NATURAL SCIENCE IN ARCHAEOLOGY

George (Rip) Rapp

Archaeomineralogy

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Archaeomineralogy

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Preface and Reader's Guide

With major limitations, the planned scope of this book is a systematic look at the mineral and rock materials that have been used from prehistoric times through the seventeenth century CE. The author has used the end of the seventeenth century as a stopping point because the expansion of the world economy and scientific knowledge at that time would have led this book to become two volumes. [The notation used for dates throughout is BCE (Before the Common Era), CE (dating to our Common Era) and BP (Before the Present) to avoid any religious connotations.]

"Archaeomineralogy" may seem like a small and arcane niche in the scholarly world. However, it turned out to be very difficult to limit the number of references cited from the large universe of publications. In preparing this volume it became obvious that the number of germane articles and books lies somewhere between 5000 and 10,000. Those publications used and referenced constitute only a small fraction of the literature. Although there are over 800 references, and almost as many additions were consulted but not used, the sheer immensity of the literature precluded comprehensive coverage. Hence, the references in this volume are in no way exhaustive.

Consideration of the use of specific ores grades imperceptibly into production technology and other aspects of archaeometallurgy. Consideration of metal ore and lithic sources leads imperceptibly into provenance studies and consideration of the color of gems can lead directly into gemology. It has been difficult at times to draw the line and stay on course to keep the content of this volume to a manageable size.

The author has taught geoarchaeology approximately a dozen times, spanning nearly 30 years at three universities, so his gathering of material and references dates back this far and even farther. He has made notes on lithologic compositions of artifacts in excavation storehouses, in museum displays, and non-display collections, particularly in Greece, Turkey, Cyprus, Israel, Jordan, Egypt, Tunisia, North America, and China. Many of these found their way into lecture notes and into this book. The reader can assume that when a reference is not given, the items are from the author's 34 years of experience in the field.

The coverage and references are often extensive but never exhaustive. In addition, there are many language and geographic gaps. This is in part because of lack of published research and also because neither the author nor his two research assistants read Far Eastern languages, particularly Chinese and Japanese. However, most relevant publications from India are in English. This book will not usually cover secondary mineral products such as patinas on archaeological artifacts. For patinas, the reader is referred to a series of three annotated bibliographies in Art and Archaeology Technical Abstracts (e.g., Volume 6, #4, 1967; Volume 7, #1, 1968; and Volume 7, #2, 1968). Many rocks and minerals of necessity are discussed under more than one topic heading. Repeating standard information each time would be inefficient. Therefore, readers are directed to the extensive mineral and rock species index to see all references to a specific rock or mineral.

This book is written for a broad group of scholars and students. Foremost would be those archaeologists (practicing and in training) who deal regularly with rock and mineral artifacts. Geoarchaeologists, diverse geoscientists, historians, conservationists, and anthropologists should find this book helpful. The diversity of this group presents a challenge. Many geoarchaeologists have at least the equivalent of a Bachelor of Science in geology. Few historians would have any background in geology. I ask your indulgence if some sections seem "elementary"; others might find these sections critical for their understanding. Behavioral archaeologists sometimes ask why a given group had certain preferences for this or that raw material. Mineral science can address only those materials that could have provided a higher quality product for human use. Many cultural preferences may well be unrelated to anything that can be measured scientifically.

I have had more than 30 years of experience identifying the **lithology** of materials excavated in Greece, Turkey, Cyprus, Israel, Egypt, Tunisia, China, and North America. The word "lithology" appears in boldface type because all the scientific nomenclature in this book that is not in common use or defined in the text appears in boldface when used for the first time and then defined in the Glossary.

The idea for this volume came from the Series Editor, Günther Wagner. In amassing and organizing the data I had the devoted and critical assistance of two of my Ph.D. students, Doris Stoessel and Edith Dunn. Russell Rothe assisted with all of the figures. The photos in this book were taken by Russell Rothe or by the author. Elaine Nissen did the stippled drawings. Nancy Nelson reviewed and improved many chapters. Although portions of this book are based on more than 30 years of the author's direct experience carrying out geoarchaeology, archaeomineralogy, and archaeometallurgy, most of what is presented herein is from the literature. Hence, the often excellent primary work, as well as the many thoughtful summaries by others, must be acknowledged as the essential basis of whatever value resides in this book. The author exercised his, perhaps idiosyncratic, judgment concerning both truth and relevance, and is thus alone responsible for any errors of fact or judgment.

Duluth, Minnesota, *George (Rip) Rapp*
January 2001

Preface to the Second Edition

First, read the Preface and Reader's Guide to the First Edition. That 'guide' is useful for understanding the focus and context of what is covered in this book. Although we can never be sure that a mineral or gem name used by Theophastus, Pliny, Albertus Magnus, and Agricola refer to the same material, this new edition attempts to untangle some of the confusion in the names used in antiquity. This is done where discussing individual minerals, rocks, and gems, not in a separate section. Overall, the reference to consult for mineral names is de Fourestier 'Glossary of Mineral Synonyms' (1999). The modern rules for naming, redefining, renaming, or discrediting a mineral species can be found in Nickel and Grice (1998). This article also has a list of references concerning the nomenclature of mineral species and mineral groups.

The First Edition [2002] focused on regions where I had been engaged in geoarchaeologic and archaeomineralogic research since 1967. This Second Edition expands the geographical coverage, especially to Eastern Europe – for help with this I acknowledge Ruslan Kostov. There is more on China, where I have been working since 1990, and on Western Europe.

Chapter 1 has been expanded to include additional information from ancient and medieval authors and a deeper look at the development of mineralogy and gemmology from earliest times through the heightened interest in rocks, minerals, and fossils in the sixteenth century. For some reason what I wrote on Agricola did not make it into the First Edition. This has been corrected.

Chapter 2 is little changed from the First Edition except for corrections to Table 2.2 and a couple of additions to the text. This chapter includes a theoretical background for mineral properties, especially color, which was fundamental in early classifications. However, many readers may want to skip this material.

Chapter 3 sets out the classification of rocks and their salient properties. There is some overlap in the coverage of rock materials in this chapter with Chap. 6, which covers carved stone, and with Chap. 11, which discusses building and monumental stone structures. There is some degree of arbitrariness concerning in which chapter important uses are noted, e.g., examples of rock sculptures are discussed in both Chaps. 6 and 11.

Chapters 4 through 9 have been expanded to include new earth materials as well as additional information on minerals, rocks, and gems uncovered since the First Edition. Although Chap. 10 is in some ways the place for discussion of materials that do not fit readily elsewhere these materials have played a major role in the lifeways of humans as technological progress has expanded the utilization of natural resources. Finally, in Chap. 11 more information is presented on those earth materials suited for the construction of mega structures.

The References have been expanded to approximately 1000. A new section, entitled Bibliography, supplements References by calling attention to important source materials not referenced in the text.

This Second Edition has been enhanced by five new drawings by Elaine Nissen. Again, carefully editing by Nancy Nelson has improved both the text and the organization of the book. Carol Kubeczko edited the photos that became six new figures. Lucy Wilson provided Fig. 2.1. I owe each of these talented women my gratitude. The Preface to the First Edition should have noted that Doris Stoessel was exceptionally helpful because she read four modern and three or four ancient languages and that Edith Dunn supplied the Arabic. Of course, I alone remain responsible for all errors in fact or judgment.

Tucson, Arizona,
August 2008

George (Rip) Rapp

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Introduction and History

1.1 Prologue

What is archaeomineralogy? The term has been used at least once before (Mitchell 1985), but this volume, now in an updated and expanded Second Edition, is the first modern publication to lay down a scholarly basis and the systematics for this subdiscipline. Students sometimes call an introductory archaeology course “stones and bones”. Archaeomineralogy covers the stones component of this phrase. Of course, archaeology consists of a great deal more than just stones and bones. Contemporary archaeology is based on stratigraphy, geomorphology, chronometry, anthropology, and a host of other disciplines in addition to those devoted to stones and bones (Rapp and Hill 2006).

To hazard a definition: archaeomineralogy is the study of the minerals and rocks used by ancient societies over space and time, as implements, ornaments, building materials, and raw materials for metals, ceramics, and other processed products. Archaeomineralogy also attempts to date, source, or otherwise characterize artifacts made from earth materials. Unlike geoarchaeology, archaeomineralogy is not yet a recognized subdiscipline. Practitioners of archaeomineralogy are mostly either (1) geoarchaeologists who specialize in geology and have a strong background in mineralogy or petrology (the study of the origin of rocks) or (2) historians of science.

In organizing the information in this book there were two competing options: (1) to do it in encyclopedic fashion, listing each mineral and rock type by name, then describing their uses in antiquity, or (2) to organize the content around specific uses of rocks and minerals such as for lithics, ornaments, pigments, or building materials. I chose the latter, both to make it more readable and to lead the reader sideways into related topics. The encyclopedic form has been utilized in the two editions of *Encyclopedia of Minerals* (Roberts et al. 1974, 1990) that I co-authored, but the projected audiences for this current volume – archaeologists, geoscientists, and historians interested in the historical aspects of rock and mineral use – would be predominantly topic rather than species-name oriented.

Many systematic mineralogy books can be consulted for information on minerals. Roberts et al. (1990) includes all mineral species identified up to the time of publication. There are many books containing systematic descriptions of rocks that

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would aid those interested in archaeomineralogy. Recent examples would be Blatt et al. 2006 or Raymond 2002. In his excellent and wide-ranging book on the birth and development of the geologic sciences, F. Adams (1938) weaves the evolution of ideas on mineral and rock classifications into the broader human view of the nature of the earth and of earth materials. By the sixteenth century the interest of practical men in the role of "fossilia" [fossils, minerals, and rocks] in pharmacy and in mining, accompanied by the long and slow shift from a dependency on classical authorities to one based on observation and experimentation, led to the accumulation of new knowledge concerning the nature of minerals and metals. Conrad Gesner (1516–1565) constructed a mineral classification based on the complexity of the crystal forms of minerals. When this new knowledge was expanded by the introduction of chemical analysis we had the basis for modern mineralogy.

1.2 Organization of the Book

First, readers are advised to go back and read the Preface and Reader's Guide, which offers valuable background information. This volume is organized more or less by the function that the mineral or rock material played in the various ancient contexts. One downside to this approach is that some minerals and rocks are covered in more than one chapter. Within limits, the same information on properties is not repeated, and the index lists all pages where a mineral or rock is discussed.

The literature of archaeomineralogy is huge, especially if one considers the abundant descriptions of mineral and rock artifacts found in many thousands of excavation reports. This volume has hundreds of references to the easily-obtained literature from more than a dozen countries but is not comprehensive in the sense that Lucas (1989) was comprehensive in his review of the mineral and rock materials utilized by the ancient Egyptians or Morey (1983) was in his exposition of the materials used in ancient Mesopotamia. Readers outside North America might not be familiar with the names, chronologies, and geographies of North American prehistoric cultures. As a reference for these items, the author would suggest *Archaeology of Prehistoric North America: an Encyclopedia* (Gibbon 1998).

As far as possible, examples are provided for the most significant ancient uses of rocks and minerals for the various purposes covered in this volume. These examples are somewhat skewed toward those geographic areas where the author has carried out research (Greece, Turkey, Cyprus, Israel, Egypt, Tunisia, and China, as well as North America) but this Second Edition has extended the coverage. Citing the hundreds or even thousands of archaeological references worldwide to the use of chert for lithics or marble for monuments would be impractical, so the examples needed to be selective.

Readers interested primarily in individual minerals, rocks, or related compounds should begin with the index of rock and mineral names. The diversity of uses of many rocks and minerals required that many materials be considered in more than one of the topical chapters. When a mineral or rock is discussed in more than one chapter, the index lists all mentions of a rock or mineral species.

Sources of rock and mineral raw materials are a vital aspect of their utilization and their archaeological context. However, the rapidly expanding field of **provenance** studies precludes this aspect from being a major component of this book. Obsidian sourcing alone is more than a "book length" subject. Specific sources are given when appropriate; for example the Afghan source of lapis lazuli. Most rock and mineral sources in ancient times were local or regional. Another ancillary area is ancient mining. There is a brief section in Chap. 3, but for coverage of this field see Shepherd (1993).

Readers should be aware of three significant aspects of mineral names. First, in ancient times mineral identification was frequently haphazard, often relying on color alone. Second, the name given to many mineral species has changed over time. Third, even today, the same mineral may have a variety of names and synonyms. The spellings used in this volume are English, although occasionally the German spelling is used if more appropriate. This volume uses American spellings rather than British, for example, sulfur rather than sulphur.

