gravels, bedrock riffles, in scour holes and at points of valley widening are all consistent with these theoretical processes. Table 14-IV and Fig. 14-16 summarize some common sites of heavy-mineral enrichment.

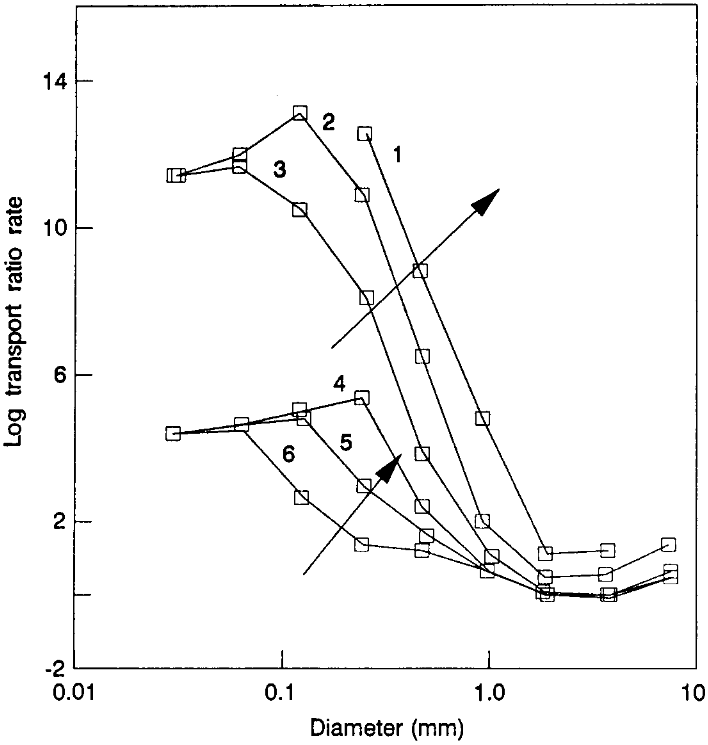


Fig. 14-15. Effect of stream gradient on transport rate ratios for quartz : gold and quartz : magnetite calculated with Einstein's bedload function. Curves (1), (2) and (3) for gold on slopes of 1, 2 and 4%, respectively. Curves (4), (5) and (6) the corresponding plots for magnetite. Arrows indicate direction of decreasing slope. Modified after Day and Fletcher (1991).

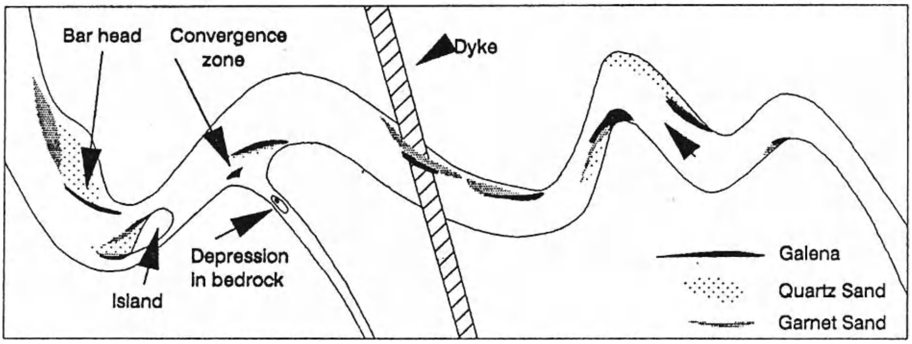
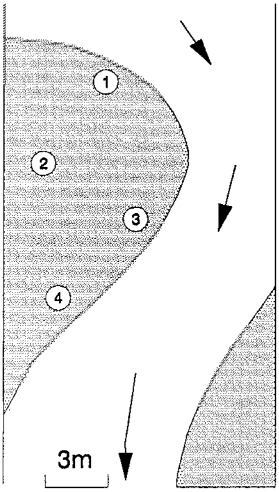


Fig. 14-16. Favourable sites for accumulation of heavy minerals on stream beds. Behaviour of gold modelled using galena. Modified after R.W. Boyle (1979b).



	HM%	mm	I/G
①	6	1.80	14/1
②	3	0.80	-5/1
③	3	0.71	-5/1
④	1	0.37	3/1

Fig. 14-17. Heavy-mineral enrichment at the bar scale. *HM%* = percent total heavy minerals, *mm* = mean size of heavy-mineral fraction, *I/G* = ilmenite/garnet ratio. Modified after Hanson (1979).

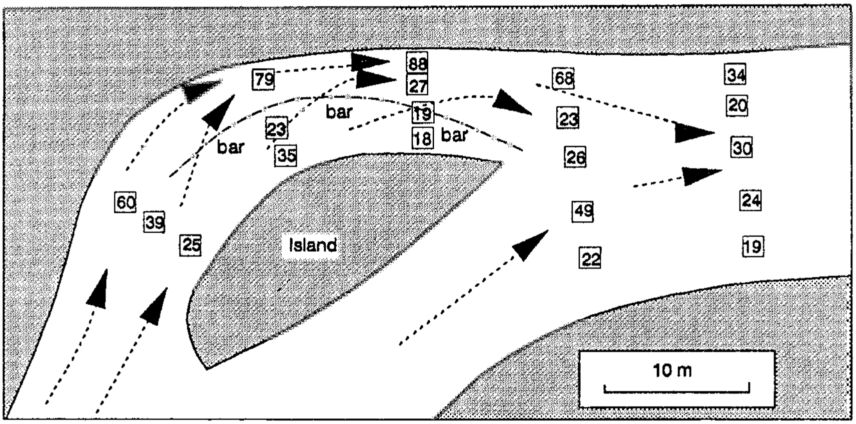


Fig. 14-18. Enrichment of magnetite (%) in a narrow sluiceway formed by flow convergence between the island and the bank. Modified after Smith and Beukes (1983).

There are few detailed sedimentological studies of gold in streams and it is necessary to draw on information on other heavy minerals as an indicator of the behaviour of gold. The existence of a systematic variation in the ilmenite : garnet ratio across a bar (Fig. 14-17) has been reported by Hanson (1979). The importance of flow convergence zones between stable banks and migrating bars as sites where heavy mineral lags develop has been demonstrated with a sample from one such sluiceway containing 88% magnetite (Fig. 14-18; Smith and Beukes, 1983). Pebble lags and constricted channelways are also recognised as controls on the accumulation of gold in Witwatersrand paleoplacers deposited in braided river systems (Smith and Minter, 1980).

In both paleo- and modern placers, pebble, rather than matrix supported, frameworks generally contain higher gold values (e.g., Toh, 1978; Smith and Minter, 1980). Pebble supported frameworks can result from extensive winnowing of the matrix over a long period. Alternatively single flood events can mobilize all bed elements and flush out the sandy matrix. Voids in the framework then rapidly fill with fines as the flood peak passes (Beschta and Jackson, 1979). Cobble-gravel pavements formed in this way are a common feature of many gravel bed streams (Parker and Klingeman, 1982). As discussed above, theory predicts that voids should form excellent traps for gold.

SAMPLE REPRESENTATIVITY CONSIDERATIONS

The importance of obtaining an adequately representative field sample is highlighted by Murphy (1982, p. 93) as follows:

"No matter how sophisticated and precise the analytical instrumentation and treatment, statistical studies and modelling, or the financial analysis of mine potential, they will have little or no significance or profitable outcome, if the samples concerned are non-representative of the material or population being sampled."

Although the problems of collecting and analyzing representative samples in the evaluation of gold deposits have long been recognized, this has not always been the case in the search for gold deposits. In many instances the exploration procedure adopted has involved the collection of a "standard sized" sample of about 500 g, appropriate for base metal exploration, followed by the analysis of a 10–20 g subsample of the traditional minus 177 μm (80 mesh) fraction. Alternatively, a heavy-mineral concentrate has been prepared by panning drainage sediments in the field and the concentrate examined visually for gold grains. In other instances separation of the "panned concentrates" or, "heavy-mineral concentrates" according to specific gravity or magnetic susceptibility has been carried out, thereby increasing the relative concentration of heavy mineral(s) by removing large quantities of lighter fractions composed of quartz or common rock forming silicates. Mineralogical or chemical analyses of such separates have in several cases indicated the presence of mineral deposits that had not been detected using the minus 177 μm fraction of stream sediment sample (Overstreet and Marsh, 1981). Such procedures have, nevertheless, frequently given rise to unreproducible results suggesting that the sample is unrepresentative of the population it is intended to represent.

Recently, the problems associated with obtaining adequately representative measures of gold content have become more widely appreciated. For a reasonable level of reliability to be placed on the results of exploration it is clearly essential that the data obtained reflect the presence of the mineral deposit sought within pre-determined levels of representativity defined by the geochemical contrast between the response to the deposit and background areas.

Gold has three features which collectively contribute to presenting a unique sampling problem: it occurs in low concentrations (with threshold values frequently below 10 ppb); it generally occurs as native gold rather than as a minor component of a major constituent; and it has very high specific gravity (19.3 for pure gold). Hence anomalous concentrations of gold can be reflected by the presence of only a very few gold particles in a sample.

The magnitude of the contrast or difference between anomalous and background concentrations frequently varies from area to area and therefore so does the necessary representativity. In situations where there is no clear distinction between anomalous and background populations, one of the conventions used in geochemical exploration is to regard the mean plus two standard deviation concentration as the threshold value. In the case of an idealized frequency distribution curve, there may be a relatively small range in concentration for population A_x (Fig. 14-19), i.e., the difference between the threshold concentration (T_A) and the mean background ($\overline{X}$) is relatively small. In such a situation a relatively high degree of representativity is therefore required to confidently distinguish between threshold and background concentrations. In contrast, in a situation where there is a relatively large difference between threshold (T_B) and the mean background, as in population B (Fig. 14-19), a lower degree of representativity would be adequate to identify anomalous concentrations. In these examples, it is assumed that the anomalous population constitutes a relatively small proportion of the entire population, as might be expected to be the case in

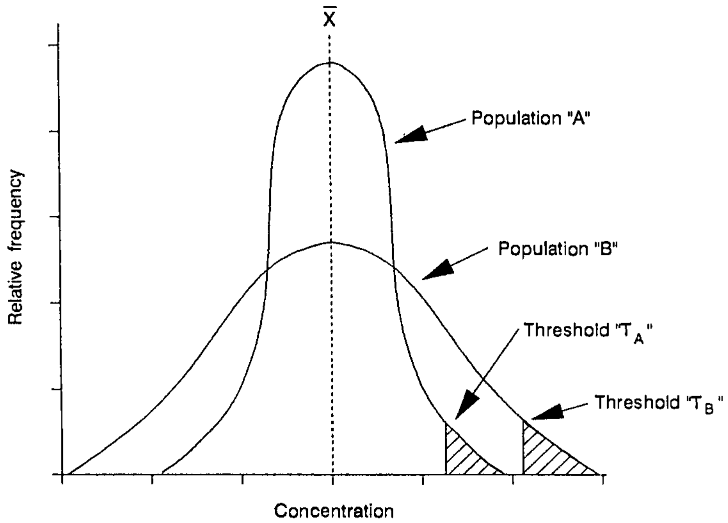


Fig. 14-19. Data distributions with varying contrast between threshold and mean background. Reproduced with permission from Nichol et al. (1989).

reconnaissance level exploration. However, in reconnaissance exploration over highly prospective terrain and in detailed exploration where a much larger proportion of the samples would be expected to contain anomalous concentrations the same sample representativity requirements apply. The essential point to be recognized is that the degree of representativity required varies from programme to programme and that the distinction of anomalous concentrations, or even degree of anomalous concentrations, must not be obscured from background populations by poor representativity.

The overall variability or variance, S^2, which is a measure of the representativity of data set can be expressed in terms of the sum of a number of individual variances as follows:

$$S^2 = S^2_{\mathrm{ntr}} + S^2_{\mathrm{smpl}} + S^2_{\mathrm{prc}} + S^2_{\mathrm{anal}},$$

where S^2 = total variance; S^2_{ntr} = natural variance; S^2_{smpl} = sampling variance; S^2_{prc} = sample processing variance; and S^2_{anal} = analytical variance.

The total variance in a set of data is the sum of the natural variance, the sampling variance, the sample processing and the analytical variance (Levinson, 1980). In exploration, it is the natural variance (or the variability between sample sites) that is of interest. Sampling, sample processing and analytical variance can be considered as sources of introduced variance that need to be controlled within acceptable limits.

If two situations in which a 10 g subsample is taken for analysis are considered the variable representativity can be appreciated (Fig. 14-20). In the first case, two 100 g samples (A and B) contain the sample gold content. In sample A, the gold is contained in a single grain, a nugget, so if 10 subsamples, each of 10 g are taken from this 100 g sample, then nine subsamples will contain no gold and one sample will contain ten times the true value. In sample B, which contains the same total gold content but in very fine grain sized gold particles, each of the 10 g subsamples will give a value that very closely approximates the true value. From this example, it is clear that for samples of equal gold content, the coarser the gold, the larger the sample analyzed must

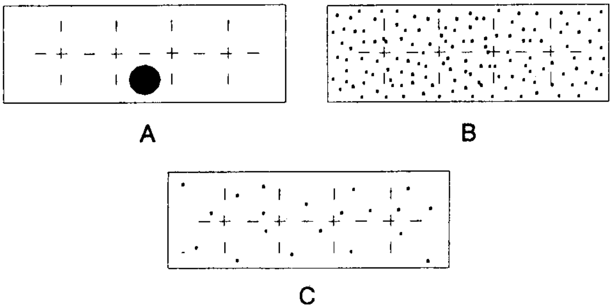


Fig. 14-20. Variation of representativity of subsample for analysis according to particle size (A and B) and concentration with constant size gold particles (B and C). Compiled from Harris (1982).

be to obtain a representative value. The second case, demonstrated by Harris (1982), considers two samples that have the same grain size of gold but with different concentrations (B and C). In the sample with low gold content (C), 10 g subsamples may have one, two, three or even no grains of gold in them. In other words, these subsamples will have highly variable gold contents and individual subsamples will have poor representativity. In the case where the gold content is much higher (B) any 10 g subsample will yield a reproducible value. From this it can be seen that for samples containing the same grain size of gold, the lower the gold content, the larger the sample required for a given level of representativity.

The classic work of Pierre Gy (1954) on sample representativity together with later work by Clifton et al. (1969) is of particular value in providing guidelines on sample representativity in gold exploration. Collectively, this information provides an excellent guideline for the appropriate collection, preparation and analyses of samples for gold exploration. A formula for establishing the representativity of ore sampling identified by Gy (1954) and subsequently described by Ottley (1966, 1983) is directly applicable to geochemical exploration:

$$S^2 = \frac{Cd^3}{M},$$

where S^2 = the relative variance (or representativity) of a data set; S = the relative standard deviation (standard deviation must be expressed in relative terms in Gy's formula); C = a sampling constant for the particular material to be sampled which is related to parameters characteristic of the sample; d = aperture of the sieve passing 95% of the sample (cm) hereinafter referred to as "maximum significant grain size"; and M = sample weight (g).

The formula can be used to determine (a) the representativity associated with a particular sample weight and type of sample; (b) the weight of sample required to achieve a particular representativity; and (c) the necessary mechanical size for a given sample weight to achieve a required representativity. The use of the formula assumes random sampling, with no bias in sample processing and takes no account of analytical precision, a feature that is very rarely true in nature but is acceptable as an initial guide.

A comparable approach was described by Clifton et al. (1969), who make the assumption, in the first instance, that all particles of gold in a sample are of the same size; and that gold particles are randomly distributed and represent less than 0.1% of all particles, samples contain more than 1000 particles in total, and analytical errors are neglected.

Clifton et al. (1969) show the level of precision and number of gold particles deteriorating as the number of gold particles in the sample decreases (Fig. 14-21). Furthermore they demonstrate that it is necessary to take a sample that contains at least 20 particles of gold to achieve a precision of ± 50% at the 95% confidence level.

They also show the relationship between weight of sample containing 20 particles of gold, particle size and gold concentration (Fig. 14-22). For example,

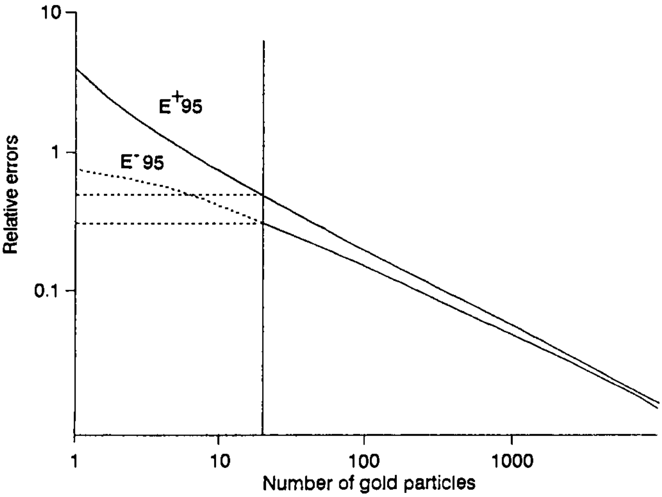


Fig. 14-21. Variation of precision with number of gold particles contained in sample. From Clifton et al. (1969).

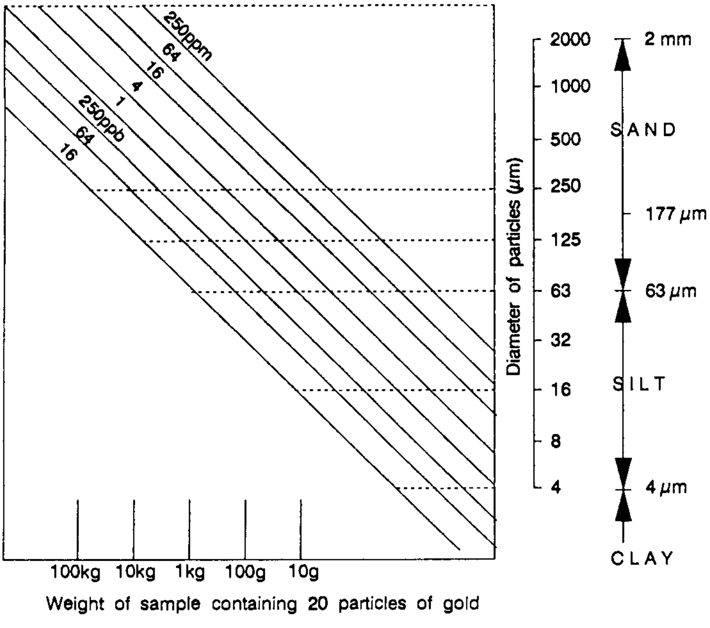


Fig. 14-22. Variation of weight of sample containing 20 particles of gold according to particle size and gold concentration. Gold particles are flakes in which the diameter is five times the thickness. Modified after Clifton et al. (1969).

in a sample containing 1 ppm gold, in which the gold occurs as discs with diameter five times the thickness (250 μm in diameter and 50 μm thick), a sample of about 1 kg would contain the necessary 20 particles. In a sample

TABLE 14-VI

Weight of sample containing twenty particles of gold (diameter is five times thickness) according to concentration of gold and size of gold particles determined by the method of Clifton et al. (1969)

Gold grain size (μm)	Gold concentration (ppb)					
	1000	250	64	16	4	1
250	950	3.8 kg	15 kg	59 kg	240 kg	950 kg
125	120	470	1.9 kg	7.4 kg	30 kg	120 kg
63	15	61	230	950	3.8 kg	15 kg
32	2.0	7.9	31	120	500	2.0 kg
16	250 mg	990 mg	3.9	16	62	250
8	31 mg	120 mg	490 mg	1.9	7.8	31
4	3.9 mg	16 mg	61 mg	240 mg	970 mg	3.9

Sample weights are in grams except where shown.

containing the same 1 ppm Au content, but as discs of 32 μm diameter, 20 particles would be contained in a sample weight of approximately 2 g. The weight of sample containing 20 particles of gold as discs with a diameter of five times the thickness, for various combinations of concentration and particle size is shown in Table 14-VI (Nichol, 1986, 1987; Nichol et al., 1989). It is clear how the necessary size of sample to be collected dramatically increases with increasing particle size for a given gold concentration and similarly increases with decreasing concentration for a constant particle size. It should be realised that the entire sample that needs to be collected must by analyzed or alternatively some procedure must be adopted to produce a representative subsample. If a sample of 10 g is being analyzed, then the area under the stepped line (Table 14-VI) is the area with adequate representativity; any combination of gold particle size and concentration over the line is unsatisfactory. For example, analysis of a 10 g sample is inadequate for samples containing 63 μm diameter discs of gold for concentrations in the range 1–1000 ppb, but adequate for samples containing 4 μm diameter gold discs for all the above concentrations. However, the suitability of analysis of a 10 g sample with gold particles in the range 8–32 μm varies within the concentration range 1–1000 ppb.

On the basis of the size of sample containing 20 particles of gold, it is possible to determine the number of gold particles expected in a 10 g sample, depending on gold particle size and gold content. Where this number falls below 20 then there are too few gold particles to give the ± 50% precision at the 95% confidence level. The combination of conditions of particle size and gold content for which the number of particles exceeds 20 (Table 14-VII) and therefore meets the ± 50% precision of representativity requirements is of course identical to the area of adequacy indicated on the basis of a 10 g sample (Table 14-VI).

A question that arises is what precision of representativity will be introduced by the collection and analysis of an inadequately sized sample. The relationship between range of analyses or representativity and the number of particles expected in a sample analyzed is illustrated by Clifton et al. (1969; Fig. 14-23).

TABLE 14-VII

Number of gold grains expected in a 10 g sample taken for analysis according to concentration of gold and size of gold particles determined by the method of Clifton et al. (1969)

Gold grain size (μm)	Gold concentration (ppb)					
	1000	250	64	16	4	1
250	0.21	0.013	0.034	0.0034	0.00083	0.00021
125	1.7	0.43	0.11	0.027	0.0067	0.0017
63	13	3.3	0.87	0.21	0.053	0.013
32	100	25	6.5	1.7	0.4	0.1
16	800	200	51	13	3.2	0.8
8	6500	1700	410	110	26	6.5
4	51000	13000	3300	830	210	51

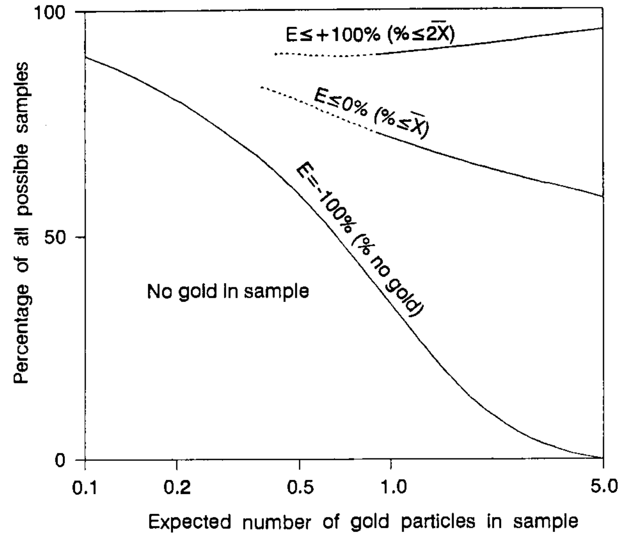


Fig. 14-23. Variation of range of values according to number of particles expected in a sample taken for analysis. After Clifton et al. (1969).

If, on the basis of the gold grain particle size, gold concentration and sample weight collected and analyzed, the particle expectancy in the sample analyzed is one (e.g., 64 ppb Au and 63 μm diameter particles as indicated in Table 14-VII) then, based on the Poisson distribution, 37% of replicate analyses will contain no particles whilst 37% will contain one particle and indicate the true value, 19% will contain two particles and give twice the true value, the remaining 7% will contain more than two particles and thereby indicate some integer of the true value greater than two. If, on the other hand, on the basis of gold concentration and particle size, the particle expectancy in the sample analyzed is 0.1 (e.g., 64 ppb and 125 μm Au) then 90% of the samples will contain no

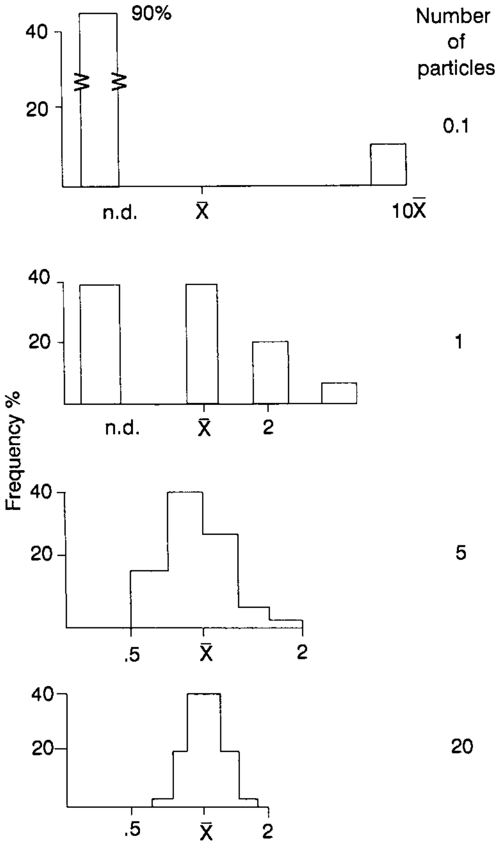


Fig. 14-24. Histograms of range of values according to number of gold particles expected in sample taken for analysis. Reproduced with permission from Nichol et al. (1989).

gold and 10% will contain some combination of 10, 20 or 30, etc. times the true value.

The decrease in precision or representativity with decreasing number of particles expected in the sample analyzed is illustrated in Fig. 14-24. It can be seen that, with a particle expectancy of 20, a ±50% precision at the 95% confidence level is achieved; however, as the particle expectancy decreases, the precision or representativity of the analysis deteriorates dramatically.

Considering these observations with respect to exploration, the relevance can be demonstrated by two hypothetical examples. In these two instances, drainage sediment associated with a significant gold mineralization contains 64 ppb Au neglecting dilution downstream. In case "A" gold occurs as 63 μm discs whereas in case "B" gold occurs as 125 μm discs. Assuming a 10 g sample is analyzed, these situations are equivalent to particle expectancies of 1 and 0.1 respectively (Table 14-VII). The resulting distribution of gold contents is illustrated in Fig. 14-25. It can readily be seen that the "noise"

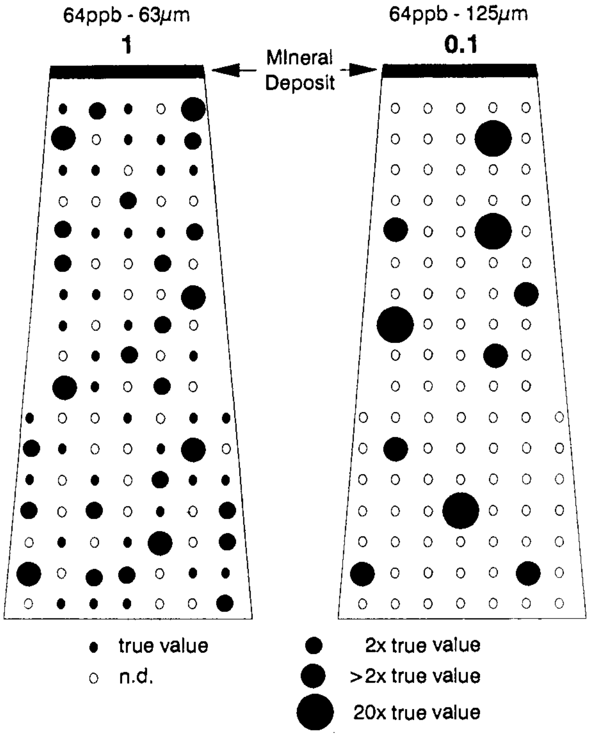


Fig. 14-25. Distribution of gold according to number of particles expected in a 10 g sample. Reproduced with permission from Nichol et al. (1989).

in data, reflecting poorer representativity, increases dramatically as the size of gold particles increases and the particle expectancy decreases. The question that arises centres on the confidence that can be placed on gold concentrations and the risk of mineralization being overlooked because of unrepresentative samples.

The previous discussion is based on the assumption that all gold particles are of the same size. In nature, gold particles generally cover a range of sizes and the magnitude of the range varies from case to case. In a situation where a sample taken for analysis contains twenty particles of gold of variable sizes the use of the average size of particles in determining the weight of samples to be analyzed to give ±50% precision will be incorrect and low. In fact, the effective grain size, by definition the grain size that can be used to determine the weight of sample to be analyzed to give ±50% precision, is greater than the average grain size.

Effective grain size may be determined on the basis of (a) the measured gold particle size distribution, (b) the variance of replicate analyses of unsized splits of a sample and (c) the maximum size of gold particles that make a significant contribution to the gold content of a sample (Clifton et al. 1969).

Prigogine (1961), Gy (1967), Clifton et al. (1969), and Nichol et al. (1989) have shown that the effective grain size, based on size distribution of the gold particles, can be determined by the equation:

$$d_e = \sqrt[3]{\sum_j \frac{M_j}{M} d_j^3},$$

where d_e is the effective grain size, or diameter; M_j is the mass of gold in size grade j; d_j is the midpoint diameter of size grade j; and M is the total mass of gold.

In several cases, exploration practice is to analyze the minus 63 μm fraction of a natural sample on the assumption that a 10 g sample will be adequately representative because of the fine-grain size of the gold particles. The validity of this assumption will now be examined. The effective grain size diameter (μm) has been calculated for hypothetical samples in which the gold is variously distributed in different size ranges within the minus 63 μm fraction (Table 14-VIII). In the case of Sample 1, it has been assumed that all gold particles are 63 μm in diameter to portray a worst case situation. Subsequently, the weight of sample containing 20 particles of gold according to the different effective diameters has been determined for gold concentrations of 1000, 100 and 10 ppb respectively (Table 14-IX). This shows that for a concentration of 1000 ppb, only when the particles are 63 μm in diameter is the sample weight containing 20 particles more than 10 g; however, at concentrations of 100 ppb and effective particle diameters greater than approximately 25 μm, the appropriate sample weight is greater than 10 g. At 10 ppb the appropriate sample weight exceeds 10 g at effective particle diameters of approximately 15 μm.

The implications of the above data are that when the minus 63 μm fraction

TABLE 14-VIII

Effective diameter of gold particles of varying size ranges in the minus 63 μm fraction of ten samples determined by the method of Clifton et al. (1969)

Sample	Size fraction (μm)					Effective diameter (μm)
	63–32	32–16	16–8	8–4	4–2	
1	100*	–	–	–	–	63
2	50	20	15	10	5	38
3	20	20	20	20	20	29
4	5	50	25	15	5	23
5	5	20	50	20	5	21
6	5	15	25	50	5	20
7	5	10	15	20	50	19
8	–	5	10	15	70	10
9	–	–	5	20	75	5
10	–	–	–	–	100	3

* In Sample 1 all grains are assumed to be 63 μm in diameter (worst case example).

TABLE 14-IX

Sample weights (g) necessary to achieve ±50% precision, at the 95% confidence limits, according to effective diameter and concentration, determined by the method of Clifton et al. (1969)

Sample	Effective* diameter (μm)	Gold concentration (ppb)		
		1000	100	10
1	63	15	150	1.5 kg
2	38	3.3	33	330
3	29	1.5	15	150
4	23	730 mg	7.3	73
5	21	550 mg	5.5	55
6	20	480 mg	4.8	48
7	19	410 mg	4.1	41
8	10	60 mg	600 mg	6.0
9	5	7.5 mg	75 mg	750 mg
10	5	1.6 mg	16 mg	160 mg

* Gold grains represented as discs with diameter equal to five times thickness. Sample weights in grams except where shown.

of natural samples is being analyzed in situations where 100 ppb gold is of interest, then the effective grain size of gold has to be reduced to some 25 μm. Similarly, if 10 ppb is considered to be significant, the effective particle size has to be reduced to some 15 μm.

Alternatively, effective grain size may be estimated on the basis of replicate analyses of unsized splits. On the basis of replicate analyses of say 50, 10 g subsamples, it is possible to determine the mean, the standard deviation and the relative standard deviation. Considering the relative standard deviation, it is possible to determine the number of gold particles per kilogram from Fig. 14-21 and thus the weight of sample containing 20 particles.

An example of determining the necessary sample weight to be analyzed to provide ±50% precision at the 95% confidence level is illustrated with reference to replicate analyses of (a) a glacial till sample associated with the Owl Creek gold deposit near Timmins, Ontario, and (b) a drainage sediment from the Carlin area of Nevada. Replicate analyses of 25 g subsamples of each sample revealed markedly skewed distributions (Fig. 14-26). On the basis of the mean contents and relative standard deviations, the effective grain sizes and sample weights required to give ±50% precision were determined. These indicate necessary sample weights of approximately 1 kg and 750 g for Owl Creek and Nevada samples, respectively (Table 14-X). The frequency distributions of replicate analyses of both samples show the existence of a few erratically high values greater than 1000 ppb suggesting the presence of erratically distributed nuggets.

A striking example of the "nugget effect" and its adverse influence on sample representativity is illustrated from the United States by Carpenter (1987). A sample comprising 13.6 kg of stream sediment sieved to 10 mesh and panned to 42 g of heavy-mineral concentrate was found by microscopic inspection to

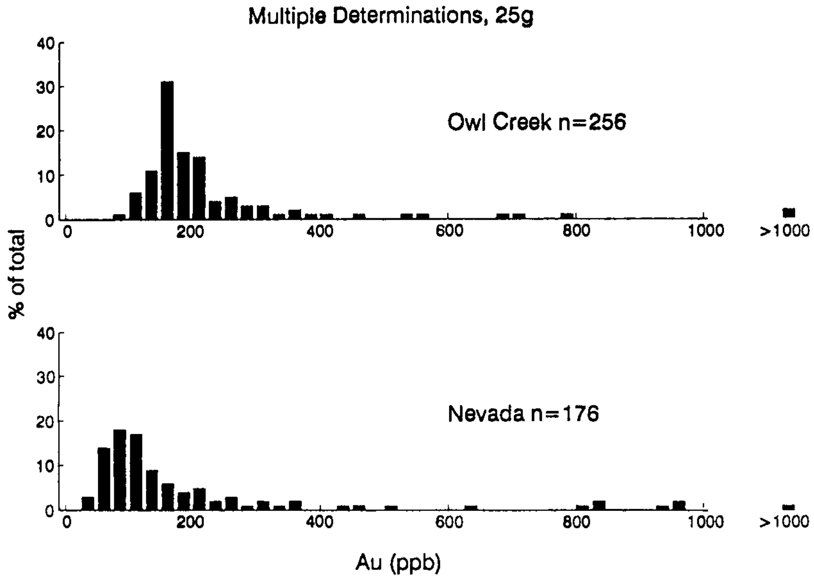


Fig. 14-26. Frequency distribution of replicate analysis of 25 g subsamples from two bulk samples. Reproduced with permission from Nichol et al. (1989).

TABLE 14-X

Sample weights necessary to achieve ±50% precision, at the 95% confidence limits, based on replicate analyses of 25 g subsamples

Sample	Number of subsamples	Mean (ppb)	Coefficient of variation	No. particles per 25 g sample	Required sample weight (g)
Nevada	176	197	1.42	0.50	1010
Owl Creek	256	235	1.23	0.64	758

contain ten grains of gold. Analysis of a subsample would always produce an unrepresentative Au concentration because nine grains in the size range 0.00005–0.00085 mm^3 contain only 5% of the total Au in the sample, while 95% is contained in a nugget of 0.06400 mm^3.

If information on the size distribution is unknown and replicate analyses of splits are not available, the appropriate sample size can be determined on the basis of considering the effective size as the size equal to the maximum significant size, a size below which 95% of the total gold is contained (Clifton et al., 1969). This approach assumes that gold particles are all the same size and equivalent to the 95th percentile size and therefore this procedure provides an additional safety margin relative to the procedures involving consideration of the size distribution of the gold and the variability of replicate analyses. A comparison of the results of these approaches on a magnetite-rich beach sand from Oregon with a content of 380 ppb Au showed a variation in the effective particle size from 170 to 270 μm, equivalent to necessary sample weights varying from 360 to 1500 g (Clifton et al., 1969). This difference in necessary sample weights reflects variations in assumptions between the different approaches.

An interesting procedure for determining the minimum analytical subsample size has been described by Cohen et al. (1992). This involves applying a binomial statistical technique to data on replicate analyses which determine the expected number of gold particles from which it is possible to infer particle dimensions. The results confirm size estimates determined by microscopy and sizing. The approach has direct application in determining the minimum analytical subsample size to provide the necessary representativity.

ANALYSIS OF GEOCHEMICAL SAMPLES FOR GOLD AND PATHFINDERS

There is a variety of analytical procedures available for the determination of gold in drainage sediment samples. Historically, the most widely adopted procedure was fire assay, involving the concentration of the gold into a silver bead and, following removal of the silver, the gravimetric estimation of the gold. This procedure, using a sample weight of 0.5 or 1 assay-ton (15 or 30 g), has practical detection limits of 170–340 ppb Au which is inadequate for many exploration programmes.

Following the advent of atomic absorption with the capability of detection limits in the range 1–40 ppb, according to analytical conditions, a number of procedures have been adopted involving variously a fire assay start, or different acid digestions followed by estimation of the gold content by atomic absorption. More recently, plasma emission spectrometry and instrumental neutron activation analyses (INAA) have been adopted as estimation procedures. All of these procedures, which are the most commonly available for geochemical exploration, usually involve the analyses of samples of between 10 and 50 g in weight. A number of procedures involving the analyses of samples up to 100 g have been reported by Lakin and Nakagawa (1965) in order to lower detection limits or increase the representativity of the sample being analyzed. An INAA method for the determination of Au in 500 g samples was described by Plant and Coleman (1973). Different digestion procedures often indicate different components of gold present in a sample; but procedures to determine total gold contents have been found to give different values (Fletcher and Day, 1988b; Hall and Bonham-Carter, 1988; Hall et al., 1989a, b; Lavin et al., 1989). A recent innovation developed with the aim of increasing sample representativity involves analyzing a 5 kg sample using the Bulk Leach Extractable Gold (BLEG) method. Gold is leached from the sample by a cyanide solution and subsequently concentrated by solvent extraction or zinc precipitation with determination by atomic absorption (Fletcher and Horsky, 1988; Sharpe, 1988; Elliott and Towsey, 1989). In some instances such procedures may only report liberated gold rather than total gold.

An ultra-sensitive method, detection limit 0.2 ppb, has been described by Xie and Wang (1991) involving the digestion of 10–20 g samples in aqua regia followed by preconcentration with activated charcoal or polyurethane foam and estimation either by emission spectrography or graphite furnace AAS. A similarly ultra-sensitive method for gold analyses with a detection limit of 0.1 ppb has been described (Kontas, 1983, 1991; Kontas et al., 1986), but involves only the analyses of 1 g samples and thereby raises questions as to sample representativity.

In natural waters, gold is sparingly soluble and the concentrations of the dissolved gold content in one litre or more of water can be determined following evaporation (McHugh, 1984), ion exchange (McHugh, 1986) or absorption onto activated charcoal (Hamilton et al., 1982; Hall et al., 1986). Concentrations as low as 0.001 ppb in water can be detected.

Pathfinders such as As, Sb, Hg, Ag and base metals tend not to pose major sample representativity problems, and are usually determined by the analyses of a relatively small quantity of the fine fraction of stream sediment. With the exception of the base metals (many of which can be determined simultaneously or sequentially on the same leachate obtained from acid digestion of the sample), most pathfinders require quite separate analytical techniques. Fletcher (1981) reports colorimetric and warm vapour flameless atomic absorption methods for arsenic, cold vapour flameless atomic absorption for mercury, flame atomic absorption or plasma emission spectrometry following solvent extraction for silver, and simultaneous determinations of As, Sb, Bi, Se and Te as their hydrides by plasma emission spectrometry.