One example of the problem with names is the various forms of hyacinth (hyacinte, hyacithe, hyacinthine, hyazinthos, hyacynthus, and similar variations). These names have been applied to zircon, spinel, vesuvianite, corundum, quartz, beryl, and garnet (de Fourestier 1999). Another example concerns the large number of names and hyphenated names based on the name opal. There are 40 listed in de Fourestier (1999). One value of the de Fourestier volume is that it gives synonyms and spellings in a number of western languages. Four volumes can aid in working through these problems with names: (1) the *Glossary of Mineral Synonyms* (de Fourestier 1999), (2) *Encyclopedia of Mineral Names* (Blackburn and Dennen 1997), (3) *Glossary of Obsolete Mineral Names* (Bayliss 2000), and (4) *Encyclopedia of Minerals* (Roberts et al. 1990). The volume by Roberts et al. presents data on mode of formation and major localities as well as the basic physical and chemical properties of all minerals.

It has been my experience that, although there are more than a thousand names given to various rock types, sorting out what rocks were exploited in antiquity is somewhat easier than for minerals. Perhaps the best guide to rock names is the *Glossary of Geology* (Neuendorf et al. 2005). That volume presents historical definitions and obsolete variations in names and meanings.

Because of the nature of the material, each chapter is structured somewhat differently. In some chapters, an Introduction incorporates a short guide to general bibliographic items that present extensive reviews of specific materials, geographic regions, or chronological periods. Many rocks and minerals were exploited for multiple purposes or products. Therefore, these appear under each of the product topics. To review everything on a given rock or mineral, please refer to the extensive index. The topics covered in most chapters are organized along obvious lines with a few rock and mineral resources or their products falling into miscellaneous categories.

We begin with an overview of the information found in the most relevant works of ancient writers in various parts of the world. For readers with a significant interest in the historical development of archaeomineralogy I strongly recommend spending considerable time with the three books that were paradigm changing:

Theophrastus's *On Stones,* Pliny's *Natural History,* and Agricola's *De Natura Fossilium* (sometimes referred to as *Textbook of Mineralogy*). Theophrastus was the first significant figure in archaeomineralogy. I have a copy of the only modern translation [in English] of *On Stones,* that of Caley and Richards (1956), which also includes the Greek text, an introduction, and a commentary. Pliny's *Natural History* was written as 37 "books". Minerals and gemstones are treated in books 33–37. I have the Loeb Classical Library edition in 10 volumes, edited by Goold (1938 and reprinted numerous times). Agricola's *De Natura Fossilium*, translated by Bandy and Bandy from the first Latin edition (1546) was published in 1955 as Special Paper 63 by The Geological Society of America. I have the Dover reprint published in 1964. In this chapter I have introduced each of these authors but most of the references to their ideas and works concerning minerals, gems, and rocks are distributed throughout this book where appropriate rather than with this introductory material.

All the scientific nomenclature in this book that is not in common use or defined in the text appears in boldface when used for the first time and are defined in the Glossary.

1.3 The Ancient Authors

Evidence for ancient utilization of minerals and rocks is available in several contexts. Cuneiform texts from Mesopotamia and Assyria and papyri from Egypt cite the use of minerals as medical treatment or drugs, building materials and embellishments on buildings, and as artifacts. In some cases topographic information is given, particularly when a mineral or a rock is a trade item. Pictorial representations also suggest how minerals and rocks were utilized or manufactured. Other information is gleaned from examination of an artifact itself. Increasing attention to archaeomineralogic research will rapidly expand our knowledge in this twenty-first century CE.

In ancient Assyria, the following minerals and metals were prescribed as drugs: white and black sulfur, iron sulfate, arsenic, yellow realgar (probably orpiment), black saltpeter, antimony, iron oxide, iron sulfide, magnetite, mercury, alum, bitumen, naphtha, and lime (Marks and Beatty 1975). In ancient Egypt doctors knew of the antacid properties of limestone (which is still in use today). To absorb water or toxins from the stomach they used kaolin, also still in use today. They also knew that antimony was effective against flukes. Precious and semiprecious stones also were used in medicinal preparations. These were diamond, ruby, sapphire, emerald, jade, jadeite, peridot, lizardite, topaz, garnet, rock-crystal, aquamarine, lapis lazuli, tourmaline, moonstone, and chrysoberyl. Pearl, coral, and shell also were similarly employed.

In the Western world we have rooted much of our scientific nomenclature in Greek and Latin (and sometimes Arabic). Chinese science developed independently, and they acquired their stock of scientific words early. We know the earliest forms of Chinese characters from the oracle bones of Anyang (Late Shang – circa 1100 BCE) [where I have worked since 1997] and from the Shang and Zhou (1100 to 256

BCE) inscriptions on bronze vessels. Needham (1956, pp. 220–230) presents an extensive table of the ideographic etymologies of important works in early Chinese scientific thinking.

Both the Greeks and Romans used mineral drugs extensively, as is attested by the numerous citations in the works of classical authors. Pliny's *Natural History* and Dioscorides's *De Materia Medica* are the foremost sources for mineral remedies in the ancient world. The latter source presents the first description of the extraction of mercury. The Arabic writers who translated the Greek and Latin sources carried on this tradition, adding their own observations and commentaries. In turn, the Arabic sources and the earlier classical writers were utilized through the Middle Ages for pharmacopoeia.

In addition to the magical and amuletic qualities of many minerals and gemstones, Pliny's list of minerals used as drugs is extensive. Eye diseases were thought to be cured by stibnite, lodestone, powdered marble, scale of iron, sulfur, marcasite, pumice, copper byproducts, and red ochre. The latter was also employed for dysentery and vomiting. Ash of biotite mica was used as a remedy for leprosy, bronchitis, and tuberculosis. Bismuth, calamine, and sulfur were used to cure the latter disease as well as skin diseases and typhoid. Orpiment was prescribed for bronchitis. Realgar when mixed with turpentine was considered a cure for asthma. Alum was prescribed as an antiperspirant, to alleviate mouth ulcers, and as a remedy for scabies. Caustic soda was used in liniments. Lead and its byproducts were used in various medical prescriptions to remove scars, as an emollient plaster, for dysentery or constipation, and were added to other mineral compounds. Powdered marble and pumice were used as tooth powders. Decomposing marcasite was used to cure toothaches and to fill cavities.

Medieval mineralogy was little advanced from Pliny. Rocks, minerals, and gems were considered valuable because of reputed medicinal and magical properties. For essentially all ancient writers, the most important property was color. However, color is of no great value in mineral classification, because many species occur in a variety of colors. Ancient writers commonly believed that different colored varieties of the same mineral were different species and, conversely, classed several different minerals into one species based on color. Until the fifteenth century CE, minerals were always listed alphabetically as the only organizing characteristic. In 1546, Agricola published his *De Natura Fossilium*, which had the first classification of minerals based on physical properties: color, weight, transparency, luster, taste, odor, shape, and texture. However, he made no distinction between individual mineral species and some rocks with more than one mineral present. It is interesting to note that Medieval scholars, believing that the essence of a substance was in its name, developed from this the discipline of etymology.

The alchemists discovered the oxides of numerous metals, and physicians adopted some of these in their practice of medicine. Arsenic was introduced in this manner, and both phosphorus and lead were used as poisons. Mercury was employed to treat syphilis. Sulfur was widely used internally as an agent for purification and externally for dressing wounds. The discovery of sulfuric acid is credited to the eighth century Arabian alchemist Jabir ibn Hayyan. Sulfuric acid was known to Medieval European alchemists as vitriol. It was an important alchemical substance, used as a philosopher's stone. Vitriol also is the old term for the sulfate minerals of the divalent metals zinc, iron, and copper. Pliny called these minerals *vitrium* (glass) because green iron sulfate looked very much like green glass. These sulfate minerals were used by European and Arab alchemists, hence the name could stem from the initial letters of a well-known alchemical theory: Visita Interiora Terrae Rectificando Invennies Occultum Laidem. The Arabs also introduced copper sulfate (the mineral chalcanthite) as a caustic and emetic.

The word alchemy came down to us through the Arabs who were the guardians of ancient Greek and Roman knowledge during the Dark Ages. The Arabs supplied the prefix 'al' (meaning *the*) to chemia [or chymia] from the Greek for *to smelt* and *to flow.* The related word chyma meant ingot. So alchemy likely owes its origin in part to metals processing and owes its zenith to attempts to transmute base metals into gold. The so-called seven metals of alchemy were gold, silver, copper, lead, iron, mercury [quicksilver], and tin. Alchemists also experimented with the minerals saltpeter, cinnabar, pyrite, orpiment, and galena and the chemical elements sulfur, arsenic, bismuth, zinc, antimony, and phosphorus.

1.3.1 Classical Authors

During the Classical Period of Greece, no specific mineralogical treatises were written. Instead, minerals and their uses are mentioned within works of encyclopedic scope that refer to broader topics such as cosmography, maps, architecture, and natural history. Although allusions to minerals, their occurrences, or their use can be found scattered throughout many well-known Classical sources such as Herodotus and Pausanias, the most comprehensive treatment of minerals can be found in the sources discussed below. A good treatment of ancient authors' writing on mineralogy is given by Moore (1978). An overview of mineral classification from antiquity through the Renaissance is given by Accordi and Tagliaferro (1981). It should be noted that prior to 1800 less than 100 *valid* mineral species had been named (Mandarino 1977).

1.3.1.1 Theophrastus (ca. 372–287 BCE)

Theophrastus was a Hellenistic Greek philosopher who was born on the island of Lesbos. He studied in Athens with Aristotle and became his devoted pupil. When Aristotle retired in 323 BCE, Theophrastus succeeded him as head of the Peripatetic School in the Lyceum, where he taught for 25 years. A prolific writer, Theophrastus composed treatises on many subjects. His treatise *On Stones*, variously known as *Peri Lithon* or *De Lapidibus*, remained a definitive reference on the subject through the Middle Ages. In this sense, although Theophrastus described only 16 minerals, he laid the foundation for the science of mineralogy, and the minerals he described led to the discovery of many of the chemical elements. Modern scholars theorize that the work in its present form is a compilation of notes, possibly those of a student, and not the complete discourse. The absence of any discussion of metals leads historians to believe that a complementary treatise on this subject was composed and is now lost. Metals are only mentioned incidentally in the section on the touchstone that references the ability of a given metal to leave a streak.

On Stones is composed of several sections that primarily discuss precious and semiprecious minerals. It is a systematic discussion of stones (Sects. 37–47) and mineral earths (Sects. 48–69) found in the Mediterranean region and the Near East. His interest is focused on the properties of stones, such as their size, color, hardness, smoothness, reaction to fire, their occurrences in nature, and their ability to attract magnetically (e.g., lodestone, meteorite, and amber). Included is the first mention of mineral fuel. He rarely mentions the magical properties with which the ancients believed stones were endowed. A case that proves an exception to this rule is his discussion of the so-called "eagle stone" in which he expresses his skepticism about its magical qualities. Additionally, he devotes sections to nonminerals such as amber, coral, pearl, and ivory that were classified by the ancients in the same category as true minerals. Although he discusses the properties of "earths", such as their colors, the method of extraction of some, their ability to harden to the consistency of stone, their association with metals, and their use as pigments, including artificial pigments, earths are not the major focus of his treatise. Apparently an avid collector, Theophrastus stressed the importance of observation and obtaining samples. Compared to Aristotle, he was much more a scientist in the modern sense. He made observations and dealt with facts rather than philosophical positions.

The new territories opened by Alexander's campaigns furthered the investigations of Theophrastus, and he acquired information on the minerals of many regions of Asia Minor, Egypt, Nubia, and the Persian Gulf. Theophrastus was the first to describe asbestos, which he said resembled rotten wood and when doused with oil would burn without being harmed. He also was the first to describe the pyroelectric effect as exhibited by a mineral which he called lyngourion. He noted its property of attracting straw and bits of wood, due to pyroelectric temperature changes. Three hundred years later Pliny gave this stone the Latin name lyncurium. Pliny kept the name of Theophrastus alive in books 36 and 37 of his *Natural History* but *On Stones* was "lost" to western scholarship for most of the Middle Ages. One Arab encyclopedist mentions *De Lapidus* [the Latin form of *On Stones*] but there is no evidence it was translated into Arabic. There are no known translations until the late fifteenth century.

1.3.1.2 Dioscorides (ca. 40–90 CE)

Pedianus Dioscorides was a Greek physician born in Cilicia (now part of modern Turkey). He was a contemporary of Pliny although there is no evidence that they met or that Pliny had read Dioscorides' works. He traveled widely in the Roman Empire including Greece, Crete, Egypt, and Petra in Jordan. In his travels he had access to the great library at Alexandria. Although some of his information was second hand he strongly supported the idea that investigation and experimentation were crucial to pharmacology. His interest in pharmacopoeia resulted in *De Materia Medica*, a five-volume work describing more than 1000 medications and treatments Dioscorides (1933). Although primarily concerned with plants and their uses, the final volume of his study describes mineral substances used in medicine. The Arabs used his treatise, and it was translated back into Latin in the tenth century and used throughout the Middle Ages. It was the central treatise on pharmacology in Europe and the Near East for fifteen centuries.

Book 5 is titled "Vines, Wines, and Metallic Stones" wherein he describes the mining, purification, and "effects" of a variety of metals and their compounds, including mercury, arsenic, copper oxide, and lead acetate. Some of the substances he mentions cannot be identified, for example "thrakias lithos". Powdered malachite was recommended as a mild abrasive for wearing off scars; arsenikon [orpiment] also was recommended as a body abrasive [but the arsenic made the hair fall out]; pumice was used as a dentifrice; gypsum aided blood clotting when applied to a wound; and magnetite drew out "gros humors" (Duffin 2005). The book ends with the health effects of sponges, coral, asbestos, emery, bitumen, and precious stones.

1.3.1.3 Pliny the Elder (ca. 23–79 CE)[*]

Gaius Plinius Secundus was born at Novum Comum (Como, Italy). He was primarily a public servant, serving under the emperors Nero and Vespasian. He was Procurator of Spain under Nero. He had a keen interest in natural phenomena and completed his encyclopedic work, the *Natural History* (*Naturalis Historia)*, in 77 CE and dedicated it to Titus, the son of Vespasian. *Natural History* is divided into 37 books. From a mineralogical standpoint the most important section of this work is Books 33 through 37, which contain Pliny's information on metals and minerals. In many cases he used secondary information from other authors, principally *De Lapidibus* of Theophrastus. However, he mentions minerals unknown to Theophrastus such as fluorspar [fluorite], tourmaline, and rhombic sulfur. He was the first to describe sulfur in detail. He frequently cites Theophrastus with some skepticism. Unlike his contemporaries, Pliny took care to name his sources, including now lost Greek texts. Pliny mentions a stone he calls "Thracian stone". It appears to be the same material that Theophrastus called "spinos" (Kostov 2007).

The "mineral" portion of *Natural History* begins with the precious metals, their alloys and compounds. This is followed by a discussion of clays and earths. The foregoing section is subdivided into paragraphs on the ceramic uses of earth, sulfur, bitumen, alum, kaolin, and chalk. Stones, minerals, and monuments are next. The work concludes with a discussion of gemstones. Interpolated within this geologic framework are two digressions: one on painters and painting, and a second on sculptors and sculpture, giving a brief history of each. A final subject addressed in the mineralogical sections is a copious amount of information on mining and the

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[*] In this book he is referred to simply as Pliny

process of **smelting**. He discusses the various techniques for discovering metals, from searching on the surface for indications of minerals to various methods of discovering underground sources.

Pliny discusses no less than 77 minerals used in medicine. Overall he gives the Latin name of more than 350 minerals. This list includes some rocks as well as natural products like petroleum. The more than 350 Latin names do not translate into that number of species in English. For example, there are 10 agates, 6 amethysts, 15 coppers [including bronze], at least 20 different marbles, and so forth.

Pliny attempted to apply scientific observations to his geologic studies. He interjected his own observations into his research and adopted a method of classifying gemstones that named them from parts of the body (*N.H.* 37.186), after animals (*N.H.* 37.187), and after a resemblance to inanimate objects (*N.H.* 37.188). He also notes that there are several tests to determine whether a gemstone is genuine: by weight (i.e., density), coldness, or by physical characteristics such as color. Pliny was, however, inconsistent or confused in the naming of some minerals. His "sapphirus" is not sapphire. He accepted that rock crystal was a hard form of water. Another interesting belief of his was that marble regenerated itself in certain quarries. Nevertheless he was suspicious of claims that certain minerals had magical properties.

Pliny used several tests to identify minerals. Among these are the use of luster (pearly, dull, metallic, greasy), transparency, hardness, streak, crystalline form, form (granularity, flake, powder), cleavage or fracture, and friability. If the mineral had special characteristics such as magnetic attraction, these are also noted. He made a major advance in describing the nature and form of crystals and was puzzled by the lack of symmetry in the terminations of quartz crystals.

Unfortunately, supposition and fiction are intermingled in his scientific observations. In general, each mineral name is given, sometimes with its derivation or foreign appellation, its geologic and geographic sources, properties, medical use (if any), uses other than medical, and its folklore or alleged magical properties. In some cases Pliny provided the formula for the preparation of a synthetic pigment. An example is the formulation of verdigris by exposing copper to an acetic solution [probably vinegar]. In addition to supposition and fiction mingled with facts and scientific observations, his mineralogic concepts are sometimes flawed, such as in instances when he classifies several minerals under one heading (e.g., *adamas*, *smaragdus*). However, some of the physical properties he noted and tests he performed are still utilized today.

He discusses many rocks in *Natural History*; not all of his conclusions have stood the test of time – he considered basalt to be a "black marble". Pliny died in the 79 CE eruption of Mount Vesuvius. The term "Plinian Eruption" used to describe violent eruptions is named after him and/or Pliny the Younger.

1.3.1.4 Vitruvius (ca. 70–25 BCE)

Marcus Vitruvius Pollio served as an artillery engineer under Augustus. His *De Architectura Libris Dicem* (*Ten Books on Architecture*) meticulously describes existing practices, not only in the design and construction of buildings, but also in what is thought of today as engineering disciplines. His books include such varied topics as the manufacture of building materials, pozzolanic cement, and dyes (material science); machines for heating water for public baths (chemical engineering); amplification in amphitheaters (acoustics); and the design of roads, bridges, and harbors (civil engineering). His mineralogical research is interspersed throughout his works. For example, the main part of Book 2 concerns mineral materials used in architecture such as bricks, sand, lime, pozzolanic cement, kinds of stone, and varieties of stone masonry, while Book 7 contains a discussion on the preparation of walls and the execution of wall paintings and frescoes, the use of lime, stucco, and the preparation of plaster, the use of quicksilver in gilding, and the source and color of natural and artificial pigments. His writing is prescriptive and gives direct advice: "I have drawn up definite rules to enable you, by observing them, to have personal knowledge of the quality both of existing buildings and of those which are yet to be constructed." As a handbook, *De Architectura* was widely read, and Vitruvius's advice was followed for centuries (see Morgan 1960).

1.3.1.5 Diodorus of Sicily (fl. ca. 58–30 BCE)

Diodorus was born in Agyrium in Sicily, hence the appellation Diodorus Siculus (Diodorus of Sicily). He was the author of the *Bibliotheke*, a 40-book history of the known world Diodorus (1950). Of these, only Books 1 through 5 and 11 through 20 are complete; the others are fragmentary. While Diodorus was primarily an historian, he mentions engineering feats in passing, and is the source for the description of gold mining techniques used in Egypt during the Hellenistic Period (first century BCE). In Book 3.12 he cites four principal steps in gold production. Fires were first set to shatter the rock, following this stone was quarried, the ore was worked, and finally the gold was washed and refined.

1.3.2 Medieval Authors

1.3.2.1 Isidore of Seville (ca. 560–636)

A prolific writer who lived in Visigothic Spain, Isidore of Seville was long associated with the schools of modern-day Seville. He continually tried to bring them up to the standard of earlier Roman schools, and for this purpose he gathered the fragments of late Roman education so that they could be the basis of his educational program. Published in a work called the *Etymologies* (*Etymologiarum Sive Originum Libri XX*) – a kind of "Encyclopedia Britannica" for the early Medieval Period – it presented a universal history of all known learning from classical sources through the ecclesiastical writers and commentators.

In this work he discusses the derivation of mineral names. A section of Book 16 discusses stones and metals with descriptions frequently copied verbatim from classical sources. It covers common and less common stones, marbles, gems, glass, and metals. Amber is included under metals. Stones were generally classified by color.

Isidore echoes Pliny's skepticism about "magical" properties of stones and adds the "current" Christian position that reflected an uneasiness about transmitting what they believed were pagan superstitions. He contributed nothing about earth materials not already given by Pliny, six centuries earlier. However, scientific understanding had been in decline the whole time between Pliny and Isidore, so he can be credited with restoring some of the "lost" knowledge.

1.3.2.2 Albertus Magnus (ca. 1206–1280)

Known as Albert the Great, this scientist, philosopher, and theologian studied at Padua and later taught there and at Bologna and Cologne. After joining the Dominican Order he was sent to the University of Paris where he read the translations of the Arabic and Greek texts of Aristotle. While in Paris he began a compilation of the entire body of information then known about natural science, logic, rhetoric, mathematics, astronomy, ethics, economics, politics, and metaphysics. He wrote commentaries on all of Aristotle's known works, supplementing them with personal observations and experiments. Among his scientific works is the *Mineralium* (or *Book of Minerals*), modeled on Aristotle, which was the most influential book on minerals until their systematic study by Agricola. This work is divided into five books, some of which are subdivided into tractates, and single tractates are subdivided into chapters.

Tractate 1 of Book 1 considers stones in general and presents the characteristics of minerals that were considered *essential*, i.e., inherent in their nature, such as their composition, greater or lesser transparency, substance, and occurrences. The second tractate considers their accidental properties, among which are: cause of color, **fissility** versus nonfissility, porosity or compactness.

Book 2 is devoted to precious stones. The first tractate examines the cause of the powers in stones. "The compilers of popular lapidaries transmitted some factual information; but their chief interest was the curative or magical powers of stones" (Wyckoff 1967:xxxiv). Albertus was therefore concerned with accounting for these so-called powers. His primary argument is a denial that these stones had an inherent soul (anima), but that its form caused each stone to be unique. "In this sense, then, the forms of stones account for whatever effects they produce. An excellent example is the "power" of magnetism, essential to an identification or definition of the mineral magnetite" (Wyckoff 1967, p. xxxiv). The second tractate is an alphabetical lapidary of precious stones that gives all the information on each gem gleaned from classical literature and previous Medieval lapidaries to which he added his own observations. The final tractate of this book treats the images or "signs" in stones, stone carving, and the meaning of these images.

Book 3 is devoted to metals in general, with the first tractate paralleling Tractate 1 of his book on stones, giving the plan of the book, its essential characteristics, the classical opinions about the composition of the metal, and the places where metals are produced. The second tractate discusses solidification and liquefaction of metals, their color, malleability, taste, odor, combustibility/noncombustiblilty, and whether there is a cyclical production of metals from each other. The book also discusses the nature, properties, and kinds of salts. These were: alum, *atrametum* (which included hydrous sulfates of copper and iron), arsenic sulfides, *marchasitum* (a group of minerals including, but not limited to, pyrite, marcasite, arsenopyrite, arsenic, bismuth antimony, and stibnite), *nitrum* (principally natron, but also included saltpeter and borax), tutty (zinc oxide [*tuchia*]), and electrum. In all he describes 96 stones.

Although much later authors wrote of his work as an alchemist there is no evidence for this. He did believe that some stones had occult properties. He was an experimenter and is credited with being the first to isolate arsenic about 1250. Like his contemporary, Roger Bacon (1214–1294), Albert was an indefatigable student of nature and applied himself energetically to the experimental sciences with such remarkable success that he was long considered the leading authority on mineralogy.

1.3.2.3 Georgius Agricola (1494–1555)

Agricola was a German, born in Saxony, with the given name of George Bauer. He was one of the great figures of the Renaissance. He lived and worked most of his life in mining communities. Agricola has been called the "father of mineralogy" for his publication *De Natura Fossilium* [now often referred to as *Textbook of Mineralogy*]. During Agricola's time *fossilia* included minerals and rocks, anything dug out of the ground. Prior to Agricola few writers attempted to classify minerals, usually just listing them alphabetically. Little was known at that time about chemical composition, so his classification of minerals was based on crystallography and physical properties [color, size, odor, strength] with chemical data where known. The book includes an extensive review of the ancient literature, and he sorted out some of the obvious misconceptions. Agricola rejected all supposition about minerals – crediting only measurements and observations. He standardized the names of minerals and described where they could be found. *De Natura Fossilium* uses 573 Latin names for minerals and 115 Greek names (Fig. 1.1).