CASE HISTORIES

The distribution of gold in different drainage systems indicates a very variable relationship exists in a variety of components of drainage sediments to mineralization that have a considerable bearing on the application of geochemical techniques in gold exploration. However, relatively few examples exist that describe comparative responses in different sample types, size fractions, analytical procedures, or sedimentological conditions to enable a reliable assessment of the relative merits of a particular procedure. The examples presented are used to illustrate the dispersion of gold in stream sediments, moss mats, heavy-mineral concentrates, lake sediments and waters together with some observations on data presentation and interpretation.

Stream sediments

In an extremely thought provoking paper, Harris (1982) described the distribution of highly variable gold results in stream sediment samples from the

Rossland area of southern British Columbia. In the programme 5 g samples of the minus 177 μm (80 mesh) fraction were analyzed using an analytical procedure with a 10 ppb detection limit, with 20 ppb Au being established as the threshold value. Difficulty was experienced in reproducing the initial analyses of reconnaissance samples by re-analyses and in order to examine the matter further 95 samples were analyzed in triplicate (Fig. 14-27). Of these 95 samples, 70 consistently displayed background concentrations in all three sets of analyses indicating their derivation from background location. However, six samples, which initially had anomalous gold contents, were shown to be anomalous in one or more of the subsequent analyses whereas six other samples, which initially had anomalous gold contents, displayed only background gold contents on subsequent analyses while a further thirteen samples that initially had background concentrations of gold, gave anomalous values in one or other or both subsequent analyses. Overall the poor reproducibility of the replicate analyses drew attention to the limited confidence that can be placed in single analyses and therefore the risk of overlooking a truly anomalous location warranting follow-up but reporting as background level gold concentrations. Similarly the risk also exists of undertaking follow-up in areas with truly background gold concentrations which reported anomalous gold contents in the first instance. In an attempt to reduce variability of replicate analyses of stream sediment samples, Harris (1982) obtained heavy-mineral concentrates of fifteen samples and analyzed them for gold. However, gold values in the concentrates were significantly higher than in the minus 177 μm fractions in only 40% of the samples, probably reflecting the occurrence of gold as inclusions in silicates, or a failure to recover fine grain sized gold. The inability of gravity systems to recover fine grain sized gold was noted by Wang and Poling (1983; Fig. 14-28). Several ways of overcoming problems identified by Harris (1982) are described in the section dealing with design of exploration programmes at the end of the chapter.

In contrast, the value of heavy-mineral concentrates in identifying gold mineralization was demonstrated over a 4900 km^2 area of the Yukon, Canada, by Boyle and Gleeson (1972); in which all known gold deposits were identified together with evidence of several new occurrences. A marked improvement was also noted in the geochemical response related to gold and silver deposits in British Columbia using the −841 +177 μm (−20 +80 mesh) heavy-mineral concentrates compared to minus 177 μm (80 mesh) fractions stream sediment (Fig. 14-29) by Barakso and Tegart (1982), in the form of responses being less subject to seasonal variations or contamination and to give enhanced anomalies.

A further example of the longer more consistent dispersion trains was also shown to be provided by gold in heavy-mineral concentrates relative to the minus 177 μm (80 mesh) fractions of stream sediments in Nevada (Fig. 14-30; I. Thomson, pers. commun., 1983). At each sample site 8 kg samples were collected and sieved to minus 841 μm (20 mesh), this fraction then being sized and separated in the laboratory and the >3.3 S.G. fraction concentrated using methylene iodide and the non-magnetic fraction analyzed for gold. The analysis of the minus 177 μm fraction displayed only a single anomalous value whereas

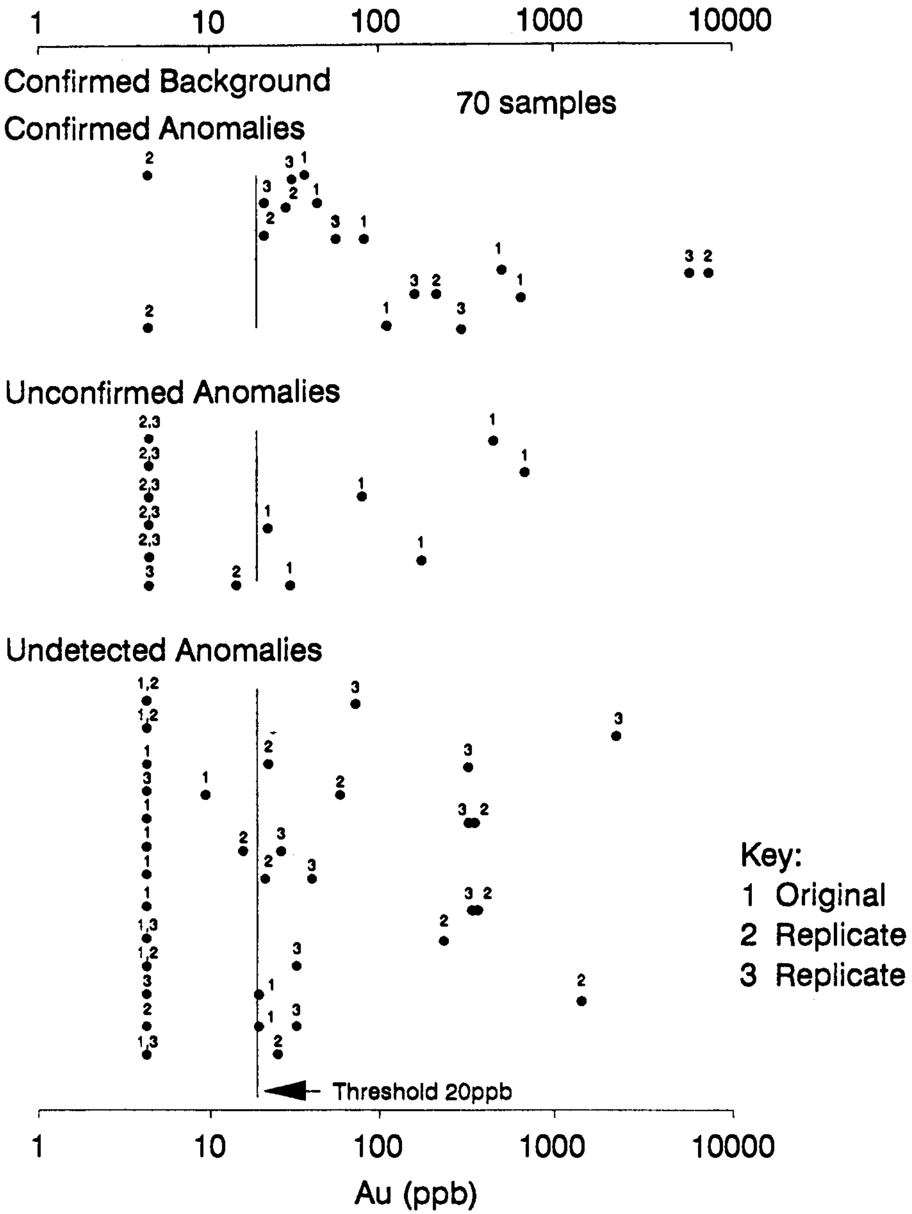


Fig. 14-27. Replicate gold analyses of stream sediments from the Rossland area, British Columbia. Compiled from Harris (1982).

analysis of heavy-mineral concentrates shows a consistent anomalous train with values of 300 ppm relative to an arbitrary threshold of 30 ppm extending at least 5 km downstream from a gold occurrence. A greater sample interval could

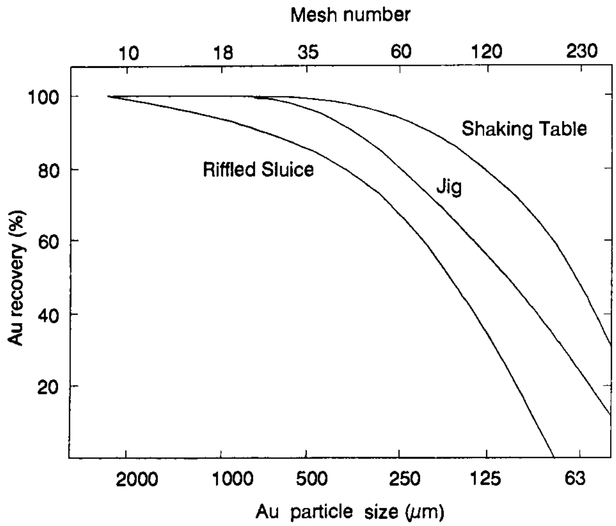


Fig. 14-28. Relative recovery of different sized gold particles by various gravity methods. Modified after Wang and Poling (1983).

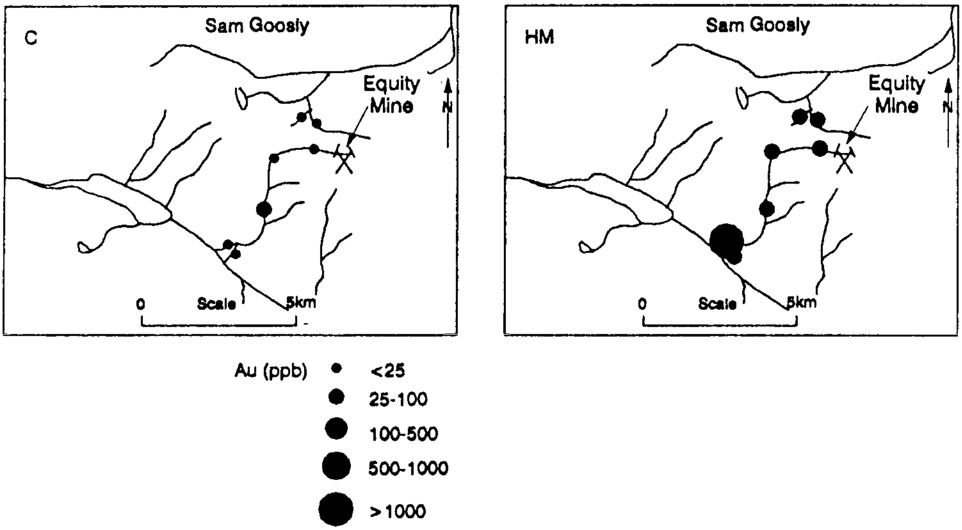


Fig. 14-29. Comparisons of gold content of −177 μm (80 mesh) C and heavy-mineral fraction (*HM*) of stream sediments in the Sam Goosly area, British Columbia. Modified after Barakso and Tegart (1982).

thus be employed with a higher level of confidence in the results. Although the cost of obtaining heavy-mineral concentrates is higher than that of minus 177 μm fractions, the higher cost is more than offset by the lower sampling density that will suffice.

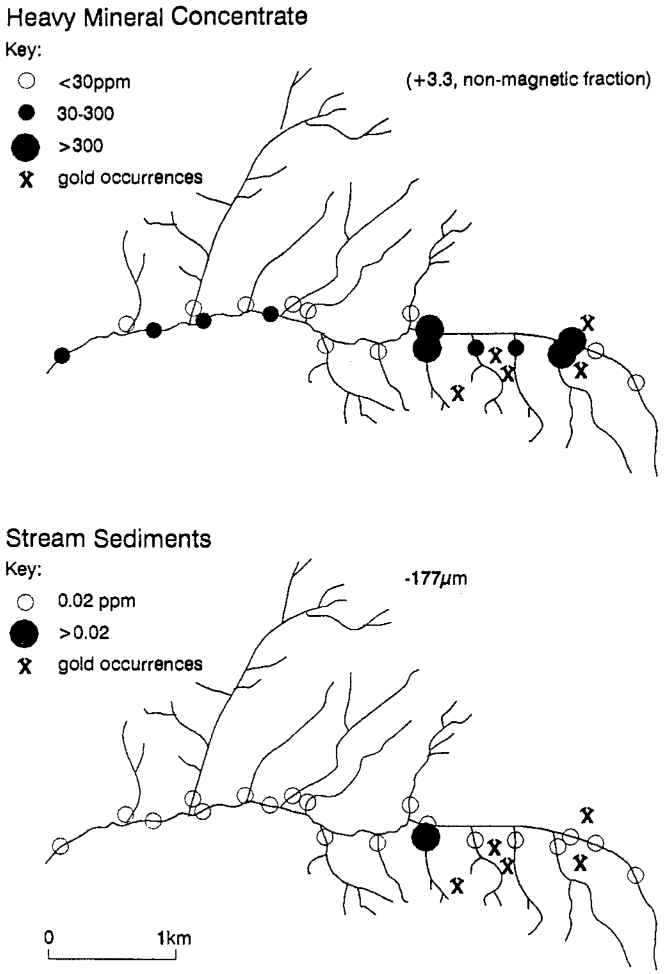


Fig. 14-30. Comparison of gold contents of heavy mineral and −177 μm (80 mesh) fraction of stream sediments, Nevada. (I. Thomson, pers. commun., 1983).

Exploration for epithermal deposits with micron-sized gold in Nevada has shown that two different techniques are effective at different stages of exploration (B. Smee, pers. commun., 1988). Initially at the reconnaissance scale 20 kg of minus 3.35 mm (6 mesh) sediment material was collected in the field at intervals of 2 km. Heavy-mineral concentrates of four size fractions were prepared utilizing tetrabromoethane. (S.G. of 2.8) and analyzed for 33 elements by neutron activation and for Cu, Pb, Zn, Ag and Bi by atomic absorption. The most reliable gold response was in the minus 106 μm (150 mesh) fraction. However, the coarser fractions displayed the best contrast for As, Sb and Bi and two of six discoveries made in the reconnaissance were reflected only by anomalous levels of pathfinder elements. Follow-up procedures involved analysis of a 5 kg sample of minus 850 μm (20 mesh) material dry sieved at sample sites 300 m (1000 ft) apart. Analysis was carried out using the BLEG (bulk leach extractable gold) method with a detection limit of 0.1 ppb Au. No anomalous concentrations of pathfinders were identified but values, >1.5 ppb Au, indicated the presence of mineralization up to 1220 m (4000 ft) down drainage. Cost comparisons of the two techniques are interesting with sample processing and analyses of the heavy-mineral concentrate costing eleven times more than analysis of unconcentrated samples. In contrast the direct analysis of the minus 75 μm fraction of stream sediments was shown to give better results than heavy-mineral concentrates or BLEG analysis in Western Australia (Mazzucchelli, 1987).

A study of gold dispersion in drainage systems in northeastern Thailand produced conflicting results that have important implications for gold exploration in the area (Nuchanong and Nichol, 1992). In two areas heavy-mineral panned concentrates and the minus 63 μm fractions of stream sediments showed markedly different responses to mineralization (Fig 14-31). In one area associated with porphyry style copper gold mineralization (Phu Tham Phra-Phu Thong Daeng) anomalous gold responses occurred in the minus 63 μm fraction whilst in the other area, Huai Hin Laep (or Lab), related to an unknown bedrock source, they are most evident in the heavy-mineral concentrates. Laboratory heavy-mineral separation techniques showed that in the second area the minus 53 μm fraction and light minerals of up to 440 μm typically contained less than 5 ppb gold whereas the heavy-mineral fractions (S.G. > 3.3) usually had in excess of 10 ppm with a maximum of 198 ppm gold (Paopongsawan and Fletcher, 1993).

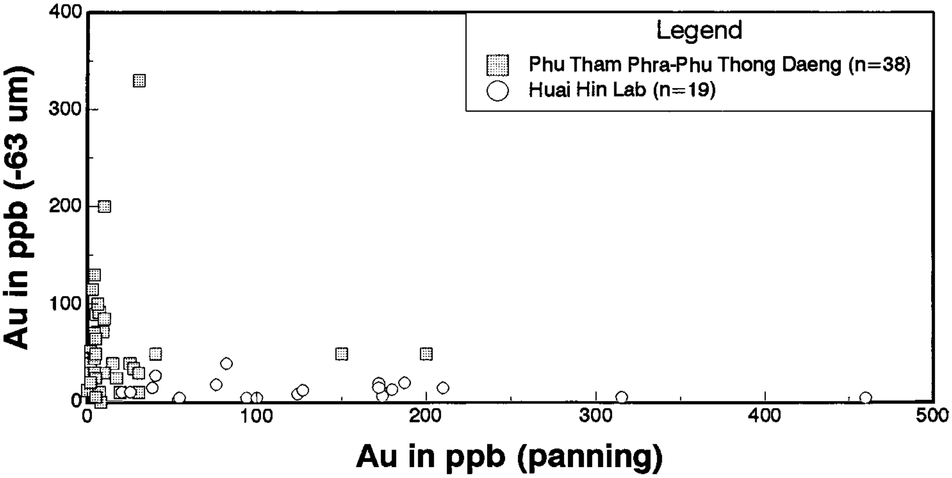


Fig. 14-31. Variation in partitioning of gold between the −63 μm fraction and panned concentrate in drainage sediments associated with two gold mineralizations in northeastern Thailand. Reproduced with permission from Nuchanong and Nichol (1992).

TABLE 14-XI

Estimated number of particles of free gold in heavy mineral concentrates and minus 53 μm sediment. From Day and Fletcher (1986)

Stream	Sample	H/L/B *	Size fraction (μm)					
			300–210	210–149	149–100	100–74	74–53	53
Tsowwin	01	L	0.5	1.0	2.1	0.0	5.0	0.0
	02	H	0.0	0.0	0.3	1.1	0.0	11.2
	03	B	0.0	0.0	0.0	0.9	0.7	0.0
Salmonberry	04	L	0.0	0.0	0.1	0.0	0.8	2.5
	05	H	0.4	0.5	0.0	0.1	0.4	5.3
	06	B	0.0	0.0	0.7	1.8	0.4	10.6
Franklin	07	L	0.2	0.8	3.7	3.0	2.7	35.6
	08	H	0.0	0.0	0.0	0.8	0.0	10.3
Harris	10	L	0.2	0.8	3.1	20.0	53.6	97.9
	11	H	0.4	1.3	1.9	2.2	2.6	16.9
	12	B	0.4	0.8	11.9	17.1	10.3	0.0
Watson-Bar	13	L	0.0	0.6	4.3	0.4	6.5	7.6
	14	H	0.0	0.0	0.0	0.7	2.2	15.8
	15	B	0.0	0.0	0.2	0.0	0.0	4.7

* H = high energy; L = Low energy; B = background.

As discussed previously, gold grains of a particular size and shape occur with much larger particles of lighter minerals (Tourtelot, 1968), contributing to the situation that one of the most important factors in the successful use of heavy-mineral concentrates for gold exploration is the selection of appropriate sample sites, i.e. sites characteristic of the depositional environments for the accumulation of gold. In a study of gold contents in five mineralized drainage systems in British Columbia, based on the collection of 20 kg of minus 5 mm sediment from high-energy sandy-gravel, and low-energy sandy environments, Day and Fletcher (1986) found that the minus 53 μm sediment fraction gave more favourable sampling statistics and a more reliable measure of gold content than the use of heavy-mineral concentrates (Table 14-XI). Suitable material was most readily obtained from low-energy sandy sites. It was estimated that if heavy-mineral concentrates were to be used, up to 300 kg field samples would have to be processed to provide adequate sampling statistics. Subsequently, a more detailed study of one of these drainages (Day and Fletcher, 1989) and a comparable study of three other mineralized drainage systems (Fletcher and Wenqin, 1989) confirmed that if samples of sufficient size are used, in this case 50 to 60 kg of minus 2 mm material, field screened from up to 300 kg of bed material, heavy-mineral concentrates provide a more reliable method of identifying the presence of gold mineralization than use of either the minus 212 μm (70 mesh) or the minus 53 μm fractions.

Investigation of gold distribution in Harris Creek, a gravel-bed stream in southern British Columbia, showed strong preferential enrichment of gold in

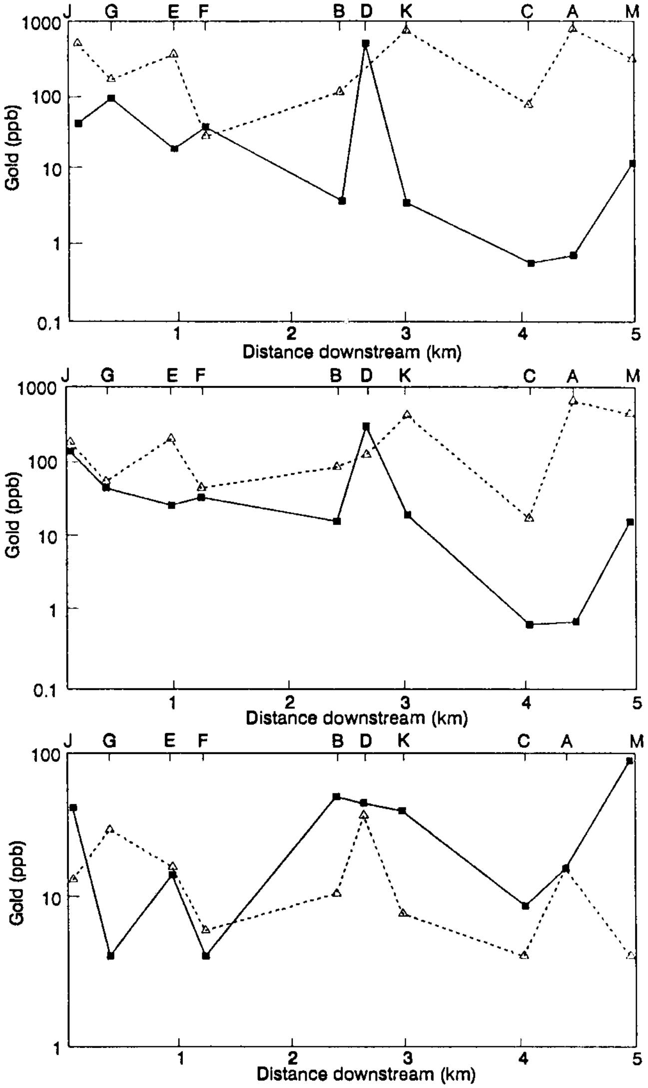


Fig. 14-32. Downstream profiles of gold in bar head gravels (solid line) and sandy pools (dashed line), Harris Creek, British Columbia. Stream flow is from left to right. (A) −105 +74 μm sediment; (B) −74 +53 μm sediment; and (C) −53 μm sediment. Open squares represent samples collected below water level from pools. Triangles represent beach deposits affected by wave action. Modified after Day and Fletcher (1991).

bar head cobble-gravels compared to sandy deposits from bar-tail pools (Figs. 14-32 and 14-33; Day and Fletcher, 1989). Accumulation of gold in the bar head gravels counteracts downstream dilution and gold values increase slightly with decreasing gradients down the 5 km study reach suggesting that a sampling density of 1 sample per 100 km^2 would be adequate to identify anomalous

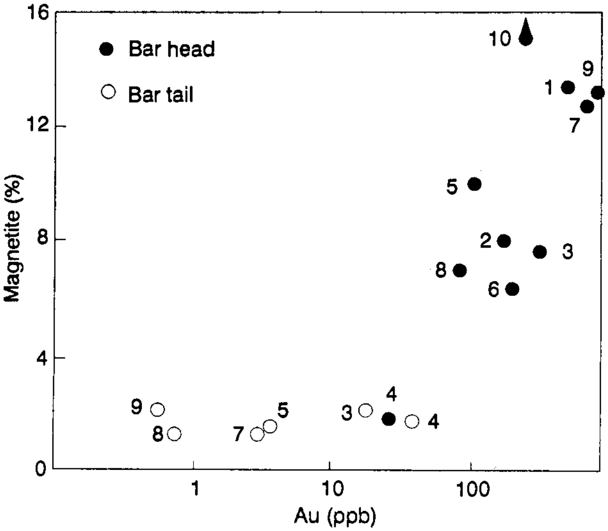


Fig. 14-33. Concentrations of gold (−105 +74 μm sediment size fraction) versus magnetite (−212 +150 μm sediment size fraction) in Harris Creek, British Columbia. Solid circles are from bar head deposits and open circles from sandy pools. Numbers adjacent to points indicate position in study reach and increase downstream. Modified after Day and Fletcher (1991).

catchments. In contrast, with the exception of very local enrichment of gold in black-sand beach swash zones, gold values in the sand deposits decrease down the reach giving a much shorter dispersion train. As the bar head cobble-gravels are the principal accumulation sites for gold and the stream flow is only capable of disrupting the coarse framework at these sites under flood conditions (Fletcher and Wolcott, 1991), transport of gold in Harris Creek is essentially restricted to periods of high discharge associated with the annual snowmelt (Table 14-XII). Anomalous concentrations of gold are therefore not always present in active sediments and there are large seasonal variations of gold content in bar head samples (Fig. 14-34) with important implications for the reliability of stream sediment and heavy-mineral surveys for gold (Fletcher and Day, 1988a, 1989). Transport of abnormally high concentrations of gold during floods can also explain why moss mats (Matysek et al., 1989), sampled above the normal water level contain greater concentrations of gold than conventional stream sediments at the same site (Fletcher and Wolcott, 1991).

As predicted by the bedload transport models, magnetite in Harris Creek is enriched to a much lesser degree than gold and enrichment of both decreases with decreasing grain size until it is insignificant in the silt size fraction (Fig. 14-35) as in the case of the mechanical recovery of gold using sluice boxes or tables (Wang and Poling, 1983).

Considering the economic importance of gold placers there is surprisingly little data on the influence of changing stream gradient on accumulation of

TABLE 14-XII

Gold content of non-magnetic heavies versus average discharge in Harris Creek, British Columbia, 1988. From Fletcher and Wolcott (1989)

Date	Discharge (m^3 s^{-1})	Gold (ppb)
April 18–May 5	4.2	<15
May 5–12	5.6	<5
May 12	9.6	<10
May 12–13	15.8	10
May 13–14	17.4	1115
May 15–17	8.8	15
May 17–22	5.9	60
May 22–23	7.5	<10
May 23–28	6.0	<10
May 28–June 17	4.1	<5

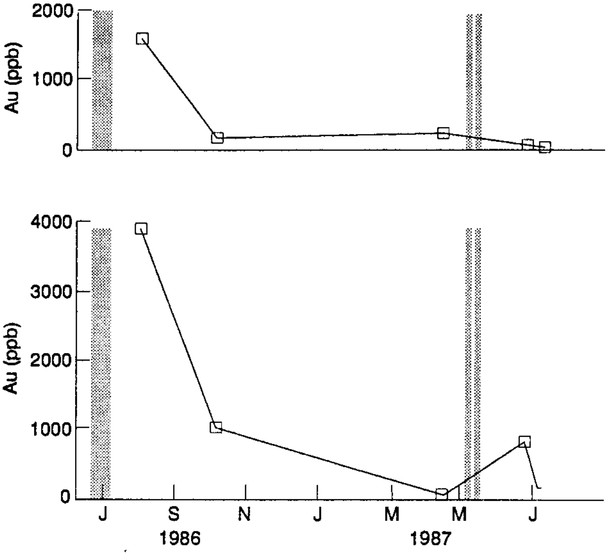


Fig. 14-34. Seasonal variations in gold content of heavy-mineral concentrates from bar head gravels in Harris Creek, British Columbia. Upper and lower diagrams the −105 +75 μm and −75 +53 μm size fractions, respectively. Shaded areas indicate flood events (discharge >10 m^3 s^{-1}). Modified after Fletcher and Day (1989).

gold. However, gold concentrations in high-energy environments in Harris Creek appear to remain roughly constant over a 5 km distance downstream (Day and Fletcher, 1989, 1991) but to increase downstream, away from the supposed source in the Huai Hin Laep, Thailand (Paopongsawan and Fletcher, 1993). Similar downstream increases in concentrations of other heavy minerals are described by Fletcher and Day (1988c, 1989). The occurrence of placers

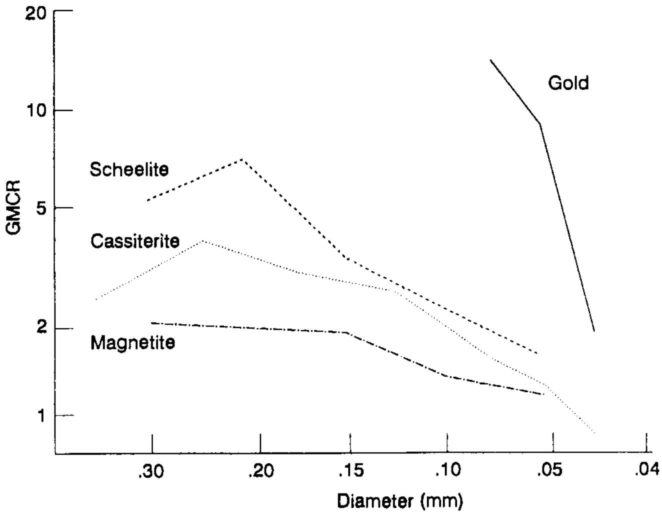


Fig. 14-35. Relation between the geometric mean concentration ratio (Saxby and Fletcher, 1986) of heavy minerals and their grain size. Modified after Fletcher and Day (1989).

at points of valley widenings or where highland valleys enter plains or larger valleys also indicates the importance of decreasing gradient (Table 14-IV). With respect to distance of transport of gold from bedrock sources "the half distance for gold is estimated to be only 15 km; which implies half the economic placer deposits of gold are nearer and half are further than 15 km from the primary source of gold" (Emery and Noakes, quoted in Taylor, 1986). Gold deposited as a thin skim on gravels after a flood, has been reported to travel up to 150 km downstream of the source in Sumatran rivers (Toh, 1978).

Sampling heavy-mineral accumulations in streams therefore generally leads to the identification of enhanced gold concentrations and longer anomalous dispersion trains downstream, sometimes for considerable distances. Such extended dispersion trains are excellent targets for low-density reconnaissance surveys. Bar head gravels and gravel pavements are a common bedform feature in many streams and provide the most consistent and easily recognizable sites for heavy-mineral enrichment. Small scale enrichments in swash zones or near sites of flow convergence caused by changes in bedrock geometry, are less likely to be sampled consistently throughout a survey area and are probably best avoided.

Because concentrations of gold in bar-head gravels do not follow the anomaly dilution model, it may be difficult to identify the cut-off point of anomalies that are gradually attenuated upstream. Thus, for follow-up exploration it may be more appropriate to collect sandy sediments from pools although care should be taken to collect samples below the surface of pools in order to avoid enrichments of heavy minerals associated with swash zones. As discussed previously these are often visible as black-sand strand lines that give erratic, anomalous gold values.

In a description of the discovery and exploration of the Wild Dog gold–silver–copper deposit in Papua New Guinea, the existence of "negligible" stream sediment and heavy-mineral concentrate anomalies is described by Lindley (1987). Concentrations of 1500 ppb in concentrates are restricted to within 200 m downstream from the deposit. No visible gold has been recognized in the concentrates and values in stream sediments are less than 50 ppb Au, probably reflecting the fine grained nature of the gold (1–12 μm) and the relatively recent exposure of the vein system.

Sampling of panned concentrates, stream sediments, visible gold, and float lead to the discovery of two epithermal gold provinces and six major prospects in Vanuatu (Hutchinson, 1987). The length of the dispersion train amongst the different sample media or indicators varied somewhat from case to case.

Of the elements associated with primary gold mineralization, some have been shown to constitute pathfinders for gold in geochemical drainage reconnaissance by virtue of longer dispersion trains, better anomaly contrast or relative ease of analytical determination compared to gold itself. Arsenic has been noted as a pathfinder that frequently best combines these criteria (Boyle and Jonasson, 1973).

Areas where gold had been noted in stream sediments in the western parts of Northern Ireland, as indicated in early reports, were found to be associated with an extensive As anomaly in the stream sediments, disclosed by multi-element geochemical mapping of Northern Ireland (Applied Geochemistry Research Group, 1973). Systematic exploration over an area of approximately 900 km^2 to the northwest of Curraghinalt, Northern Ireland is described by Woodham et al. (1988). Most of the area is underlain by late Pre-Cambrian–Cambrian metasediments covered by thin glacial till, with a well developed stream network. An initial survey involving the analysis of the minus 80 mesh fraction of stream sediments for eleven elements, including arsenic and gold, indicated that gold concentrations were mostly below the limit of detection of 5 ppb, and anomalies were difficult to reproduce. A further survey was carried out using 10 kg of unsieved stream sediment which was panned and inspected visually. Subsequent improvement in representativity was achieved by sieving a 100 kg sediment sample at each site to <1 mm, and panning the sieved material to give a mineral concentrate of 30–40 g, which was analyzed for Au and Ag. Threshold values of approximately 5 ppm Au in the heavy-mineral concentrate, 12 ppb Au in the <1 mm fraction and 2 ppb Au in the bulk sample were established. Clustering of anomalies reflected a gold-mineralized shear zone, and other gold occurrences.

The multi-element analyses of heavy-mineral concentrates of wadi samples together with limonitic alteration recognised on the basis of remote sensing served to identify several gold targets considered to be worthy of further exploration in Saudi Arabia (Raines and Allen, 1985).

Exploration for gold in the Red Sea Hills province of Sudan, has been shown to be hampered by variations in the surface environment (Fletcher, 1985). The region variously consists of areas of flat-lying wind-blown sand and transported alluvium; areas of deeply weathered bedrock and residual soils related to an earlier weathering surface, and areas of steep incised drainage with poorly developed stony soils. The most universally applicable reconnaissance procedure was found to be provided by the gold contents of heavy-mineral concentrates of drainage sediments at a frequency of one sample per 10 km^2. Although the minus 250 μm fraction of stream sediments may reflect mineralization the superiority of the heavy-mineral fraction in terms of greater contrast between background and anomalous values is clearly evident (Fig. 11-14). The use of the heavy-mineral fraction avoids the problem of the fine fraction of stream sediment samples being variously diluted by aeolian material. In this particular case distinctly anomalous concentrations of arsenic are also apparent but the recorded variation in the mineralogical associations amongst different gold occurrences would indicate in this case the desirability of basing exploration on the analyses of gold rather than potential pathfinders.

In a programme aimed at the discovery of bedrock gold mineralization in Gabon, variable anomalous responses were noted in heavy-mineral concentrates of stream sediments, soils and saprolite related to bedrock mineralization (Wilhelm and Essono Biyogo, 1992). This situation was attributed to the existence of variable weathering histories throughout the area, the implication being that anomalous gold responses in the heavy-mineral concentrates and drainage sediments should serve only as a "qualitative" guide to identifying areas warranting further investigation.

In a former placer-gold mining area in Quebec, heavy-mineral concentrates of stream sediments have been shown to contain anomalous gold contents (Maurice, 1988). Many of the anomalies occur outside the known placer areas and the gold is thought to have be derived by erosion of (a) the gold-enriched regolith which extended over the area prior to Quaternary glaciation, (b) gossanised upper parts of primary gold and gold-bearing polymetallic deposits and (c) pre-existing placers.

In a drainage survey in three areas of the Austrian Alps essentially coincident anomalies were indicated by analyses of both the heavy-mineral concentrate and the minus 64 μm fraction although the latter fraction displayed a longer dispersion trail and generally a clearer impression of the regional gold distribution (Reimann, 1988).

The case history examples cited hitherto variously involve the determination of gold in the heavy-mineral concentrate or a particular size fraction of the drainage sediments utilizing analytical procedures with detection limits in excess of 1 ppb. Attention has in many cases been paid to obtaining a representative sample having regard to the expected grain size and concentration of the gold on identifying concentrations well in excess of the detection limit. In marked contrast to the emphasis on collecting large samples in the interests of meeting representativity requirements, the occurrence of significant regional scale low order concentrations attributable to sub 5 μm or "ultrafine" gold in drainage sediments surrounding mineralized centres has been reported in China (Xie and Wang, 1991). In reconnaissance programmes samples are collected at a frequency of one sample per km^2 with samples from 4 km^2 being composited. The minus 250 μm (60 mesh) or 177μm (80 mesh) fractions are pulverised to minus 75 μm (200 mesh) and 10–20 g samples analyzed by an analytical method with a detection limit of 0.2 ppb. Results indicate regional thresholds in the 2–4 ppb range with concentration centres of 4–8 ppb defining targets for follow-up surveys. Subsequent follow-up has confirmed the reliability of the reconnaissance results and the overall approach has contributed "to the discovery of hundreds of new gold occurrences, some of which are or will soon be producing mines" (Xie and Wang, 1991).

In a drainage sediment survey over a 1600 km^2 schist belt in Sierra Leone anomalous arsenic values (>3 ppm) were identified in the minus 177 μm fraction stream sediments, (Fig. 14-36; Nichol et al., 1966). In the south of the area, at Baomahun, values exceeding 15 ppm As, occur over auriferous quartz–arsenopyrite mineralization and in the centre of the area, at Yirisen, the high arsenic values occur over gold and sulphide-bearing veins. More recently, however, gold mineralization independent of any arsenic association has been located.

Over the last two decades, the importance attached to stream sediment dispersion patterns of arsenic is reflected in its inclusion in geochemical reconnaissance mapping programmes. Plant et al. (1989b) document 38 stream sediment surveys, each covering an area of 5000 km^2 or more, of which at least 25 incorporate arsenic in the suite of elements determined on the samples. By contrast, only seven of the surveys involve the analysis of samples for gold.

Antimony has a lower natural abundance than arsenic and poses greater analytical problems, but it is a useful pathfinder. Boyle and Jonasson (1984) report dispersion trains of up to 6 km in sediments of streams draining gold mineralization at Keno Hill, Yukon, and Plant et al. (1989a) describe how anomalous arsenic and antimony concentrations in stream sediments reflect three known gold deposits in the southwest Highlands of Scotland.

Silver and mercury are pathfinders for epithermal gold deposits, and it is common practice to analyze stream sediments routinely for Au, Ag, As, Sb and Hg in gold exploration projects. Other elements associated with gold mineralization, such as Se, Te, Bi and Tl, have attracted less interest as pathfinders in drainage geochemistry, due to their low natural abundances and necessity for element-specific analytical procedures.

Moss mats

Prospectors and placer miners have traditionally recognised the value of moss mats, growing above normal stream level, as traps for gold. In McKay Creek, Vancouver Island, sands separated from moss mats have been shown to provide better contrasts and longer dispersion trains for gold than stream sediments (Fig. 14-37; Matysek et al., 1989). Higher concentrations of gold in moss mats relative to stream sediments and suggest that the moss traps sediment being transported under flood conditions when deeply buried gold is released from the stream bed (Fletcher and Wolcott, 1991).

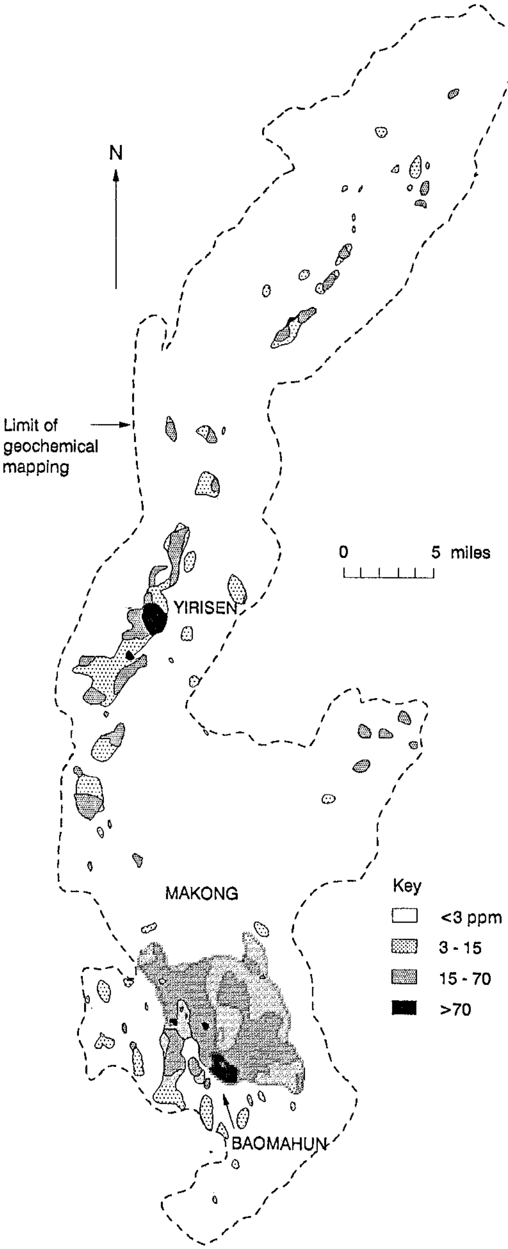


Fig. 14-36. Distribution of arsenic in the −177 μm (−80 mesh) fraction of stream sediments in region of gold mineralization, Sierra Leone. Reproduced with permission from Nichol et al. (1966).

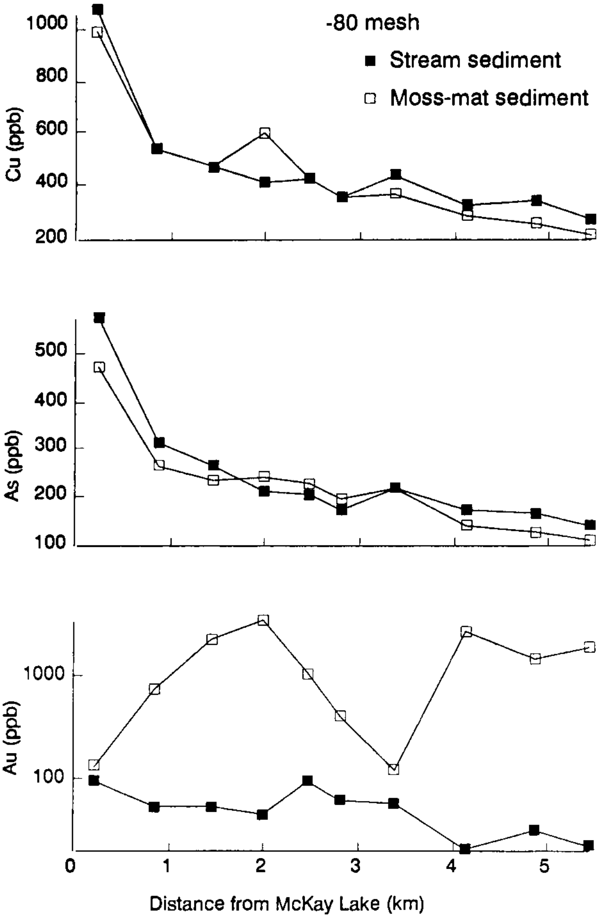


Fig. 14-37. Stream sediment and moss-mat sediment dispersion patterns in McKay Creek, Mount Washington. Estimated background levels for copper, arsenic and gold are 50 ppm, 20 ppm, 24 ppm and 13 ppm, respectively, in moss-mat sediments. Modified after Matysek et al. (1989).

Waters

Based on the analysis of spring well, stream and sea waters from the United States it was concluded that background concentrations of gold in natural waters are 0.001–0.005 ppb, and anomalous concentrations are 0.010–2.8 ppb (McHugh, 1988). However, considerable overlap in the data from mineralized and unmineralized areas was noted (Fig. 14-38). Many of the anomalous Au concentrations are for waters draining mines or brine wells, although not all mine drainages are anomalous. Concentrations of up to 0.130 ppb Au have also been reported in stream waters draining disused gold mines in southeastern Australia (Hamilton et al., 1983). Stream waters in a creek in British Columbia (Fig. 14-39), draining an area postulated to be an epithermal system, and

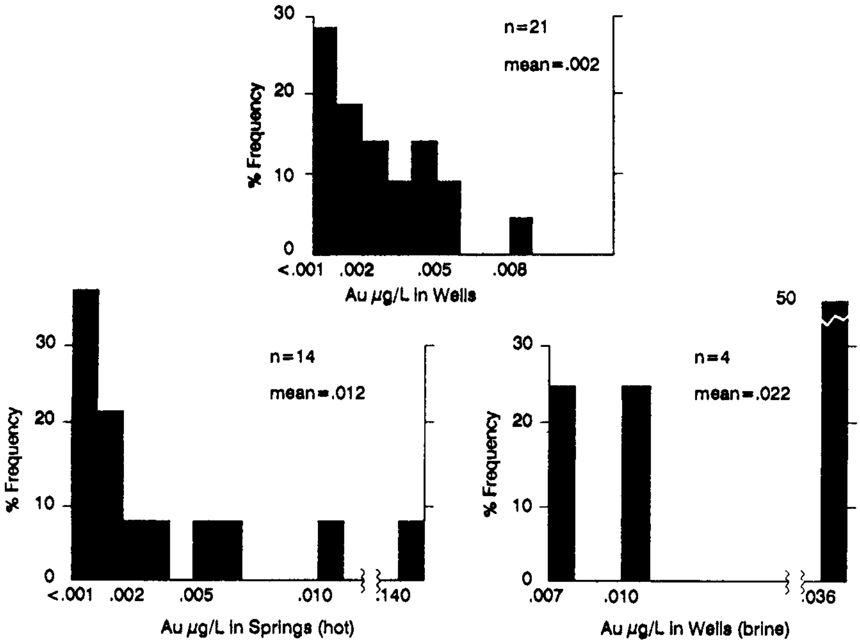


Fig. 14-38. Distribution of gold in well, well brine and hot spring waters. Modified after McHugh (1988).

characterised by downstream placer gold, contained anomalous gold contents of 2.5 ng/l Au (0.0025 ppb) near the headwaters suggestive of gold mineralization being associated with the epithermal system (Hall et al., 1986).

Lake sediments

Conventional geochemical exploration techniques utilising drainage sediments have found limited application in areas of exotic glacial overburden and/or indefinite and disorganized drainage systems characteristic of large areas of Canada, particularly those underlain by the Canadian Shield. A unique feature of many of these areas is the high density of lakes. It has been shown that the composition of lake sediments can be used as an indicator of several types of mineral deposits.

Organic-rich lake-centre sediments from the centre of lakes have been shown to reflect the presence of gold deposits in Saskatchewan (Coker et al., 1982). Gold concentrations in organic-rich lake-centre samples have also been shown to reflect the Kempt Back Lake gold occurrence in Nova Scotia, and the Hemlo gold camp, together with anomalous concentrations of As, Mo and Sb.

Anomalous gold contents in organic-rich lake sediment samples have been shown to reflect mineralization in Newfoundland, with a sampling density of 1 sample per 4–5 km^2 using lakes less than 0.1 km^2 in size, providing adequate

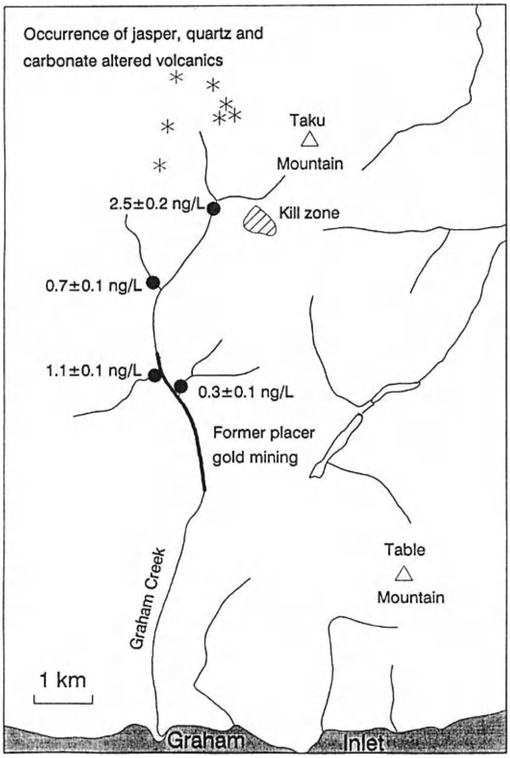


Fig. 14-39. Distribution of gold in stream water associated with placer deposit in British Columbia. Modified after Hall et al. (1986).

consideration is given to topography and glacial processes (McConnell and Davenport, 1989). Gold, Sb, As, Se, W and Cr determinations were carried out on 1200 lake sediment samples collected at a density of one sample per 6 km^2. Gold concentrations reflected known mineralization in one area but failed to detect mineralization in a topographic low in a second area. The pathfinder distribution was considered to reflect faulting in the hydrothermal systems and constitute broader exploration targets (Davenport and McConnell, 1988).

In Nova Scotia, analysis of organic-rich lake-centre samples indicated anomalous gold contents associated with known gold occurrences, and identified additional anomalous locations warranting further investigation (Rogers, 1988). Examination of heavy-mineral concentrates of the organic-rich sediments indicated the presence of particulate gold indicative of mechanical dispersion.

Gold appears to occur in organic lake sediments either in the particulate form or associated with organics. On the one hand no relation has been noted between Fe, Mn and LOI with gold, indicative of gold not being associated with Fe and Mn oxides and hydroxides or organics, whereas on the other

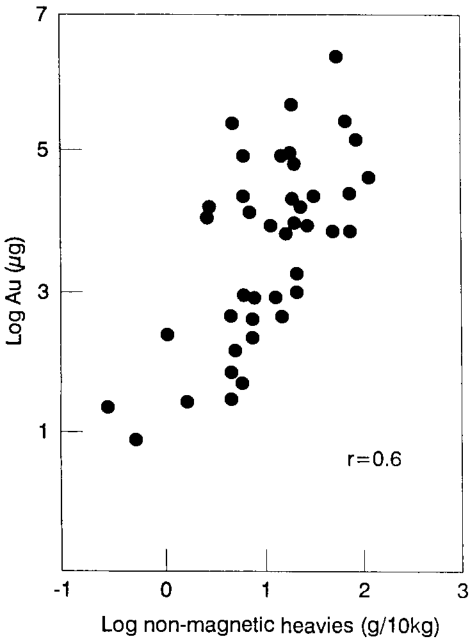


Fig. 14-40. Gold content of −500 +106 μm non-magnetic heavy minerals versus weight of the non-magnetic heavy-mineral fraction for 51 stream sediments from Nevada. Note that gold concentrations increase fivefold for a threefold increase in non-magnetic heavies. Modified after Fletcher and Day (1989).

hand improved reproducibility of gold analyses with increasing organic content indicative of the association of gold with organics has been noted in another instance (Hornbrook, 1989).

Data presentation and interpretation

Sedimentological behaviour of gold is also relevant to the choice of data presentation. Theory (Fig. 14-12) and field observations (Fig. 14-35) indicate that whenever heavy minerals are enriched on the bed of a stream in response to local hydraulic effects, the very high density of gold results in it having the greatest enrichment as illustrated with data for a drainage survey in Nevada (Fig. 14-40; Fletcher and Day, 1988c, 1989). It follows that, where streams are eroding lithological units with reasonably similar heavy-mineral contents, such variations can be minimized by presenting data as relative concentrations of gold (i.e., ppb) gold in the heavy-mineral fraction. Calculation of an absolute gold value (i.e., ppb Au × weight heavy-mineral fraction analyzed), sometimes advocated as a means of correction for catchment basin size and eliminating downstream anomaly dilution, will actually increase local variability due to hydraulic effects and change anomaly rankings (Table 14-XIII).

TABLE 14-XIII

Anomalous gold contents in 10 out of 51 heavy mineral concentrates ranked according to (i) relative concentrations of gold (ppm); and (ii) absolute abundance of gold (μg) in a 10 kg bulk sediment sample. From Fletcher and Day (1988c, 1989)

Au (ppb)	Au (μg)	Rank by ppm out of 51	Rank by μg out of 51
>99	>2380	1	1
66	235	2	3
40	435	3	2
26	91	4	7
20	47	5	13
18	86	6	10
16	54	7	12
16	37	8	15
10	90	9	8
10	15	10	24

In addition to identifying anomalous sites or catchments, interpretation requires that anomalies be ranked for follow-up. Ideally samples should be collected systematically from similar sites and be accompanied by relevant field information that identifies features of the sample sites. This is not always possible, however, particularly where gold is not the principal target of the survey. In these circumstances, variations in the heavy-mineral content of samples provides a useful indicator of changing parent material, poor sampling on sampling variability. Ratioing gold to magnetite contents, or to another ubiquitous heavy mineral, can help to identify anomalies that reflect local hydraulic conditions (e.g., Figs. 14-31 and 14-32).

DISCUSSION AND CONCLUSIONS

From the examples discussed it must be clear that the response of stream sediments to gold mineralization varies according to the sample type, size fraction, and mineral fraction analyzed, the number of replicate analyses and, most importantly, the area over which the gold mineralization outcrops. Hence there are considerable problems in the interpretation of drainage sediment data based solely on gold concentrations.

Moreover, the reliability of some commonly applied geochemical procedures is low. Thus although geochemical techniques have played an important role in the discovery of some deposits, other deposits may have been overlooked because inappropriate techniques have been used.

The theoretical aspects of gold geochemistry and sedimentology draw attention to some particular problems that must be considered in the design and implementation of geochemical surveys for gold exploration. Reviews of case histories also indicate that there are considerable variations in the type of response for gold mineralization shown by drainage sediments.

DESIGN OF GOLD EXPLORATION PROGRAMMES USING GEOCHEMISTRY

For success in gold exploration, the nature of gold (i.e., low abundance, occurrence as gold and the high specific gravity) necessitates particular care in designing an effective exploration programme by paying attention to sampling, sample processing, analysis and interpretation of the data.

The variability in size of gold particles, gold concentration, and degree of representativity necessary to achieve success are fundamental features characteristic of a given exploration area; features that we have no control over but need to take into account in designing and implementing an exploration programme. The fundamental requirement is to obtain an adequately representative sample to meet necessary representativity levels. In this way attention must be focussed at the outset of an exploration programme to undertaking an orientation survey aimed at identifying the nature of gold dispersion in the drainage systems associated with mineralization as a basis for identifying the optimum methodology rather than assuming a particular methodology appropriate in one area will by suited to another area.

Orientation studies should include a range of potentially useful sample types collected at different distances downstream of mineralization to identify the optimum sampling media and density. Sampling of background areas should also be carried out over the full range of lithological and surface environments present.

The features that warrant attention are shown in Table 14-XIV (modified after Harris, 1982) and discussed below under the aspects sampling, sample processing, analysis and interpretation.

TABLE 14-XIV

Aspects to be considered for increasing the reliability of data in gold geochemistry

Stage	Focus
Sampling	Type Location Season Collection Size Treatment
Sample preparation	Bulk Reduction Concentrate Subsample
Analysis	Weight Replicate Quality control
Interpretation	

Sampling

In drainage sediment surveys appropriate sample type may be very coarse gravel or fine silt depending on the size of gold particles characteristic of the deposit being sought. Every effort must be made to ensure that samples are comparable and of the same type, or where this is not possible differences must be taken into account during interpretation. The identification of the location or environment (bedform) where the appropriate sample can be obtained is particularly important. Gold is expected to be relatively medium or fine grained respectively in high- or low-energy depositional environments in stream sediments. Moreover, in areas of highly variable rainfall or meltwater or run-off the appropriate season for sampling should be considered.

The collection procedure adopted to obtain an adequately representative sample is particularly important in gold exploration and consideration needs to be given to methods for obtaining a representative sample. Considerable variation in gold contents has been shown to exist within very short distances in drainage systems (Harris, 1982).

The success of surveys depends critically on the collection of samples of adequate *size*. This varies according to the size of gold particles and inversely with the content of the gold concentration and level of representativity required. Sampling gravel bars may require large bulk samples (>100 kg) to be field screened to obtain representative subsamples (Day and Fletcher, 1986, 1989). Consideration therefore needs to be given to the adequacy of any on-site sample treatment with particular reference to the potential loss of any significant gold-bearing component of the sample during sample treatment. Gold may be lost, for example, during the collection of the fine-grain fraction of stream sediments.

Sample preparation

The purpose of the sample preparation stage is to prepare the sample collected in the field into a form suitable for analysis. It is important that the entire *bulk* sample collected is processed to generate as large and homogeneous a subsample as possible. The appropriate sample particle size *reduction* procedure should be examined, e.g. sieving or concentrating. Grinding should be avoided since this tends to smear gold on sampling equipment and is a source of cross contamination. The separation of samples into different size fractions by sieving helps to identify the grain size distribution of gold.

Heavy-mineral concentrates can be prepared either by field panning or under laboratory conditions to concentrate gold from a large sample into a smaller sample that is representative for analysis. The efficiency of gravity tabling depends on the particle size of the gold grains and it is necessary to ensure that fine-grain sized gold is not lost during the process. The limited efficiency of gravitational methods in recovering fine-grained gold, has long been recognized by placer miners.

The final stage of sample preparation, involving splitting to generate representative subsamples for analyses requires particular care.

Analysis

Analytical methods commonly used for gold determinations involve the analyses of 10–50 g samples. These methods include adaptions of the traditional fire assay procedures, acid digestion and neutron activation with estimation of the gold content by gravimetry, atomic absorption, plasma or activation neutron analysis. Considerable variations in technique are possible to suit individual analytical requirements according to e.g. the bulk composition of samples, the concentration range of interest, and the accuracy and precision required. The exploration geochemist should discuss the nature of exploration programmes and analytical requirements with the analyst to ensure that appropriate analytical procedures are employed (Burn, 1984). The size or weight of the sample being analyzed, or alternatively the number of replicate analyses, can be increased to improve representativity.

A system of quality control to monitor the representativity of different stages in the exploration sequence is essential. Duplicate field samples, and sample processing subsamples, and samples of known composition (reference materials) can be used to monitor sampling, sample processing and analytical error, respectively. This is best achieved by inserting at random, control samples that cover the concentration range of interest at an overall frequency of some five percent. It is important that the sampling and sample processing stages be monitored by submitting replicate subsamples from each stage for analysis. To quote from Burn (1984, p. 474), "Control of the quality of sampling and preparation processes is very often a blind spot for many people, who may lavish excessive efforts on checking the assay laboratory but fail to recognise the shortcomings in the preceding stages. Control of assaying is the easier and more obvious procedure to implement. Even so, however it is carried out, if it is not backed by control in the preceding stages, its results can lead to unjustified confidence in the reliability of the results. In the worst cases highly precise, accurate assays may be produced by the analyst, from the small subsamples he has received, which bear little relationship to the values of the samples from which they were originally derived".

Interpretation

At the interpretation stage it is important that consideration be given to identifying criteria which can be used to evaluate the relationship of data to mineralization. In particular, consideration needs to be given to the type of sample, and the type of the surface environment to which the analytical data relate.

Adoption of an exploration method should also take into account factors such as (a) financial resources, (b) time constraints, (c) personnel, (d) equipment,

(e) accessibility and (f) past experience. The exploration methodology will thus represent a compromise between the technically desirable and the economically practicable. Nevertheless, it is critically important to know the confidence that can be placed in the results and their limitations. The cost of an orientation survey in relation to the total cost of an exploration programme is small and the cost always repays the initial investment.

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Chapter 15

DRAINAGE GEOCHEMISTRY IN URANIUM EXPLORATION

ARTHUR W. ROSE

INTRODUCTION

During the late 1970's, the number and coverage of water and sediment surveys conducted for geochemical exploration and evaluation of uranium resources probably exceeded that of all other types of geochemical surveys. For instance, in the NURE (National Uranium Resource Evaluation) program in the USA, over 700,000 sediment samples and 300,000 water samples, representing about 67% of the total land area of the USA, were collected and about 14 million element determinations were preformed (Everhart, 1981). Similar programs were conducted in Canada, Britain, France (Soyer, 1984) and many other countries. Extensive orientation surveying and testing of methods were also carried out. The groundwork had been laid during an earlier period of uranium exploration from 1950 to 1958, when a considerable number of geochemical test surveys and small geochemical exploration surveys had been conducted.

This chapter presents a review of the published information on this work. The study is not comprehensive, but an attempt has been made to review key studies published in journals as well as the extensive NURE studies in the USA. The emphasis is on North America, but encompasses some work from other regions. Most of the chapter deals with stream water, stream sediments and groundwater, in temperate, desert and tropical environments. Lake water and sediments are discussed separately in Chapter 7. A number of general references provide a guide to the literature on geochemical exploration for uranium (Table 15-I).

Radioactivity associated with decay of the ^{238}U series provides the basis for the radiometric surveys which dominate in detailed exploration, but in reconnaissance exploration, drainage surveys have gained a status comparable to that for base and other metals. Drainage surveys are capable of detecting concealed deposits and uraniferous regions that are not easily detected as radioactivity anomalies.

TABLE 15-I

Some general references covering geochemical exploration for uranium and its literature

Author	Title
Boyle (1982)	Geochemical prospecting for uranium and thorium deposits
Bowie et al. (1972)	Uranium prospecting handbook
IAEA[a] (1970)	Uranium exploration geology
IAEA (1973)	Uranium exploration methods
IAEA (1974)	Formation of uranium ore deposits
IAEA (1976)	Exploration for uranium ore deposits
IAEA (1977)	Recognition and evaluation of uraniferous regions
IAEA (1979a)	Evaluation of uranium resources
IAEA (1979b)	Uranium deposits in Africa: Geology and exploration
Hawkes (1982)	Exploration geochemistry bibliography (to January 1981)
Hawkes (1985)	Exploration geochemistry bibliography (January 1981 to October 1984)
Dyck (1978)	The mobility and concentration of uranium and its decay products in temperate surficial environments
Dyck (1979)	Application of hydrogeochemistry to the search for uranium
United Nations (1956)	Geology of uranium and thorium

[a] IAEA = International Atomic Energy Agency.

GEOCHEMICAL CONSIDERATIONS

Supergene geochemistry of uranium

A key factor affecting the dispersion of U in the surficial environment is the general immobility of U in the tetravalent oxidation state (U^{4+}) and its generally high mobility in the hexavalent oxidation state, as UO_2^{2+} (uranyl) or as its complexes with CO_3^{2-}, HPO_4^{2-}, OH^-, F^- and other anions (Langmuir, 1978). Hence uranium is generally soluble in oxidizing surface waters and shallow groundwaters but is insoluble in near-surface reducing environments and in most deep-seated environments (Fig. 15-1). Uranium may also be dispersed as colloidal UO_2, or as U adsorbed on colloidal Fe-oxides or organic matter (Giblin et al., 1981). The mobility of U in oxidizing environments is limited, however, by its mineralogical form; for example, where it occurs as a trace substitution in resistant minerals such as zircon, it is moved mainly mechanically.

During weathering of U ore bodies or halos around ore bodies, marked anomalies are commonly formed in groundwaters and other media in the vicinity of deposits. The mobility of U is similar to that of Mo (MoO_4^{2-}) and As (AsO_4^{2-}) and is significantly greater than that of most common base metals (Cu, Ni, Pb). As a result, a considerable emphasis has been placed on surveys

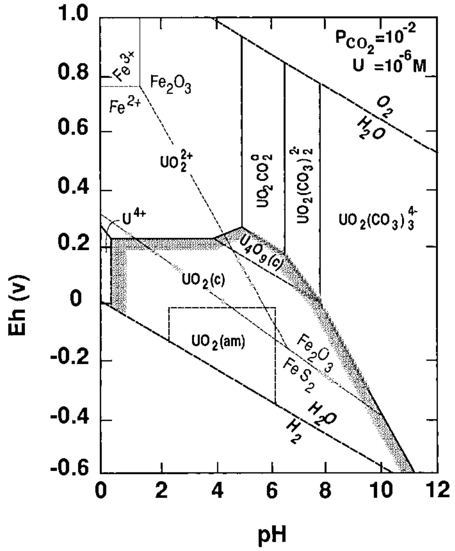

Fig. 15-1. Eh–pH diagram for the system U–O–H–CO_2 at 25°C, 1 atm total pressure, $P_{CO_2} = 10^{-2}$ atm, and U solubility of 10^{-6} M. Uranium is immobile in the hachured area. U_4O_9 field indicates approximate effect of nonstoichiometry of uraninite. UO_2 (am) shows approximate field in which amorphous UO_2 is expected to precipitate. Short dashes show stability of Fe species at 10^{-4} M sulfur and Fe^{2+} at 10^{-6} M (reprinted from Langmuir, 1978, Uranium solution-mineral equilibria at low temperatures with applications to sedimentary ore deposits, Geochimica et Cosmochimica Acta, Vol. 42, by kind permission of Pergamon Press Ltd.).

using natural waters, although stream sediments can give useful results in most environments.

Once dissolved, UO_2^{2+} is susceptible to significant adsorption by several materials, of which organic matter and iron oxyhydroxides are the most important (Szalay, 1964). Van der Weijden and Van Leeuwen (1985) show that U is enriched in peat by a factor of up to 6 × 10^5 relative to coexisting water at pH 4.6, with lower enrichments at more acid pH. Kochenov et al. (1965) and Rose et al. (1977) suggest similar enrichment factors, based on natural samples. Ishak and Dunlop (1985) show enrichment of U to levels of 100 to 500 ppm in the organic fraction of stream sediments, compared to values of 6 to 11 ppm in total stream sediment. Adsorption of U on organic matter is high at pH values greater than about 4, and is significant even at pH values of 3. In many situations, the adsorbing organic matter forms part of the solid phase (stream sediment or lake sediment), but in some situations, adsorption of U to colloidal suspended organic matter may allow dispersion of U "in solution". This process is suggested to operate in the drainage of lakes in the southern Canadian Shield and to result in greater dispersion of U than Cu, Zn and Pb (Cameron, 1980). The uranyl ion is also complexed by soluble humates and fulvates, so that some mobility of U can occur in organic environments.

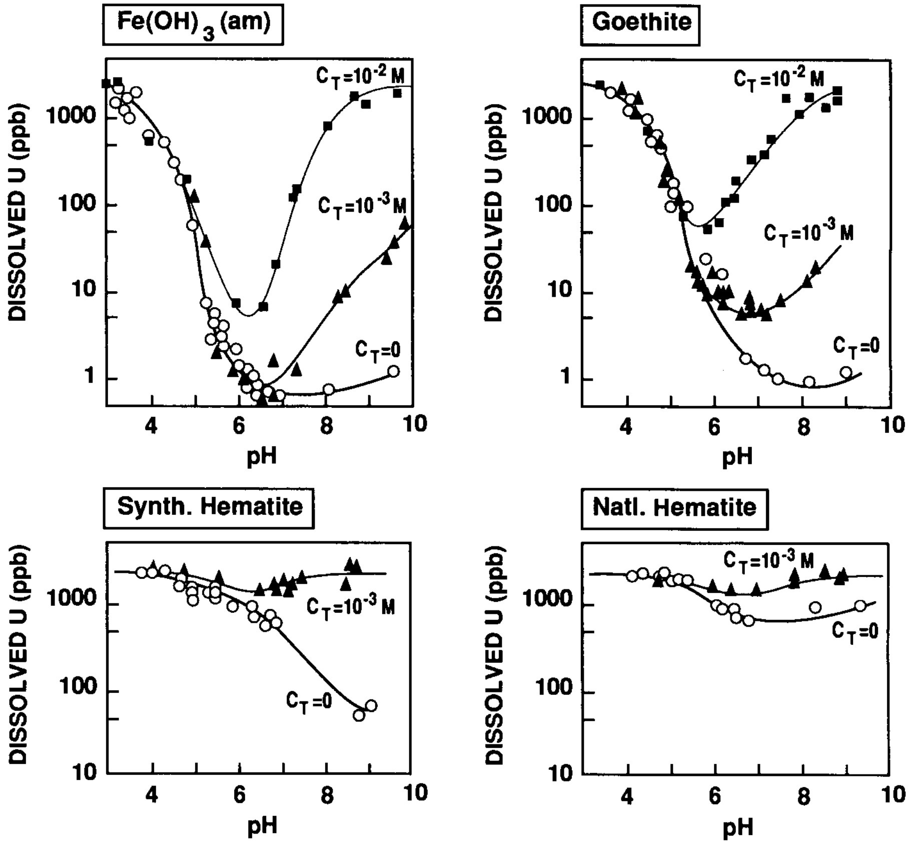

Fig. 15-2. Adsorption of UO_2^{2+} on Fe-oxides as a function of total carbonate (C_T), for $\Sigma U = 10^{-5}M$ and $\mu g/l$ Fe-oxide suspensions in 0.1 M $NaNO_3$ at 25°C (reprinted from Hsi and Langmuir, 1985, Adsorption of uranyl onto ferric oxyhydroxides: application of the surface complexation site-binding model, Geochimica et Cosmochimica Acta, Vol. 49, by kind permission of Pergamon Press Ltd.).

Freshly precipitated iron oxides strongly adsorb U above pH 5–8, with adsorption decreasing in the presence of CO_2 above about pH 6.5 (Fig. 15-2; Hsi and Langmuir, 1985; Ho and Miller, 1986). Ratios of U in Fe oxide to U in solution are about 10^6 for slightly acid solutions. Considerably less sorption is found on crystalline Fe oxides, such as goethite, hematite and organic matter at the rank of bituminous coal. Moderate concentrations of complexing elements, such as CO_3^{2-} and possibly PO_4^{3-} and fulvates, inhibit adsorption and are probably responsible for much of the observed mobility of U in natural waters. Relatively alkaline, carbonate-rich waters may allow dispersion of U through rocks containing Fe oxides, but in near-neutral or carbonate-free waters, U is relatively immobile because of sorption on Fe-oxides. Michel et al. (1983) show that the U content of sediment correlates with surface area of sediment grains as a result of adsorption.

The most important process controlling the background content of U in natural waters, especially in arid regions, is concentration by evaporation and by transpiration of plants. In contrast, U is extensively leached from rocks and soils in regions of high rainfall, to leave very low amounts of U to be dissolved and leached by later soil waters and groundwaters. As a general rule, the background values of U in water of humid regions, such as the eastern United States, are commonly 0.1 μg/l or less, accompanied by low contents of dissolved solids, whereas in arid regions such as the western United States, background values of 1 μg/l or more are typical, with high contents of dissolved solids (see also Fig. 8-21). Although this difference in U content may partly reflect U enrichment in rocks of the western United States, the major part is related to much higher values of U and all other soluble components in western waters, mainly because of concentration by evapotranspiration. This trend toward enrichment of soluble U in arid regions reaches a peak in the precipitation of carnotite in calcrete deposits, as at Yeelirrie, Australia. Evapotranspiration in irrigated areas can also lead to very high dissolved U values (Benson and Leach, 1979). The high concentrations of U in groundwaters of arid regions probably favoured the formation of sandstone-type ores in arid climates during the past. The background content of U in waters is discussed further in the sections discussing uranium anomalies in stream water and groundwater.

Supergene geochemistry of thorium

Thorium generally accompanies uranium in igneous processes. A relatively constant Th/U ratio of 2 to 4 is characteristic of most unmineralized igneous rocks and many metamorphic and sedimentary rocks (Rogers and Adams, 1970). The concentrations of both elements are very low in ultramafic rocks, low in mafic and intermediate rocks, and are highest in granites, rhyolites, and in some alkaline syenites and similar rocks.

Thorium is nearly immobile in the surficial environment because Th lacks the mobile hexavalent oxidation state of U. The Th^{4+} ion, if released by decomposition of its host-mineral phase, tends to precipitate or to be strongly adsorbed by silicates, oxides or other phases, and thus migrates at most only short distances (Langmuir and Herman, 1980). Thorium values in waters are always extremely low compared to U. The potential exists for recognizing depletion or enrichment of mobile U in weathered or altered rocks by examination of the Th/U ratio.

Radioactive decay products

Uranium and Th are unique in producing an extensive series of radioactive decay products (Fig. 15-3), most of which have chemical properties distinct from those of their parent nuclides ^{238}U, ^{235}U, or ^{232}Th (Dyck, 1978; Ivanovich and Harmon, 1982). In particular, ^{4}He (formed from alpha particles that have captured electrons) and ^{222}Rn are extremely mobile and tend to escape

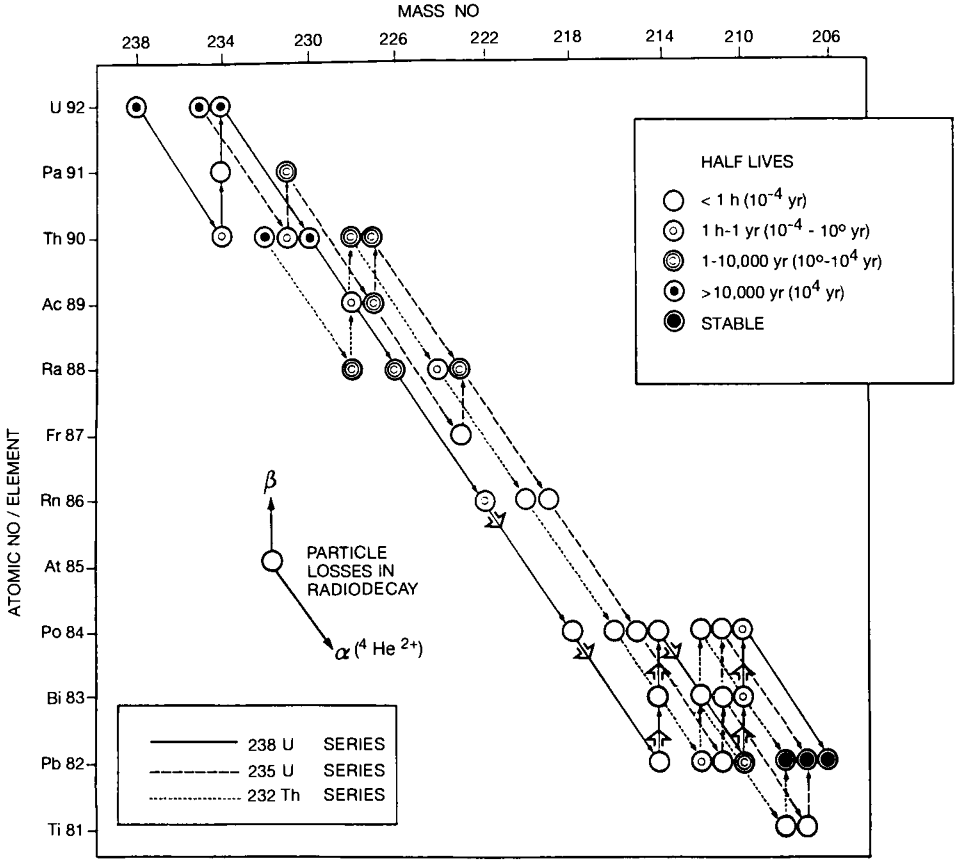

Fig. 15-3. Uranium and thorium disintegration series, showing half-lives and mode of decay (alpha and beta).

from their host, while ^{226}Ra, ^{234}U, ^{210}Pb and ^{206}Pb may migrate in solution independently of ^{238}U under certain conditions (Fig. 15-4). Conversely, ^{230}Th, ^{234}Th and ^{234}Pa are extremely immobile and tend to remain behind along with their daughters for significant periods of time, thus indicating the former presence of U. The distribution and relative proportions of the various U decay products can aid considerably in the detection of uranium ores. Most gamma radiation detected in airborne and ground surveys is from ^{214}Bi, a daughter nine steps down the decay chain of ^{238}U. The distribution of ^{214}Bi and certain other decay products can thus be determined by radiometric methods. Also, the use of radiometric surveys in geochemical exploration can require considerable knowledge of geochemical mobility of the daughters for proper interpretation.

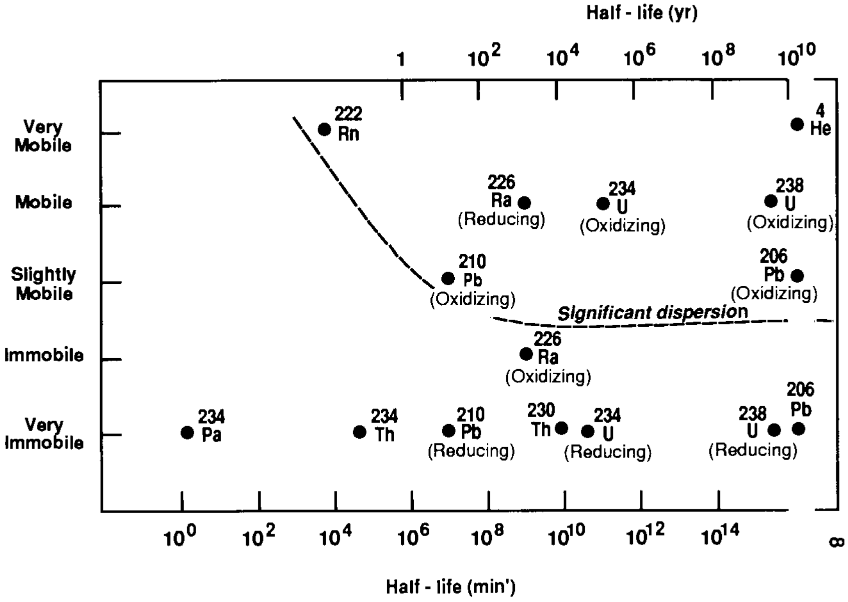

Fig. 15-4. Chemical mobility and half-life of ^{238}U and some of its decay products (reproduced with permission from Rose and Korner, 1979).

Non-radiogenic pathfinders associated with uranium mineralization

Table 15-II lists pathfinder elements for several important types of U deposits.

In igneous environments, U is enriched with Th, F and other incompatible elements (K, P, Ti, Zr, Mo, Re, rare earths) and commonly is most enriched in high-alkali (commonly peralkaline), relatively oxidized syenitic to granite plutons and volcanic rocks. This association of elements is common in the ores as well as in the associated igneous rocks, and is only slightly modified in the placer deposits and stream sediments derived from such sources. The coherence of Th^{4+} with U^{4+} is very close in magmatic phenomena because of their common valence and similar ionic size.

Under high-temperature hydrothermal conditions, U is accompanied by various combinations of Ni, Co, As, Ag, Cu, Pb and Zn. The hydrothermal deposits most closely association with igneous sources commonly contain F.

During weathering, especially under semi-arid to arid conditions, U forms very soluble uranyl carbonate complexes in surface and groundwaters. It tends to be accompanied by selenate, vanadate, molybdate, arsenate and similar anion complexes. These constituents are concentrated with U in sandstone-type deposits, calcretes, and possibly in lignites, as well as unconformity-type deposits and black shales, because this suite of elements are all precipitated by reduction.

TABLE 15-II

Pathfinder elements for major types of uranium deposits (modified after Mickle, 1978; Mathews et al., 1979)

Type of deposit		
I. Sedimentary association		
1. Placers	NE Florida; Idaho batholith (USA)	U,Th,Ti,Zr,P,RE(Au,Sn)[a]
2. Quartz-pebble conglomerates	Witwatersrand (South Africa)	U,Au,Ti
3. Marine black shales	Alum Shale (Sweden)	U,P,S(Mo,Cu,Ni,V)[a]
4. Phosphorites	Phosphoria Fm. (USA)	U,P,F
II. Magmatic association		
1. Pegmatites	Bancroft (Canada)	U,Th,F,Zr,Mo(RE,Nb)[a]
2. Autometasomatic-contact metasomatic type	Mary Kathleen (Australia) Ross-Adams (Alaska)	U,Th,F,RE,Nb
3. Anatectic type	Rossing (Namibia)	U,Th,F(RE,Zr)[a]
4. Volcanic association	Pena Blanca (Mexico)	U,F,Mo(Be,Sn,W,Li,Hg)[a]
III. Hydrothermal and groundwater association		
1. Magmatic hydrothermal	Radium Hill (Australia), Marysvale (USA)	U,F(Pb,Zn,Cu)[a]
2. U–Ag–Ni–Co veins	Echo Bay (Canada)	U,Ni,Co,Ag,As,Bi,Cu,Pb
3. Unconformity-type	Jabiluka (Australia), Rabbit Lake (Canada)	U,Ni,As,Cu,Pb,Zn,Au
4. Sandstone	Colorado Plateau (USA)	U,V,Se,Mo,As(Cu,Pb,Zn,Co,Ni)[a]
5. Uraniferous calcrete	Yeelirrie (Australia)	U,V
6. Uraniferous lignite	N. Dakota (USA)	U(Ni,Co,V,Sn,RE)[a]
IV. Universal pathfinders		^{234}U,^{226}Ra,^{222}Rn,^{214}Bi,He,etc.