De Natura Fossilium was published in 1546 and translated into Italian in 1612 and into German in 1809–10. Using the first Latin edition of 1546, it was translated into English by M. and J. Brady in 1955 and published as Geological Society of America Special Paper 63. I have the Dover reprint of 2004. It is divided into 10 books [chapters]: Book I treats the properties of minerals in great detail, giving many examples; Book II covers the uses of "earths", including agricultural uses. Book III describes four classes of minerals: (1) salts (halite and "nitrium"), (2) alum and related minerals, (3) sulfur minerals and bitumen, and (4) "vein ores" including chrysocolla and other copper minerals; Book IV takes up jet, "natural carbons", "thracian stone", amber, some gems, and mentions localities where these minerals are found; Book V treats more materials in detail including lodestone, marble, diamond, hematite, gypsum, asbestos, mica, and quartzite; Book VI discusses what it takes to be considered a gemstone, where gems may be found, and offers extensive

Fig. 1.1 Georgius Agricola, author of *De Natura Fossilium*, the leading book on mineralogy at the end of the Middle Ages

details concerning many precious and semi-precious stones including quartz crystal, beryl, prase, topaz, lapis-lazuli, amethyst, sard, jasper, agate, and pearl; Book VII treats marble in great detail, sand, bricks, and petrified wood; Book VIII is devoted to metals: gold, silver, mercury, copper, lead, bismuth, tin, and iron, and then covers alloys; Book IX discusses natural and artificial color in metals, luster, smelter products, and verdigris; Book X treats mixtures and combinations of earth materials and their uses, Most of these are based on metallic elements. The book ends with a long list of writers whose works were consulted.

Probably Agricola's most famous book is *De Re Metallica*, which covers the development of mining methods, metallurgical processes, geology, mineralogy, and mining law. It went through 10 editions in three languages and was for over 180 years the textbook for mining. *De Re Metallica* was translated by Herbert and Lou Henry Hoover from the first Latin edition of 1556. This volume has 638 pages in the 1950 edition that I have. This first edition of 1556 was published a year after Agricola's death. In it he rejected the Biblical, alchemical, and astrological views of his day. It drew the attention of Ming Dynasty officials who ordered a Chinese version (Needham 1999:39–40). Agricola decided that the black rock of his region was the same as Pliny's basalt, so he introduced this name into petrology. He did have a few mistaken ideas. He thought that arsenic was a lead-tin alloy and that zinc was a lead-silver alloy.

1.3.3 Arab Authors

In the Postclassical Period, the Arabs not only preserved Greek sources but also wrote new treatises on mineralogy. The Yemenie geographer Al-Hamdânî wrote a treatise in the tenth century CE describing the deposits of gold and silver in the Muslim world. Arab historians and geographers recorded hundreds of mining sites in the Arabian Peninsula. Copper was mentioned as occurring in Saudi Arabia and plentiful in Oman. A major tract was written by Teifaschi (Ahmed ben Ioussouf al-Teifaschi) about 1242 CE, which is composed of a preface in which the author states his objective, followed by 24 chapters, each discussing a separate precious or semiprecious stone. In each section he describes the properties of these minerals generally including the theory of gem formation, statements from earlier sources (such as Aristotle and Pliny), occurrences, physical and magic properties, the ability to enhance or change the color of a gem through heating or dyeing, and the cost of precious and semiprecious gems. He also includes the overall price of these gems and the defects that reduce their value. The principal minerals described are pearl, emerald, beryl, and *yaqut.* The latter word covers descriptions of the true diamond, ruby, corundum, zircon, and hyacinth.

1.3.3.1 Al-Biruni (973–1048)

Abu Ar-Rayhan Muhammad Ibn Ahmad Al-Biruni was born in Khwarezm, a province of ancient Persia. He traveled extensively, eventually reaching India to study and publish on its culture. He was known to have corresponded with Avicenna. His

Fig. 1.2 Al-Biruni, author of the *Book of Precious Stones*, was the most influential Islamic scholar of his time

wide knowledge of the sciences included themes on astronomy, mathematics, medicine, history, and physics. In his book *al-Athar al-Baqia* he discussed the rotation of the earth and gave correct values of latitude and longitude for various places. Six hundred years before Galileo he knew the earth rotates on its axis daily and moves around the sun yearly. He explained the geologic workings of springs, artesian wells, and volcanic eruptions (Fig. 1.2).

In the science of mineralogy his book *Kitab-al-Jamahir* [Book of Precious Stones], written late in his life, discusses the properties such as color, odor, hardness, and density of approximately 100 precious stones and often gives their names in Arabic, Persian, Greek, Syriac, Hindi, and Latin. It is in two parts: precious stones and metals. In it he reported the specific gravity of 18 minerals, elements, and compounds – accurately to three decimal places. This was the most complete book on mineralogy of his time. Under the title *The Book Most Comprehensive In Knowledge of Precious Stones* it is available in an English translation by H. Said (Islamabad 1989).

1.3.3.2 Avicenna (980–1037)

Abu Ali al'Husain ibn Abdullah ibn Sina Avicenna was one of the most influential Arabic scholars. He was both a physician and a civic administrator by profession. Because of his wide-ranging interests, he wrote extensively on the subjects of philosophy, mathematics, natural sciences, chemistry, astronomy, medicine, and music. These treatises significantly influenced not only the Arab World, but also the European Middle Ages. He was the author of *The Canon of Medicine*, an encyclopedic compendium of Greek, Roman, and Arabic medical achievement that he supplemented with his own observations. His treatise on minerals was one of the main medieval sources for geologic information.

Other Arab scholars who contributed to the field of mineralogy were Fakhr ad-Din ar-Razi (1149–1209) and the Egyptian, al-Kalka-shandi (died 1418).

1.3.4 Chinese and Indian Authors

In China the oldest known listing of minerals dates to the fourth century BCE with the *Ji Ni Zi* book that lists 24 minerals. By Han times (206 BCE to 220 CE) the number of known rocks and minerals [*shi*] and metals [*jin*] had risen into the hundreds. In parallel fashion to the development in the western world, by 1070 CE Su Song in his *Ben Cao Tu Jing* used a systematic approach to recording the use of minerals in medicine. In early Chinese writings on mineralogy, stones and rocks were distinguished from metals and alloys, and were further separated by color or other physical properties. Mineral remedies were contained in the pharmacopoeias of Shen Nong [or Shen Nung] (100–180 CE), which contained 23 species of minerals used as drugs, and that of Li Shih-chen (ca. 1578), which described the use of

375 minerals (for example, the use of mercury and iron to cure anemia). Some of the minerals employed were magnetite (*magnatitum*), red ochre clay, goethite, mica, and pyrite (Qin and Li 1992).

Readers interested in Chinese archaeomineralogy should read Needham (1959), Sects. 23 (geology) and 25 (mineralogy), where, although he complains of the dearth of information in Chinese or Western languages on Chinese contributions to the development of geology and mineralogy, he provides a detailed history of Chinese mineralogy, mainly from early Chinese sources. Among other things, Needham illustrates the reasonably accurate geomorphology in ancient Chinese art. By the late first century BCE the Chinese believed in the alchemical principle of the transformation of one mineral into another. From Han times (206 BCE–220 CE) to the last Chinese Dynasty, the Ching (Qing, 1644–1912 CE), most mineral descriptions were contained in pharmacopoeias. Mineral remedies were included from the earliest times. Cinnabar, alum, saltpeter, hematite, and amethyst were of greatest value. Orpiment, realgar, marble, and azurite had modest value and stalagmites, iron, lead carbonate, lime, and fuller's earth were among those with least value. (Needham 1959:643) As early as 815 CE a Chinese Synonymic Dictionary listed 335 synonyms of 62 chemical substances. An eleventh century Chinese book on geology and mineralogy discusses the formation of rocks and such minerals as gold, jade, arsenolite (as being poisonous), cinnabar, alum, green vitriol, and halite. (Needham 1959:637) As elsewhere in the world, color played a prominent role in classifying minerals. From the Han Dynasty on the practical uses of minerals were noted: cinnabar for red inks and paints and also in medicines to promote longevity, powdered steatite as a filler in paper, lead salts in glazes, kaolin as an antacid, and calcium sulfate in the preparation of the Chinese national dish *tou fu.*

Early Indian medicine consisted mainly of drugs made from native plants. However, some medications employed minerals. Sanskrit texts mention the use of bitumen, rock salt, yellow orpiment, chalk, alum, bismuth, calamine, realgar, stibnite, saltpeter, cinnabar, arsenic, sulfur, yellow and red ochre, black sand, and red clay in prescriptions. Among the metals used were gold, silver, copper, mercury, iron, iron ores, pyrite, tin, and brass. Mercury appeared to have been the most frequently used, and it is called by several names in the texts. Physicians in India used mercury from 800 BCE to 1000 CE for skin diseases, smallpox, and later, for syphilis. No Indian source for mercury or its ores has been located, leading to the suggestion that it may have been imported (Murthy 1983).

Chapter 2
Properties of Minerals

2.1 Mineral Chemistry

Mineral chemistry as a science was established in the early years of the nineteenth century by Joseph-Louis Proust's proposal of the Law of Constant Composition in 1799, John Dalton's Atomic Theory in 1805, and the development of accurate methods of chemical analysis. By definition, a mineral has a characteristic composition expressed by its formula, e.g., halite ($NaCl$) or quartz (SiO_2).

Atoms are the basic building blocks of all matter, including minerals. Atoms are extremely small, about 10^{-8} cm, and are themselves composed of smaller particles: electrons, protons, and neutrons. Only the electron portion of atoms will concern us in this book. Because mineral color was so critical in many ancient uses of minerals, the relevant electronic structure of atoms is presented and related to color variation in Sect. 2.3.

A basic understanding of archaeomineralogy requires knowledge of 38 of the 92 naturally occurring chemical elements, including their chemical symbols, because mineral formulas use these symbols. Many symbols are derived from their ancient (often Latin) name rather than their modern name. Examples are: Au, gold from the Latin *aurum*; Ag, silver from the Latin *argentum*; and Na, sodium from the Latin *natrium.* Table 2.1 is a list of the chemical elements and their symbols. Those in italics are important for an understanding of archaeomineralogy.

2.2 Mineral Structure

A mineral species is defined by two distinct properties: (1) its chemical composition and (2) its crystal structure. Each mineral has a distinct three-dimensional array of its constituent atoms. This regular geometry affects its physical properties such as cleavage and hardness.

How the atoms are held together in a mineral is governed by the nature of the chemical bonds formed between elements in the structure. An advanced

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Table 2.1 Elements of the Periodic Table

Actinium	Ac	*Gold*	*Au*	Praseodymium	Pr
Aluminum	*Al*	Hafnium	Hf	Promethium	Pm
Americium	Am	Helium	He	Protactinium	Pa
Antimony	*Sb*	Holmium	Ho	Radium	Ra
Argon	Ar	*Hydrogen*	*H*	Radon	Rn
Arsenic	*As*	Indium	In	Rhenium	Re
Astatine	At	*Iodine*	*I*	Rhodium	Rh
Barium	*Ba*	Iridium	Ir	Rubidium	Rb
Berkelium	Bk	*Iron*	*Fe*	Ruthenium	Ru
Beryllium	*Be*	Krypton	Kr	Samarium	Sm
Bismuth	Bi	Lanthanum	La	Scandium	Sc
Boron	B	*Lead*	*Pb*	Selenium	Se
Bromine	Br	Lithium	Li	*Silicon*	*Si*
Cadmium	*Cd*	Lutetium	Lu	*Silver*	*Ag*
Calcium	*Ca*	*Magnesium*	*Mg*	*Sodium*	*Na*
Californium	Cf	*Manganese*	*Mn*	*Strontium*	*Sr*
Carbon	*C*	Mendelevium	Md	*Sulfur*	*S*
Cerium	Ce	*Mercury*	*Hg*	Tantalum	Ta
Cesium	Cs	*Molybdenum*	*Mo*	Technetium	Tc
Chlorine	*Cl*	Neodymium	Nd	Tellurium	Te
Chromium	*Cr*	Neon	Ne	Terbium	Tb
Cobalt	*Co*	Neptunium	Np	Thallium	Tl
Copper	*Cu*	*Nickel*	*Ni*	Thorium	Th
Curium	Cm	Niobium	Nb	Thulium	Tm
Dysprosium	Dy	*Nitrogen*	*N*	*Tin*	*Sn*
Einsteinium	Es	Nobelium	No	*Titanium*	*Ti*
Erbium	Er	Osmium	Os	*Tungsten*	*W*
Europium	Eu	*Oxygen*	O	*Uranium*	U
Fermium	Fm	Palladium	Pd	Vanadium	V
Fluorine	F	*Phosphorus*	P	Xenon	Xe
Francium	Fr	Platinum	Pt	Ytterbium	Yb
Gadolinium	Gd	Plutonium	Pu	Yttrium	Y
Gallium	Ga	Polonium	Po	*Zinc*	*Zn*
Germanium	Ge	*Potassium*	K	*Zirconium*	*Zr*

understanding of crystal structures and bonding is unnecessary in the context of this book, so only a brief introduction is provided.