[a] () indicate minor association in some deposits.

In most situations, U is the most effective indicator element for uranium deposits, because of its very high enrichment in ores. However, for deposits associated with magmatic rocks, Th can be a useful pathfinder in stream sediments because it is essentially insoluble in surface and groundwaters (Langmuir and Herman, 1980), whereas U can be extensively leached in oxidizing conditions. The association of U with F in many environments can be useful because of the relatively high solubility of F in natural waters.

PRACTICAL CONSIDERATIONS

Sampling and sample treatment

The most problematic aspects of sampling concern waters. Some workers consider that filtration of water samples can remove significant amounts of suspended and colloidal humic or other material and thereby weaken anomalies (Boyle, 1982, p. 278) or that dissolved U will be adsorbed on filter paper (Soyer, 1984). Others recommended filtration as a means of avoiding the variability that arises because of different amounts of U in suspended material at different sites and between aliquots from the same sample, and also to allow meaningful calculations of saturation states (Wenrich-Verbeek, 1977a). Waters are commonly acidified (after filtration) to avoid adsorption of U onto container walls or other modes of loss from solution, though U in most waters seems to be relatively stable (Wenrich-Verbeek et al., 1976; Boyle, 1982, p. 279). Acidification of non-filtered waters is generally to be avoided because particulates are dissolved, as demonstrated by Wenrich-Verbeek (1977a). Filtration of turbid waters is essential for reproducible results, especially if waters are acidified (Wenrich-Verbeek et al., 1976), but for clear waters it is generally not needed. The value of the different procedures may vary from one area to another, but the writer prefers to filter (0.45 μm Nuclepore or Millipore filters) and acidify in order to obtain values for only dissolved constituents (plus the finest suspended material that will pass a filter). However, in areas with clear waters containing little or no suspended or colloidal material, the time spent in filtration may not be justified.

An alternative method of sample treatment is to pass waters through a cation–anion exchange resin at the sample site and retain the resin for laboratory analysis (Parslow and Dwairie, 1977; Price, 1979; Ward and Price, 1980). If this procedure is used, the fate of suspended matter and its significance should be considered. Filtration may be desirable.

Additional measurements and observations which should be carried out on waters at the sample site or laboratory include pH, specific electrical conductivity, dissolved oxygen (groundwaters), alkalinity and evidence of reducing conditions (such as H_2S). Measurement of conductivity is especially important because this easily measured parameter can be used as a guide to the content of total dissolved solids (TDS) of waters, and can be used to infer many kinds of dilution or concentration processes affecting background levels of U, as discussed later.

Problems in the collection and treatment of stream sediments for U exploration are similar to those encountered in exploration for other elements. In general, U tends to concentrate in the fine size fractions (Fig. 15-5) because of adsorption onto Fe-oxides and organic matter, which are concentrated in these fractions. However, in localities with appreciable U-bearing accessory or ore minerals such as zircon and brannerite, there may also be enrichment of U in coarser fractions (Wenrich-Verbeek, 1977a). Pradier (1985) recommends the <63 μm fraction (<230 mesh), Wenrich-Verbeek (1985) the <90 μm fraction (<170 mesh), Plant (1971) the <150 μm (<100 mesh) fraction, and Beeson (1984) the <70 μm fraction, although most of these conclusions were based on high contrast or absolute values of U without consideration of variability, as recommended by Rose et al. (1979, p. 328). Stier and Friedrich (1982) have shown that U-rich accessory minerals can also concentrate in the fine fraction of sediments and give rise to false anomalies.

The analysis of readily extractable U and comparison of extractable U with total U in stream sediments can be extremely valuable in detecting weak anomalies and interpreting the origin of anomalies. Methods for readily ex-

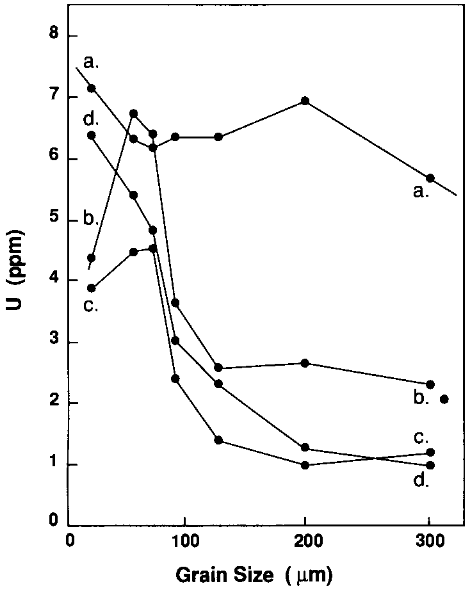

Fig. 15-5. U concentration vs. grain size in four samples of stream sediment, showing high values in the fine sediments (from Wenrich-Verbeek, 1976).

tractable U include carbonate–H_2O_2 and acetic acid–H_2O_2 solutions (Fletcher, 1981). Low ratios of ex U/total U suggest that most U is in resistant minerals (zircon, monazite), and high ratios, especially with high total U, indicate mobile U, possibly from dissolution of uraninite or similar relatively soluble minerals in an orebody.

Analysis for uranium

Three main methods have been used in recent years for the determination of U in different media (Ward and Bondar, 1979; Ward and Price, 1980).

In the fluorometric method, the sample is fused with an alkali fluoride and the fluorescence under ultraviolet light is measured. This method is simple, rapid and adequate for many purposes. It is subject to interference from Fe and Mn at high levels (>0.1% Mn, >30% Fe) but this is not generally a problem if care is used in identifying the samples with high concentrations of these elements. The detection limit of about 0.1 ppm in solid samples and 0.05–0.2 ppb in waters is adequate for most exploration programs, although precision may be poor at low levels. The fluorimetric method is generally well suited to U determination on solutions derived by partial extractions of stream sediments and other materials.

The delayed neutron activation method measures the neutrons emitted from fission products of ^{235}U at times up to 60 seconds after the neutron-induced fission of ^{235}U. The method is rapid and accurate, the main limitations being the availability of a reactor, and the cost of such a facility. Thorium also emits delayed neutrons on fission, but by appropriate adjustment of irradiation and counting conditions the interference can be minimized or used to determine both U and Th (although the detection limit generally is not as good for Th as U). The delayed neutron method can be used with partial extractions of sediments (Rose and Keith, 1976) but has most commonly been used for total U analysis. Water samples are usually analyzed following adsorption of U on an ion exchanger or adsorber (Fe oxide).

Laser-induced fluorescence is the basis of instrumentation developed by Scintrex Ltd. (Robbins, 1978). The fluorescence is measured directly in aqueous solution, after removal of potential interfering elements and compounds by suitable complexing. A detection limit of <1 ppb in solution is possible, and analyses can be carried out in field laboratories.

Other techniques that have been used successfully for determination of U include X-ray fluorescence and the fission track method. The X-ray fluorescence method is capable of a 1 ppm detection limit in solids, although matrix effects can be considerable, and the equipment is moderately expensive. The fission track method employs tracks formed in plastic detectors when U fissions in a neutron flux. The method can be very accurate for the determination of low U levels in waters, but requires access to a nuclear reactor and entails relatively time-consuming microscopy to determine the track density. Methods for uranium-series radioactive decay products mainly involve counting of radioactive decays (Ivanovich and Harmon, 1982), or mass spectrometry for ^{4}He.

Scale of surveys

Drainage surveys for U are performed on three scales:

(1) regional reconnaissance to identify uraniferous provinces (sample spacing $\geq$5 km^2/sample);

(2) more detailed reconnaissance surveys aimed at detecting anomalies from individual deposits or groups of deposits (sample spacing 1/2–5 km^2/sample); and

(3) detailed surveys to identify exploration targets within known mineralized districts.

In the following sections, case studies at a variety of scales are considered first, followed by discussion of the effect of various climatic and geologic factors on U anomalies.

CASE HISTORIES

Northwest Canada

Regional reconnaissance surveys using low sample densities were conducted extensively in the USA and Canada during the 1970's. Some of the most successful surveys were carried out in the Canadian Shield of the Northwest

Territories, where, for example, Cameron and Allan (1973) showed that the Bear Province, which contains uranium deposits at the Port Radium and Rayrock mines, has a mean U content of 5.3 ppm in about 1200 lake sediments, compared to 1.3 to 1.9 ppm in similar sets of samples in the adjacent Slave Province. The differences in the background level of U in the lake sediments thus reflect differences in U content of bedrock and in U metallogeny. At a more detailed scale, Cameron (1980) showed that anomalies in lake sediments extend over a 20 × 8 km area around the Rabbit Lake deposit in northern Saskatchewan. Lake waters show less extensive anomalies. This large extent of the sediment anomaly appears to originate by extensive glacial dispersion from the deposit.

Central Africa

The most valuable orientation surveys are those near major undisturbed ore bodies. Unfortunately, very few of these are reported, but the few that exist are instructive.

Grimbert (1963) described the distribution of U in stream sediment and stream water around the large sandstone-type U deposits of Mounana and Boyindzi in Gabon in central Africa. Two other sandstone-type deposits, the Oklo and Okelobondo, are about 2 km to the south. Over the Mounana deposit, a soil anomaly about 250 m in diameter with values of up to 80 ppm U in soils 3 to 6 m thick has developed. The vegetation is tall-grass savanna with local forest. Annual rainfall is seasonal, totalling about 2 m, and the area is cut by deep valleys. Sampling was conducted in 1956–7, prior to mining the deposits and shortly after the discovery of a small radiometric anomaly.

Figure 15-6 shows the distribution of U in stream sediments for the Mounana area. The highest value is 15 ppm U compared to a background of 1 ppm U (hot 2.5 M HNO_3 leach). Anomalous values of 4 and 5 ppm U extend for about 1.5 km downstream, and slightly anomalous values of 2 ppm extend for about 3 km downstream, although two intervening samples are not anomalous.

Stream water anomalies (Fig. 15-7) are not obvious near the deposit, but Grimbert (1963) showed that the regional background is about 0.5 μg/l U, so that the entire region is anomalous. The survey was conducted during the rainy season, and Fig. 15-8 illustrates the large seasonal variability in U levels in an anomalous stream near the deposit. The middle of the rainy season was concluded to be a favourable time for stream water surveys, because anomalous values in the dry season fall below 0.1 μg/l U and are therefore difficult to resolve. No data are available to establish whether ratios to TDS or conductivity would stabilize the seasonal effects.

Northern Australia

Relatively few geochemical investigations have been published for the large U deposits of the Alligator Rivers region of northern Australia. Some samples

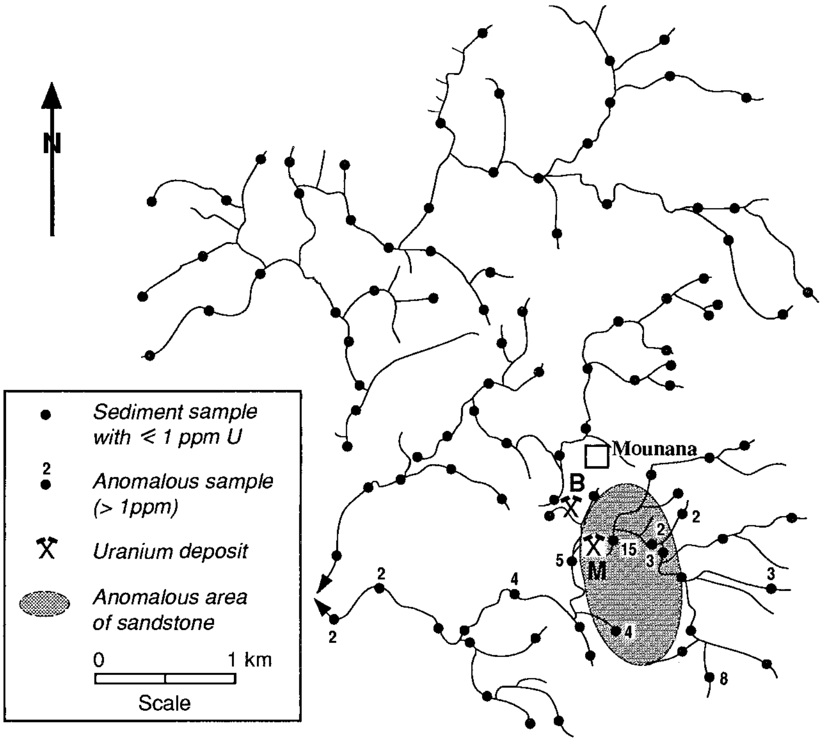

Fig. 15-6. Uranium (ppm) in stream sediments at the Mounana deposit in Gabon (modified after Grimbert, 1963). *M* indicates Mounana deposit, which crops out at the surface; *B* indicates Boyindzi deposit, which is blind at about 200 m depth. The Oklo deposit is about 2 km south of the Mounana deposit.

from a small suite of groundwaters from drillholes and auger holes at the unconformity-type Jabiluka deposit (Fig. 15-9) have U contents of 3–9 μg/l U in waters with TDS contents of 50 to 200 mg/l (Deutscher et al., 1980). Although these U values are not high, they are anomalous relative to the TDS contents of these waters. The extensive leaching and high and seasonal rainfall of the region are probably not conducive to the development of the higher U values found in more arid regions. A second type of water in nearby flood plain sediments has much higher TDS (500 to 7000 mg/l) with very high SO_4, low pH, and appreciable Fe^{2+} content. These waters appear to have undergone more extensive interaction with underlying pyritic schists. They contain 1–12 μg/l U, but are not clearly anomalous in view of their high TDS contents. In summary, the limited groundwater data suggest that anomalous U values occur near the Jabiluka deposit, but the hydrogeology and hydrochemistry are complex. Few stream sediment data are available, and the published results are not encouraging (Foy and Gingrich, 1977).

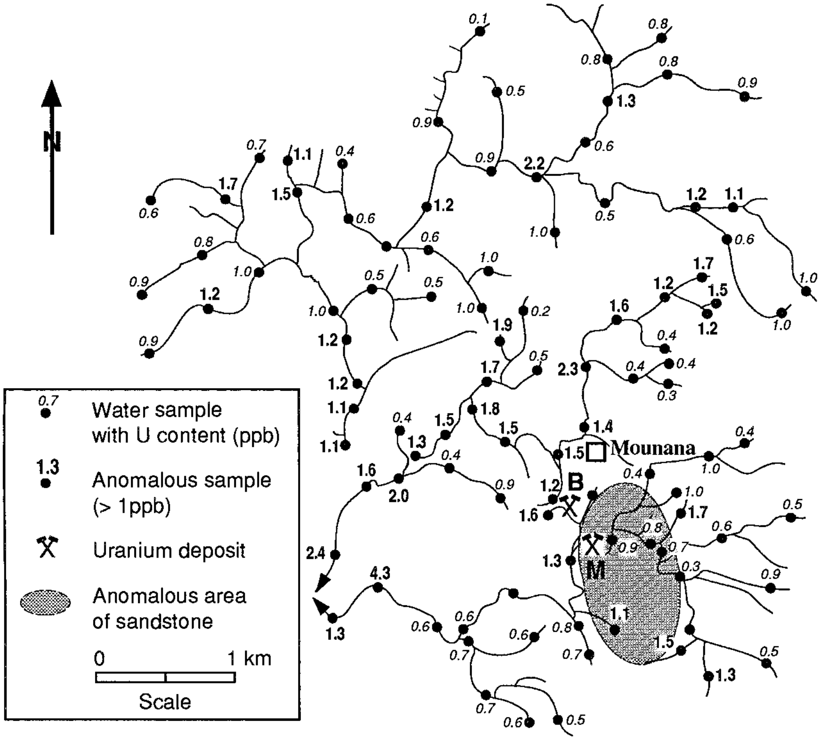

Fig. 15-7. U content of stream water (ppb) near the Mounana deposit in Gabon (modified after Grimbert, 1963). See Fig. 15-6 for *M* and *B*.

Western USA

Several sets of data available for waters near the Colorado Plateau and Wyoming sandstone-type U deposits of the western USA. Figure 15-10 shows the content of U in groundwaters near the Gas Hills ore deposits in Wyoming. Concentrations of 20 to 1300 μg/l are common near the deposits compared to background levels of 1–10 μg/l. Total dissolved solids are 300 to 2000 mg/l in the Gas Hills area (LaDelfe, 1980), and similar or somewhat lower in background samples.

Figure 15-11 illustrates the U contents of stream sediments near uranium deposits of the Tallahassee Creek area, Colorado. Several very small shallow sandstone-type deposits have been mined in this area, but the largest deposit (Hanson Creek, 13,600 metric tonnes U_3O_8) is buried and was discovered by drilling (Shannon, 1979). Total U values of stream sediments in the vicinity are indistinguishable from background, with values in the stream draining the deposits generally <4 ppm for a distance of 4.5 km downstream. Of the two anomalous values (>5 ppm), one is adjacent to a small mine; the other (14.7 ppm) may reflect undiscovered mineralization. Thus, these orebodies would not

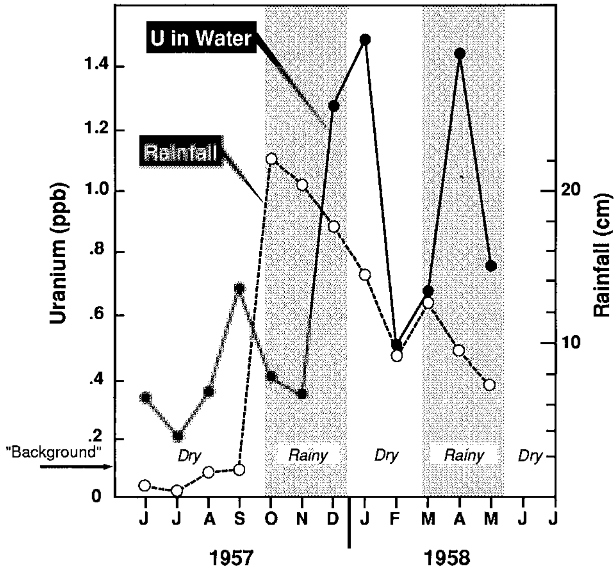

Fig. 15-8. Variability of U with time in stream water below prospect in Gabon (from Grimbert, 1963).

be easily discovered by stream sediments alone. Precambrian granitic rocks just to the east are U-rich, however, and give rise to distinct anomalies, commonly in the range 5–10 ppm (Shannon, 1978, 1979). Also, oxalic acid leaches of stream sediments along the stream draining the deposits (Carpenter, 1980) show distinct although weak anomalies which persist for several kilometres downstream (Fig. 15-12). This result is typical of a number of investigations that show much stronger anomalies in extractable U than in total U. The level of extractable U in the area underlain by granite is not known.

The Grants region of New Mexico, which contains the largest uranium reserves in the USA, has deposits of sandstone type in gently dipping Jurassic and Cretaceous sandstone, in the Ambrosia Lake, Laguna, Smith Lake, Crown Point, Churchrock, Noserock, and Marquez sub-districts. Figure 15-13 illustrates data for U in groundwater of the region, based on the NURE surveys (Maassen and Bolivar, 1979; Maassen and LaDelfe, 1980; Purson, 1981). A strong anomaly with U values >5 ppb parallels the outcrop of the Morrison Formation, the main host for ore (and probably the source rock for ore as well). Undoubtedly some of the high values, especially near the oldest mines north of Grants, result from contamination by mining operations or disturbance of the groundwater by mining, but many high values, especially over the western portion of the belt, are in areas with no mining at the time of sampling, and no contamination was recognized by the samplers. These data suggest that the region and the small ore bodies along the Morrison outcrop could have been detected by reconnaissance water sampling, although the discovery of major ore bodies down-dip beneath

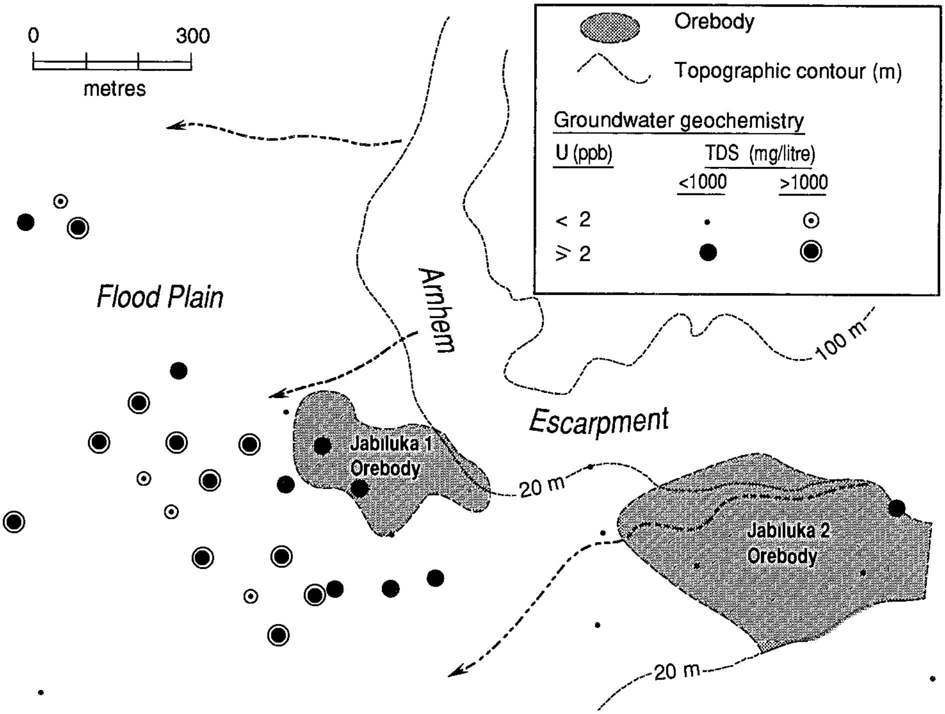

Fig. 15-9. Content of U and U/TDS in groundwater near Jabiluka deposit, Australia (from Deutscher et al., 1980).

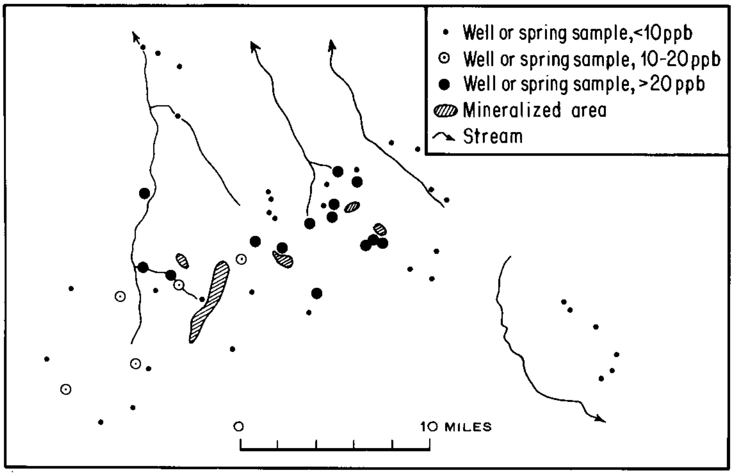

Fig. 15-10. U content of groundwaters, Gas Hills area, Wyoming (from Denson et al., 1956).

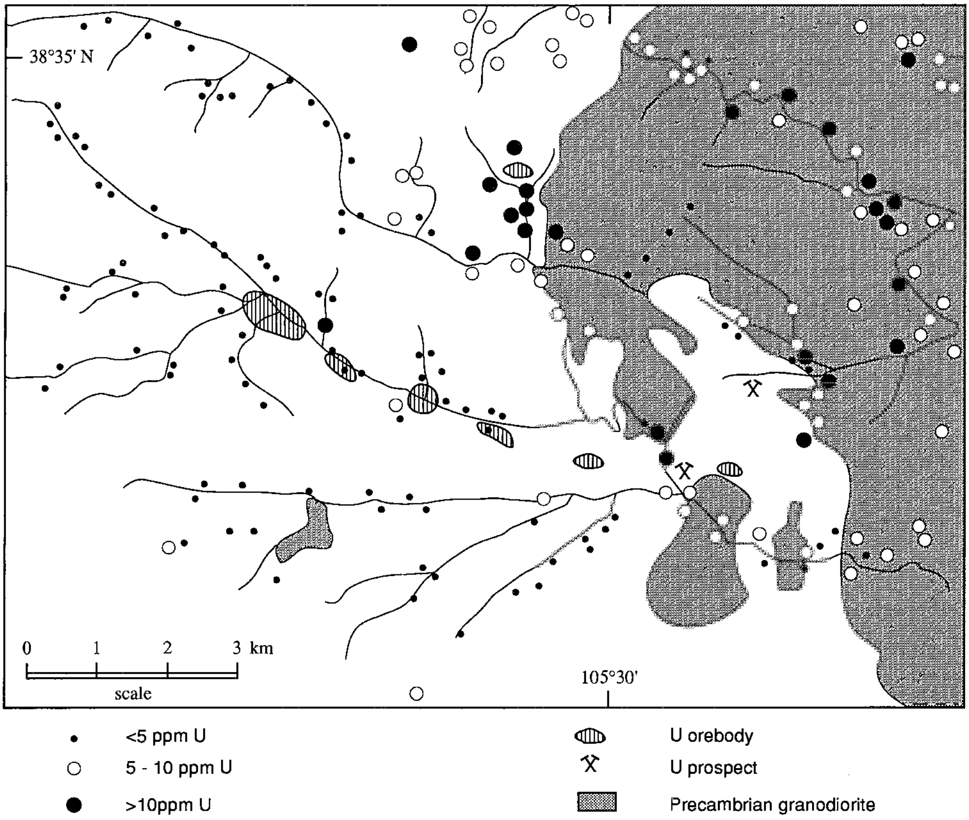

Fig. 15-11. Uranium in stream sediments from the Tallahassee Creek area, Colorado: total U in stream sediments (from Shannon, 1979).

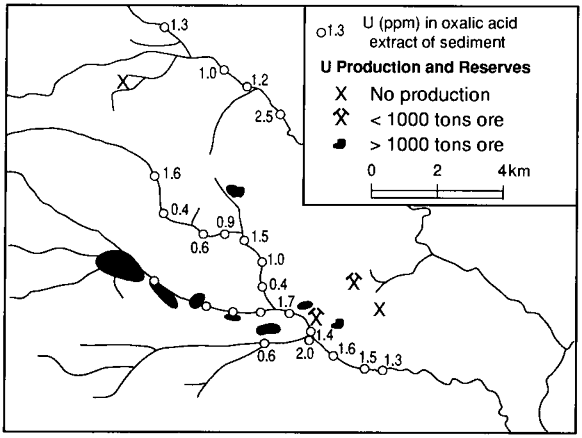

Fig. 15-12. Uranium in stream sediments from the Tallahassee Creek area, Colorado: oxalic acid extractable U (from Carpenter, 1980).

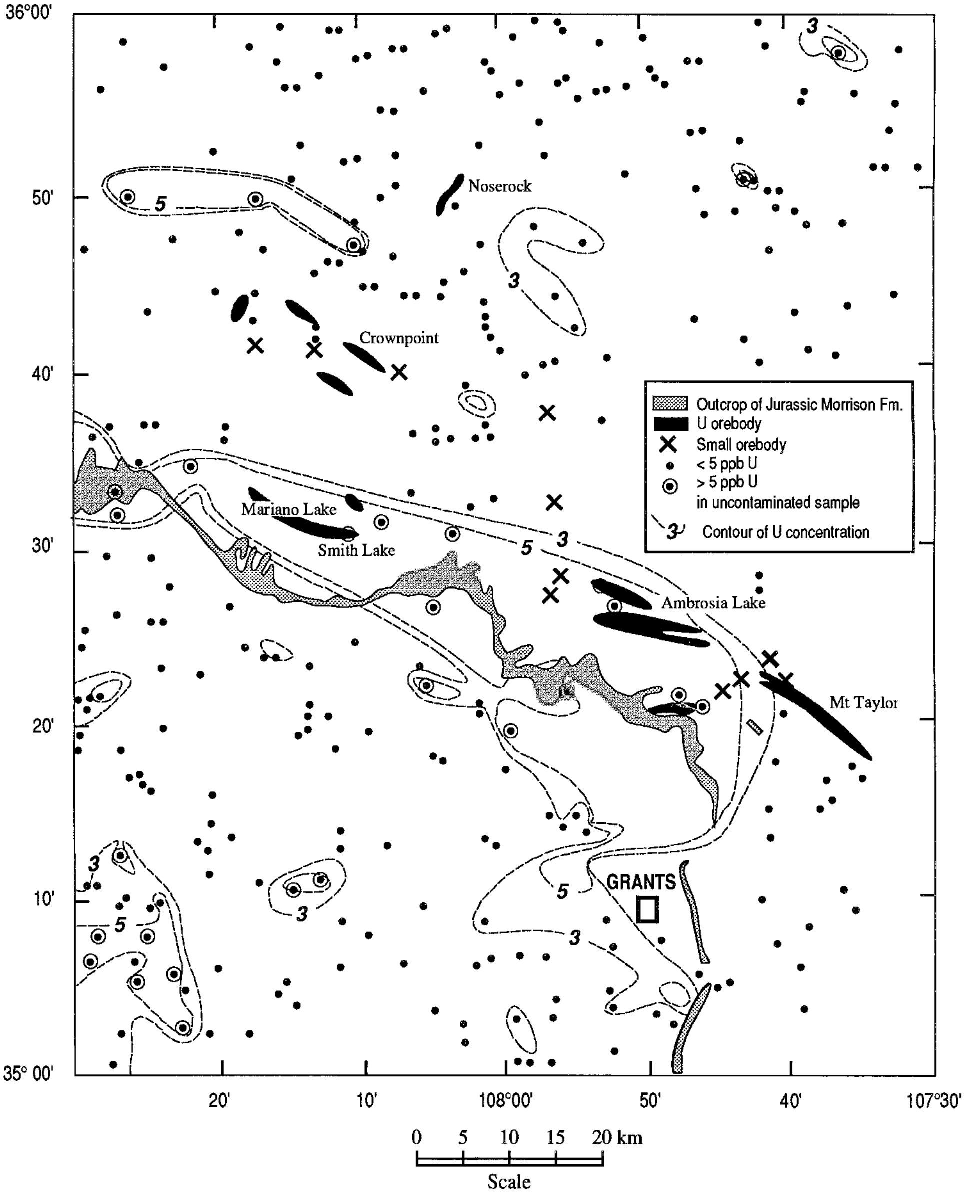

Fig. 15-13. Uranium in groundwaters, Grants Mineral Region, New Mexico, showing regional anomaly along the shallower parts of the district (compiled from data from Maassen and Bolivar, 1979, Maassen en LaDelfe, 1980, and Purson, 1981).

200 to 1000 m of Cretaceous rocks would have required considerable additional exploration. Also, a considerable proportion of samples in the Albuquerque quadrangle, to the east, are equally anomalous (Maassen and Bolivar, 1979).

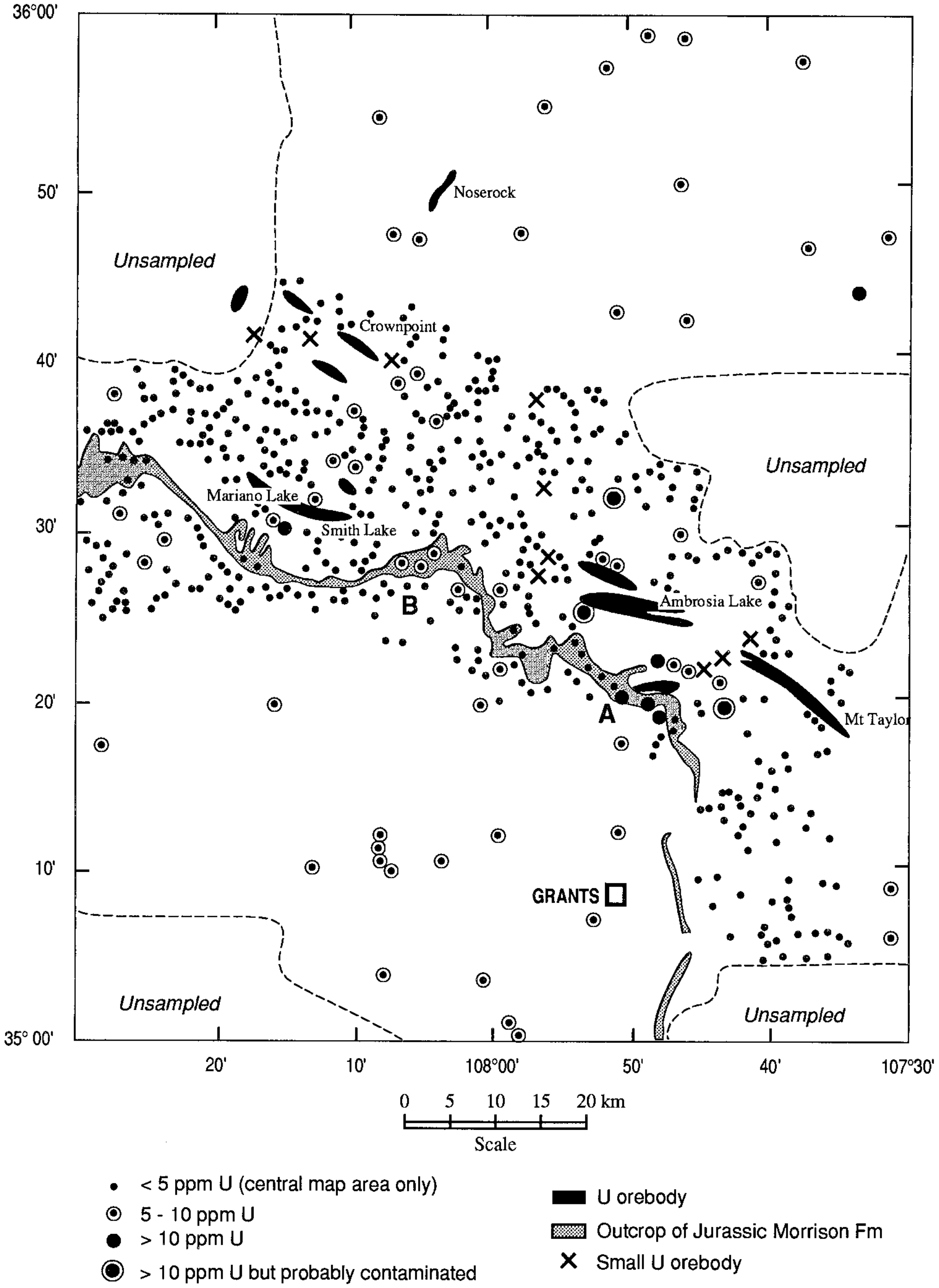

Fig. 15-14. Uranium in stream sediment (total U) in the Grants Mineral Region (compiled from Purson, 1981). All samples are shown in Central belt along the mineralized region; only samples with >5 ppm U outside this zone, but sampling has similar density.

Figure 15-14 shows stream sediment U data for the Grants uranium region. The sediments were collected at a density of about 1 sample per 2 km^2 (Purson, 1981). The median value for the survey area is 2.9 ppm U, with a mean value of 3.17 ppm. These data indicate that stream sediments in the 80 × 120 km area around this world-class uranium region are not anomalous, probably because the host Morrison Formation is exposed at the surface only along a narrow belt. A cluster of anomalous samples does occur in the vicinity of point A on Fig. 15-14, where a number of shallow ore bodies were mined. The significance of this cluster is uncertain because of the likelihood of contamination from mining activities. A distinct anomaly probably was present in some of these drainages prior to mining. Further west along the belt, between A and B, about seven samples are weakly anomalous, in the range 5 to 10 ppm U. These values seem likely to represent uncontaminated sediments derived from the weakly mineralized Morrison Formation. However, many samples from streams draining the Morrison Formation are not anomalous, and sediments with 5 to 10 ppm U are scattered over the entire map area. The recognition that the relatively weak U anomalies in the Morrison outcrop reflect the presence of major U deposits down the dip would have required considerable sophistication in data interpretation in the presence of widely scattered weak anomalies, most of which are probably non-significant.

In western Nebraska, the Crow Butte U deposit near Crawford was discovered by geologic techniques after the regional NURE surveys were conducted and reported (Union Carbide Corp., 1980; Collings and Knode, 1984; Spalding et al., 1984). The deposit, which is of sandstone-type with ore reserves exceeding 13,000 metric tons of U_3O_8 at an average grade in excess of 0.25% U_3O_8, is approximately 200 km east of the extensive deposits in the Powder River basin, Wyoming. The mineralized zone extends for more than 10 km and is up to 0.8 km wide at depths of 100 to 300 m. The host rock is gently dipping fluvial sandstones of the Oligocene Chadron Formation, overlain by clay-rich units and underlain by the marine Cretaceous Pierre Shale. The ore-bearing unit crops out a few kilometres to the north of the deposit. The Oligocene sediments above the ore horizon include regionally extensive tuffaceous units that are a possible source of the U in the deposit.

Figure 15-15 shows the distribution of U in stream sediments of the region. No clear stream sediment anomalies are evident within about 10 km of the deposit, the U contents being generally less than 3 ppm. Scattered slightly anomalous values of up to about 10 ppm occur along the outcrop of the mineralized unit and in some streams draining the Pierre Shale, but values at this level and higher are also common in Wyoming, Colorado and other adjacent states. For example, a threshold of 14 ppm U in stream sediments (exceeded by 5% of samples, with 13.5% greater than 8 ppm) was chosen in the NURE survey of the uraniferous Casper, Wyoming quadrangle to the west (LaDelfe, 1980); and a mean U of 6 ppm was found in stream sediments of the eastern Greeley and Denver, Colorado, quadrangles, which have geology similar to the Alliance quadrangle in which Crow Butte occurs (Bolivar et al., 1978). Thus, stream

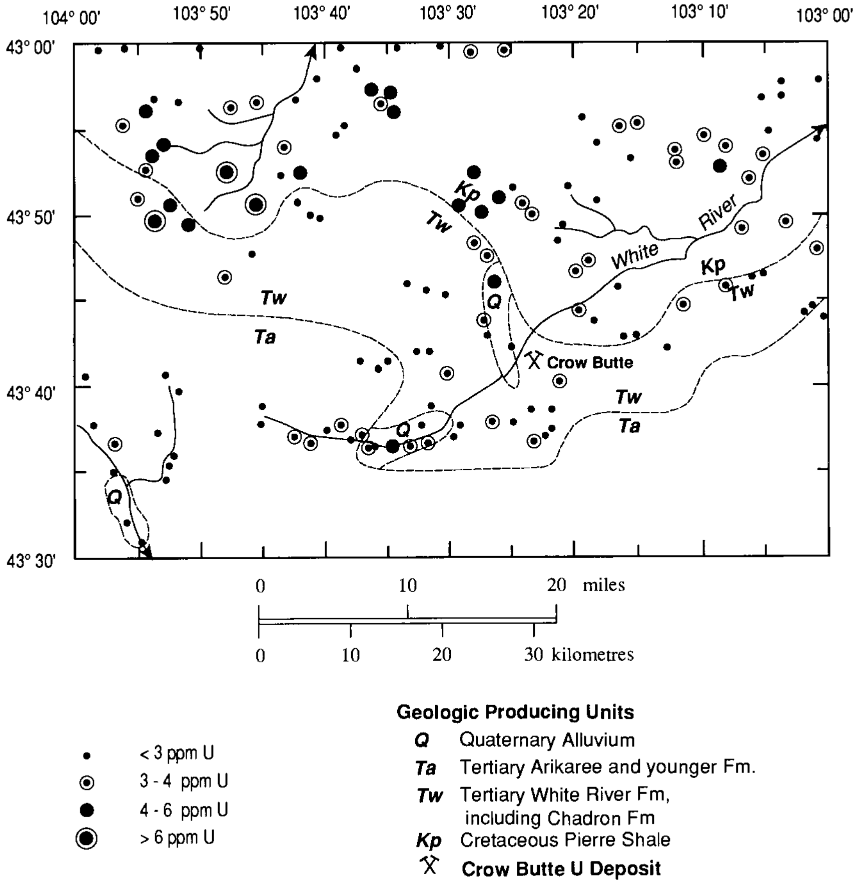

Fig. 15-15. Uranium in stream sediment (ppm acid extract) near the Crow Butte U deposit near Crawford, Nebraska (modified after Union Carbide Corp., 1980).

sediment geochemistry appears to be a dubious reconnaissance technique for this type of buried ore body.