There are three basic types of chemical bonds: metallic, covalent, and ionic. The metallic bond is responsible for the cohesion of a metal. Metals readily lose their outer electrons, so the geometry of crystal structures is determined by the manner in which the positively charged atoms can be "packed" in space. The detached electrons dispersed among the atoms are freely mobile. This mobility is responsible for the good electrical and thermal conductivity of metals.

The most stable configuration for an atom is one in which the outer shell of electrons is completely filled (see Sect. 2.3 for a description of the structure of atoms). One way to achieve this stable configuration is for two or more atoms to share electrons in their outer shells. The best mineralogical example is diamond, in which every carbon atom is surrounded by four other carbon atoms, each sharing one electron with the central atom. This arrangement is repeated throughout the structure. This type of bond is called covalent.

Another way for an atom to achieve a completely filled outer shell of electrons is for it to gain or lose the precise number of electrons required to reach this configuration. A neutral chlorine atom lacks one electron for a filled outer shell. By accepting one additional electron it becomes a stable, negatively charged ion with a filled outer shell. Sodium has only one electron in its outermost shell. By giving up this electron sodium has its outermost shell filled and becomes a stable positively charged ion. Sodium and chlorine ions combine readily to give an ionic structure, bonded by electrostatic attraction. Each ion is surrounded by ions of opposite charge, the number being determined by their relative sizes. This ionic bonding is the most common bonding in minerals. Practically all minerals, except native elements (such as gold or copper) and sulfides, are predominantly ionic.

The hardness of a mineral is defined as its resistance to scratching. Hardness was quantified by the Austrian mineralogist Friedrich Mohs, who proposed the following scale of relative hardness in 1922: (1) talc, (2) gypsum, (3) calcite, (4) fluorite, (5) apatite, (6) orthoclase, (7) quartz, (8) topaz, (9) corundum, (10) diamond. Each of the minerals lower in the scale can be scratched by those higher in the scale. The scale is not linear; in absolute hardness, diamond is three orders of magnitude harder than talc. Hardness does vary with crystallographic direction in a mineral.

Hardness is an important diagnostic property in the field identification of minerals. In addition to the minerals in the scale, the following materials serve as handy references for the hardness (on the Mohs scale): fingernail: 2–2.5; copper coin: approximately 3; pocket knife: 5–5.5; window glass: 5.5; steel file: 6.5.

Because there is a general link between hardness and chemical composition, the following generalizations can be made: (1) most hydrous minerals are relatively soft ($H<5$), (2) halides, carbonates, sulfates, and phosphates are also relatively soft ($H<5.5$), (3) most sulfides are relatively soft ($H<5$) with pyrite being an exception ($H<6$ to 6.5), (4) most anhydrous oxides and silicates are hard ($H>5.5$).

Rock hardness is a very different matter. Rather than based on the Mohs hardness of its constituent minerals rock hardness as used in geology denotes the cohesiveness of a rock and usually is expressed in terms of compressive fracture strength. Geologists also use the qualitative terms “hardrock” to refer to igneous and metamorphic rocks and “softrock” to refer to sedimentary rocks. These terms originated as mining terms indicating how difficult it was to mine a given rock type. The fracture strength of rocks varies from “weak” in poorly cemented **clastic** sedimentary rocks, through “medium” in competent sedimentary rocks, through “strong” in most igneous and metamorphic rocks, to “very strong” in quartzites and dense fine-grained igneous rocks.

For metals and alloys, in particular, a group of properties called *tenacity* are important. These are:

malleability:	capable of being flattened under the blows of a hammer into thin sheets without breaking or crumbling in fragments. Malleability is conspicuous in gold, silver, and copper. Most of the native elements show some degree of malleability.
sectility:	capable of being severed by the smooth cut of a knife. Copper, silver, and gold are sectile.
ductility:	capable of being drawn into the form of a wire. Gold, silver, and copper are ductile.
flexibility:	bending easily and staying bent after the pressure is removed. Talc is flexible.
brittleness:	showing little to no resistance to breakage; separating into fragments under the blow of a hammer or with the cut of a knife. Most silicate minerals are brittle.
elasticity:	capable of being bent or pulled out of shape but returning to the original form when relieved. Mica is elastic.

Specific gravity (G) is a number that expresses the ratio between the mass of a substance and the mass of an equal volume of water at 4°C. The specific gravity of a mineral depends on (1) the atomic weights of all the elements of which it is composed, and (2) the manner in which the atoms are packed together. If two minerals, e.g., graphite and diamond, have the same chemical composition, the differences in specific gravity reflect the difference in internal packing of the atoms or ions (diamond with $G=3.51$ has a much more densely packed structure than graphite with $G=2.23$).

Minerals may break by fracturing or cleaving. *Cleavage* and *fracture* are two separate phenomena. Cleavage is planar rupture, controlled by the atomic arrangement in the mineral’s crystal structure. For example, mica cleaves into sheets because of the sheet structure of mica. Cleavage planes are symmetrically disposed within minerals, and different minerals have from zero to six directions of cleavage.

Those without cleavage break by fracturing along **parting** surfaces not related to cleavage planes. Different kinds of fracture are designated as follows. Conchoidal fracture is curved and resembles the interior surface of most shells. This is the type of fracture observed in glass and the mineral quartz. Some minerals exhibit a fibrous or splintery fracture. A hackly fracture results in jagged and sharp edges. Fractures producing rough and irregular surfaces are called irregular fractures. The most common fracture for the production of lithics is the conchoidal fracture exhibited by obsidian, chert, quartz, and quartzite.

The term luster refers to the appearance of a mineral surface in reflected light. Metallic luster is that of a shiny metal. Minerals with a metallic luster are opaque. Galena and pyrite are common minerals with a metallic luster. A metallic luster has also been added artificially to give decorative effects to glazed ceramics. This technique was created by Arab ceramists in the ninth century (Darque-Ceretti et al. 2005) and spread over the Mediterranean basin especially to Spain and Italy. This technique is based on firing of the glazed pottery in a reducing atmosphere in the presence of metallic salts. This produced a metallic-appearing surface with a gold, brown, or red luster. The luster was a result of metal particles of nanometer size dispersed in a glassy matrix.

Minerals with a nonmetallic luster are generally light-colored and transmit light, at least through thin edges. The following are the important types of nonmetallic luster:

Vitreous:	The luster of glass. Example: quartz.
Pearly:	An iridescent pearl-like luster, usually observed on mineral surfaces that are parallel to cleavage planes. Example: cleavage surface of talc.
Greasy:	Appears as if covered with a thin layer of oil, resulting from light scattered by a microscopically rough surface. Examples: some specimens of sphalerite and massive quartz.
Silky:	Silk-like, caused by the reflection of light from a fine fibrous parallel aggregate. Examples: fibrous gypsum and serpentine.
Adamantine:	A hard, brilliant luster like that of a diamond, due to the mineral's high index of refraction. Example: the transparent lead mineral cerussite.

See Sect. 2.4 for further information about the causes of luster in minerals.

2.3 Mineral Identification Methods

2.3.1 Element Analyses

Modern instrumental techniques are all capable of multi-element analysis. These techniques can be used to determine well over half of the elements in the Periodic Table. They provide high precision and accuracy over a range of elemental concentrations. However, each technique has one or more limitations, so one must evaluate the relative merits of the competing systems. Most are destructive so not applicable to museum specimens. Detailed explanations of these instruments and instrumental techniques are readily available in all libraries (for example, see Ewing 1997).

The dominant techniques used by geologists for multi-element analyses are atomic absorption spectrometry (AA), inductively coupled plasma spectrometry (ICP), X-ray fluorescence spectrometry (XRF), and instrumental neutron activation analysis (INAA). Although analysts conducting archaeological provenance studies have favored INAA, this technique is best for trace elements.

Since the mid-1950s, atomic absorption spectroscopy (AA) has developed rapidly and is now a convenient and rapid "work horse" analytical method in most geology and biology departments in universities and major museums. Atomic absorption spectroscopy developed from emission spectroscopy, to gain more sensitivity. This method requires that the sample be put into solution that is then aspirated into a flame. The absorption spectra are compared with standards with curves of absorbency plotted against concentration. For mineral analyses, the primary problem is getting a small sample into solution. Whatever technique is used for this digestion, there is a real danger of contamination.

In the author's view, the major utility of AA is determining of which metal or metals an artifact is composed when one has only a few milligrams of sample. This is most often the case with museum artifacts that are subjected to destructive analysis. INAA can also identify small metal samples but is not available to most researchers, whereas AA should be. Inductively coupled plasma emission spectroscopy (ICP) is an efficient technique for multi-element analyses, but the instrumentation is quite expensive. Like AA, it suffers from possible contamination as the artifact sample is dissolved.

X-ray fluorescence spectrometry achieved prominence in the 1960s and has been used widely ever since. In this technique, a sample irradiated by an X-ray beam emits a secondary X-ray fluorescence spectrum characteristic of the elements in the sample. The principal advantage of XRF is that it is a bulk technique and, like INAA, can be applied to the raw sample. This overcomes concerns about sample homogeneity and resistance to dissolution. XRF systems can be highly automated, provide high precision analyses for many elements, and can be designed to be both nondestructive and portable–extremely desirable when dealing with museum artifacts. The principal disadvantages of XRF are (1) matrix and interference problems, and (2) an instrument cost perhaps four times as great as AA.

Neutron activation analysis is a physical method of analysis where a wide range of elements can be measured simultaneously with no loss in precision. Neutron activation analysis requires only a small sample (50 mg for metals, 200 mg for silicates), no complex sample preparation, and no extraction techniques. A sample analyzed by this technique is subjected to irradiation by slow (thermal) neutrons in a nuclear reactor. Various constituent atoms capture these neutrons producing unstable daughter elements. These unstable **isotopes** emit gamma rays characteristic of the original element present in the sample, and the gamma ray intensity is a measure of the concentration of each original element present. The gamma ray spectrum from the decay is measured in a multichannel gamma-ray spectrometer.

Neutron activation methods can achieve high accuracy and precision for some elements but only moderate or poor results for others. As a technique, neutron activation has a different sensitivity (detection limit) for each chemical element.

Sensitivities vary with irradiation time and intensity, delay time, counting conditions, and composition of the sample. Where a reactor is accessible and set up for automated INAA, the per sample cost is very competitive. A major advantage of INAA is the lack of matrix interference, which is a major problem with AA and ICP. The principal disadvantage for most investigators is the need for access to a reactor. Other disadvantages include the need for compromises when setting the counting routine and the need to monitor the neutron flux. Neutron activation analysis is one of the prominent means used to find the geologic sources of raw materials used by prehistoric human groups. It has often been employed by those interested in trading patterns, population territories, and migration.

Nondestructive activation analyses using isotopic neutron sources may also be appropriate in many cases. The author has not used this technique because of limited sensitivity compared to INAA. However, it has the major advantage of being nondestructive. For example, for the determination of the precious metal content of ancient coins, see Cosma et al. (1988).

2.3.2 Petrographic Analyses

Rock and mineral specimens can be examined using polarized light microscopy in two different ways; either by making a thin transparent section 0.03 mm thick, or by crushing to a convenient size to be examined as grains. Thin sections reveal the mineralogy, texture, grain size, and relative proportions of different minerals in a rock. Figure 2.1 is a photomicrograph of a thin section of a quartzite tool from the Lower Paleolithic of France.

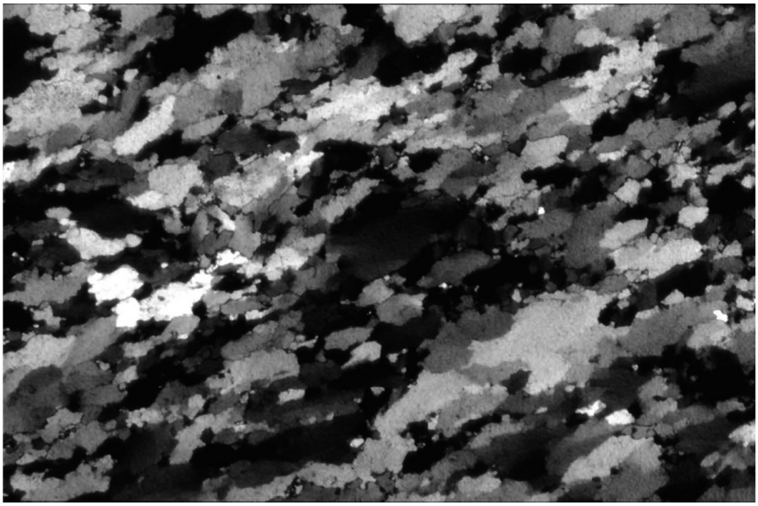


Fig. 2.1 Petrographic thin-section of a quartzite used as a lithic tool in Paleolithic France

Grain mounts have the advantage of more easily identifying minerals by their most diagnostic optical property, refractive indices. In my view, microscope methods are woefully underutilized in archaeological investigations. Most lithic and ceramic materials and products are composed of minerals (obsidian–a volcanic glass–is an exception). Minerals are crystalline, so **petrography** is based on crystal symmetry and crystal chemistry. The coarsest categorization of crystal symmetry classifies minerals into seven crystal systems: isometric, hexagonal, tetragonal, trigonal, orthorhombic, monoclinic, and triclinic. For petro-graphic analysis it is the optical symmetry and optical parameters of minerals that allow identification and interpretation.

Isometric minerals are optically isotropic, i.e., they have only one index of refraction. Hexagonal, tetragonal, and trigonal minerals are uniaxial – they have one optical axis and two indices of refraction. Orthorhombic, mono-clinic, and triclinic minerals are biaxial. They have two optical axes and three indices of refraction. Uniaxial and biaxial crystals are said to be **anisotropic** (i.e., not isotropic). Mineral grains can be immersed in oils of known indices of refraction to measure the refractive indices and other optical characteristics and thereby be identified. Clay minerals are too fine-grained to be studied by the methods of optical mineralogy.

In grain mounts the grains should be of approximately the same size, between 0.10 and 0.15 mm. This can be done by passing the crushed material through a 100-mesh screen and retained on a 150-mesh screen. The useful grain size limits for this technique are from 0.01 to 0.2 mm. If refractive indices are to be determined, one needs a set of refractive index oils in which the grains can be immersed and compared.

When a polarizing microscope is available, microdebitage can be studied, and chert and obsidian are easily distinguished because obsidian is a glass with only one index of refraction. There are dozens of standard textbooks on optical mineralogy and petrography for those who would find this method to be useful. Thin sections of rocks or ceramics when studied under polarized light allow investigation of textures and chemical alteration as well as mineral identification. A note on nomenclature–petrology is the study of the origin of rocks, petrography is the description of rocks. American usage follows the strict definition. The description of rocks or ceramics in thin section is *petrography.* British usage is to call thin-section analysis *petrology.*

Thin-section petrography requires the use of a polarizing microscope. The polarizing microscope has two functions: (1) to provide an enlarged image of an object placed on the microscope stage, and (2) to provide plane and crossed polarized light and convergent light. The *polarizing lens* below the rotating microscope stage constrains light to vibrate only in a front-back (north-south) direction. A converging lens is also mounted in the substage. Above the microscope stage (and above the object under study) is a second polarizer called an *analyzing lens* that constrains light to vibrate only left-right (east-west). The substage polarizing lens is fixed in place, but the analyzer can be moved in or out of position. Minerals exhibit a host of distinguishing characteristics in plane and crossed (both lenses in position) polarized light and in convergent polarized light. As with other compound microscopes, polarizing microscopes contain a variety of other lenses and devices that can modify the transmission of light for specialized studies.

Thin sections of rocks allow identification of mineral constituents, their relative abundances, associations and states of alteration; grain orientations and related fabric features; the size, shape, and orientation of voids; and post-use **diagenetic** recrystallization. The mineral grains exhibit distinct size, shape, sorting, roundness, and sphericity characteristics. All these parameters can provide diagnostic data.

Those using the thin-section method of rock identification and characterization will find the following volumes very helpful: for igneous rocks MacKenzie et al. (1982), and for metamorphic rocks Yardley et al. (1990). Each of these volumes has large numbers of colored photographs of rock thin sections.

2.3.3 Physical Methods of Identification

To go very deeply into X-ray diffraction methods (XRD) would require that the reader be familiar with the fundamentals of crystallography and the physics of electromagnetic radiation. This section will only outline what XRD seeks to do and a segment concerning how one goes about it. In archaeomineralogy, the primary use of XRD is to identify crystalline materials. Glassy or amorphous substances are not amenable to diffraction techniques.

XRD encompasses two distinct recording methods: film and diffractometry. Both methods require that the specimens be in powdered form. The main advantage of using the camera/film technique is that one can obtain a strong pattern with very little material, much less than with diffractometry. The diffractometer technique has the advantages of getting better angular resolution, and the low-angle limit is much lower than with an ordinary powder camera. The latter advantage is quite important when identifying minerals with large spacings between planes of atoms. Clays and other sheet silicates have one, very large, spacing.

Once an X-ray diffraction pattern is obtained, one can identify the mineral or minerals by comparing the pattern with the known patterns of all mineral species. As part of recent powder diffractometer instruments, a computer will do the matching. Otherwise one can do the matching “by hand” using the American Society for Testing Materials (ASTM) powder data file and the ASTM index. XRD works because each mineral has a unique structure.

Density is a fundamental and characteristic property of each mineral and, as such, is an important determinative property. Specific gravity is a number, the ratio of the mass of a substance to the mass of an equal volume of water at 4°C. Density is defined as the ratio of the mass of any quantity of a substance to its volume normally expressed in g/cm^{-3}. If you look up the density or the specific gravity of a mineral, you will normally find its specific gravity recorded. For small artifacts, density can be used to distinguish the two jade minerals. Nephrite has a specific gravity of 3.0, whereas jadeite is denser (heavier) at 3.3.

Although there are many methods of density determination, only four types will be introduced briefly here. The first is the displacement method. This method is based on direct weighing of the mineral followed by measuring the volume of liquid displaced when the mineral is immersed in it. In its simplest form, the volume is determined by immersing the mineral in a graduated cylinder, and the volume increase read off. All laboratories will have both weighing scales and graduated cylinders.

The second method is called pycnometry. The principle underlying this method requires that the weight of the mineral is measured directly, and the volume obtained by weighing the volume of the liquid displaced from the pycnometer by the minerals. This method entails the successive weighing of the empty pycnometer, the pycnometer with the sample alone, the pycnometer with the sample and liquid and the pycnometer with liquid only. Water can be used if it is not absorbed by, nor reacts with, the mineral. N.H. Winchell (1938) modified the basic technique to achieve accuracies of ±1.0%. The primary disadvantage of this method is that most universities and major museums might not have a pycnometer. The major advantage is that one can use many small fragments when a larger sample is not available.

The third method is based on hydrostatic weighing. For most small artifacts, less than 50 g or so, the well-known Jolly balance (Fig. 2.2) is quite suitable. This is the technique preferred by the author. The mineral is first weighed in air and then reweighed in a liquid of known density. From the apparent loss in weight, the volume of the mineral may be computed and hence its density. Most geoscience departments should have a Jolly balance. The fourth, most accurate, method is based on comparison of the mineral or metal artifact with heavy liquids. However, few institutions have the requisite set of heavy liquids (many of which are toxic). All of these density methods are valuable in small artifact identification because they are nondestructive.

Geologists use a 10- or 20-power hand lens as an aid in identifying rocks and minerals in hand specimens. Use of a hand lens is valuable in seeing the relict sand

Fig. 2.2 The author using a Jolly balance

grains that identify quartzite; the cleavage or fracture diagnostic of many minerals; and fine-grained textural features common in some rocks. Specimens that are polished by geologic or human action are much harder to identify than those showing natural features of cleavage, fracture, crystallinity, and color.

2.4 Color of Minerals

Color has always been important to the human psyche, from protecting against evil spirits to attracting the opposite sex. In the modern Western world black is the symbol of mourning, white of purity, and red of passion or danger. To some groups in East Africa black is the color of joy. In ancient times purple pigment was rare and expensive, so it was a royal color.

For thousands of years humans have marveled at the variety of colors found in "stones" and have attributed magical, curative, and protective powers to certain minerals, especially the varicolored gems. The beauty of amethyst was secondary to its value as a safeguard against intoxication; hematite, from the Greek word for blood, was believed to cure all manner of blood diseases, and beryl to promote conjugal love. Even today certain colors are considered appropriate on some occasions and inappropriate on others. Colors as symbols, magic or otherwise, have retained their authority: brides wear white, priests black; red signals stop, and so on.

Alchemists, in many ways forerunners of modern experimental scientists, equated color with the essence or true nature of a substance. They tried to find a way to dye, tinge, alloy, or otherwise color metal, believing that such an alteration would indeed transform one substance into another. If their "synthetic gold" tarnished, they knew they had failed. The alchemists' lack of understanding of the structure of matter was matched, and in some measure governed, by their ignorance of the nature of the color of light. If there is no light, there is no color.

Although it is the color of individual minerals that has attracted nearly all of the scientific study, some rocks have been investigated. An example of a study where a rock has been studied carefully to account for its color is that of the color changes in purple-green slate from North Wales (Borradaile et al. 1991). The normally purple slate changes to green in patches parallel to the bedding. The green color is seen where there is a diffusion of Fe^{3+} away from the green material leading to a replacement of hematite (red) with magnetite (black). The green material also has twice as much **chlorite** (green). Mineral and compound descriptions in Chaps. 5, 6, 7, 8, and 9 often describe color and its role in defining the value of the material.

The Nature of Light and Color. Information gathered by the human eye as it perceives light governs the way we think about the material world. As knowledge of the nature of light increased, so, correspondingly, has knowledge of the materials and forces that make up the universe.

Beginning in the seventeenth century, when scientists first devised experiments to check their ideas on the nature of the physical world, a running controversy developed on the nature of light. Experiments like those showing that light could be made to go around corners, that it could interact to produce "beats" similar to those produced by sound waves, and that sunlight could be separated into colors and then recombined seemed to indicate that light traveled in "waves." However, Sir Isaac Newton proposed that light consisted of a series of particles, which, because they traveled in straight lines, could be considered "rays". Experiments conducted from Newton's time until the beginning of the twentieth century gave ever-increasing support to the wave theory as opposed to the particle theory. In fact, it became the custom in science to designate a particular color in terms of its "wavelength." This system is still used.

In the latter part of the nineteenth century, James Clerk-Maxwell showed that visible light as well as infrared and ultraviolet radiation are forms of *electromagnetic radiation* (Fig. 2.3). All forms of electromagnetic radiation travel at a constant speed in empty space, approximately $3\times10^{10}\,\mathrm{cms}^{-1}$. Types of radiation differ only in their wavelengths (λ in Fig. 2.3).

Shortly after Clerk-Maxwell's work, radio waves (with wavelengths longer than infrared radiation) and X-rays (with wavelengths much shorter than ultraviolet) were discovered. Thus the "electromagnetic spectrum" was greatly extended at both ends of the range of visible light, and today it is known that visible light occupies only a very narrow portion of that spectrum (Fig. 2.4). The only other portion of the electromagnetic spectrum that humans can sense is the infrared, the region of heat radiation. We feel the warmth of infrared radiation generated by particles colliding in the hot gases of the sun, as well as the infrared radiation from a hot stove, electric iron, and similar heat-producing implements.

At about the time radio waves and X-rays were discovered, Albert Einstein created a "new physics" by relating electromagnetic energy to the mass concept of matter and the velocity of light. We were back to light consisting of particles. According to this concept, radiation comes in discrete packets, later called *photons.* The more energetic photons correspond to radiation with short wavelengths; the less energetic, to radiation with long wavelengths. Light, then, can be considered either an electromagnetic wave with a specific wavelength or a stream of light particles called photons, each possessing a specific amount, or quantum, of energy. The narrow band of the electromagnetic spectrum occupied by visible light, or light that registers on the average human eye, can be further broken down by wavelength into colors (Fig. 2.5). The longest waves in the visible spectrum form the color we call red; the shortest waves produce blue or violet; the remainder of the rainbow hues falls in-between. Wavelengths of light recognized by the human eye range from

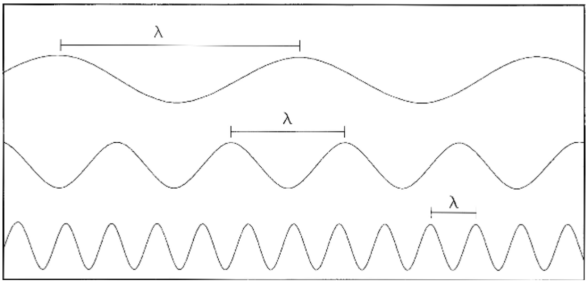


Fig. 2.3 The wave nature of light

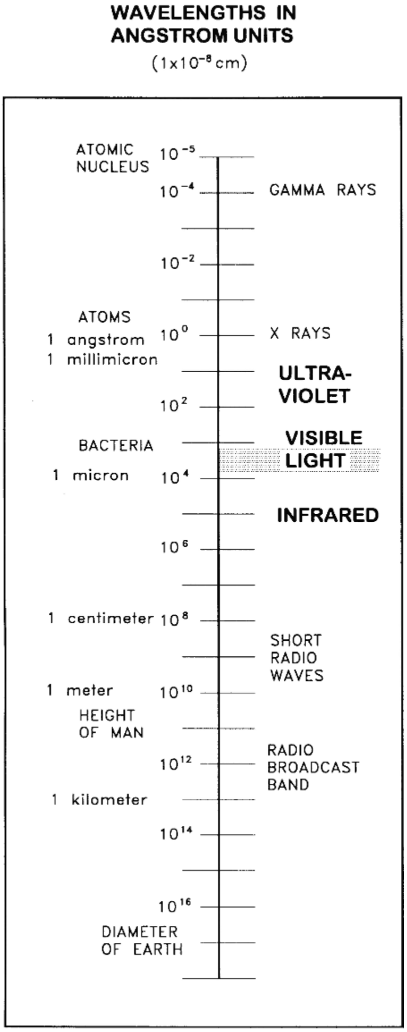
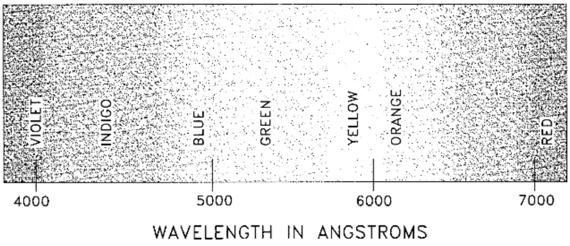


Fig. 2.4 Types of electromagnetic radiation



COLOR	RANGE	AVERAGE
VIOLET	3900–4300	4100
INDIGO	4300–4600	4450
BLUE	4600–5000	4800
GREEN	5000–5700	5350
YELLOW	5700–5900	5800
ORANGE	5900–6100	6000
RED	6100–7500	6800

Fig. 2.5 Wavelengths of light in the visible spectrum

about 4000 to 7500 angstrom units. *One angstrom equals one hundred-millionth of a centimeter* (10^{-8} cm), about the diameter of an atom.