Groundwater U contents are illustrated in Fig. 15-16. Again, the Crow Butte deposit is not clearly indicated by strong anomalies. However, a boundary between high and low U in groundwater approximately follows the contact between the Pierre Shale and the ore-bearing Chadron Formation across the northern part of the Alliance quadrangle. Values in the Pierre Shale and lower Chadron are mostly greater than 20 μg/l U, whereas values to the south are usually less than 10 μg/l. The hydrology of the region is not well understood, but a generally southward flow direction is inferred (Bard, 1982). Any component of southward flow or downward flow would result in an oxidizing to reducing transition in the general vicinity of the ore zone, and indicate the presence of a favourable zone for mineralization. The U con-

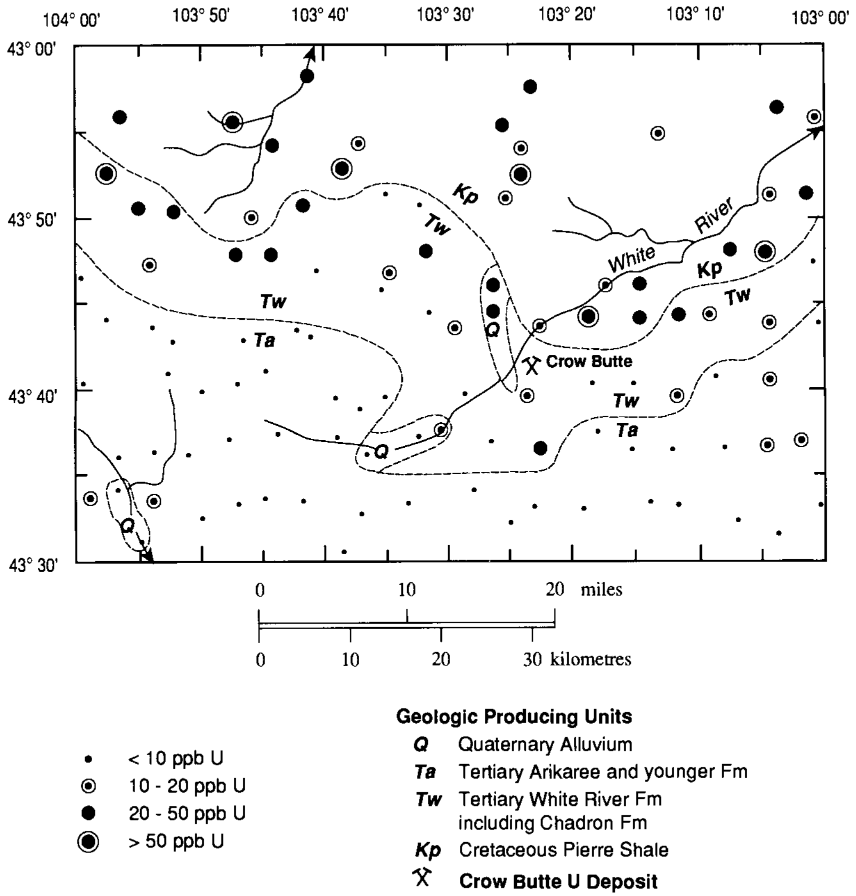

Fig. 15-16. Uranium in groundwater (μg/l) near the Crow Butte U deposit near Crawford, Nebraska (modified after Union Carbide Corp., 1980).

centration of groundwater to the north of the deposit compares favourably with those of the Casper quadrangle. A zone of erratically high ratios of U to specific conductivity also trends along the boundary (Fig. 15-17). Thus, the groundwater values might attract attention to the mineralization area and its extension to the east and west. Bard (1982) shows that rapid decreases in Ca, Mg, B, Na, K, Li, SO_4, HCO_3, conductivity, Se, As and the ratio of U to specific conductivity also occur along the same zone as the U decrease.

In more detail, Spalding et al. (1984) show that U contents of groundwater from within the ore body are highly variable, ranging from 5 to 2000 μg/l, compared to values commonly less than 5 μg/l in other formations of the area, and in basal Chadron Formation more than 1 km from the ore body. These investigators also show that excess ^{234}U (dissolved ^{234}U above the amount in

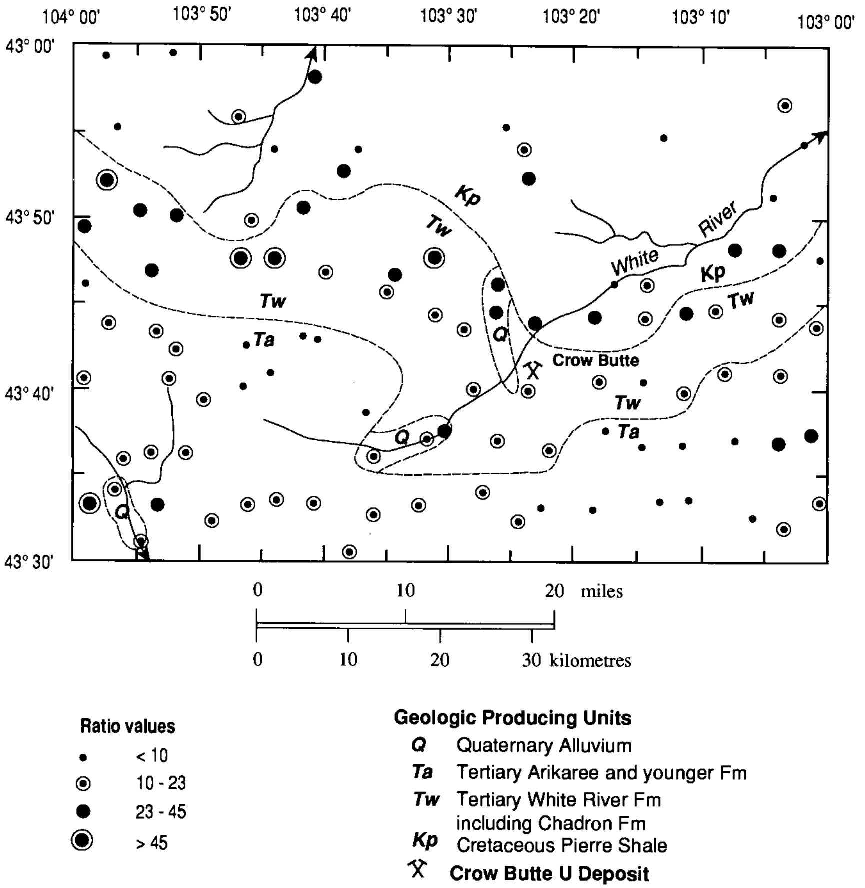

Fig. 15-17. Uranium/specific conductance for groundwaters near the Crow Butte U deposit near Crawford, Nebraska (modified after Union Carbide Corp., 1980). Ratio values are 1000 × U (μg/l)/Spec. Cond. (μmho).

equilibrium with dissolved ^{238}U) is high in and near ore, and declines to low values in non-mineralized areas.

DISCUSSION

Uranium anomalies in stream sediments

Stream sediment shares importance with water as a medium used in geochemical surveys for uranium. Table 15-III lists examples of critically appraised orientation surveys on well delimited, undisturbed deposits or occurrences in a variety of geologic and climatic regions. The method clearly detects large exposed deposits and mineralized regions with a high degree of responsibility,

TABLE 15-III

Characteristics of U anomalies in stream sediment

Locality	Anomaly		Method[b]	Climate[c]	Relief[d]	Geology[e]	Reference[f]
	Intensity at 1 km (background)	Train length (km)					
A. Significant deposits or districts							
Grants, N.M.	5 (2.9) ppm	1–3(?)	T	Arid, cont.	Slight	Strat.	1
Tallahassee Cr., Colo.	4 (3[a])	<1	T	Mod., cont.	Strong	Strat.	2
Midnite Mine, Wash.	35 (4)	2.5	E	50 cm, cont.	Mod.	Contact	3
Coutras, France	0.9 (0.5)	9?	E	Mod., temp.		Strat.	4
St. Hippolyte, France	10–20 (>5)	1–2	E	Mod., temp.		Strat.	5
Lassie Lake, B.C.	>8 (<8)	2–5		Mod., temp.	300 m	Strat.	6
Mounana, Gabon	9 (1)	2	E	200 cm, hot	Mod.	Strat.	7
Koongarra, Australia	<20 (5)	0.5	T?	140 cm, hot	300 m	Unconf.	8
Crow Butte, Nebr.	No anomaly (4)	0	E	Arid, cont.	Slight	Strat.	9
Anderson Mine, Ariz.	~7 (5)	~1	E	20 cm, hot	600 m	Strat.	10
B. Prospects or small deposits							
Westmoreland, Australia	16	2		70 cm, hot	250 m	Strat.?	11
Una May, Australia	>20 (7.4)	2	?	70 cm, hot	150 m	Vein?	12
Lower Buller Gorge, N. Zealand	8–15 (2.5)	?	T	200 cm, hot	High	Strat.?	13
Ben Lomond, Australia	None	0.3(?)	?	70 cm, hot		Volc.?	14
Randbodol, Greenland	5 (3)	1	T	Cold	1000 m	Volc.	15
Monticello, N.Y.	0.9 (0.7)	<1	H	100 cm, temp.	100 m	Strat.	16
N. Andes, Colombia	Yes	?	E	200 cm, hot	>1000 m	Vein?	17
S.W. Antolia, Turkey	3 (0.5)	1–3?	E	45 cm, warm	Mod.	Strat.	18
Muhlbach, Austria	Very local		E	Mod., temp.	High	?	19
Forstau, Austria	No anomaly		E	Mod., temp.	>1000 m?	Vein	19
Bancroft, Ont.	>33 (4)	1	E?	Mod., cool	Low	Vein	20
Torrington, Australia	>12 (6)	1	E	80 cm, var.	750 m	Vein	21

[a] Threshold value.

[b] T = total U; E = hot HNO_3, ext.; H = hot HNO_3–$HClO_4$.

[c] Climate: Precipitation (arid, moderate, or cm/yr); Temperature (cool, temperate, continental, warm).

[d] Local topographic relief.

[e] Character of U deposit: *Strat.* = stratabound in sediments; *Volc.* = volcanic association; *Unconf.* = Unconformity type, vein type in igneous/metamorphic rocks.

[f] References: (1) Maassen and Bolivar, 1979; Maassen and LaDelfe, 1980; Rose and Wright, 1980; Purson, 1981; (2) Shannon, 1979; (3) Bramlette, 1979; (4) Soyer, 1984; (5) Pradier, 1985; (6) D.R. Boyle, 1979; (7) Grimbert, 1963; (8) Foy and Gingrich, 1977; (9) Union Carbide Corp., 1980; (10) Butz et al., 1981; (11) Rossiter, 1976; (12) Rossiter, 1980a; (13) Cohen et al., 1969; (14) Watters, 1983; (15) Steenfelt et al., 1976; (16) Rose et al., 1982; (17) Premoli, 1983; (18) King et al., 1976; (19) Smith et al., 1976b; (20) Morse, 1971; (21) Ishak and Dunlop, 1985.

but the reliability for moderate-sized deposits, covered deposits, and other more difficult targets is not so clear. False anomalies are not uncommon, but also have not been appraised systematically.

At the reconnaissance stage of exploration, a distinction of two major types of targets seems useful. The easier type of target to detect is a district or region where uranium deposits are geometrically and geographically associated with felsic igneous rocks, such as the Erzgebirge in Central Europe, Marysvale area, Utah, or Bokan Mountain area, southeastern Alaska. The large volume of felsic rock, usually with above average uranium contents and with resistant uraniferous accessory minerals, typically creates extensive easily detectable anomalies in the drainage of the region. Surveys detecting anomalies of this type have been reported by Simpson (1977) in Caledonian granites of Scotland; Olade and Goodfellow (1979) in the Tombstone batholith, Yukon Territory; Howarth et al. (1981) in central Colorado; Chu et al. (1984) in Malaysia; Armour-Brown et al. (1983) at the Illimaussaq alkaline intrusion in Greenland; Beyth and McInteer (1982) for Tertiary granitic plutons in Alaska; and Stier and Friedrich (1982) for granite bodies in Bavaria. The detection of small economic orebodies in this type of environment may be more difficult than the detection of plutons, as discussed later, and false anomalies due to heavy-mineral concentrations or accumulation of mobile U may be formed (Stier and Friedrich, 1982). Smith et al. (1976a) show, however, that extractable U detects all areas of apparent potential U deposits in a portion of Greece, but screens out a granitic body with anomalous radioactivity but no mineralization.

The second major type of target is that of districts containing stratabound uranium deposits in a sedimentary sequence. Examples are the sandstone uranium deposits of the western USA and elsewhere, and possibly palaeoplacer deposits such as the Witwatersrand or Blind River. The restriction of U deposits to a specific stratigraphic unit, which in many districts is relatively thin and poorly exposed, can make this type of deposit difficult to detect. Some of these deposits are associated with uraniferous granites or felsic volcanics of regional extent, so that they are readily detected using stream sediments, but many districts seem to provide only local weak anomalies in stream sediments, for example, the Tallahassee Creek deposit, Colorado (Fig. 15-11), the Alligator Rivers deposits in northern Australia, and possibly the Grants district, New Mexico. In part these difficulties arise from post-ore cover, but in part they reflect the relatively small size and the stratigraphic-structural controls of the U orebodies and the weakness or absence of U enrichments in host formations away from the orebody.

Climatic, topographic and geomorphic effects on the intensity of U anomalies in stream sediments are also proposed by several workers, although convincing evidence is lacking. The effects arise mainly because of the high mobility of U under oxidizing conditions. Varying proportions of U are leached from soil and bedrock (to depths of 100 m or more), and carried off in groundwater. If adsorbents, such as Fe-oxides or organic matter, are present in moderate to high quantities in the stream sediment, then false anomalies may be formed during youthful erosion stages. Conversely, if waters are alkaline with high levels of HCO_3^- to inhibit adsorption, or in ancient deeply weathered terrains, the soluble U may be almost completely leached from the surface and the zone of groundwater circulation, leading to very weak stream sediment anomalies.

A case history demonstrating leaching and hydromorphic enrichment in a rugged temperate region is reported by Dall'Aglio (1971) in the Alps of northern Italy. Stream sediments in an area of gneiss, schist and pegmatite commonly show anomalous U values (15–45 ppm U by hot 5 M HNO_3 digestion, compared to 8 ppm background) but no U concentrations could be found in rocks of the area. Waters are highly enriched in U (1–15 μg/l), especially considering the very low TDS content (110 mg/l). The dried residue from leaching of crushed rocks contains 10 to 20 times as much U as the original rock, indicating that U is selectively leached by weathering. Uranium in stream sediments is concentrated in organic matter, probably by adsorption from stream water. The high-U sediments are deficient in U daughters, indicating very recent fixation of U in the sediment. Thus, in rapidly eroding, recently uplifted areas of crystalline rocks where stream sediments contain appreciable organic matter, surveys based on U in stream sediments may give false anomalies.

Clear examples of the opposite situation, where anomalies are lacking in areas of prolonged weathering, are not documented. In the Alligator Rivers region of Australia, however, where rainfall is high, anomalies in stream sediment are weak downflow from at least some U deposits, possibly reflecting past leaching plus the present high rainfall and high water table. A granite in Bavaria contains some uraniferous quartz veins, but has been deeply weathered to a depth of 150 m (Von Gaertner, 1963). No anomalies are found in the stream sediment, except for U-rich peat fed by a small spring draining from a quartz vein. In the Philippines, Tauchid et al. (1983) report very low U values in sediments (<0.2 ppm) near U occurrences, but more distinct U anomalies in heavy minerals.

Dall'Aglio (1972) suggests that U anomalies are weak in arctic climates because weathering and groundwater leaching are inhibited by permafrost, but more recent work in the Canadian arctic indicates that weathering and leaching are relatively active in such environment. Jonasson and Dunsmore (1979) suggest that sediment anomalies in the Arctic Islands are weak because of deep weathering, but the U occurrences are very small and the resulting anomalies are weak and relatively diluted in the streams. Distinct U anomalies are detected in stream sediments in rugged arctic terrain in Greenland (Steenfelt et al., 1976; Armour-Brown et al., 1983).

Stream sediment surveys for U have been used at a variety of scales. Regional reconnaissance with a density of 1 sample per 5 to 10 km^2 has been applied to detect regions or even geochemical provinces with potential for U deposits. As noted previously, this procedure appears successful if the region contains a significant area of U-rich granite, but it is not necessarily successful for regions containing sediment-hosted U deposits. The use of total U determinations in sediments detects uraniferous granitic areas, but the use of extractable U appears to give better results for sediment-hosted districts, since hydromorphic dispersion may be involved in creating anomalies in this environment.

At more detailed scales, aimed at identifying individual deposits or the associated halo, relatively dense sampling (1 sample/km^2 or closer) is generally used, and measurement of extractable U is generally preferable. Care must be taken to evaluate the effects of organic matter and Fe oxides, for example, because elevated amounts of these adsorbent may create false anomalies which can be stronger than anomalies from an ore body.

Seasonal or weather-related effects on U anomalies in stream sediments have been detected by several workers. Steenfelt and Kunzendorf (1979) show a five-fold decrease in U content of sediment from a large river in Greenland over a three month period, correlated with an increase of U in water. Rose and Keith (1976) found a seasonal variability in extractable U of only about ±50% for sediments from small streams draining U prospects in Pennsylvania. The variability was attributed to the time required for newly deposited sediment to acquire U from the stream water. The variability was much less than the 70-fold variability in U content of stream water.

Regression methods have been used by several workers to correct for varying contents of organic matter and Fe-oxides. Rose et al. (1976) found significant correlations of U with Fe, Mn and organic matter (estimated as loss on ignition, LOI) in stream sediments from a region of sedimentary rocks containing small U prospects. Adjustment of background using a regression against LOI eliminated some apparently false anomalies in samples with a high content of organic matter. Ishak and Dunlop (1985) found a strong correlation of U with LOI in stream sediments of the Torrington district, Australia, and by using a regression method were able to distinguish drainages with U occurrences from drainages lacking U occurrences (Fig. 15-18).

Uranium anomalies in stream water

Stream waters were probably the earliest natural medium used for geochemical surveys for uranium, although their use has decreased markedly in recent years. The high mobility of U and ease of collection of stream waters makes them attractive for reconnaissance surveys. Disadvantages and problems, however, include the large temporal changes relating to rainfall and seasons, the very low background and threshold levels in humid regions, and the rapid disappearance of anomalies downstream in some regions.

Table 15-IV summarizes stream water surveys near known U deposits and prospects. The data indicate that significant uranium deposits exposed to weathering usually produce detectable anomalies in stream water, but the anomalies may be relatively weak, especially in areas of high rainfall and deep weathering, as over the Mounana deposit, Gabon (Fig. 15-7). The anomalies may extend only a short distance downstream, probably because of adsorption on organic matter and Fe–Mn oxides in the sediment. Comparison with Table 15-III suggests that dispersion trains in stream water are usually shorter

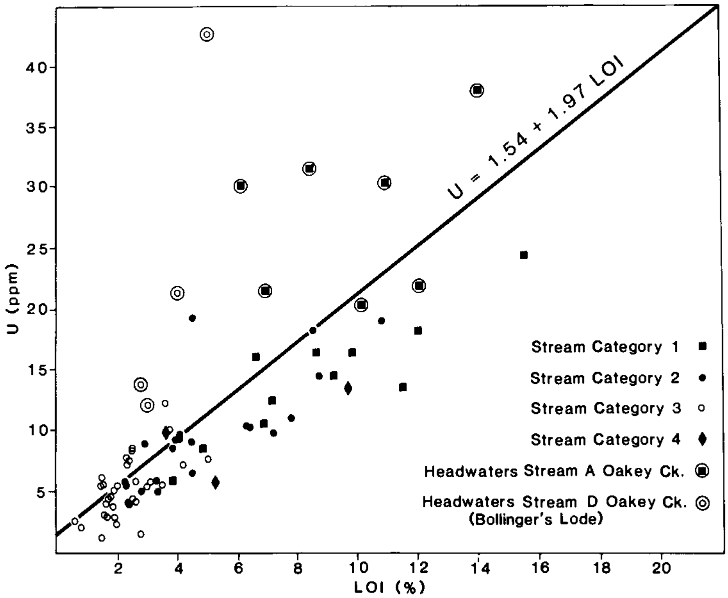

Fig. 15-18. Scatter plot of uranium and organic matter (as loss on ignition) in minus 180 μm stream sediments from the Torrington area, New South Wales, Australia; only streams A and D of Oakey Creek drain mineralization (from Ishak and Dunlop, 1985).

than stream sediment trains for extractable U. Prospects and small deposits commonly produce anomalies, but these may be very weak, even in regions of active erosion.

Figures 15-8 and 15-19 illustrate the variability of U with time in stream water as reported by Murakami et al. (1958), Wodzicki (1959), Grimbert (1963), Rose and Keith (1976), and Steenfelt and Kunzendorf (1979). The time variations are up to a factor of 70-fold (Rose and Keith, 1976) and may result in "disappearing anomalies". In some instances, these variations can be markedly decreased by taking the ratio of dissolved U to TDS or dissolved U to specific conductivity of the water, but this method is not always affective (Rose and Keith, 1976). The ratio appears to improve resolution of anomalies if the variability of U is due to dilution by rainfall or to groundwater of varying residence time, but it does not work if U variability results from changes in oxidation rate caused by water table variations or occasional flushing of

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Fig. 15-19. Changes in U content of stream water with time. A = Storelv River, Greenland (redrawn with permission from Steenfelt and Kunzendorf, 1979); B = Lower Buller Gorge, New Zealand (redrawn from Wodzicki, 1959, New Zealand Journal of Geology and Geophysics, Vol. 2, p. 607, by kind permission of SIR Publishing); C = Small stream draining U prospect, Jim Thorpe area, Pennsylvania (from Rose and Keith, 1976). High values follow a period of early fall rainfall that is inferred to have flushed out U-rich groundwater.

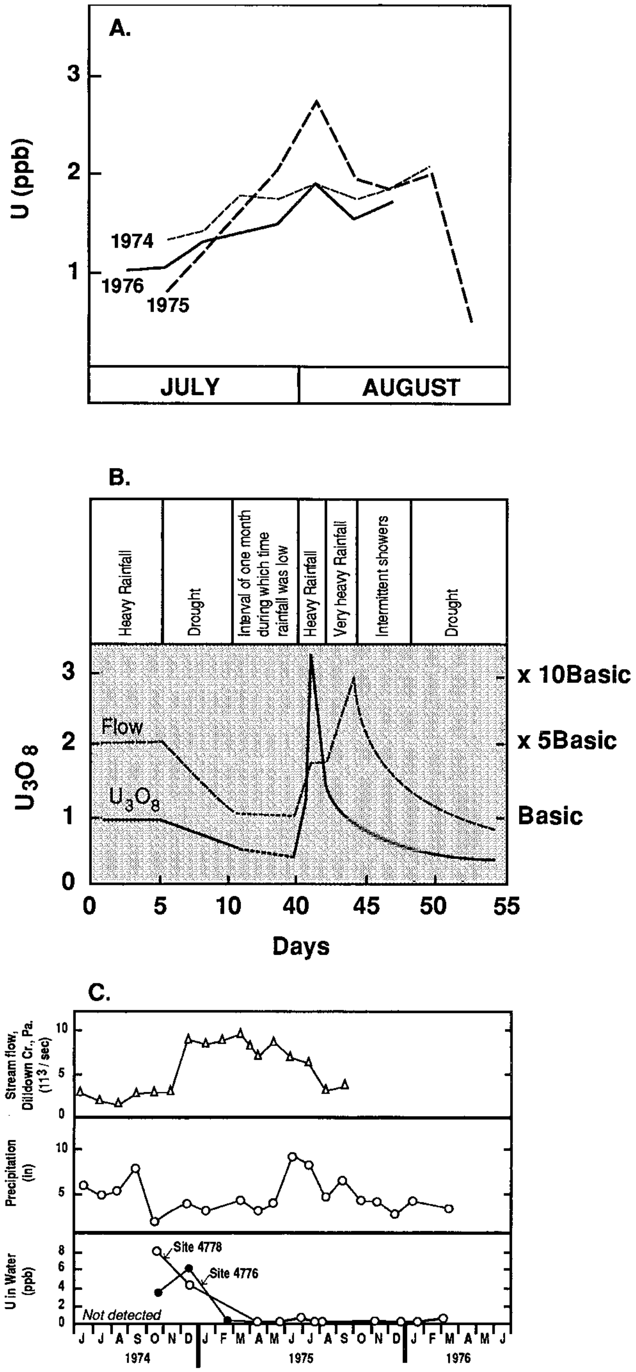

A.
U (ppb)
3
2
1
1974
1976
1975
JULY
AUGUST
B.
Heavy Rainfall
Drought
Interval of one month during which time rainfall was low
Heavy Rainfall
Very heavy Rainfall
Intermittent showers
Drought
U_3O_8
3
2
1
0
Flow
U_3O_8
x 10Basic
x 5Basic
Basic
Flow of Water
0
5
10
40
45
50
55
Days
C.
Stream flow, Dilldown Cr., Pa. (113 / sec)
10
5
0
Precipitation (in)
10
5
U in Water (ppb)
8
6
4
2
0
Site 4778
Site 4776
Not detected
J J A S O N D J F M A M J J A S O N D J F M A M J
1974
1975
1976

TABLE 15-IV

Uranium anomalies in stream waters near deposits

Locality	Anomaly		Climate[c]	Relief[d]	Geology[e]	Reference[f]
	Intensity[a] (background)	Length[b] (km)				
A. Significant districts and deposits						
Mounana, Gabon	1.3? (0.5) μg/l	<1?	200 cm, hot	Mod.	Strat.	1
Lassie Lake, B.C.	2–4 (0.5)	<1	Mod., temp.	300 m	Strat.	2
Midnite Mine, Wash.	1	1	50 cm, cont.		Contact	3
Coutras, France	14 ppm (0.5)	10	Mod., temp.		Strat.	4
Ningyo-Toge, Japan	5.2 (0.1)	<1	Mod., temp.		Strat.	5
Beaverlodge, NWT, Can.	>2.8 (0.5)	2?	Mod., cold	100	Vein	6
B. Prospects and small deposits						
N. Michigan	>3.2 (0.5)?	>1.5	Mod., temp.	Mod.	?	7
Tombstone Batholith, Yukon	0.1–5 (0.12)		Low, cold	1500	Granite	8
Monticello, N.Y.	0.2 (<0.1)	0–2	100 cm, mod.	300	Strat.	9
Sonestown, Pa.	0.2 (0.1)	2	100 cm, mod.	100	Strat.	10
Randboldal, Greenland	1.6 (0.1)	1	cold	1000	Volc.	11
Bancroft, Ont.	1.7 (<0.6)	1?	Mod., cool	Low	Vein	12
Philippines	No anomaly		High, hot		?	13
Forstau, Austria	4.5 (1?)	3	Mod., temp.	High	Vein	14
Black Forest, Germany	10 (0.8)		Mod., temp.	Mod.–high	?	15
Lower Buller Gorge, N. Zealand	1? (0.5?)	?	200 cm, hot	High	Volc.	16
Boulder Batholith, USA	4.3 (0.1)	3	Mod, cool	Mod.–high	Vein	17
Moye Pegmatite, Ga.	0.05 (0.01)		Mod, hot	Mod.	Pegmatite (Granite?)	18

[a] U concentration near deposit (background concentration).

[b] Downstream length of anomalies.

[c] Annual precipitation and typical temperature (hot, temperate, cool).

[d] Relief between hilltops and valleys in vicinity of deposit.

[e] Geology of orebody or prospect.

[f] References: (1) Grimbert, 1963; (2) D.R. Boyle, 1979; (3) Bramlette, 1979; (4) Soyer, 1984; (5) Murakami et al., 1958; (6) Dyck et al., 1971; (7) Illsley et al., 1958; (8) Olade and Goodfellow, 1979; (9) Rose et al., 1982; (10) Price, 1979; (11) Steenfelt et al., 1976; (12) Morse, 1971; (13) Tauchid et al., 1983; (14) Smith et al., 1976b; (15) Fauth, 1973; (16) Wodzicki, 1959; (17) Fix, 1956; (18) Ferguson and Price, 1976.

accumulated oxidation products. Moreover, the use of ratios tends to reduce variability in background values. Ratios of dissolved U to HCO_3 have a similar damping effect, mainly because HCO_3 is the main anion of most dilute waters, but possibly also because of carbonate complexing with a resulting inhibition of adsorption as well. Wenrich-Verbeek et al. (1976) show that the U content in streams is inversely related to stream discharge, and in the western USA is correlated with conductivity.

Uranium anomalies in groundwaters

As mentioned previously, the content of U in background water samples tends to increase with TDS or with conductivity, which correlates closely with TDS. This relation is clear for groups of samples covering a wide range of climatic regions, but for small areas the correlation may be poor. However, some variability with time caused by variations in discharge is corrected for by use of the U/TDS ratio (Wenrich-Verbeek, 1977b).

If U is being dissolved from rocks and soils in the same proportion as major elements (Ca, Na, Mg, K), then the U content of the evaporated solids (i.e., TDS) is a relatively constant amount, varying only because of differing U content of the bedrocks and varying content of residual quartz and Fe–Al-rich hydrolysates left in the residual weathering products of the drainage. For example, given an average granodiorite with 2 ppm U being weathered to form a natural water containing bicarbonates of Ca, Mg, Na and K, the calculated U content of the evaporated solids is 12 ppm. In Fig. 15-20 the waters would fall along the lines labeled "Granodiorite". A line calculated for average shale with 3 ppm U has a similar position when calculated as U content in TDS.

However, the graphs of Fig. 15-20 show that most groundwaters and may stream waters have lower U contents than the line for weathering of granodiorite, and the slope of the curve for U vs conductivity tends to be much steeper. In the Albuquerque and Pueblo quadrangles groundwaters clearly have lower U than stream waters of the same conductivity. On the other hand, the absolute U content of groundwater commonly exceeds that of nearby stream water, because of the generally higher TDS of the groundwaters.

A possible explanation for the high conductivity but low U content of some waters in Fig. 15-20 is dissolution of evaporites, which is possible in the Albuquerque and Oklahoma areas, but not in the Scranton area. A more likely cause, especially in the Scranton area, is that leachable U has been dissolved out of the soils and rocks along groundwater flow paths, so that present-day groundwaters encounter little U, although major elements are still available. Conversely, in regions of strong relief and vigorous physical erosion, such as the Pueblo area, New Mexico (Shannon, 1978), or the Alpine region, northern Italy (Dall'Aglio, 1971), U is being leached preferentially relative to major elements. Groundwaters that have encountered reducing conditions or had lost U because of adsorption during their evolution would also tend to yield low values of U/conductivity.

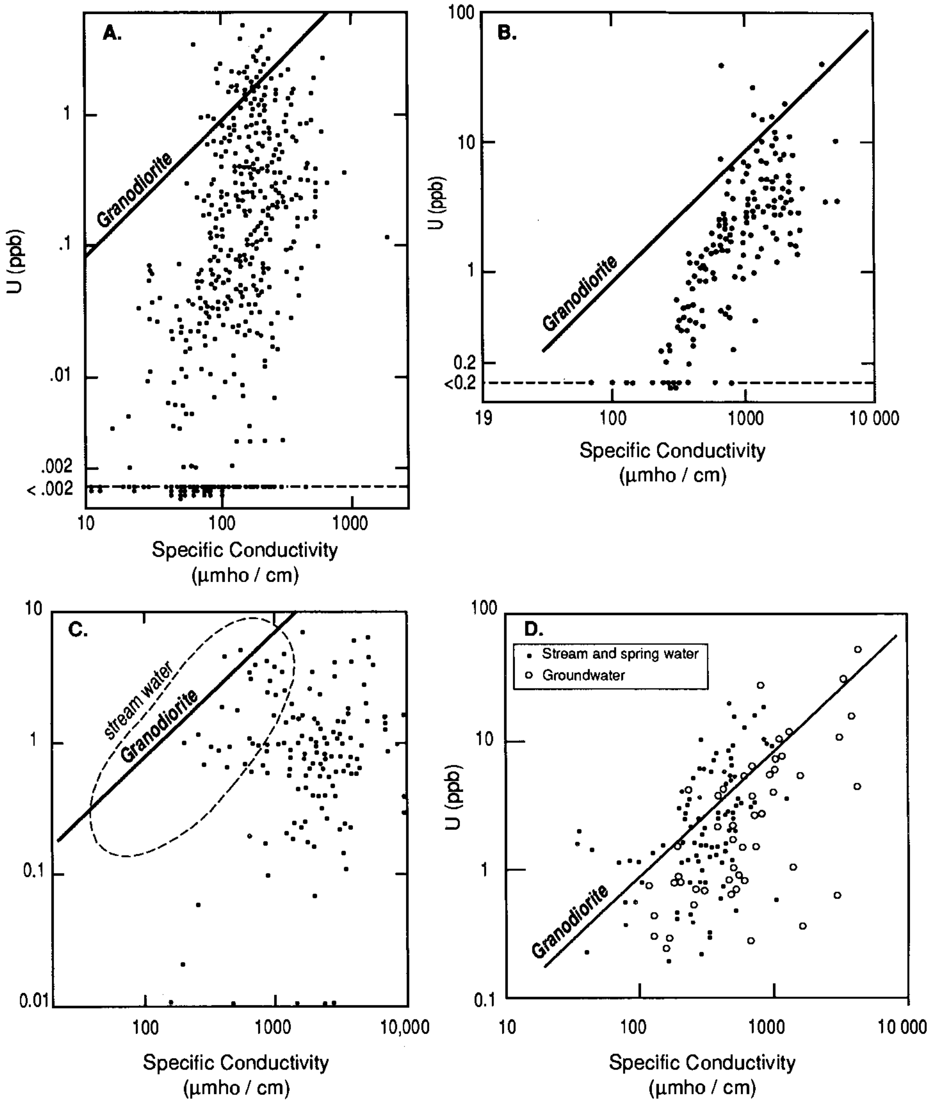


Fig. 15-20. Relations of U in groundwater to specific conductivity. A = Scranton quadrangle, Pennsylvania (compiled from data from Ferguson and Jones, 1979); B = Southwest Oklahoma (compiled from data from Bard et al., 1979); C = Groundwaters, Albuquerque quadrangle, New Mexico (compiled from data from Maassen and Bolivar, 1979); D = Pueblo quadrangle, Colorado (compiled from data from Shannon, 1978, 1979). See text for line labeled "Granodiorite".

Germanov et al. (1958, fig. 7) show a similar plot of U/TDS with a steep slope for water from springs and small streams from an area in the Tien Shan Mountains in Kirghizia (former USSR). They relate the change in U/TDS to climate. In areas of granitic rocks, waters of the high mountains (>2000 m) have U/TDS ratios of 1 to 4 × 10^{-6}, whereas lower mountains have ratios of 10 to 30 × 10^{-6}. The reasons for this climate-related pattern of U/TDS are not clear. Van der Weijden et al. (1985) report adsorption and leaching experiments and calculations that suggest U contents of natural waters similar to those of Fig. 8-21.

It is apparent that the background U content of waters tends to increase with TDS when taken over large regions, but within a small survey area the relation is likely to be more complex. The U/TDS or U/conductivity ratios may be helpful in interpretation, but obviously they do not solve the major problems of variability in U background of waters.

Table 15-V summarizes data on U in groundwater near U deposits, and Figs. 15-9, 15-10, 15-13, 15-16, 15-21, 15-22, 15-23 and 15-24 show maps of U in groundwater near some deposits. Essentially all significant deposits have anomalous U contents in some groundwaters near or in ore, but there are commonly also samples with very low (background) values near ore. At some deposits the low U may be caused by reducing conditions (Langmuir and Chatham, 1980; Runnells et al., 1980) and in other instances the low-U samples may lie along flow paths not intersecting ore. At some deposits, groundwater in the ore is nearly stagnant, with circulation occurring only in a near-surface zone (Deutscher et al., 1980). In general, well defined plumes or fans downflow from ore are lacking. Thus, it is evident that, to be successful, groundwater surveys for U require careful consideration of hydrology and hydrogeochemistry.

A technique suggested as an aid to interpretation of groundwater data is the use of a saturation index (SI), defined as

$$\mathrm{SI} = \log \frac{Q}{K_{\mathrm{sp}}},$$

where K_{sp} is the solubility product of a uranium mineral (i.e., the product of chemical activities in solution for components of the saturated mineral) and Q is the observed product of the activities of the same species in the water in question (Langmuir and Chatham, 1980; Runnells et al., 1980; Chatham et al., 1981; Runnells and Lindberg, 1981). Groundwater in contact with uranium minerals in a deposit will generally be near saturation in minerals of the deposit, so that the SI is approximately zero. Normal groundwaters in most regions are extremely undersaturated , with SI values of −3 to −8 (Rose et al., 1983). Saturation indices are most valuable in localities with reducing groundwaters, in which U contents are commonly very low even at saturation, or where appreciable changes in Eh or pH occur under conditions approaching saturation.

Comparison of the distribution of U and SI values at a deposit in Texas (Fig. 15-21a) shows that the SI values clearly identify the zone of deposits, despite a somewhat erratic behaviour of dissolved U values (Fig. 15-21b).