The possibility of separating sunlight into its different wavelengths or colors was first recognized by Sir Isaac Newton, who allowed a narrow circular beam of light to pass through a glass prism and fall onto a white surface. The individual colors contained in sunlight were spread out in a rainbow-like display, recorded by Newton as red, orange, yellow, green, blue, indigo, and violet. Thus sunlight, or *white light*, which appears to have no color, is really a mixture of all colors.

Interaction of Light with Crystals. For color to be perceived, light waves must interact with the object. Light striking the surface of a crystal undergoes reflection, refraction, scattering, and absorption. Reflection is the return to the original medium, normally air, of a portion of the light striking a surface. The amount of light reflected depends on the composition and structure of the solid object. Metals reflect a high percentage of the incident light. If the metal is colored, the reflection will also be colored. Light reflected from the surface of a transparent substance, on the other hand, is generally not colored even if the substance is colored.

Refraction is the change in direction of a light ray when it enters a material of a different optical density at an angle (other than 90°). Differential refraction causes the color spectrum seen by Newton in his experiment with a prism. Each wavelength (color) of light has a different angle of refraction, so the colors separate as they emerge from the prism. Blue light is bent the most; red, the least.

Scattering arises from imperfections or flaws in the regular arrangement of atoms in a crystal. In this process, light energy is taken from the light beam and reradiated as spherical light waves from each "scattering center." Thus, an amount of energy is lost by the beam as it travels in an altered direction. Solids that transmit light scatter and reduce it to such an extent that transmitted patterns that cannot be seen are *translucent*; solids that transmit light with no appreciable loss in clarity are *transparent*; solids that transmit no light are *opaque.*

Absorption in crystalline substances is the process by which certain wavelengths in the visible spectrum are neither transmitted nor reflected. If some portions of the spectrum are absorbed and others transmitted or reflected, the wavelengths that are reflected combine to make the apparent color of the substance. For some substances the absorption is general, or approximately the same for all wavelengths. If the absorption is general and complete, or nearly so, we see the object as black–a complete lack of color. The object is seen as white if there is little or no absorption and all wavelengths are reflected or scattered, so the whole visible spectrum is contained in the reflected light. The difference between a white material and one that is clear or colorless is that the white material reflects or scatters all wavelengths without selective absorption, while a colorless substance transmits the light without appreciably altering anything but the path of the light as it enters and leaves the substance.

When a board that has been painted red is viewed in sunlight, it appears red because pigment in the paint selectively absorbs all the wavelengths shorter than red. However, if this same "red" board is viewed in light from a light source containing only the shorter (bluer) wavelengths, the board appears black because all the blue light is absorbed and there is no incident red light to be reflected. An otherwise "white" board appears red if illuminated by exclusively red light.

Color Development in Crystals. The following sections relating to atomic structure use the convenient diagrammatic approach that allows one comprehend physical interactions. Although physicists would say this does not adequately describe the underlying physics it is quite sufficient for our purposes. To understand how electrons can absorb electromagnetic energy in the visible light region, one must understand the electronic structure of atoms. The element iron contributes heavily to the color of many minerals. Figure 2.6 shows a highly simplified diagram of its electron shells. These shells are more or less spherical and concentric with the nucleus. Within the shell each electron is restricted to a certain energy level called an *orbital.* The orbitals, designated *s*, *p*, *d*, and *f*, each have a certain number of "positions" for electrons. The *s* orbital electrons have the lowest energy, and the energy increases through the *p*, *d*, and *f* orbitals. Not all shells have all types of orbitals. In some atoms the electron positions in the orbitals are not all filled. It is in these atoms with partially filled orbitals that mechanisms exist to develop many of the colors observed in minerals.

For every distinct quantity of energy contained by Einstein's photons or light packets, there is one, and only one, associated wavelength. When light of a specific wavelength enters a crystal and encounters an electron that can accept the amount of energy associated with that particular wavelength, the light is absorbed. A given electron is able to accept and absorb the amount of energy stored in the light photon if the energy corresponds exactly to the amount necessary for the electron to "jump" from its normal position to a position of higher energy.

Conversely, when an electron drops to a lower energy level, a photon is emitted containing energy equivalent to the energy difference between the new and old positions of the electron (Fig. 2.7). The whole field of spectroscopic analysis is based on this principle. Each chemical element has a unique set of energies associated with its particular set of electron orbitals and, there-fore, has its own distinguishing emission wavelengths. For example, common table salt (sodium chloride) placed in a

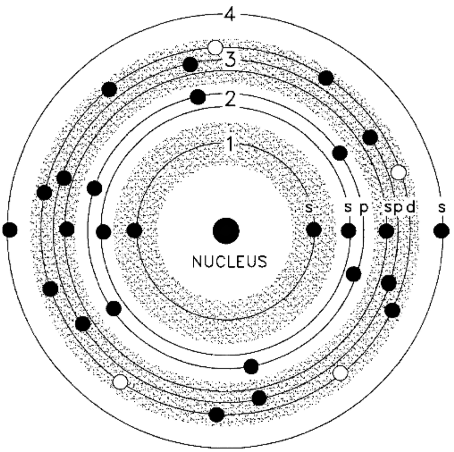


Fig. 2.6 Atomic structure of iron

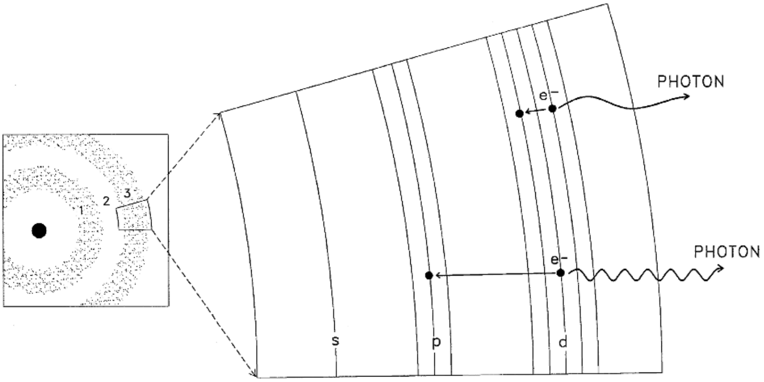


Fig. 2.7 Electron jumps producing light rays (photons)

nonluminous flame will emit a strong yellow color. This color is due to the photons of light emitted when electrons in sodium, having been "excited" by the heat, return from a higher to a lower energy level. At ordinary temperatures electrons lack the energy to jump from one type of orbital to another. However, electron jumps from one orbital to another orbital of the same type within the same shell require only a small amount of energy, and the associated wavelength often lies in the visible region.

Sources of Color in Minerals: Transition Elements. It takes two electrons to fill the *s* orbital of a shell in an atom, six to fill the three *p* orbitals, ten to fill the five *d* orbitals, and fourteen to fill the seven *f* orbitals. See Table 2.2 for electronic configuration in the chemical elements. Whenever an atom with a partially filled *d* or *f* orbital is present in a mineral, there is a good chance that the electrons will jump between the various *d* or *f* orbitals, absorbing energy in the visible region. Because the energy differences between electron positions in these orbitals correspond to the wavelengths of visible light, the mineral will be colored. The *transition elements* (Fig. 2.8) have such partially filled orbitals and play the major role in mineral color.

Elements like iron, manganese, chromium, and vanadium have partially filled *d* orbitals. Elements in the so-called lanthanide and actinide series have partially filled *f* orbitals.

A given element does not always cause the same color, however. This is because the energy required for an electron jump from one position to another is influenced by the environment of the atom – the types and number of nearby atoms – and also by its *oxidation state* – the number of electrons it has in excess or in deficit of its atomic number Z (the number of protons). Some elements, notably the transition metals, can assume more than one oxidation state. For example, manganese can assume oxidation states +2, +3, +4, and +7, corresponding to a deficit of 2, 3, 4, or 7 electrons.

The large majority of highly colored minerals contain transition metals. Iron, the most abundant transition metal, is the coloring agent in a great variety of minerals. In addition to having unfilled *d* orbital positions, iron can exist in two oxidation states (+2 and +3); this leads to further complexities that result in the absorption

Table 2.2 Electronic configuration of the first 36 elements (transition elements are in capital letters; *s*, *p*, *d*, *f* are orbital designations)

Atomic number	Name of element	Symbol	First shell	Second shell	Third shell	Fourth shell
			s	s p	s p d	s p d f
1	Hydrogen	H	1			
2	Helium	He	2	Inert gas		
3	Lithium	Li	2	1		
4	Beryllium	Be	2	2		
5	Boron	B	2	2 1		
6	Carbon	C	2	2 2		
7	Nitrogen	N	2	2 3		
8	Oxygen	O	2	2 4		
9	Fluorine	F	2	2 5		
10	Neon	Ne	2	2 6 Inert gas		
11	Sodium	Na	2	2 6	1	
12	Magnesium	Mg	2	2 6	2	
13	Aluminum	Al	2	2 6	2 1	
14	Silicon	Si	2	2 6	2 2	
15	Phosphorus	P	2	2 6	2 3	
16	Sulfur	S	2	2 6	2 4	
17	Chlorine	Cl	2	2 6	2 5	
18	Argon	Ar	2	2 6	2 6 Inert gas	
19	Potassium	K	2	2 6	2 6	1
20	Calcium	Ca	2	2 6	2 6	2
21	SCANDIUM	Sc	2	2 6	2 6 1	2
22	TITANIUM	Ti	2	2 6	2 6 2	2
23	VANADIUM	V	2	2 6	2 6 3	2
24	CHROMIUM	Cr	2	2 6	2 6 5	1
25	MANGANESE	Mn	2	2 6	2 6 5	2
26	IRON	Fe	2	2 6	2 6 6	2
27	COBALT	Co	2	2 6	2 6 7	2
28	NICKEL	Ni	2	2 6	2 6 8	2
29	COPPER	Cu	2	2 6	2 6 10	1
30	Zinc	Zn	2	2 6	2 6 10	2
31	Gallium	Ga	2	2 6	2 6 10	2 1
32	Germanium	Ge	2	2 6	2 6 10	2 2
33	Arsenic	As	2	2 6	2 6 10	2 3
34	Selenium	Se	2	2 6	2 6 10	2 4
35	Bromine	Br	2	2 6	2 6 10	2 5
36	Krypton	Kr	2	2 6	2 6 10	2 6 Inert gas

of light. A given iron ion, say **ferric** iron (Fe^{3+}), does not have a characteristic color since the specific absorption will be modified by the environment of the ion. The colors of compounds where the same ion is surrounded by a nearly identical arrangement of other ions are quite similar. For instance, the two iron silicates olivine, $(FeMg)_2SiO_4$, and tremolite-actinolite, $Ca_2(MgFe)_3Si_8O_{22}(OH)_2$, are both green since the **ferrous** ion (Fe^{2+}) has a similar environment. Consider also the