Given the regional variability of background in U content related to climate and previous weathering history, one may ask whether regional anomalies in groundwater and streamwater can be used as a guide to major uranium

TABLE 15-V

Groundwater anomalies related to uranium deposits

Locality	Anomaly (background)		U/TDS[b]		Climate[c]	Geology[c]	Reference[d]
	At deposit (μg/l)	District or region[a] (μg/l)	At deposit (ppm)	Regional (ppm)			
A. Major deposits and districts							
Jabiluka, Australia	9 (1)	–	10–65	1-5	Hot, wet	Unconf.	1
Koongarra, Australia	80–1000 (0.6)	–	50–1000	6–40	Hot, 150 cm	Unconf.	2
Yeelirrie, Australia	>100	5–15	–	–	Hot, dry	Strat.	3
Grants, N.M.	–	5–50(0.8)	–	4–80(4)	Cont., dry	Strat.	4
Gas Hills, Wyo.	40–300	5–20(3)[e]	–	13[e]	Cont., dry	Strat.	5, 6
Crooks Cap, Wyo.	250	1–2(3)[e]	100[e]	13[e]	Cont., dry	Strat.	5, 6
Oakville, Tex.	100 (1)	–	50	–	Temp., mod.	Strat.	7
Catahoula area, Tex.	30 (0.3?)	–	20	–	Temp., mod.	Strat.	7
Crawford, Nebr.	5–1000 (1)	5–15(1)	80	25	Cont., dry	Strat.	8
Powder River basin, Wyo.	40–22,000	2–5(1?)	–	–	Cont., dry	Strat.	5
Shirley basin, Wyo.	20	(3)[e]	70	13[e]	Cont., dry	Strat.	6
Athabaska basin, Sask.	10–2000 (0.4)	–	–	3	Cold, mod.	Unconf.	9
B. Prospects and small deposits							
Catskill Fm., Pa.	0.7–10 (0.1)		5–60	2.3	Temp., mod	Strat.	10
Monticello area, N.Y.	2–10 (0.2)		20–80	3.4	Temp., mod	Strat.	11
Slim Buttes, S.D.	10–100		–	–	Cont., dry	Strat	5
S. March, Ont.	80–700 (0.3)		150–1300	2.6	Cool, mod	Strat.	12
Carboniferous basin, E. Canada	5–30 (0.1)		–	0.8	Temp., mod	Strat.	13
Powder River basin, Wyo.	100–10,000 (<10)		200–20,000	–	Var., dry	Strat.	7
Thailand	63? (0.2)		–	–	Hot, wet	?	14
S.W. Anatolia, Turkey	10–50(2)	2	–	–		Strat.	15
Pueblo County, Colo.	190(0.2?)		–	–	Cont., dry	Strat.	16

[a] Regional values are listed to examine the possibility of regional anomalies indicative of a mineralized region.

[b] U/TDS = U content in Total Dissolved Solids, to examine whether this variable connects for regional background differences.

[c] See Table 15-III for abbreviations.

[d] References: (1) Deutscher et al., 1980; (2) Giblin and Snelling, 1983; (3) Cameron et al., 1980; (4) Purson, 1981; (5) Denson et al., 1956; (6) LaDelfe, 1980; (7) Langmuir and Chatham, 1980; Chatham et al., 1981; (8) Spalding et al., 1984; (9) Earle and Drever, 1983; (10) Rose and Korner, 1979; (11) Rose et al., 1982, 1983; (12) Dyck, 1980; (13) Dyck et al., 1976; (14) Hahn, 1983; (15) King et al., 1976; (16) Runnells and Lindberg, 1981.

[e] Background estimated as median U in groundwater in the Casper quadrangle, and TDS from median conductivity (LaDelfe, 1980).

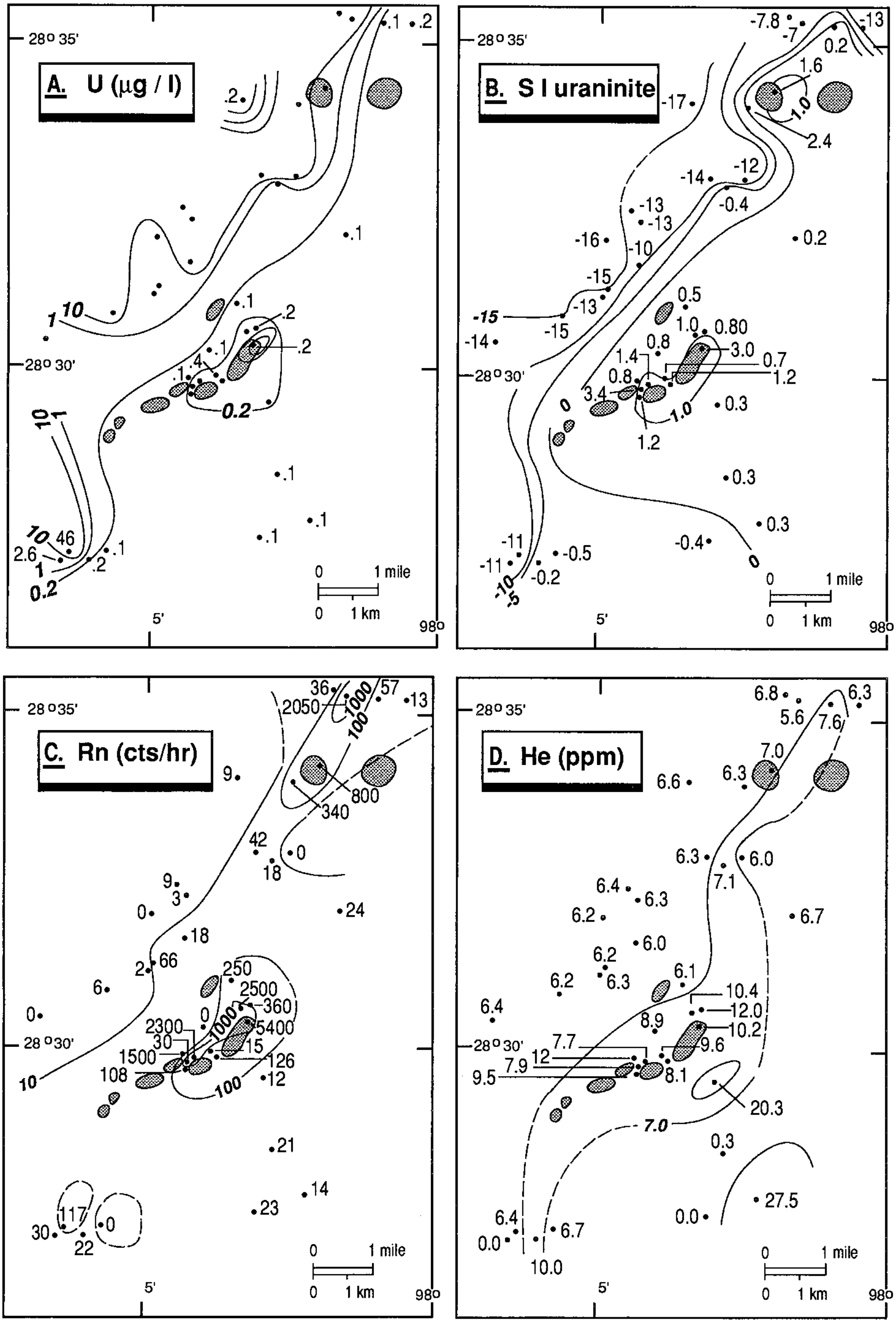


Fig. 15-21. Groundwater geochemistry of ores in the Live Oak County area, Texas (modified after Chatham et al., 1981). A = Uranium (µg/l); B = Saturation index of uraninite; C = Radon (cts/h); D = Helium (ppm by volume).

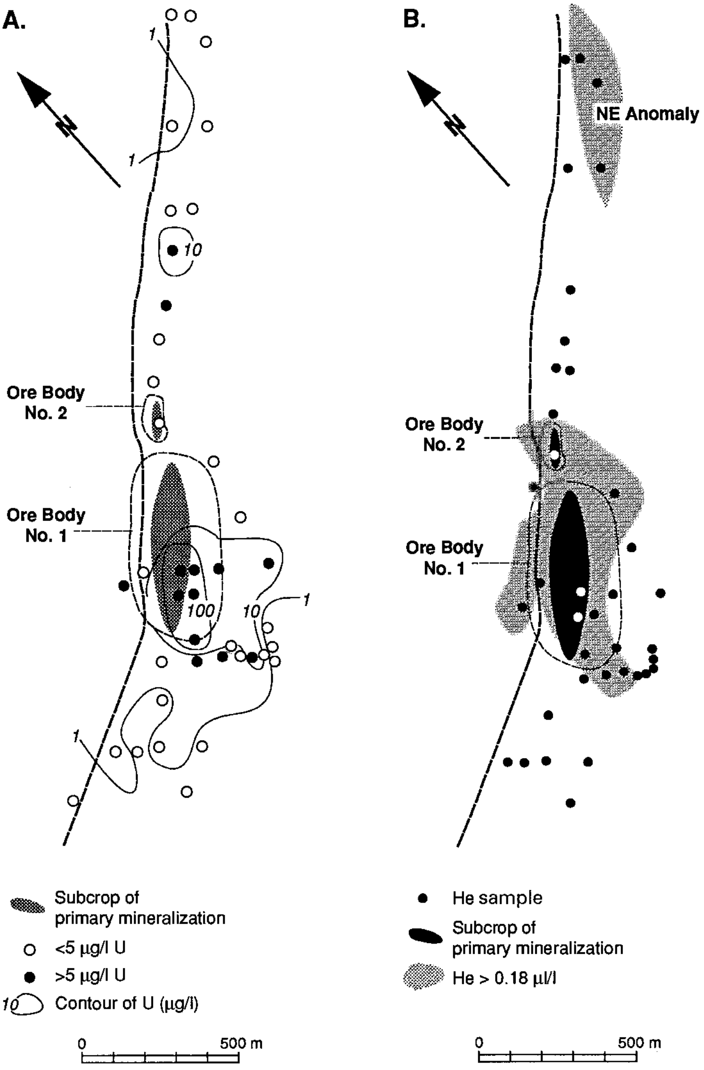


Fig. 15-22. Groundwater geochemistry near the Koongarra U deposit, Australia. A = Uranium in groundwater (from Giblin and Snelling, 1983); B = Helium in groundwater (from Gole et al., 1986).

districts. A preliminary assessment of the extensive NURE data suggests mixed results. As indicated on Fig. 15-13, an extensive groundwater anomaly appears to exist around the Grants uranium region; and groundwater in the western USA generally has high U contents, perhaps because it is a major continent-scale uranium-rich region. However, the ability to recognize major U districts within the western USA, such as within the state of Wyoming, is questionable. Although high dissolved U values are associated with most of the mining

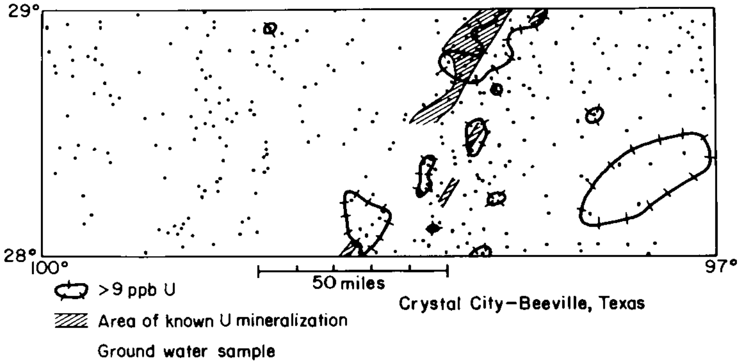


Fig. 15-23. Uranium in groundwater, Crystal City-Beeville area, Texas (from Butz, 1977).

districts, there are many values as high or higher that are not related to known mineralization. The use of regional U anomalies in groundwater as a guide to uranium districts, especially in sedimentary environments, requires further study.

Anomalies of radioactive decay products of uranium

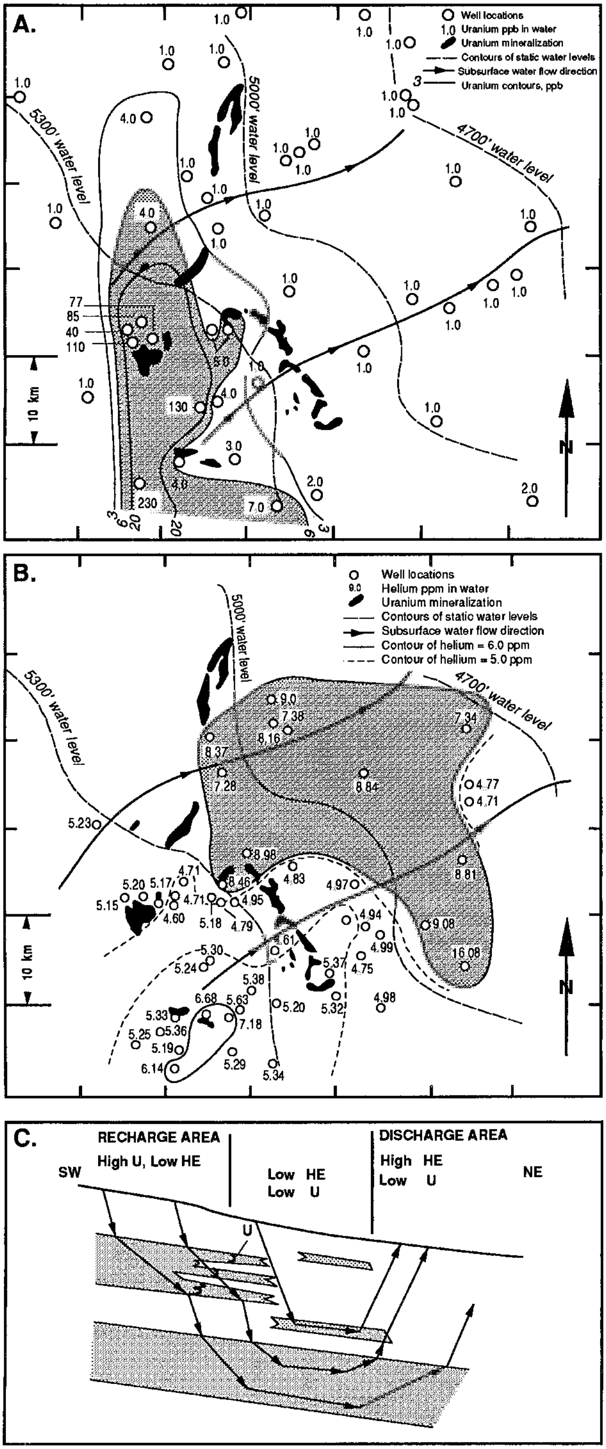
The diverse chemical and radioactive behaviour of various nuclides in the uranium decay series leads to potential dispersion patterns in groundwater that are of interest in exploration (Osmond and Cowart, 1982). Two general geologic cases may be distinguished:

(1) uranium ore body exposed to groundwater flow that is oxidizing throughout the flow system (dispersing system); and

(2) uranium ore body localizing at a redox boundary, probably in sediments, with oxidizing conditions upflow and reducing conditions in ore and downflow (accumulating or stable system).

Case 1 might apply to many uranium ores in igneous host rocks. In general, U and some of its decay products are dissolved from ore in small quantities and carried downflow. The amounts of daughter nuclides may tend to be enhanced over ^{238}U by effects of recoil and lattice damage, although Russian results (Levinson et al., 1982, pp. 336–366) suggest that this does not always occur. The distance of downflow transport will depend on solubility, adsorption and radioactive half-lives. Anomalies of ^{238}U, ^{234}U, He and possibly ^{226}Ra in groundwater might be expected to extend downflow for a considerable distance, whereas most other nuclides are either chemically immobile (^{230}Th, ^{210}Pb, ^{206}Pb) or have short enough half-lives that they show very limited anomalies (Rn).

Case 2 applies to many ores in poorly consolidated sandstone. Uranium may be relatively high in oxidizing upflow groundwaters, but precipitates at the redox boundary to form ore. Downflow U contents are very low. However, recoil


A.
Well locations
1.0 Uranium ppb in water
Uranium mineralization
Contours of static water levels
Subsurface water flow direction
3 Uranium contours, ppb
5300' water level
5000' water level
4700' water level
10 km
N
77
85
40
110
130
230
4.0
5.0
3.0
2.0
7.0
1.0
3
6
20
B.
Well locations
9.0 Helium ppm in water
Uranium mineralization
Contours of static water levels
Subsurface water flow direction
Contour of helium = 6.0 ppm
Contour of helium = 5.0 ppm
5300' water level
5000' water level
4700' water level
9.0
7.38
8.16
8.37
7.28
8.84
7.34
4.77
4.71
5.23
8.98
8.46
4.83
4.97
8.81
4.71
5.20
5.17
5.15
4.71
4.95
4.60
5.18
4.79
4.94
4.99
9.08
16.08
5.30
5.24
5.61
5.37
4.75
5.38
6.68
5.63
5.20
5.32
4.98
5.33
5.25
5.36
7.18
5.19
6.14
5.29
5.34
10 km
N
C.
RECHARGE AREA
High U, Low HE
Low HE
Low U
DISCHARGE AREA
High HE
Low U
SW
NE
U

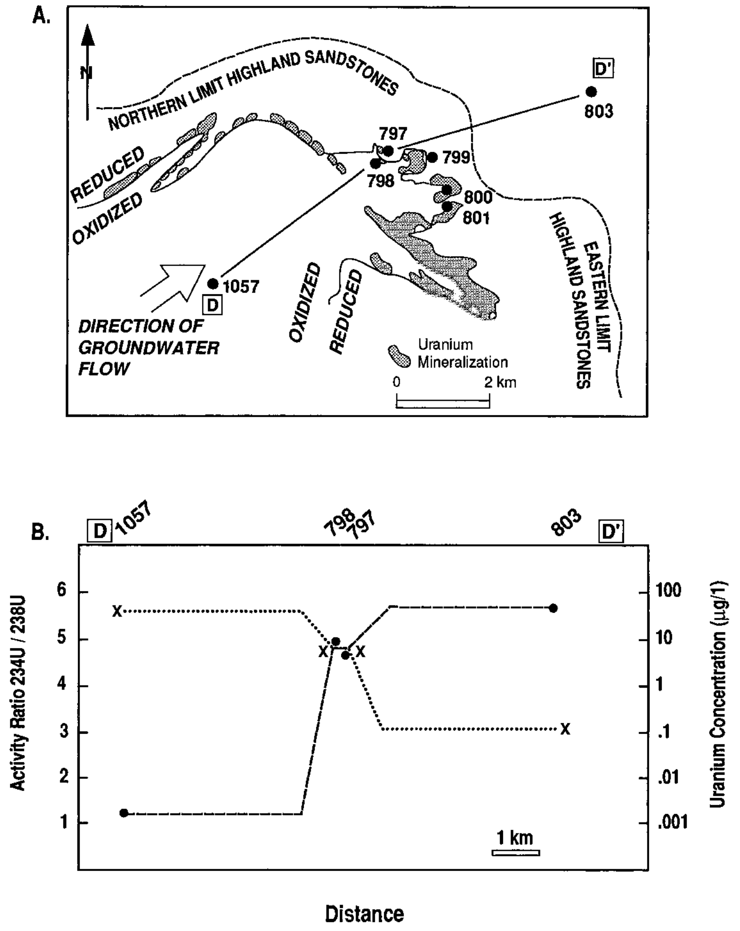


Fig. 15-25. Ratio of $^{234}U/^{238}U$ for groundwaters of the southern Powder River basin, Wyoming (from Cowart and Osmond, 1977). A = Location of groundwater samples; B = Profile showing changes in U content and $^{234}U/^{238}U$ of groundwater.

and lattice damage effects lead to enhanced ^{234}U values in groundwater passing through ore, along with other nuclides selectively leached from ore, to give ^{4}He anomalies extending well downflow, and relatively extensive anomalies in the $^{234}U/^{238}U$ ratio and possibly ^{226}Ra. Examples of patterns of ^{4}He, U and $^{234}U/^{238}U$ are illustrated in Figs. 15-24 and 15-25 for the Powder River Basin uranium district of Wyoming. However, Chatham et al. (1981) found more

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Fig. 15-24. Groundwater geochemistry near the U deposits of the southern Powder River basin, Wyoming (from Devoto et al., 1980). A = Uranium anomaly in recharge zone; B = Helium anomaly downflow from ore; C = Sketch of inferred hydrology.

complex results for the Oakville area in Texas. A distinct decrease in U content of groundwater occurs from oxidized to reduced waters in the mineralized area, but the $^{234}U/^{238}U$ activity ratio is erratic and does not show the values above 2.0 that Cowart and Osmond (1980) indicate are expected in and down dip from an actively accumulating U ore. Possibly this discrepancy results from the complex hydrology and mixing of waters in the Oakville area. Spalding et al. (1984) also found complex relations of $^{234}U/^{238}U$ to dissolved U content and ore at the Crow Butte deposit in Nebraska.

Among the daughter products of U that can be traced in groundwaters, Rn and He have attracted the most attention. Devoto et al. (1980) conducted test surveys of He in groundwater in the Grants and Powder River Basin regions. Some waters downflow from U ore are weakly to moderately anomalous in He in both districts. In eastern maritime Canada, Dyck et al. (1976) found a regional correlation of He and Rn with U in broad belts considered to be related to the "geochemical cells" forming sandstone-type U ores. Some anomalies are in the vicinity of known U occurrences. In the St. Lawrence Lowlands, ^{4}He anomalies in groundwater appear to indicate fault zones and regional groundwater discharge (Dyck, 1980). Groundwaters near some known small U deposits do not have He anomalies, but do show Rn and U anomalies. Similar results are reported by Zaikowski et al. (1982) for a deposit in Wyoming. In general, the very rapid diffusion rate of He leads to He loss from natural waters near the water table or Earth's surface, so He does not seem a good pathfinder in detailed surveys, but may be useful in reconnaissance.

Surveys of Rn in groundwater generally show anomalies in the immediate vicinity of deposits (Rose and Korner, 1979; Dyck, 1980; Chatham et al., 1981, fig. 22; Zaikowski et al., 1982). Groundwaters from favourable sedimentary units also tend to have elevated Rn contents (Rose and Korner, 1979; Rose et al., 1983). The short half-life of Rn (3.8 days) means that it will not migrate far from its parent, ^{226}Ra, at the flow rates of normal groundwaters.

Dean et al. (1983) and Dickson et al. (1983) have examined the significance of Ra isotopes in exploration (^{226}Ra in the ^{238}U series, ^{223}Ra in the ^{235}U series, and ^{228}Ra and ^{224}Ra in the ^{232}Th series). In theory, because of the short half-life of ^{223}Ra (3.64 days) compared to ^{226}Ra (1600y), a high ratio of $^{223}Ra/^{226}Ra$ should indicate waters close to the source of the Ra (and U). Dean et al. (1983) report reasonable results for groundwater in and near uranium ore in Saskatchewan, but Dickson et al. (1983) found many samples with high $^{223}Ra/^{226}Ra$ that are not near known ore. The latter workers were able to classify Ra-bearing waters from radioactivity anomalies into two groups, one representing a U ore source, and the other a rock source containing background Th and U values.

Morse (1971) has tested the Ra content of stream sediment as an exploration method in the Bancroft area, Ontario, where uraniferous veins and pegmatites associated with syenites occur in an area covered by till and numerous lakes. Uranium and Ra in stream sediments were found to be equally effective in detecting orebodies. Both show a few false anomalies in organic-rich sediments. Radon anomalies were found in some stream waters, but false anomalies detracted from the method. Morse (1971) suggests that stream sediment is the major source of Rn in stream water, but other workers (Rogers, 1959) have generally found that local influx of Rn-rich groundwater creates high values, and that anomalies decay rapidly downstream due to degassing of Rn, especially in turbulent streams. Ketola and Sarikkola (1973) showed a good correlation of Rn in streamwater to U occurrences in Finland.

CONCLUSIONS

The geochemical properties of uranium and its radioactive daughters are sufficiently distinctive that optimum techniques for uranium exploration differ from those for the common base metals. In particular, water sampling is more widely applicable to exploration for U than for most other elements, and the existence of radioactive decay products is unique.

Case studies indicate that outcropping uranium ore is readily detected by standard drainage methods using stream sediments. At a reconnaissance scale, uraniferous igneous bodies are also readily detected. However, stratabound U deposits in sedimentary environments may be difficult to detect. Some of these deposits or districts may lie within uraniferous regions, but in the western USA these are so large that simple geochemical guides do not exist. A combination of geochemical methods, especially groundwater sampling, with careful interpretation of hydrology, geochemistry and geology, is required for success in this environment. Particular attention to identifying the source aquifer for water samples and the existence of redox boundaries is necessary. As reported by Ostle et al. (1972), some mineralized bodies are detectable with stream sediments but not water, and vice versa, so conducting both types of surveys is commonly warranted.

Climatic and physiographic factors also determine the character of anomalies. Areas of high relief and vigorous physical erosion generally show good response in detrital materials, but may also show significant false anomalies of hydromorphic origin, owing to preferential dissolution of U minerals and adsorption onto organic matter. In regions of low relief, the groundwater may circulate very shallowly, through zones from which U has been leached, to give at best only weak anomalies. In stream sediments, analysis for acid-soluble or readily-extractable U is generally preferable to total U, though both measurements can be useful.

In the future, planning of surveys should take into account the lessons to be learned from the extensive surveys of the 1970's, as indicated here, in order to achieve optimum design. Also, comprehensive orientation studies at a variety of stratabound deposits are needed to improve our knowledge of the complexities of dispersion around buried deposits.

Drainage Geochemistry
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Chapter 16

SELECTIVE EXTRACTIONS AND CONTRASTING SAMPLE MEDIA IN DRAINAGE GEOCHEMISTRY

J.S. COATS, R.C. LEAKE and D. PEACHEY

INTRODUCTION

Geochemical processes taking place at the Earth's surface are extremely complex and the pathways taken by elements from primary sources in rocks and mineral deposits to their temporary location in drainage sediments are many and varied. Some material goes straight from weathered rock to particles in the stream load by direct mechanical erosion, but most mineral grains pass through one or more intermediate stages of mechanical and chemical breakdown within tills or soils. Drainage sediment predominantly consists of a detrital material of varying grain size down to clay grade material, colloids, hydrous oxide/hydroxide precipitates which may coat the detrital grains, and organic matter in various stages of decay. The proportions of the above vary enormously depending on catchment geology, physiography and present and past climatic regime.

Compositions of drainage sediments are not fixed but change with time and physico-chemical conditions. Seasonal changes in composition have been recorded (Rose et al., 1979) but ageing processes, such as crystallization of iron colloids, take place in buried sediment and these may well affect the trace element contents. The range of physical and chemical processes that takes place in the surficial environments means that some elements, originally closely associated in the rock or mineral deposit, may take widely differing dispersion paths. Exploration objectives can be promoted by acquiring and analyzing drainage sediments by methods designed to obtain information about particular dispersion pathways.

As discussed by Lovering and McCarthy (1978, p. 254) no single sample type fulfils all the requirements of an ideal medium with respect to all types of ore deposit, under all combinations of geologic and geographic variables. The aim of this chapter is to describe methods of resolving some of the complexity in the relationship between drainage sediments and mineralization in the catchment and to show the potential exploration value of these. This is particularly important for the more difficult exploration environments and targets such as where there is heavy contamination from previous mining, from other human activity or where mineralization may have suffered extensive near surface leaching.

In mineral exploration it may be advantageous to reduce some of the variability within a drainage sediment and to accentuate the contribution of a particular component which shows a stronger positive correlation with mineralization than the sediment as a whole. This can be achieved by separation of different components chemically, using partial dissolution methods, or physically by sieving, gravity separation or magnetic separation so as to select a particular grain-size, density range or magnetic susceptibility. Combination of data from different fractions of drainage sediments is particularly valuable in obtaining a better understanding of dispersion pathways from mineralization. This approach, using two contrasting physically separated fractions, has been used successfully by the British Geological Survey in its Mineral Reconnaissance Programme and is illustrated by data from various parts of Britain.

All these methods have the same aim of making use of variation in dispersion pathways to facilitate the detection of particular types of mineralization. Orientation work defining the chemical and physical parameters of the dispersion is one of the first essentials in any detailed mineral exploration study. The "why" and "how" of the metal dispersion needs to be known rather than the simple fact, "the element is dispersed downstream of the source".

PARTIAL DISSOLUTION OF STREAM SEDIMENTS

When a stream sediment sample is completely dissolved in a reagent the solution contains trace metals released from all the components of the sample from background detrital grains to hydromorphic material derived from a weathering orebody. By using a partial rather than "total" dissolution procedure it is possible to extract selectively trace metals from hydromorphic phases, and to enhance the contrast between data for anomalous and background samples. The phases commonly investigated are "exchange sites" on clays and silicates, organic matter, carbonates and secondary oxides of Fe and Mn. Preferential leaching of a sulphide mineral fraction is also possible.

Partial dissolution work is commonly carried out on the fine fractions of stream sediments collected for conventional determinations of "total" amounts of trace metals. However, some workers have also investigated secondary oxides of Fe and Mn as coatings on pebbles (Chao and Theobald, 1976; Carpenter et al., 1978) or as nodules (Nowlan, 1982; Nowlan et al., 1983).

The simplest form of partial dissolution technique involves leaching a sample at ambient temperature and analyzing the extractant by atomic absorption spectrophotometry (AAS) or colorimetry. The results are then referred to as "cold extractable", "weakly bound" or "acid soluble". Reagents commonly used include aqueous solutions of EDTA (Cagatay, 1984), dilute hydrochloric acid (Agemian and Chau, 1976) and the ammonium citrate/hydroxylamine hydrochloride solution used in the "Bloom test" (Bloom, 1955). An alternative approach is to leach samples with a reagent that will selectively extract a specific phase together with any associated trace metals. More detailed studies involve leaching samples sequentially with a number of selective extractants.

In addition to the enhancement of contrast between anomalous and background samples, partial dissolution techniques have been used to identify phases involved in metal bonding, to select suitable sample matrices and appropriate extractants, and to recognise "false" anomalies. An account of partial dissolution techniques (including sequential leaching schemes) has been given by Chao (1984).

Exchange sites

Ammonium acetate solutions are widely used to determine exchangeable cations from clays but they also have some solvent action on carbonates and sulphates. Alternatively solutions of salts of alkali earth metals can be used (Tessier et al., 1982; Hickey and Kittrick, 1984), although trace metals associated with exchange sites on organic matter as well as clay minerals may be extracted (Slavek et al., 1982).

Organic matter

There are two main approaches to the determination of organically-bound trace metals. First, organic matter is oxidised and the released trace metals are determined. Second, organic matter is removed by extraction with an aqueous alkaline solution and the extract analyzed for trace metals.

Gregoire (1985) compared the efficacy of 5% sodium hypochlorite and 30% hydrogen peroxide as oxidants during an investigation into organically-bound Au in soils and sediments and concluded that the former should be used. Losses due to sorption of Au extracted by the reagent on to inorganic phases occurred, but for organic-rich stream and lake sediments the losses were not important if all the organic matter was oxidised and if the levels of Au were sufficiently high to avoid analytical problems. For soils and stream sediments with low levels of organic matter the losses were more significant, although not necessarily precluding the recognition of anomalous samples. Hydrogen peroxide oxidations may also result in the formation of oxalates which can then extract secondary oxides or Fe and Mn (Farmer and Mitchell, 1963).

Organic matter in sediments can be operationally fractioned into three parts: "humin" which is insoluble in alkaline solutions; "humic acid" which is soluble in alkaline solutions but precipitates at pH 7; and "fulvic acid" which is soluble in alkaline and acid solutions. Breward and Peachey (1983) used an ammoniacal solution to extract organic matter from sediments, prepared humic and fulvic acid fractions from the extracts and then determined trace metals in them. Other workers (Wilhelm et al., 1979; Learned et al., 1981) have used alkaline sodium pyrophosphate solutions to extract organic matter and analyzed them without further fractionation.

Carbonates

Carbonates can be extracted using an aqueous buffer solution of sodium acetate/acetic acid (pH 5.0). However, Tessier et al. (1982) consider that metals extracted from their Canadian sediments using this reagent are derived from specific adsorption on to surfaces — probably on to secondary Fe oxides.

Secondary oxides of iron and manganese

Secondary oxide coatings may be extracted with a solution of 1 M hydroxylamine hydrochloride in 25% acetic acid (Chester and Hughes, 1967). Chao (1972) used a solution of 0.1 M hydroxylamine hydrochloride in 0.01 M nitric acid to selectively dissolve secondary oxides of Mn from soils and sediments. Gatehouse et al. (1977) used hydrazine chloride for the extraction of Fe oxides from soils. Solutions of oxalic acid and ammonium oxalate have been used to dissolve secondary oxides although serious problems can arise when extracting from calcareous samples due to the formation of insoluble calcium oxalate. Filipek et al. (1982) found a 0.25 M hydroxylamine hydrochloride/25% acetic acid solution was preferable to oxalic acid for enhancing anomalies, particularly when calcareous or clay-rich samples were investigated. Both reagents will also extract exchangeable cations, and some organic phases, so that detailed partition studies require sequential extractions.

Due care is required when selecting partial dissolution reagents for use in a particular project. Robinson (1984) applied three established sequential leaching schemes to composite samples representing secondary oxide coatings but none of these schemes proved to be entirely efficient in removing coatings nor in being phase-specific. An alternative scheme was developed but partitioning of metals was found to be variable and primary rock fragments susceptible to chemical attack.

Provided that exchangeable cations, Mn oxides and organic matter have previously been excluded from samples, the secondary oxides of Fe can be selectively extracted using "Tamm's" reagent. This is a solution of 0.175 M ammonium oxalate and 0.1 M oxalic acid (pH 3.3). In the dark, amorphous phases are extracted, whereas under UV light, more crystalline Fe oxides were removed (Sondag, 1981). Breward (1988) extracted amorphous Fe oxides from samples of fine sediment (<150 μm) from Plynlimon, mid-Wales, from which exchangeable cations, Mn oxides, and organic matter had been previously removed. He found that ammonium oxalate extractable Cu, Pb and Zn levels indicated the position of mineralized faults (Fig. 16-1, sites 6 and 8) more clearly than the total metal contents of the samples.

Martin et al. (1984) applied a two-stage sequential leaching scheme (ammonium acetate at pH 4.5 and ammonium oxalate at pH 3.3) to stream sediments. The acetate solution performed well for samples from calcareous environments, whereas the oxalate solution was preferred for those from a silico-aluminous environment; the acetate solution removed carbonates so that interference from

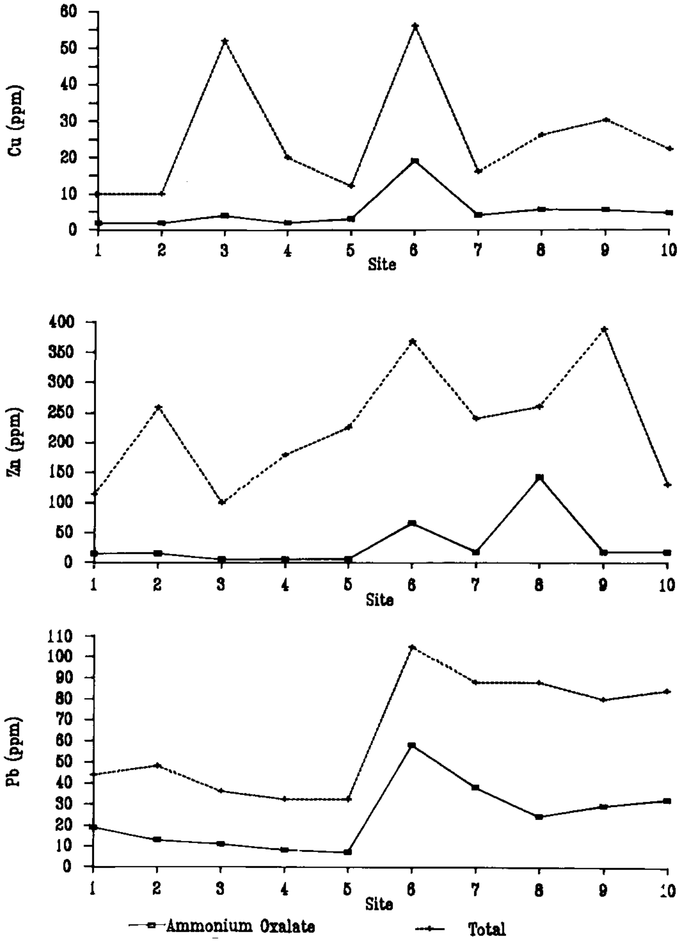

Fig. 16-1. Comparison between total and ammonium oxalate extractable Cu, Pb and Zn concentrations in stream sediments from Plynlimon, mid-Wales (compiled from data from Breward, 1988).

precipitated calcium oxalate during the second stage was avoided. The dispersal pattern shown by the two selective chemical attacks was compared with that produced by an electromagnetic separation method (Fig. 16-2, from Martin et al., 1984). Both the selective chemical extractions and the physical separation of the paramagnetic phase produced an improvement in the geochemical response compared to conventional methods. The oxalic acid extracts can be analyzed directly by inductively coupled plasma atomic emission spectroscopy (Motooka and Sutley, 1982) and this rapid method may be suitable for large regional, multi-element geochemical surveys, particularly in a carbonate environment.

A related method, using direct laser ablation of coatings rather than a selective chemical extraction of the oxides, for simultaneous multi-element

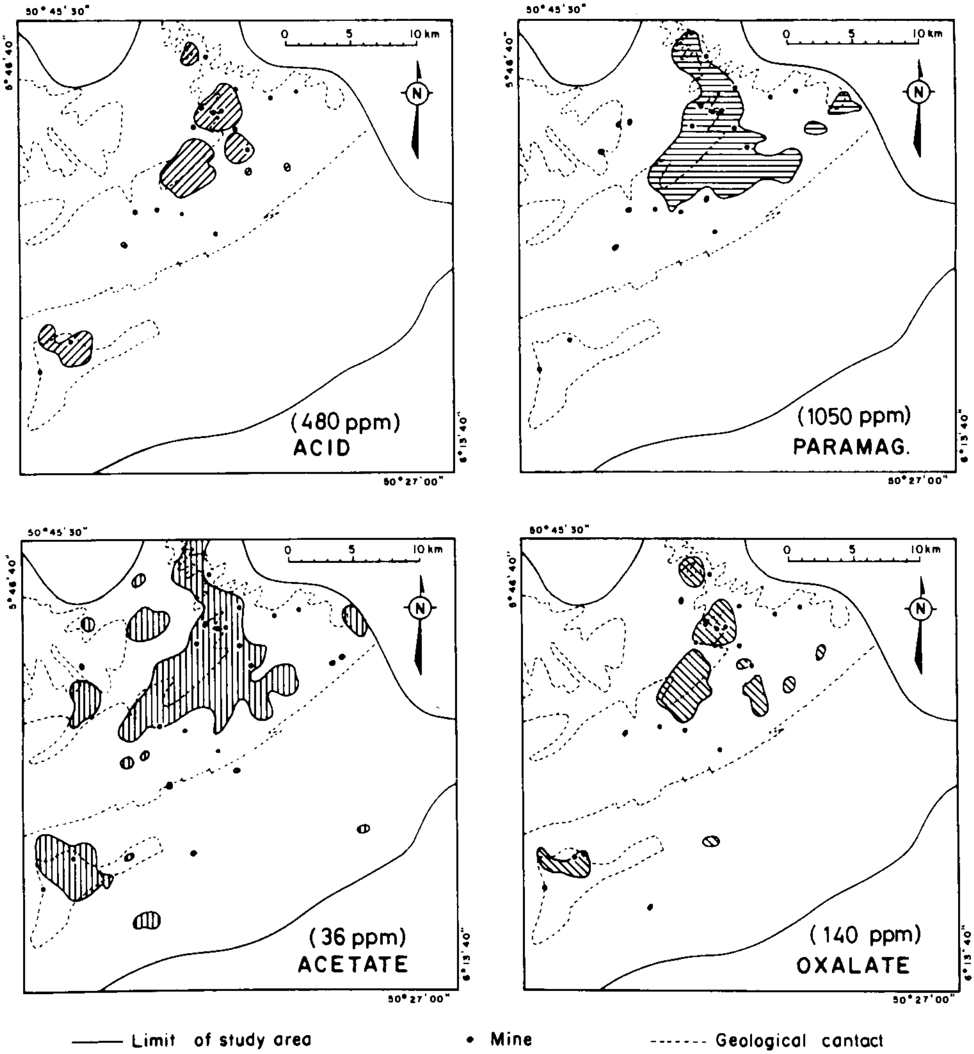

Fig. 16-2. Mapping of anomalous areas for Pb in different chemical and physical extractions from 815 stream sediment samples from a predominantly carbonate rock area in the northeast part of the Ardennes, Belgium. The extractions comprise a conventional hot HCl-HNO_3-HF acid attack, a paramagnetic fraction obtained from a Franz Isodynamic Separator, an ammonium acetate extraction and an ammonium oxalate extraction. Anomalous areas are dashed and threshold values shown in parentheses (from Martin et al., 1984).

analysis by ICP-AES, is described by Hale et al. (1984). This technique permits the determination of a pathfinder element in oxide coatings, which would otherwise be difficult to determine in chemical extracts, but lacks some of the selectivity of the latter method.

Sulphides

The dissolution of sulphides in sediments requires strong oxidising agents and salt solutions. It is necessary, therefore, to remove organic matter and exchangeable cations prior to the extraction of sulphides or to make allowances when the data are interpreted. For example, Peachey and Allen (1977) used a hydrogen peroxide/ascorbic acid extraction (Lynch, 1971) followed by leaching with ammonium acetate solution to re-dissolve any Pb precipitated as sulphate. Manganese oxides were also extracted with hydrogen peroxide/ascorbic acid and allowances made for their trace element contents. Although dissolution of sulphide was incomplete it was possible to distinguish between anomalous samples reflecting mineralized locations from those in which trace metals were elevated solely as a result of adsorption of background concentrations on to secondary oxides. Chao and Sanzolone (1977) also found incomplete dissolution of nine sulphide minerals using hydrogen peroxide/ascorbic acid; the dissolution of stibnite and orpiment was only slight. They found that leaching with potassium chlorate-hydrochloric acid (Olade and Fletcher, 1974) followed by an additional boiling with 4 N nitric acid dissolved all nine minerals.

Problems associated with partial dissolution techniques

In view of the complexity of many sediments, the specificity and effectiveness of a particular reagent for all sediments in general cannot be assumed. Considerable care is required in sequential schemes to ensure that each step does not interfere with succeeding steps by introducing artifacts or causing a re-distribution of trace metals amongst the phases. Tipping et al. (1985) found on sequential leaching of a sample — previously examined by electron microscopy and microprobe — that the Ca and Pb distributions were rearranged. The reagents used were 0.1 M hydroxylamine hydrochloride/0.01 M nitric acid followed by 0.2 M ammonium oxalate/0.2 M oxalic acid (pH 3). The differences were attributed to extraction of Ca from Fe oxides by the hydroxylamine treatment, and the re-adsorption of Pb originally released from Mn oxide. Slavek et al. (1982) studied the selective extraction of "available" or "exchangeable" metals sorbed into humic acid. During these studies they considered four established sequential schemes and concluded that each scheme would produce a different result for metal "bound to organic matter" and that in partial extraction techniques much care must be paid to chemical equilibria and competition between various chemical reactions.

Kheboian and Bauer (1987) applied a sequential leaching scheme (Tessier et al., 1979) to a number of well-characterised, prepared phases, each spiked with a particular trace metal. The phases were calcite, Fe hydroxides, Fe sulphide and humic acid; three model sediments were prepared by combining various phases together with illite or silica. While admitting that their models do not represent real sediments, the authors claim that sequential leaching techniques are fundamentally flawed since their experiments demonstrate that serious re-distribution of metals occurs. They are also dubious about the operational efficiency of partial extractions when applied to comparative regional geochemistry.

Rendell et al. (1980) found that extracted metals may be lost from solution during overnight leaching of river sediments with various reagents. Comparison of results by different sequential leaching schemes is also very difficult since there is a lack of standard materials for direct comparison. However, Tessier et al. (1980) have applied their scheme (Tessier et al., 1979) to a US Geological Survey marine mud (MAG-1).

Further complications may arise during sample storage and pre-treatment. The extractability of some metals in 1 M ammonium acetate can vary depending upon whether samples are air-dried or oven-dried at 105°C (Breward and Peachey, 1983). Similarly, Shuman (1980) found that levels of DTPA-extractable Mn, Fe, Cu and Zn were affected by soil moisture and air-drying. Rapin et al. (1986) used a sequential leaching system to study the partitioning of trace metals in sediments and found that the results could be influenced by the conditions of sample storage prior to analysis, and that elements in anoxic sediments need to be extracted in the absence of oxygen. The authors concluded that freeze-drying and oven-drying should be avoided and suggest that freezing or short-term storage at 1–2°C should be used.

The cost-effectiveness of a proposed extraction scheme should also be considered (Sandström, 1984). Whereas a single extractant could be used for large batches of samples, a sequential leaching technique is only appropriate for relatively few samples without incurring large additional costs.

However, some findings from partial dissolution techniques have been corroborated. For example, Hale et al. (1984) obtained similar dispersion patterns for Pb to Fe ratios and Zn to Mn ratios using laser ablation/ICP-AES and selective leaching (Whitney, 1975) of pebble coatings. Sequential leaching using ammonium acetate and ammonium oxalate solutions of sediments has been demonstrated by Martin et al. (1984) to give an improvement in geochemical response compared to conventional methods. This was shown by an increase in the size and contrast of anomalies and in the detection of new anomalies.

Provided that the problems involved in partial dissolution techniques are carefully considered during their design and in the interpretation of data, this approach may usefully be applied to well-defined exploration problems. These techniques are most valuable for geochemical exploration problems not readily amenable to simple physical methods of sampling. Hydromorphic leakage anomalies above a concealed ore deposit represent one example where orthodox physical stream sediment samples may not produce an adequate response because of lack of dispersion of anomalous detrital grains. Thus selective extraction techniques may become increasingly important in the search for buried ore deposits.

PHYSICALLY-SEPARATED FRACTIONS OF STREAM SEDIMENTS

The behaviour of an element in drainage depends on its mode of occurrence at source and the chemical and mechanical stability of its host minerals within the surficial environment. Table 16-I summarises the mode of occurrence of several elements of economic interest and their typical means of dispersion in drainage in temperate climatic regimes. A particular drainage sediment fraction can be collected which enhances one size, density or magnetic susceptibility range at the expense of others, facilitating the detection of anomalies from particular mineralization types. Commonly, orientation work is carried out by studying the dispersion in drainage from known mineralization to identify a single sample type likely to be most efficient in the detection of similar mineralization in the same general geological and physiographical environment (e.g., Plant, 1971).

The use of a fine fraction of stream sediment has been highly successful in the detection of mineralization where hydromorphic dispersion is important, as in the case of many porphyry copper deposits. However, such a sample, e.g., a <150 μm fraction, would not reflect mineralization which is dispersed as coarser detrital grains. This is commonly the case for Cr mineralization, which occurs as relatively coarse-grained and mechanically and chemically resistant grains of chromite. Furthermore the coarse ore chromite may have to be distinguished from a background of disseminated chromite and possibly elevated Cr concentrations in other minerals. Podiform chromite mineralization on Unst, Shetland (Prichard and Neary, 1981) occurs within dunite and, to a lesser extent, harzburgite units within an ophiolitic complex. Between 80 and 95% of the chromite in the background ultramafic rocks is coarser than 150 μm and in samples derived from mineralization the proportion is higher still (Gunn et al., 1985). In such an environment it is necessary to explore specifically for the most coarse-grained chromite.

The potential importance of grain size variation in drainage geochemistry can also be illustrated by dispersion of Sn and W from mineralization in southwest England. The regional background, especially of Sn, is relatively high. A long history of mining in the region has disturbed the natural patterns of dispersion from mineralization in many places, but little mining activity has taken place in one section of the aureole of the Dartmoor Granite where cassiterite and wolframite-bearing stockwork mineralization occurs. Different size fractions of panned concentrates from four sites along a stream draining this stockwork zone have been analyzed (British Geological Survey, unpublished data). The concentrations of a number of elements including Sn and W were determined in <250 μm, <500 >250 μm and >500 μm fractions of these samples and the proportions of each element in each fraction calculated. The first sample site was above the mineralized zone while the second, third and fourth were progressively further downstream from the mineralization. Figure 16-3 demonstrates that proportions of Sn and W in the coarsest fraction are much higher in the sample collected immediately below the mineralization than in the sample from above it. The proportion of the coarsest mineral decreases

TABLE 16-I

Mode of occurrence and properties in the secondary environment of some elements of economic interest

	Source	Mineral	Form	Contrast	Chemical stability in sec. environ.	Mineral in sec. environ.	Mechanical stability	Form in sediment	Grain size effect
Ti	Basic rocks	Ilmenite	Dissem.	Low	High		High	Detrital	Important
V	Basic rocks	Magnetite	Dissem. or vein	Low	High		High	Detrital	Important
Cr	Ultra basic rocks	Chromite	Pod or layer	Low	High		High	Detrital	Important
Ni	Sulphide in basic rocks	Pyrrhotite, pentlandite	Dissem., network	Low	Low	Soluble, gossan		Fe oxide detrital	
Cu	Sulphide	Chalcopyrite	Dissem., massive veins	High	Low	Soluble, malachite		Clay, organic, sec. mins.	
Zn	Sulphide	Sphalerite	Dissem., massive, veins	High	Low	Soluble		Sec. mins., oxide clay	
As	Sulphide	Arsenopyrite	Dissem., veins	High	Low	Sec. mins., soluble		Sec. mins., Fe oxide	
Mo	Sulphide	Molybdenite	Dissem.	High	Low	Sec. mins.		Sec. mins. Mn/Fe oxide	
Sn	Hydrothermal in granite veins	Cassiterite	Veins, stockwork	High	High		Med. high	Detrital	Important
Sb	Hydrothermal	Stibnite	Veins, dissem.	High	Low	Sec. mins.	Low	Sec. mins., Fe oxide	
Ba	Hydrothermal	Baryte	Massive veins	Low	High	Baryte	Med.	Detrital	Important
W	Hydrothermal	Wolframite, scheelite	Veins, strata-bound	High	Med., high	Sec. min., scheelite	Med.	Detrital	Important
Pb	Hydrothermal	Galena	Veins, strata-bound	High	Med.	Sec. min.	Med.	Detrital	

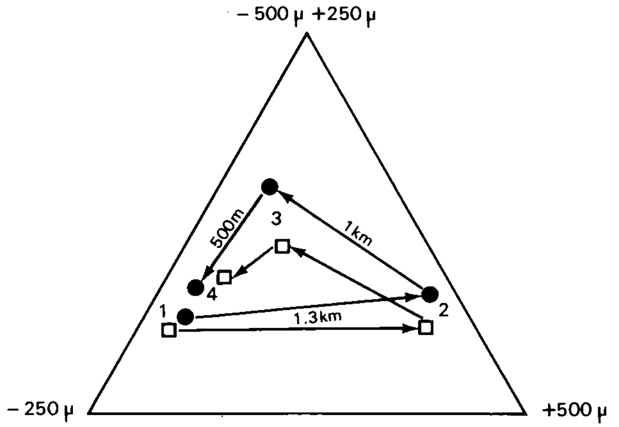

Fig. 16-3. Proportions of Sn ● and W □ in three size fractions of four panned concentrate samples from the aureole of the Dartmoor granite, southwest England. Site 2 is immediately downstream of mineralization.

with distance away from source. The ratios of the total Sn content of the anomalous samples (samples 2, 3, and 4) to the background (sample 1) decrease from 9.4 to 3.0 and to 0.7 with increasing distance from the source. When the Sn contents of the coarsest fractions are compared, the corresponding ratios are 36.6, 5.1 and 1.0. For the finest fraction the ratios are 0.69, 1.24 and 0.47, showing only a weak anomaly displaced 1 km from the source. Tungsten behaves similarly, although the magnitudes of the corresponding ratios for the coarsest fraction samples are lower, at 18.6, 1.4 and 0.5, respectively.

CONTRASTING SAMPLE TYPES

In order to optimise the acquisition of information about the sources of anomalies in drainage, more than one sample, comprising contrasting fractions, can be analyzed from the same site. These fractions should preferably overlap but be biased towards different size or density components, reflecting different geochemical pathways. The chemistry of most drainage samples is strongly related to grain size (Plant, 1971), as the proportion of chemically active clay and oxide precipitate increases markedly in the finest grain sizes. It is therefore advantageous to compare a fine-grained fraction with a coarser fraction, especially if the heavier detrital grains in the latter are upgraded at the expense of lighter grains of similar size by panning. This approach has been used successfully by the British Geological Survey in its Mineral Reconnaissance Programme by comparison of a <150 μm wet-sieved fraction with a <2 mm fraction panned to constant volume to upgrade the heavier detrital grains and to remove the finest clay, organic and precipitate fractions.

Comparison of populations

A powerful method of comparing chemical data for two contrasting sample types is to analyze their frequency distributions and this can be achieved by means of cumulative frequency plots (Sinclair, 1974). Panned concentrate samples can usually be considered as mixtures of a background population of mineral grains and rock fragments containing low levels of a metallic element of interest and a population of metal-rich grains. Most ore minerals have a relatively simple chemistry, with one main metallic element forming a major proportion or phase, e.g., sphalerite contains around 67% Zn. Secondary ore minerals also frequently have a high metal content, such as 76.3% Pb in pyromorphite. The ore minerals can be thought of as representing the mineralized population extreme, with the actual concentration of an element also dependent on the proportions of other heavy minerals present at source. Mixing of ore and background components in differing proportions results in cumulative frequency graphs with steep increases in gradient where the concentration of metal-rich material becomes significant. The concentrate cumulative frequency plots of Pb, As, Cu and Zn from southwest England, Pb and Ba from Galloway and Pb, Cu and Zn from the Harlech Dome (Figs. 16-4 to 16-7) are of this type. In several cases the level of an element in the background component is below the detection limit of the analytical method used and this results in the presence of only the upper, higher gradient part of the cumulative frequency plots of Sn and W in southwest England, Pb, Ba and Zn in the Northumberland Trough, and Cu in Galloway being visible. This type of cumulative frequency plot is relatively easy to interpret and seems to be of very wide occurrence, regardless of background geology and physiographic or climatic environment.

In some cases, the pattern shown by a cumulative frequency plot is more complex due, for example, to the presence of additional mineral species containing an element at the few percent level, which is well above the background but significantly lower than the level within typical ore minerals. Such a situation could arise where Cu associated with a porphyry system is present both as chalcopyrite and as a minor component of pyrite. Nevertheless, analysis of the gradients of different sectors of a more complex cumulative frequency plot can resolve such a case.

The composition of the fine fraction of a stream sediment sample is often more complex and variable than that of the panned concentrate. For some elements the mode of occurrence is the same in both sample types, e.g., Sn in the form of detrital grains of cassiterite. In other cases an element may be split among several component phases, each of which could contain differing anomalous levels of a metal. Apparently anomalous levels of some elements may be of environmental origin due, for instance, to the scavenging effect of Mn oxide co-precipitation in peaty upland areas. In consequence, it is more difficult to interpret these complex mixtures from the shapes of cumulative frequency plots.

Comparisons of the plots of the two sample types for various elements of economic interest from different areas of Britain are discussed below, and are given in order of increasing complexity. This provides valuable information on dispersion pathways which can assist in the recognition of the more significant anomalies.

Tin and tungsten

The cumulative frequency plots of Sn and W for the two sample types from southwest England (Jones, 1981) are compared in Fig. 16-4. The shape of the two curves is very similar, approximating to a straight line of steep gradient. The panned concentrates are greatly enriched in Sn relative to the corresponding fine sediments (medians: 500 ppm for concentrates compared to 25 ppm for fine sediments). This difference is due to a combination of upgrading of the heavy-mineral cassiterite, the form in which virtually all the Sn occurs, and the presence of a significant amount of this mineral coarser in grain-size than 150 μm.

The degree of W enrichment in the concentrate, relative to the fine sediment, is much lower than for Sn (medians: 40 ppm in concentrate and 10 ppm in fine sediment). In southwest England the majority of tungsten mineralization is in the form of wolframite, a mineral mechanically and chemically less stable than cassiterite. The wolframite tends to break down into relatively fine-grained secondary oxides of lower density which occur in close association with hydrous Fe oxides and are not upgraded to a large extent by panning.

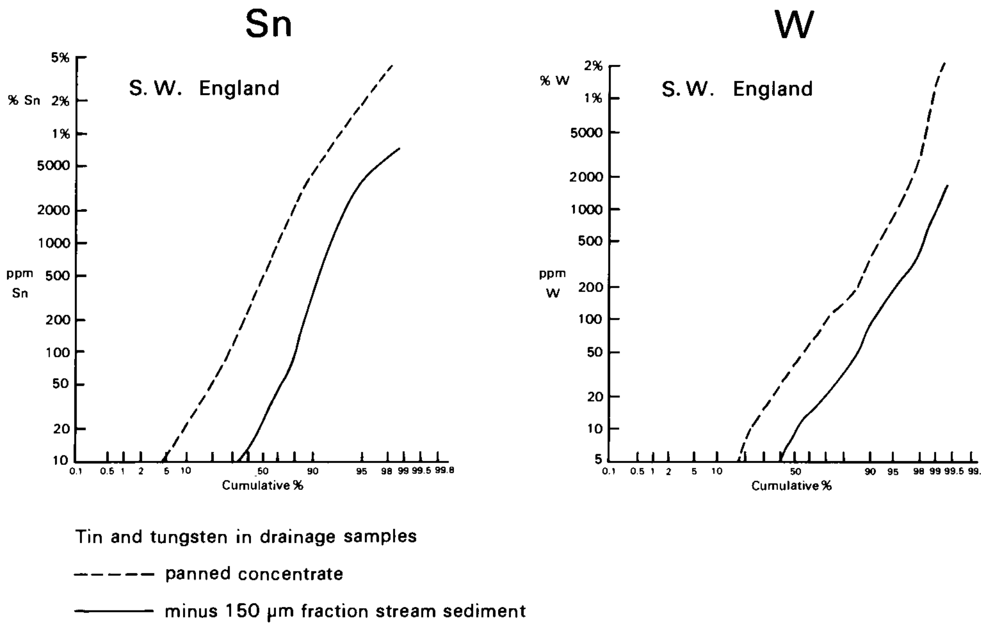

Fig. 16-4. Cumulative frequency plots of Sn and W contents of paired <150 μm fraction and panned concentrate samples from south Devon and east Cornwall, southwest England; 1072 sites for Sn, 134 sites for W.

Arsenic

The behaviour of arsenic in drainage samples is more complex than that of Sn and W because of its relative solubility and its tendency to be scavenged from solution by hydrous Fe oxide precipitates. The cumulative frequency plots for southwest England (Fig. 16-5), where As, usually as arsenopyrite, is an important constituent of the higher temperature vein and stockwork mineralization (Dines, 1956), are similar, with a sharp increase in gradient around the 90th percentile level. The lower gradient section of the plots represents the background for southwest England, where low-grade enrichments in As, e.g., within pyrite, are widespread. Irregularities represent ill-defined subpopulations related to different degrees of enrichment in different lithologies. Enrichment of As in the concentrate relative to the fine sediment indicates that detrital dispersion is of greater importance than hydromorphic dispersion in this area.

The cumulative frequency plots for As in the two types of drainage sample from the Preseli Hills in Dyfed, Wales, differ markedly from those from southwest England, both having a relatively low gradient and curving only slightly upwards. Furthermore there is a significantly higher level of As in the fine sediments compared to the panned concentrates. In this area no significant arsenic mineralization is known, though As is a minor constituent of base-metal mineralization, chiefly of vein type, but possibly also of shale-hosted style (Cameron et al., 1984). These plots indicate that dispersion is largely hydromorphic from relatively diffuse source regions.

Barium

Barium is present in minor, but significant, amounts in many common rocks, but in ore deposits it is mostly present in the minerals baryte and to a lesser extent witherite. The cumulative frequency plots of Ba in fine sediment from the Northumberland Trough (Bateson et al., 1983) and from Galloway (Leake et al., 1978a) both show (Fig. 16-5) a marked increase in gradient between the 90th and 99th percentile. In the Northumberland Trough the abrupt increase in gradient reflects the incoming of detrital baryte derived from widespread vein mineralization, which is superimposed on the background level contained within clay and other fractions derived from local bedrock. In the Galloway data the lower gradient of the upper portion of the fine sediment plot reflects the presence of an anomalous population containing clay derived from feldspar in the granitoid rocks containing a moderately high concentration of Ba. This clay-rich material is more widespread than the minor amount of baryte mineralization in the area. In the Galloway concentrates the upper section of the plot reflects baryte rather than the granite-derived clay, which is not retained during panning. A difference in the nature and grain-size of the country rocks between the Galloway and Northumberland Trough areas probably accounts for the absence of a lower gradient sector in the latter concentrate plot. Detrital grains of greywacke, the predominant rock in Galloway, are more easily retained in the pan and generally may have a higher Ba content than the mixture of pure quartz sandstones, limestones and shales which make up the country rocks of the Northumberland Trough.

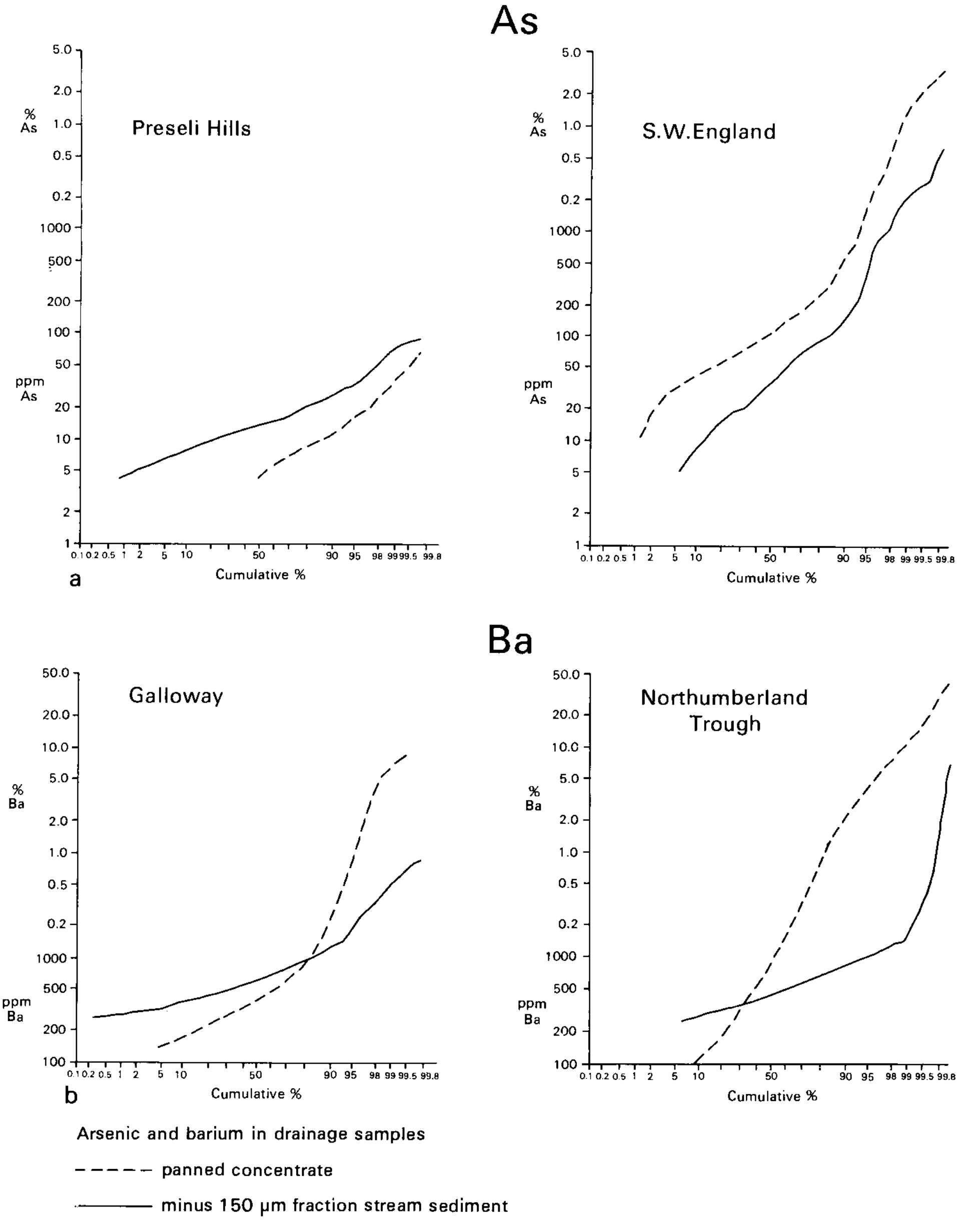

Fig. 16-5. (a) Cumulative frequency plots of As in paired <150 μm fraction and panned concentrate samples from 358 sites in the Preseli Hills, southwest Wales, and from 650 sites in south Devon and east Cornwall, southwest England. (b) Cumulative frequency plots of Ba in 381 <150 μm fraction samples and 217 panned concentrate samples from sites over the Criffel granitoid pluton and its environs in Galloway, Scotland, and of similar sample pairs collected from 1878 sites in the Northumberland Trough, north England.

Lead

The cumulative frequency plot of Pb in drainage samples from southwest England (Fig. 16-6) resembles that for As but with a more pronounced break in slope. The Pb plot for the Northumberland Trough (Fig. 16-6) is similar to the corresponding Ba plot but with a smaller enrichment in concentrate relative to fine sediment. This reflects the greater ease with which lead minerals are mechanically broken down.

The plots of Pb in samples from the Harlech Dome, an upland area in Wales with minor vein and strata-bound lead mineralization (Cooper et al., 1985), show very little difference between concentrations in the upper part of the curve for each sample type (Fig. 16-6). This indicates that hydromorphic dispersion is more important for Pb in this area than the lowland Northumberland Trough and southwest England areas.

The importance of hydromorphic dispersion of Pb is even more marked in the case of the samples from Galloway (Fig. 16-6), an upland area of southern Scotland also with minor vein and strata-bound mineralization (Leake et al., 1978b; Stone et al., 1984). In this area Pb contents in fine sediment are generally much higher than those in concentrates. Much of the Pb in the fine fraction originates from alkali feldspars from the granitoid rocks which, on weathering, produce a clay in which the Pb is fixed. In both Galloway and the Harlech Dome there is extensive development of peat on the higher ground. This organic-rich material concentrates Pb relative to mineral-rich soils and forms a significant proportion of drainage sediment at some sites. Both these factors result in relative enrichment of Pb in the fine sediment compared to the concentrate. In the Galloway data a mineralization-derived anomalous population is only discernible in the concentrate data.

Copper

Copper data from four areas are compared in Fig. 16-7. The plots of Cu in panned concentrate samples from the Harlech Dome and southwest England show breaks in slope at around the 90% level. The upper populations represent the presence of significant numbers of grains of copper-rich minerals derived from widespread vein or disseminated mineralization. The lower populations probably reflect a minor, but significant, amount of copper within pyrite or perhaps iron oxides. The cumulative frequency plot of Cu in panned concentrate samples from Galloway shows no break in slope and lower gradient sector. This reflects a lower general abundance of copper mineralization in Galloway and an absence of significant amounts of cupriferous pyrite.

The distribution plot for concentrate samples from central Argyll is approximately linear with an indication of a very small higher gradient sector at about the 99.5% level. The gradient of the main part of the line is similar to that of the lower part of the Harlech Dome plot and is thought to reflect the nature of the mineralization in the region, where copper is mostly associated with stratiform pyrite. In this mineralization copper is present as fine inclusions of chalcopyrite within the pyrite with a maximum concentration of a few per-

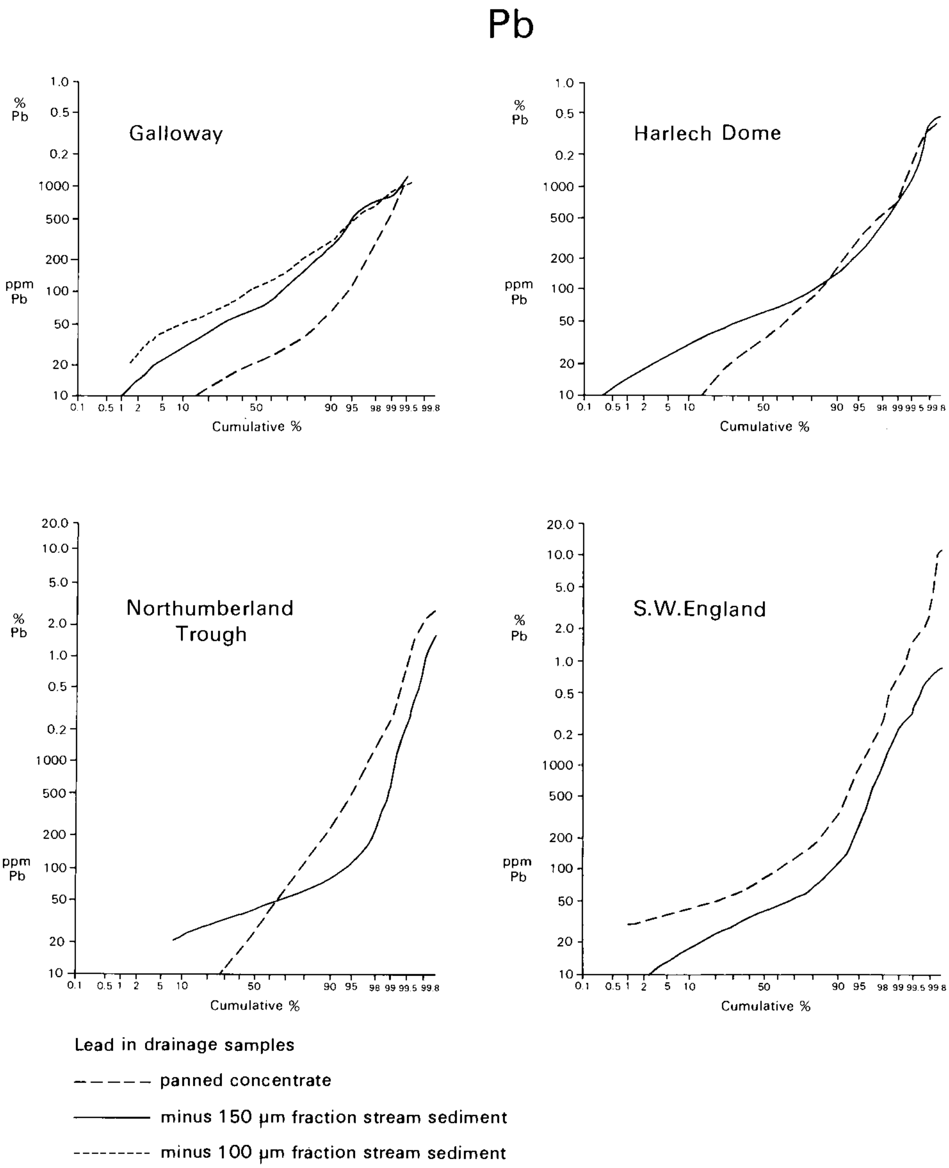

Fig. 16-6. Cumulative frequency plots of Pb in <100 μm and <150 μm fractions and panned concentrate samples from the same 196 drainage sites in Galloway, Scotland, and paired <150 μm fraction and panned concentrate samples from 888 sites in the Harlech Dome, north Wales, 1878 sites in the Northumberland Trough, north England, and 1570 sites in south Devon and east Cornwall, southwest England.

cent copper (Coats et al., 1982) in contrast to the 34.5% copper in chalcopyrite.

The plots for Cu in the <150 μm fraction samples each show a marked inflexion point but the proportion of each population is highly variable between

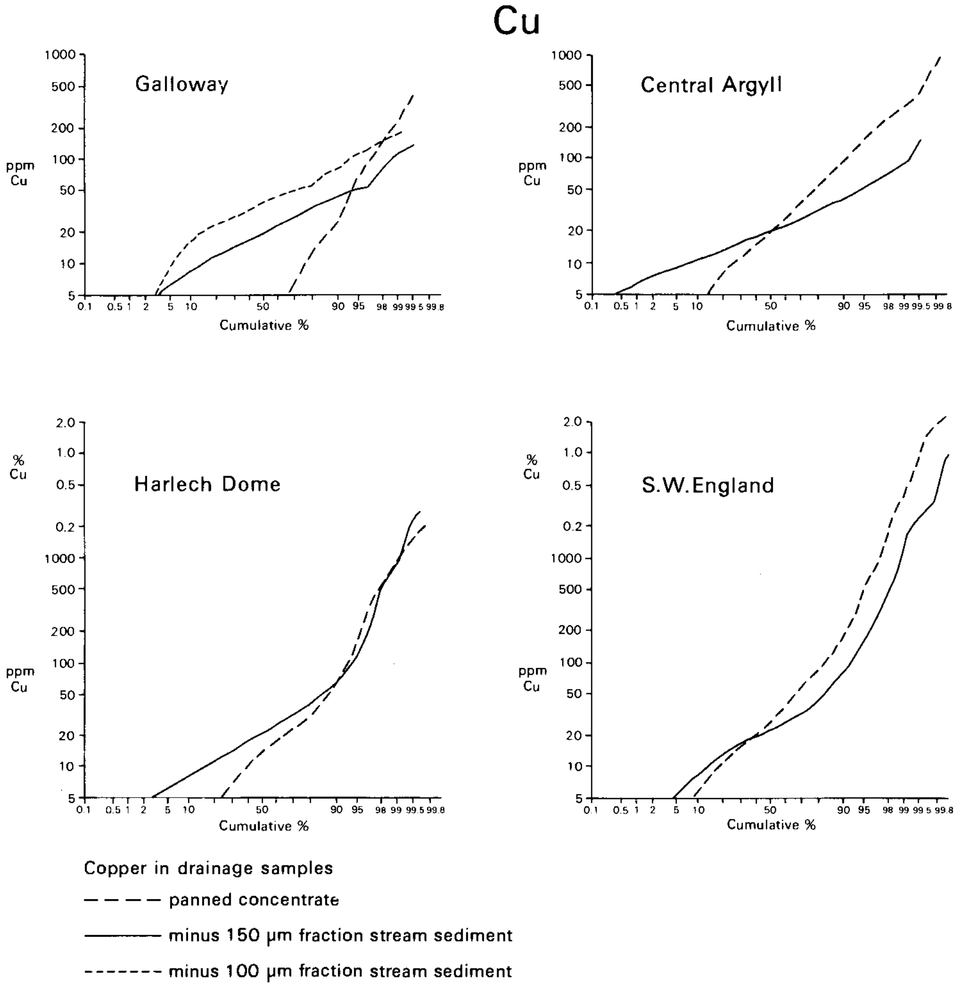

Fig. 16-7. Cumulative frequency plots of Cu in <100 μm and <150 μm fractions and panned concentrate samples from the same 196 drainage sites in Galloway, Scotland, and paired <150 μm fraction and panned concentrate samples from 761 sites in Central Argyll in the Scottish Highlands, 888 sites in the Harlech Dome, north Wales, and 1554 sites in south Devon and east Cornwall, southwest England.

the different areas. The upper high-gradient sector is most obvious in the southwest England samples while lower gradient part of the plot is better developed in the Harlech Dome data and even more so in samples from Galloway and Central Argyll. In Galloway much of the copper is associated with a fine clay or organic-rich fraction and the concentration of Cu in the <100 μm fraction is on average twice that in corresponding <150 μm fraction (BGS, unpublished data). In the Harlech Dome the fine sediment Cu levels are higher relative to those in the concentrates than in the other areas. This reflects a greater degree of hydromorphic dispersion from porphyry-style copper mineralization in the Harlech Dome (Cooper et al., 1985).

Zinc

The relative solubility of sphalerite, the commonest zinc mineral, has a considerable influence on the mode of dispersion of the element in drainage. Coarse-grained sphalerite, such as may occur in relatively low-temperature vein mineralization, can show detrital dispersion. The Zn in fine-grained sphalerite, especially if subject to surficial leaching, can be entirely removed in solution, and its dispersion in drainage sediment is then governed by secondary precipitation of manganese oxide and scavenging of Zn from solution.

The complexity of the dispersion of Zn in stream sediment can be illustrated by cumulative frequency plots from four areas in Britain shown in Fig. 16-8. In concentrate samples from southwest England and the Harlech Dome, well marked breaks in slope occur. The upper population in both cases reflects the presence of detrital sphalerite derived from vein mineralization.

In contrast, in the Central Argyll data a high-gradient sector is hardly recognisable. In this area there is little evidence of a significant amount of zinc mineralization. Moreover, because of its upland nature, with acid waters derived from accumulations of peat, Zn is rapidly leached from rocks at surface, leading to its widespread general hydromorphic dispersion.

The near straight line form and intermediate gradient of the cumulative frequency plot of Zn in concentrate samples from the Northumberland Trough is considered partly to reflect the fact that mineralization carrying Zn in the region is spatially closely related to the doleritic Whin Sill. This rock is a favoured host for alteration and replacement leading to more widespread elevated Zn concentrations in the fabric of the rock rather than discrete grains of sphalerite (Bateson et al., 1983). Zinc within fragments of altered Whin Sill, or possibly within ankeritic carbonate, is thought to be the main form in which Zn is detritally dispersed.

The shape of the fine fraction sediment plot in the southwest England data is similar to that of the concentrate plot but there are significant differences between the two sample types in the other three areas. In Central Argyll the small but well marked high-gradient population in the fine sediment and the generally higher concentrations of Zn in the fine sediment compared with the concentrates reflect the greater importance of hydromorphic dispersion of Zn. In the Northumberland Trough the well-defined, high-gradient population in the fine sediment data also reflects the importance of hydromorphic dispersion of Zn from sphalerite mineralization. The relatively low gradient and the small magnitude of the increase in the upper part of the sieved sediment plot for Harlech Dome samples contrasts with the other comparable plots in Fig. 16-8. Factor analysis of the data (Cooper et al., 1985) shows the environmentally controlled hydromorphic general dispersion of Zn, particularly from argillaceous rocks in the upland areas, to be more important than the dispersion of Zn from vein mineralization.

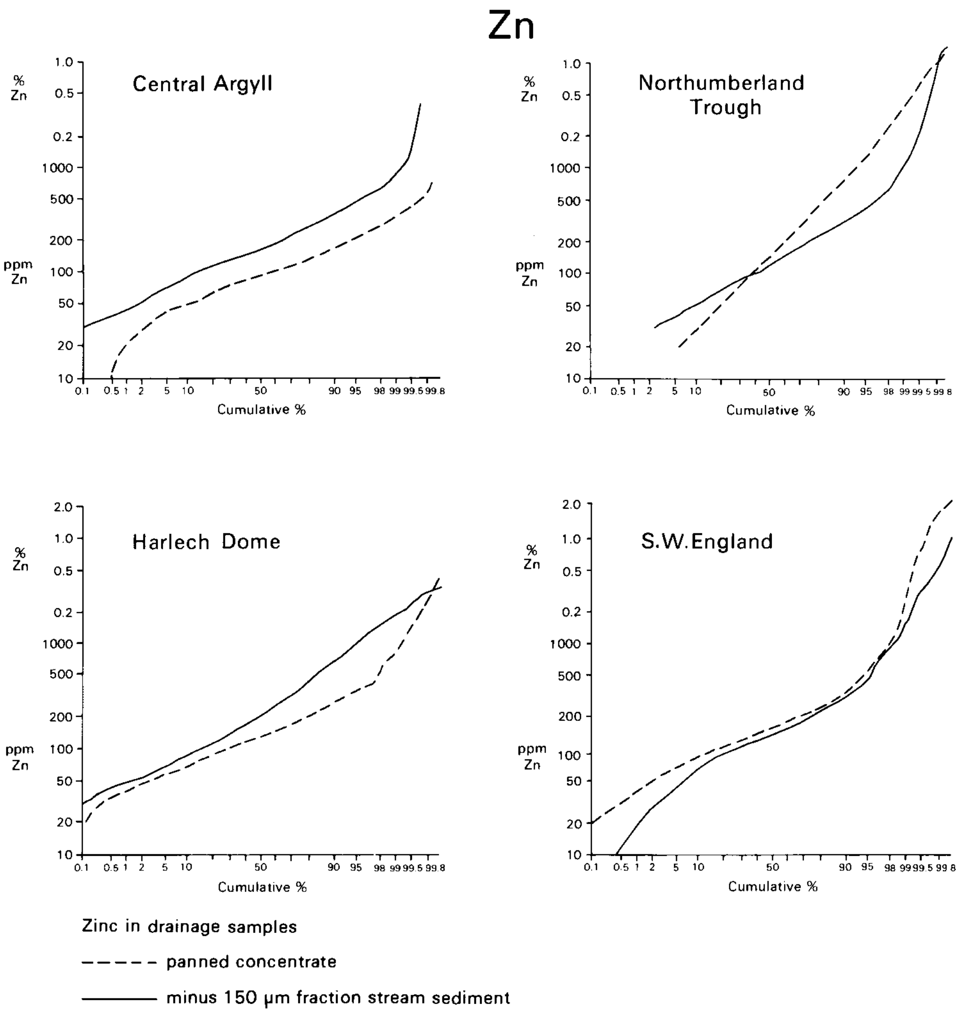

Fig. 16-8. Cumulative frequency plots of Zn in paired <150 μm fraction and panned concentrate samples from 761 drainage sites in Central Argyll in the Scottish Highlands, 1878 sites in the Northumberland Trough, north England, 888 sites in the Harlech Dome, north Wales, and 1547 sites in south Devon and east Cornwall, southwest England.

Comparison at individual sites

Much can be deduced about the source of an anomaly from the proportion of a given element in contrasting drainage sediment samples collected simultaneously at the same site. Anomalies can arise (a) naturally from mineralization of different varieties and size, (b) from contamination due to various types of human activity, including old mining operations, and (c) from the enhancement of the concentration of a particular element due to the scavenging activity of environmentally-controlled precipitation of chemically active material like hydrous manganese oxide. In addition, anomalies can arise over background rocks as a result of the presence in drainage sediment of significant amounts of a weathering product such as residual clay which is itself enriched in certain elements. Anomalies of elements present as heavy resistant minerals can also arise from natural "panning" at sites with favourable flow characteristics, particularly in the larger streams and rivers in upland areas.

Complexity in anomaly distribution patterns apply particularly to the more common metallic elements which occur in a wide variety of deposit types, have a significant background concentration in common rocks and are also present in many common contaminants. An assessment of the relationship between element concentrations in equivalent panned concentrate and fine sediment samples and anomaly sources for Pb, Cu and Zn in various regions in Britain are described below. Data sets have been chosen where mineralogical examination of panned concentrates has been carried out to identify metal-bearing phases and where monitoring of sources of contamination has been undertaken.

Lead

Except in areas of carbonate rock, in Britain most anomalous lead of natural origin in concentrate samples is in the form of secondary minerals, which can often be relatively inconspicuous. Lead is a very common contaminant in areas of human habitation and agricultural activity, quite often in the form of discrete grains of lead shot, battery plates, solder from tin cans or lead glass. In areas where tin mineralization is absent, Sn is often a useful general contamination indicator and there is often a close positive correlation between Sn and Pb in such contaminated samples. Another source of contamination of several metals, including sometimes Pb, is in association with effluent from sewage or agricultural slurry, where metals are often present in close association with organic matter. The Pb content of samples of $<150\ \mu m$ sieved sediment and <2 mm panned concentrates collected simultaneously from a number of sites in Galloway within the Southern Upland belt of Scotland, from southwest England and from the Harlech Dome in North Wales are shown in Fig. 16-9. In each area, samples containing discrete lead-bearing contaminants have high levels of Pb in the concentrate samples, relative to the fine fraction of the sieved sediment, a consequence of the relatively coarse grain size of such contaminants as lead shot and their mechanical and chemical stability.

Two samples from Galloway in which lead is accommodated in galena are highly enriched in Pb in the concentrate relative to the sieved sediment. These samples are thought to have been derived, in part, from old mine waste from worked vein mineralization. Such dump material contains relatively coarse-grained galena, which has not had time to equilibriate to the surface environment and occurs near source in the drainage as relatively coarse grains, sometimes of a composite nature. The surface expression of Pb in undisturbed stratabound and associated vein mineralization in Galloway tends, as a result of surface leaching, to be as secondary minerals like plumbogummite and

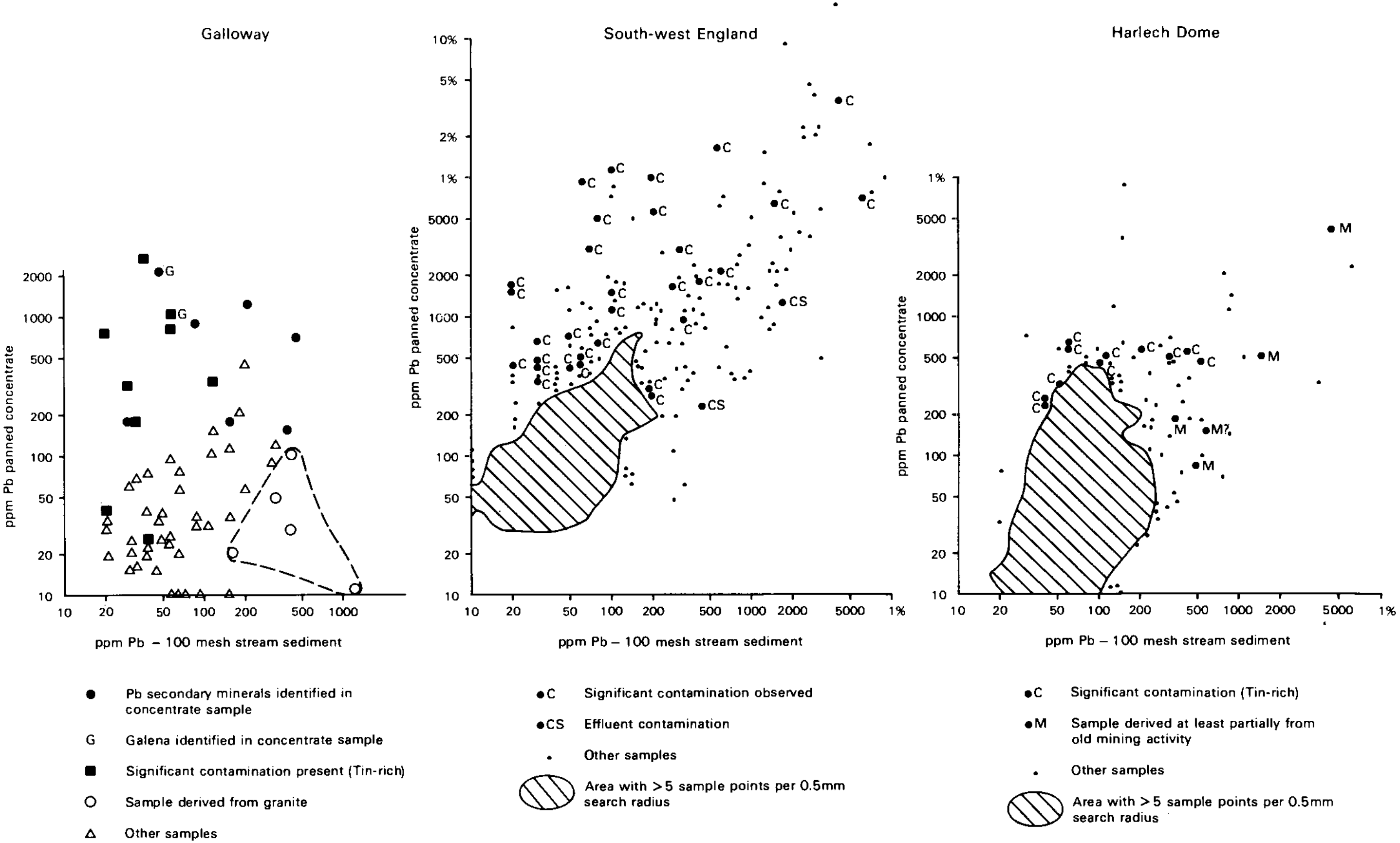

Fig. 16-9. Comparison of Pb concentrations in paired <150 μm fraction and panned concentrate samples from Galloway, Scotland (63 samples), south Devon and east Cornwall, southwest England (1570 samples), and the Harlech Dome, north Wales (888 samples).

pyromorphite (Stone et al., 1984). The drainage samples which contain material derived from this mineralization show Pb enrichment in both sample types of roughly the same order of magnitude.

Figure 16-9 also shows a group of samples that are derived from the Fleet granitoid complex and exhibit marked Pb enrichment in the fine sediment relative to the corresponding concentrate. At these sites the Pb is mostly present in the clay and organic fractions of the drainage sediment. This Pb is derived from the minor amount present in the alkali feldspar of the intrusion, which is concentrated on weathering and retained in clays.

Similar sample pairs from southwest England, a region with much greater abundance of mineralization and disturbance both from old mine workings and general human activity, are also plotted in Fig. 16-9. The samples were taken from the sedimentary rocks of east Cornwall and south Devon and the marginal areas of the granite bodies but not their interiors. Generally there is a much closer correlation between the Pb content of the two samples than in the Galloway data set. Nevertheless there are several sites where Pb is enhanced in the concentrate relative to the fine sediment. At many of these sites, contaminants of household or farming origin were either observed during sample collection and/or laboratory mineralogical examination. Material derived from old mining activity is also present though site selection was carried out to avoid such sources as far as possible.

Distinguishing between Pb anomalies derived from natural dispersion from unworked mineralization and those derived from mineralization that has been disturbed by old working is particularly difficult, especially where there has been a long history of small scale mining activity. Anomalies influenced by the presence of old workings tend to show greater enrichment in the concentrate sample relative to the sediment as in Galloway, but this is not likely to be universally the case. At two sites contamination from sewage effluent was noted and in these Pb is enriched in the fine sediment relative to the concentrate.

Comparison of the size distribution of Pb in single concentrate samples can also provide significant information about the source of anomalies. This may be particularly valuable in areas where general metallic contamination is high. A number of concentrate samples from a part of south Devon where there is very little, if any, old mining activity but where general contamination is widespread, were split into three size fractions prior to analysis (Leake et al., 1988). A triangular plot of the proportions of Pb in >500 μm, <500 μm to >250 μm, and <250 μm fractions of anomalous panned concentrates is shown in Fig. 16-10. The points close to the coarsest fraction apex represent samples in which the Pb is present as a few, relatively large grains of artificial contaminants, like metallic lead. Other samples plotting in a straight line from the coarse towards the medium fraction apex also probably only contain contaminant lead. In contrast, the Pb in the sample plotting most towards the finest fraction apex of the diagram is partly of natural origin, derived from minor polymetallic mineralization which is dispersed in drainage as relatively fine grains of lead-rich secondary minerals (BGS, unpublished data).

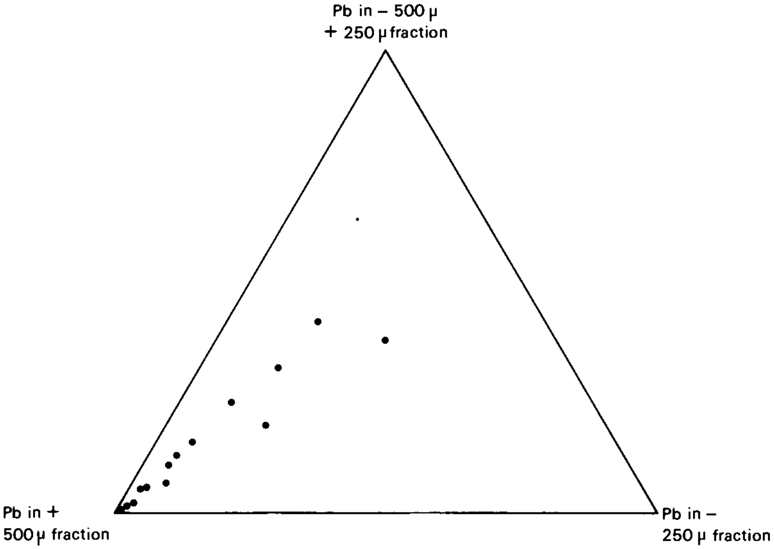

Fig. 16-10. Triangular plot showing the proportion of Pb in three size fractions of panned concentrates from south Devon containing anomalous total Pb.

The plot of Pb in corresponding sample pairs from the Harlech Dome in Fig. 16-9 shows a steeper gradient in favour of the panned concentrate samples at the lower part of the concentration range than for southwest England samples, together with a positive intercept on the Pb in fine sediment axis. This high background reflects regional low-grade concentration of Pb in mudstones (Cooper et al., 1985) and secondary enhancement of Pb due to the presence of acid organic-rich soils in an upland area. The greatest concentrations of Pb in fine stream sediment are in areas marginal to the higher ground, where precipitation is favoured by environmentally-controlled sharp changes in pH and Eh. Samples derived, at least in part, from old mining activity show a more uniform enrichment in Pb in both sample types than those containing older contaminants.

Copper

Though chalcopyrite and malachite are the commonest of several Cu-rich minerals found in drainage sediment, a small but significant amount of Cu can also occur as very fine inclusions, typically of chalcopyrite, within pyrite. The detection of Cu in this form can be as important as the location of Cu-rich minerals. Copper contamination originating from general human activity does not seem either to be as widespread or as intense as Pb contamination. Copper wire and brass are the most frequent contaminants observed in concentrates. Because of the wide variety of styles of copper mineralization and the greater mobility of copper in the surface environment compared to that of lead, the relation between source and proportions of copper in different sample types is

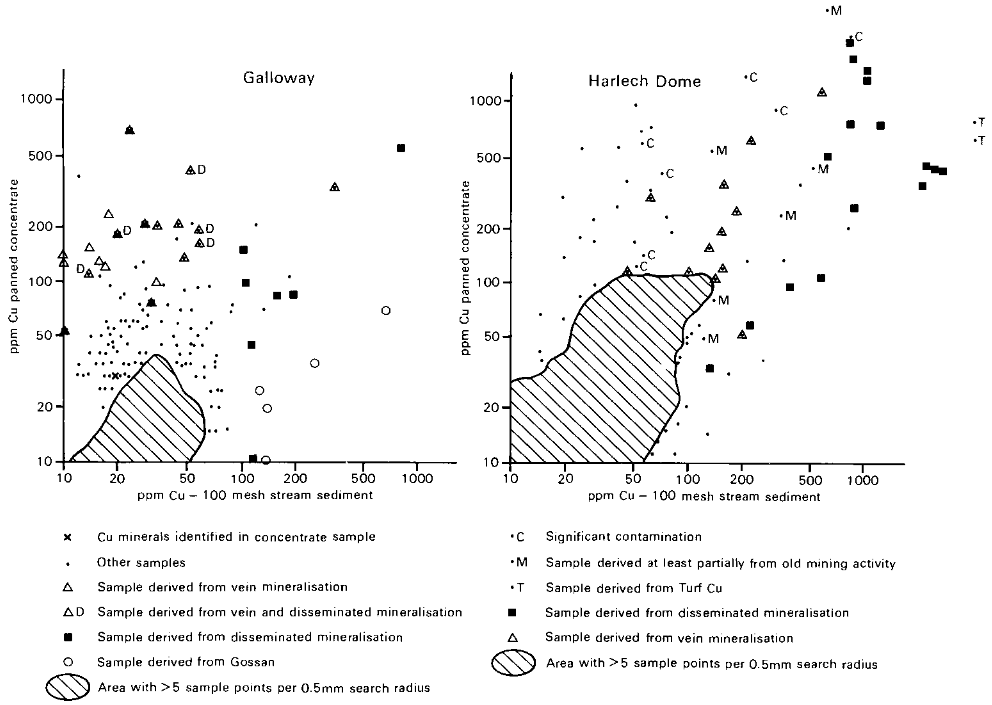

Fig. 16-11. Comparison of Cu concentrations in paired <150 μm fraction and panned concentrate samples from Galloway, Scotland (247 samples), and the Harlech Dome, north Wales (888 samples).

often clearer than for lead. The Cu contents of simultaneously collected <150 μm sieved sediment and <2 mm panned concentrate samples from Galloway and from the Harlech Dome are shown in Fig. 16-11.

The source of many copper anomalies in Galloway has been established by mineralogical examination of the concentrates and by further mineral exploration (Leake et al., 1978a; Leake et al., 1978b; Brown et al., 1979). Fig. 16-11 shows that samples derived from vein mineralization generally have higher proportions of Cu in the concentrate sample than those derived from disseminated mineralization. Grains of chalcopyrite or malachite have been identified in sufficient quantity to suggest that detrital dispersion of relatively coarse-grained material is the dominant dispersion pathway for such mineralization. Samples derived from disseminated pyrite-rich porphyry copper type mineralization, in contrast, show roughly equal levels of Cu in each sample type. Figure 16-11 also shows a group of samples in which Cu is enriched in the fine sediment relative to the concentrate. These samples contain material derived from a structure that has been heavily leached to produce a friable gossan containing a minor amount of visible malachite. The detrital material derived from this structure is readily broken down mechanically and therefore tends to be fine-grained. Furthermore, during periods when the water table is high, hydromorphic dispersion of copper also occurs and mobile Cu is fixed in the fine sediment fraction.

A similar distinction is also apparent between vein and disseminated mineralization in samples from the Harlech Dome. On the other hand, several samples derived from old mines on copper veins are slightly more enriched in Cu in the fine sediment than samples derived from unworked vein mineralization. This could reflect increased hydromorphic dispersion of the Cu through acid groundwater tapped by the workings. There are also differences in the ratio of Cu in the two sample types which reflect different zones within the area of porphyry-style copper mineralization. Copper is relatively enhanced in the fine sediment fraction in samples derived from the Cu-rich central zone and from the area of the Turf copper deposit, an area of organic-rich soil which has become greatly enriched in Cu due to adsorption of metal from acidic groundwaters derived from the deposit (Cooper, 1976). In contrast, a second group of samples derived from disseminated mineralization, showing greater concentrations of Cu in the concentrate samples in Fig. 16-11, largely originate from the peripheral pyrite-rich zone of the mineralization (Cooper et al., 1985). All sites known to be contaminated with material of domestic or other artificial origin show relative Cu enrichment in the concentrate, generally to a greater extent than samples derived from the vein mineralization.

Zinc

Two factors influence the interpretation of drainage data for Zn to a much greater extent than for either Cu or Pb. Firstly, Zn is generally more abundant, and is present as a trace constituent of many common rock-forming minerals. This factor has to be recognised particularly in the interpretation of the concentrate samples. Though sphalerite is the main zinc-bearing mineral likely to derived from mineralization, the presence of small amounts may be difficult to identify in the presence of large amounts of a rock-forming mineral containing significant amounts of Zn. Secondly, Zn is relatively mobile and readily scavenged by hydrous manganese oxide precipitation, a factor of importance in the interpretation of the data for Zn in fine sediment in upland areas in temperate climates. Because of these complexities in controls of Zn dispersion, comparison of the two sample types is particularly useful in the recognition of Zn anomalies derived from mineralization rather than from other sources. Contamination with Zn of artificial origin is less frequent in panned concentrates than either Pb and Cu. Brass and galvanised sheet are the commonest particulate contaminants but there is potential for more contamination of the fine fraction of the sediment from Zn-bearing runoff from slurry of agricultural origin. The Zn contents of sample pairs from Galloway, the Berwyn Dome in mid-Wales, southwest England and the Aberfeldy area of the Scottish Highlands are compared in Fig. 16-12.

Only concentrates from Galloway that have been analyzed mineralogically are compared in Fig. 16-12. Sphalerite has been identified in most concentrates containing >150 ppm Zn, but in three samples Zn is present in a spinel which

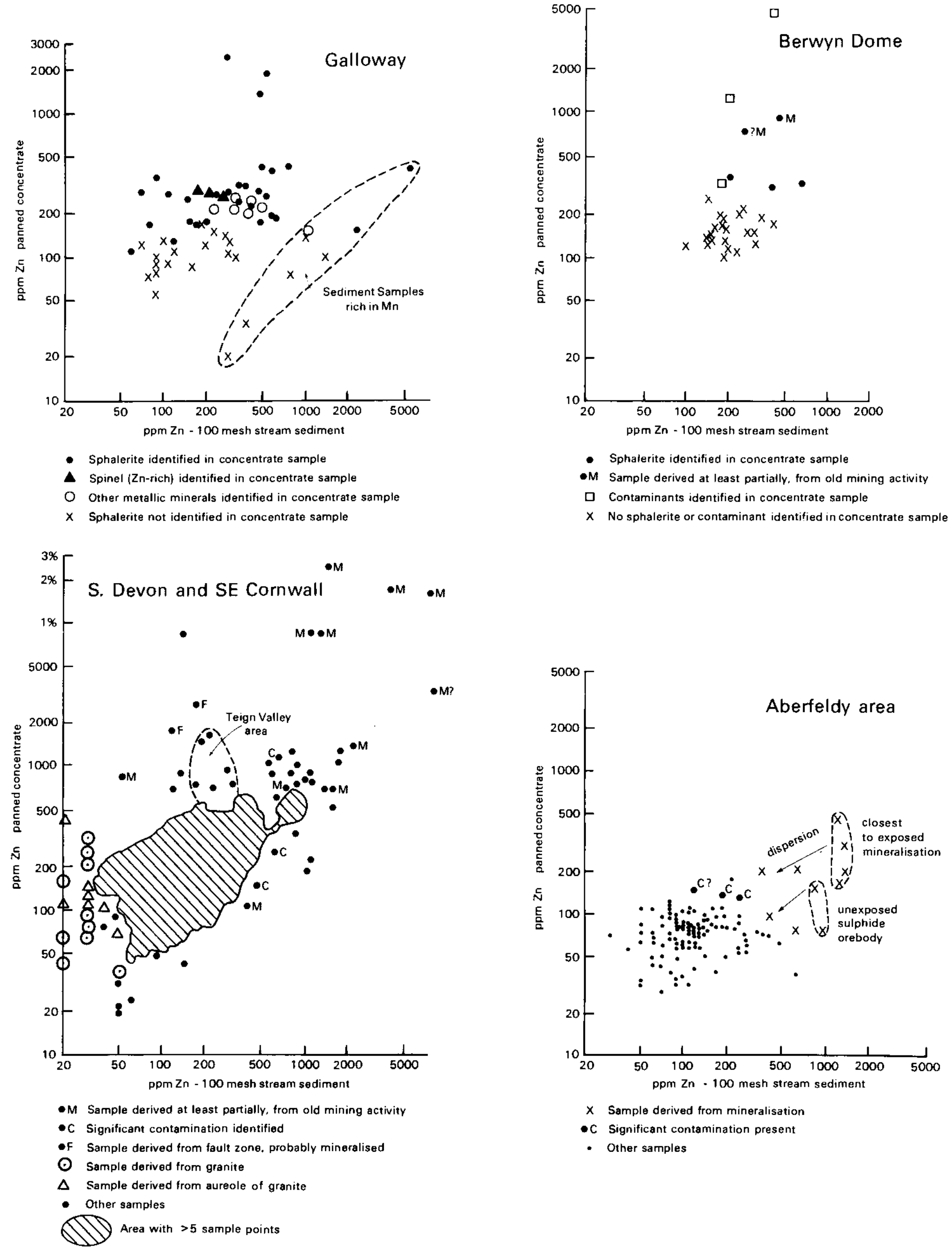

Fig. 16-12. Comparison of Zn concentrations in paired <150 μm fraction and panned concentrate samples from Galloway, Scotland (63 samples), the Berwyn Dome, north Wales (30 samples), south Devon and east Cornwall, southwest England (1547 samples), and the Aberfeldy area of the Scottish Highlands (112 samples).

contains a significant amount of the gahnite endmember ($ZnAl_2O_2$) (Stone et al., 1984). Three samples contain very much higher levels of Zn in the concentrates than the fine sediments and of these, two are known to be derived from old mine workings of relatively coarse-grained vein mineralization. Most of the other samples containing sphalerite are derived from a variety of sources of structurally-controlled disseminated or vein mineralization, probably of minor significance. A distinct group of samples with Zn greatly enriched in the fine sediment relative to the concentrate can also be recognised in Fig. 16-12. All of these samples contain secondary Mn oxide in significant amounts, with Mn concentrations varying from 2.2% to 16%. This fraction of the drainage sediment has the capacity to adsorb Zn from solution producing anomalies that can be unrelated to the Zn content of the catchment bedrock. There is no evidence of a significant positive correlation between Zn and Mn in these samples and there is a considerable range in the Zn-to-Mn ratio. Sphalerite has been identified in the corresponding concentrates of only the two most Zn-rich sediment samples.

There is no obvious enrichment of Zn in Mn-rich stream sediment samples in the Berwyn Dome comparable with that in Galloway, in spite of the upland nature of much of the area and the high concentration of Mn reached (max. 7.3% Mn). Known Zn-bearing mineralization in the area is confined to locally developed quartz–sulphide veins (Cooper et al., 1984). As in Galloway, samples derived partly from old mine dump material are enriched in Zn in the concentrate relative to the fine sediment. In addition, in two samples containing metal-rich contaminants the ratio of Zn in the concentrate to Zn in the sediment is even higher.

Most of the samples from southwest England with the highest levels of Zn in either sample type contain a component derived from the residue of old mining activity. There is some evidence of a relationship between types of Zn-bearing mineralization source and ratio of Zn in the two sample types in that material from a restricted area, e.g., the Teign Valley, plot in a well-marked field in Fig. 16-12. In the Teign Valley, baryte–quartz lodes carry variable amounts of sphalerite (Beer and Ball, 1977) which is possibly coarser in grain size than in some other types of vein. The sphalerite may also be relatively protected from chemical attack within large volumes of baryte which would inhibit hydromorphic dispersion relative to detrital dispersion. Most of the other samples with a component derived from Zn-bearing mineralization but probably uncontaminated by mine dump material, have greater concentrations of Zn in the fine sediment. However, some samples clearly contaminated with mine dump material also plot in a similar field. In Fig. 16-12 there are also two contaminated samples with relatively high Zn in fine sediment compared to the concentrate which contain a component probably derived from farm slurry effluent.

A group of samples containing moderate levels of Zn in concentrates but very low concentrations in the fine sediment, derived from the margins and immediate aureoles of the Dartmoor and Bodmin granites, can be distinguished in Fig. 16-12. Although minor amounts of sphalerite are known to occur in the granites (T.K. Ball, pers. commun., 1977), it is probable that Zn in these concentrates is accommodated mostly in tourmaline, which is common in this geological environment and is both mechanically and chemically stable.

The Aberfeldy area in the Scottish Highlands contains two major baryte and base metal ore deposits, one of which is currently being exploited for baryte. The deposits are poorly exposed and, apart from small trials, were unknown until discovered by follow-up of Zn anomalies in the drainage sediments (Coats et al., 1980). Some high Zn values in the Aberfeldy samples owe their origin to general contamination from human activity, identified as such by microscopic examination and by enhanced contents of Sn, Sb and Pb, and have higher panned concentrate levels of Zn than the normal range of uncontaminated drainage sediments. In the uncontaminated samples, Zn levels in the panned concentrates (Fig. 16-12) are generally lower than in the other three areas, because of rapid breakdown of sphalerite by the acid groundwater derived from the overlying organic-rich soil and oxidising pyrite. Downstream from the better exposed Foss deposit the panned concentrates contain higher Zn levels relative to those downstream of the largely unexposed Ben Eagach orebody. Because of the lack of active erosion of the orebody at Ben Eagach, sphalerite originally in the overburden is more likely to have dissolved and Zn dispersed hydromorphically than at Foss, where mechanical erosion is the more dominant process.

Comparison of downstream dispersion

Detailed study of the Zn dispersion (Fig. 16-13) downstream of the exposed baryte and base metal mineralization at Foss in the Aberfeldy region shows only a slight rise in Zn content of the panned concentrate sample reflecting the addition of detrital sphalerite. The <150 μm stream sediment sample rapidly reaches a maximum 150 m downstream of the source and then declines to background levels after 3 km.

A similar detailed study of Ba and Zn dispersion was carried out at the Loch Lyon baryte and base metal mineralization (Coats et al., 1984a, b). This prospect occurs at the same stratigraphic horizon as in the Aberfeldy region but is interpreted as a distal rather than proximal deposit in a small separate basin. Zinc in the panned concentrate shows a rapid rise immediately the narrow mineralized horizon is cut by the stream and declines steadily downstream (Fig. 16-14). In the <150 μm fine fraction, however, the rise is not immediate but occurs over a broad 500 m interval and begins to decline after 1 km. The fine fraction is clearly better for regional exploration in this upland environment, and may better detect unexposed ore deposits, but the panned concentrate sample provides much more accurate delineation of the very narrow (1–2 m wide) outcropping mineralized horizon.

Barium in the panned concentrates from Loch Lyon shows a similar pattern to Zn, with a dramatic rise from <200 ppm to nearly 1% Ba on crossing the

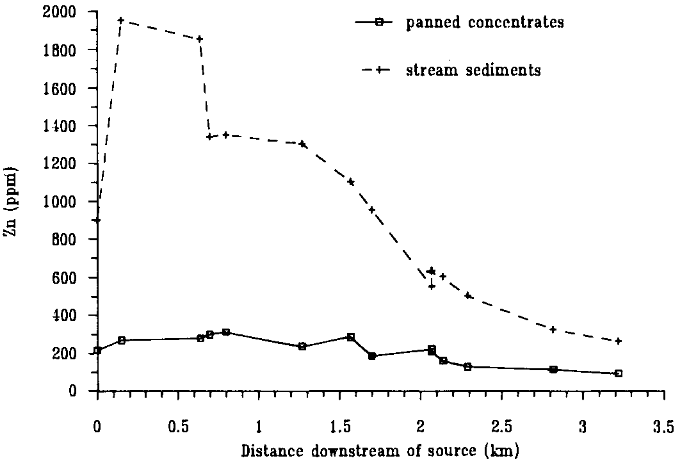

Fig. 16-13. Downstream dispersion of Zn in <150 μm fraction and panned concentrate samples downstream of the Foss baryte deposit, near Aberfeldy in the Scottish Highlands.

mineralized horizon and an exponential fall downstream (Fig. 16-14). The Ba content of the fine fraction of the stream sediment, however, begins to rise slightly before the horizon is reached, and peaks once over the mineralization and again 500 m downstream. The first peak is interpreted as the incorporation of fine baryte from the larger lithogeochemical and/or overburden halo derived from Ba in micas or feldspars. The peak 500 m downstream is probably related to the occurrence of Ba adsorbed on to clays or co-precipitated with Fe and Mn oxides after the final breakdown and dissolution of the finest baryte. Beyond 1 km downstream, the levels of Ba are similar in the stream sediment and panned concentrate, and the two sample media are similarly effective at the reconnaissance stage of exploration. The panned concentrate sample is clearly better at the follow-up stage because it accurately delineates the mineralization and is less influenced by the scavenging effects of Fe and Mn oxides.

Relation between source and drainage response

Some general and empirical conclusions can be drawn about potential sources of anomalies from the comparison of the concentrations of metallic elements in contrasting sample types. These are unlikely to be universal but can be useful in initial interpretation of anomalies. Sites where contamination derived from general human activity is present are likely to contain much more metallic elements in the panned concentrate compared with the corresponding fine fraction sediment. Extremely contaminated sites with some industrial input are often highly anomalous in both sample types but identifiable from the range of elements present. In contrast, contamination of drainage with farm slurry or sewage effluent should result in much greater concentration of the more soluble elements like Zn in the fine sediment compared with the concentrate. Samples

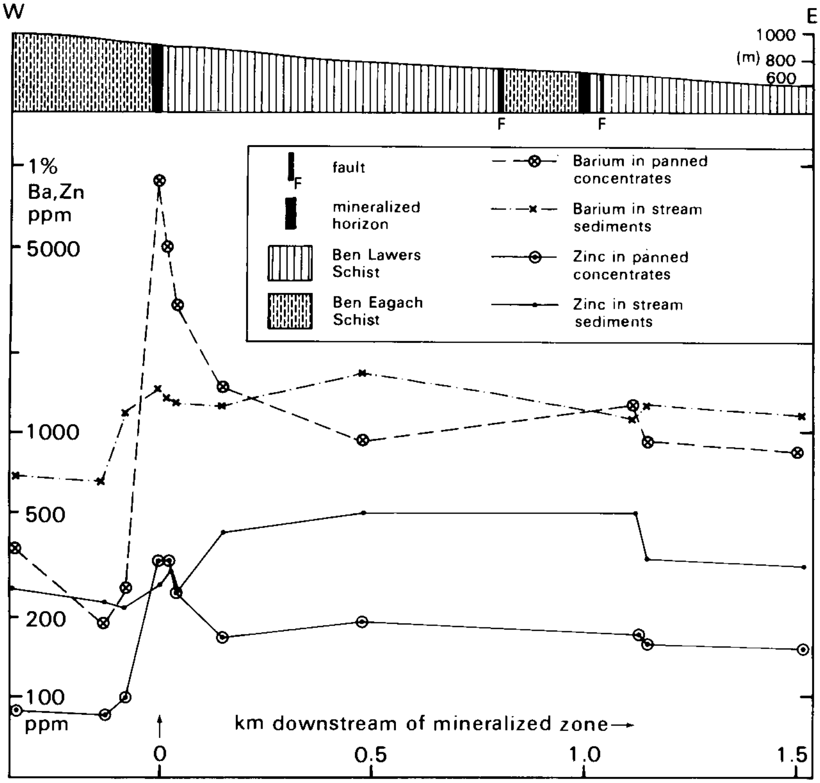

Fig. 16-14. Downstream dispersion of Ba and Zn in <150 μm fraction and panned concentrate samples downstream of stratabound mineralization at Loch Lyon in the Scottish Highlands (modified after Coats et al., 1984b).

derived from old mining activity, overwhelmingly in Britain working vein mineralization, may be expected to have significantly greater concentrations of metals in panned concentrates relative to fine fraction sediment unless mine waters from old workings contaminate the stream. To a lesser extent a similar relation could characterise drainage sediment derived from unworked minor vein mineralization of relatively coarse grain size. Disseminated and stratabound mineralization, especially within a relatively large volume of rock, tend to give more nearly equal amplitude anomalies in each sample type. If the predominant metal in such mineralization is Zn in an area where surficial leaching by acid waters is prevalent, as in peat-covered upland areas of Britain, very little response in the panned concentrate sample may be apparent and such sites may be difficult to distinguish from those where environmental enhancement of metals derived from the weathering of common rocks has occurred in drainage.

DISCUSSION AND CONCLUSIONS

Drainage sediments are a part of the complex geochemical cycle and elevated levels of an element can arise from a variety of causes. Even multivariate statistical analysis of data from a single sample medium may not provide the identification of all factors controlling the chemistry of elements of economic importance. This chapter has attempted to provide examples of selective or multi-sample approaches to the general problem of the recognition of the different dispersion pathways taken by such elements from mineralization sources through drainage.

The use of partial dissolution techniques allows identification of the chemical phases that contain the trace elements of interest. Conclusions can be drawn about the actual sites where the metals are bound and the choice of suitable sample matrices and appropriate extractants can be made to facilitate detection of a particular type of mineralization. For example, it is possible to distinguish between anomalous samples reflecting detrital sulphide dispersion from mineralized locations from those in which trace elements are elevated as the result of adsorption on to secondary oxides (Peachey and Allen, 1977). Some elements are, however, dispersed hydromorphically under temperate conditions and simple detrital sulphide dispersion is very limited in extent. Partial dissolution of the secondary oxides of Fe and Mn precipitated under these conditions can prove a valuable technique in identifying this hydromorphic dispersion and enhancing the geochemical response. For example Martin et al. (1984) found a marked improvement in geochemical response with detection of new anomalies, better detection of mobile elements and an enhancement in geochemical contrast. They found that the physical separation of the paramagnetic phase is more appropriate for clastic dispersion, while the selective chemical extraction more suitable for tracing hydromorphic transport. Similarly, organic phases are often powerful scavengers of metals from solution and the resultant organometallic complexes can be very stable. A possible dispersion pathway is from a sub-outcropping, weathered sulphide body which releases metals to the highly reduced and acid groundwater from which metals are adsorbed and fixed on the organic-rich soil and subsequently eroded into the stream sediment.

Comparisons between two or more partial extractions can yield important information about the most suitable phase to analyse in subsequent large scale surveys. Orientation studies of this kind, particularly downstream of typical deposits, are extremely useful in planning large regional surveys and avoiding following up false anomalies or those resulting from small surface manifestations rather than deeper buried deposits. The differentiation of anomalies into predominantly hydromorphic or detrital assists the exploration geochemical in widening the search for buried or blind ore deposits.

Detailed sequential leaching of anomalous samples can determine the adsorption sites of metals in the fine fraction of stream sediment, which is difficult to study by mineralogical techniques. Interpretation of fine sediment anomaly patterns is often hedged with qualifications because of the lack of knowledge about the actual dispersion pathway and adsorption sites of the metals. In the coarser-grained heavy-mineral concentrate it is comparatively simple to identify the density or magnetic fraction containing the metal of interest and then identify the host mineral.

Comparison of the fine fraction of the drainage sediment and the heavy-mineral concentrate is another method of demonstrating different pathways. The <2 mm heavy-mineral concentrate is dominated by the detrital fraction of the sediment, except for minor secondary oxide coatings on some of the grains, whereas the fine fraction is more important for providing sites for the adsorption of metals from solution on to clays, colloids, organic material or secondary oxides.

Comparison of two sample media using cumulative frequency plots allows general principles of metal dispersion in a given area to be characterised. In detailed studies of small mineralized areas, where the maximum amount of information about the sources of the metals needs to be gained, comparison of metal concentration in both sample types from the same site is extremely useful. Dispersion pathways from mineralization of significance may be more varied than from relatively minor mineralization and recognition of this is important in delineating potentially the more important anomalies at as early stage as possible during exploration. Multi-element analysis of a single sample medium is often not as informative as a similar multivariate study using several elements in contrasting sample types.

As regional geochemical surveys using drainage sediments are completed over increasingly large areas of the globe, there will be an expanding need for more detailed studies within particular metallogenic provinces. These studies might be directed, for example, towards the discovery of buried ore deposits within a previously prospected region where the surface geochemical expression of the orebody may be very small and subtle. The recognition of these anomalies becomes increasingly difficult as their magnitude converges with that of the background geochemical variation. Similarly in old mining areas the distinction between minor contamination resulting from mining activities and small anomalies caused by blind orebodies is important. Geochemical methods will need to become increasingly sophisticated to cope with these and similar problems and this chapter has attempted to offer several different approaches to the problem of sampling drainage sediments. Increasing the selectivity of chemical methods of sample dissolution allows more information to be gained from the different sites in which metals are held and is especially important in hydromorphic dispersion, which may be the only expression of a buried orebody. As one of the major costs in collecting a geochemical sample is getting to the sample site, the collection of one or more further sample types in addition to the conventional fine fraction of the stream sediment does not add proportionately to the cost and increases significantly the effectiveness of the survey.

We therefore envisage an increase in sophistication of geochemical techniques applied to drainage geochemistry away from a simple grab or single fine fraction sample towards a variety of sample media. Waters, colloids, organics, Fe–Mn coatings and heavy-mineral concentrates are seen as becoming more important and they will be analyzed by a variety of selective chemical techniques.

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