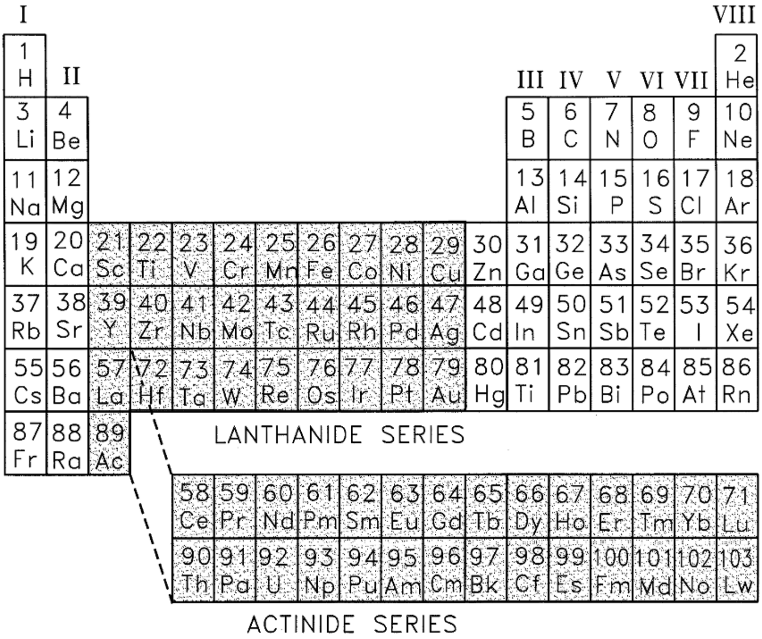


Fig. 2.8 Periodic Table of the elements

coloring effect caused by varying amounts of the transition metal iron in these two minerals. Both olivine and tremolite-actinolite are magnesium-iron silicates, which means that magnesium and iron may substitute for one another at the same site in the crystal structure. The magnesium ion (+2) has all orbitals and shells filled (an inert gas configuration) and does not contribute to absorption in the visible region. Therefore, as the transition metal iron replaces magnesium in the structure of these minerals, the minerals range from white to dark greens.

The intensity of the color seems to increase when the transition element in the mineral is present in more than one oxidation state, a situation made possible by a process called charge transfer. Many minerals containing only the ferrous ion (Fe^{2+}) or only the ferric ion (Fe^{3+}) are relatively pale in color, whereas iron-containing silicates like **pyroxenes** and **amphiboles** that contain both ions are dark green to black. This feature is shown dramatically by the mineral vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$. The fresh mineral is usually colorless, but exposure to air, with the accompanying partial oxidation of ferrous to ferric iron as the ferrous ion gives up an electron to an oxygen atom, causes vivianite to turn bluish-black.

Charge transfer among atoms, a mechanism related to light absorption, may also take place when an element capable of more than one oxidation state is present. Since an electron is a charged particle, a transfer of an electron from one ion to another is a charge transfer. This transfer is possible when the energy difference between the different oxidation states of the same element is small. Under these circumstances, an electron may transfer or jump from one ion to another, thus changing the oxidation state of both. The small energy difference between Fe^{2+} and Fe^{3+} causes the deep color of magnetite, Fe_3O_4, and is a contributing factor in the color of biotite, $K(MgFe)_3(Si,Al)_4O_{10}(OH)_2$, and tourmaline, $(Na,Ca)(AlFe,Li,Mg)_3B_3Al_2(AlSi_2O_9)_3(O,OH,F)_4$. A broad and intense band of optical absorption spectra in ferrous and ferric iron garnets is attributed to charge-transfer transitions. (Taran et al. 2007) Charge transfers can also occur between ions of different chemical elements. The $Fe^{2+} \hat{=} Ti^{2+}$ charge transfer gives sapphire its blue color.

When a small amount of chromium, another transition element, is present in corundum (Al_2O_3), a red color develops and the corundum is called ruby. Both natural and synthetic rubies are colored in this manner. However, if a large amount of chromium is forced into the corundum structure, the resulting color is green. The same phenomenon occurs in chrome spinel, $Mg(Al,Cr)_2O_4$. Minor amounts of chromium produce a red color; larger amounts, green. This may be interpreted as follows: placing the chromium ion, which is larger than the aluminum ion, in the aluminum position results in a squeezing of the chromium. The strain energy from the squeezing causes the red color by absorption of the blue-green portions of the spectrum. When sufficient chromium replaces aluminum to expand and distort the structure, the strain energy changes and the absorption shifts, producing the green. Chromium is also the green coloring agent in uvarovite garnet, $Ca_2Cr_2(SiO_4)_3$, chromium muscovite, $K(Al,Cr)_2AlSi_3O_{10}(OH)_2$, and emerald, $Be_3Al_2Si_6O_{18}$.

Manganese usually lends a pink, lavender, or violet color to silicates and carbonates such as lepidolite, $K(LiAl)_3(Si,Al)_4O_{10}(OH,F)_2$; rhodonite, $MnSiO_3$; rhodochrosite, $MnCO_3$; and thulite (zoisite), $Ca_2Al_3Si_3O_{12}(OH)$. The prefix "rhodo-" is used to indicate a rose color. Manganese oxides such as manganite, $MnO(OH)$, and pyrolusite, MnO_2, however, develop a deep black color as a result of charge transfer in the manganese.

Copper minerals occur in a variety of colors. When copper is bonded to oxygen in minerals such as malachite, $Cu_2Co_3(OH)_2$, and azurite, $Cu_3(CO_3)_2(OH)_2$, the resulting colors are green and blue, respectively. The copper sulfides, however, display a variety of colors due to the interaction of the copper ion with loosely held electrons of the sulfur atoms. Different structures and different copper/sulfur ratios produce absorption in different portions of the visible spectrum. Exposure to a moist atmosphere causes oxidation and tarnishes the metallic gray of chalcocite, Cu_2S, and the metallic pink of bornite, Cu_5FeS_4, to an iridescent purple. These color changes are in response to the chemical change on the surface of the mineral. The material beneath the surface does not change color.

Some transition metal ions whose *d* orbitals are either empty or completely filled do not cause coloring. An example is Ti^{4+}, which, when in its neutral state, has two *d* electrons in the third shell. However, in becoming a +4 ion, titanium loses these two *d* electrons, along with the two *s* electrons in its fourth shell. Therefore, no electrons are present in the *d* orbitals to jump around from one *d* orbital to another. The intense absorption observed in rutile, TiO_2, is due to an excess of titanium over the Ti/O ratio of 1: 2. The excess titanium results in the development of Ti^{3+} with one electron in a *d* orbital. There may also be charge transfer between Ti^{3+} and Ti^{4+}.

Zinc minerals display a variety of colors, depending on their impurities, because zinc is not a transition element and does not contribute to color in minerals. Sphalerite, ZnS, is colorless when pure and assumes its typical honey-brown color when iron substitutes for zinc in the structure. Willemite, Zn_2SiO_4, is also colorless when pure but develops a variety of colors through chemical substitution of other elements in the structure. The following transition elements produce the color indicated in parentheses when introduced into willemite: copper (light green), iron (gray), manganese (yellow), chromium (gray), and cobalt (intense blue).

It is often difficult to determine completely the cause of color when transition metals are present, because effects arising from partially filled *d* orbitals may be masked by the strong absorbing power of charge-transfer phenomena also common in minerals containing transition metals.

The Effects of Chemical Bonding. "Free" electrons give metals their characteristic opacity (by absorption), their high reflecting power ("metallic" luster), and, in many cases, their color. Two distinct mechanisms, both dependent on the different manner in which the electrons in metals respond to different parts of the visible spectrum, are important in defining the optical properties of metals. One is *selective reflection*, and the other is *selective absorption.* Selective reflection may be the dominant mechanism in highly reflecting minerals such as metals. Gold exhibits a yellow color due to selective reflection of yellow light, not selective absorption. Light transmitted through thin gold foil is bluish green; the yellow has been reflected and the red absorbed.

Finely powdered metals show a strong general absorption and appear black due to the large number of small light traps between the particles. Light is continually reflected back and forth among the small metal grains. On each contact with a metal surface a little more light is absorbed, ultimately resulting in total absorption and extinction of the light.

The color absorption characteristics of covalently bonded minerals depend on how tightly the bonding electrons are held in the elements. In diamond these electrons are held securely, resulting in electromagnetic wave absorption only in the ultraviolet region; therefore, a diamond crystal appears colorless and transparent. In silicon the electrons are not as tightly held, so absorption occurs in the visible spectrum, and the material is colored or opaque. Tin has the same crystal structure as diamond and silicon, but the electrons are so loosely held that pure tin is opaque and has properties we normally associate with metals, although it is not a true metal.

The element carbon illustrates well the color variations due to different bond strengths in the same element. In diamond the strong bonding results in a dense, very hard mineral that is transparent and colorless. The mineral graphite, however, is also composed solely of carbon. Here a different type of bonding produces a large number of loosely bonded electrons that absorb almost the entire visible spectrum, resulting in a deep black opaque mineral (Fig. 2.9).

Pure quartz, SiO_2, is transparent and colorless. Crystals of quartz are transparent to wavelengths of electromagnetic radiation ranging all the way from 1800 to 300,000 angstrom units. However, since impurities are often included in the crystal, colored varieties of quartz are common. Some amethystine quartz owes its

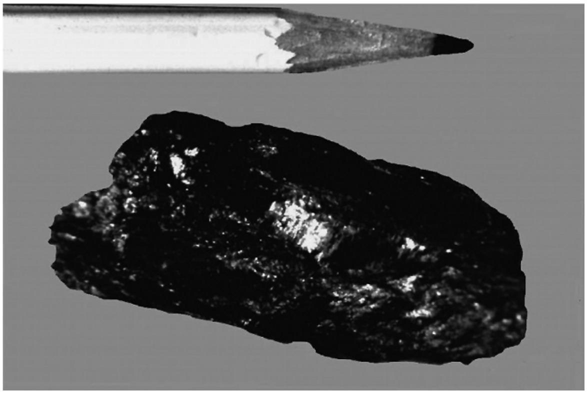


Fig. 2.9 Graphite's *deep black*, opaque appearance is the result of its atomic bonding

color to thin films of iron oxide incorporated in the surface planes of the growing crystal. It has been suggested that the lemon color of citrine quartz is produced either by **colloidally** dispersed particles of hydrous iron oxide too small to be seen with a microscope or by the presence of Fe^{3+} in noncrystalline surroundings. Amethyst may be decolored or changed to the citrine color by heating. Some blue quartz is found in igneous and metamorphic rocks. The blue color of light reflected from this quartz is due to selective scattering of the blue wavelengths by the oriented patterns of needlelike inclusions of rutile within its structure. Milky quartz owes its color to the light scattered by the large number of tiny cavities or flaws in the crystals. Small flakes or bands of mixed material often impart a distinct color to otherwise colorless or pale-colored minerals. For example, the red color of some feldspar, $KAlSi_2O_8$, is produced by the distribution of small flakes of hematite, Fe_2O_3, within the crystal.

Reflection and refraction of light from layers of dissimilar optical properties near the surface of a mineral produce the play of colors observed in some varieties of opal, $SiO_2 \cdot nH_2O$, and labradorite, $(Ca, Na)(Al, Si)AlSi_2O_8$.

Color Centers. Another mechanism that produces color in crystals is the selective absorption of light by certain imperfections in the crystal structure called *color centers.* An imperfection may be a foreign atom or ion, or it may be a "vacancy" in the structure as, for example, an excess of positive ions accompanied by "negative" vacancies. A negative vacancy would be a site where a negative ion belonged but was missing. Such a negative vacancy may be filled by an electron that has become trapped there through displacement from its normal position by bombardment with X-rays or other high-energy particles.

The energy of an electron trapped in a negative vacancy may be the proper magnitude to absorb light; this energy will depend on the environment of the site in which the electron is located. When a crystal is irradiated with white light, any photon in this light with the appropriate amount of energy will be absorbed by the electron and excite it to jump to a higher energy state. An induced color center is usually easily bleached by exposure to strong light or by heating, since supplying enough energy will release the electron from the color center.

Impurities in a crystal may cause color by:

1. acting as direct absorbers of a portion of the visible spectrum,
2. straining the structure sufficiently to produce imperfections if the impurity is a larger ion than the normal ion, or
3. promoting positive or negative vacancies allowing for color centers if the impurity is an ion of different charge.

The so-called colloidal colors result from the inclusion of colloid-sized impurities in solid material. Glass manufacturers have long added colloidal gold, copper, cadmium, and selenium to glass for color effects. These colloidal particles promote color by direct absorption, *selective scattering* (removing part of the optical spectrum by scattering and thus destroying some colors), and the development of *strain imperfections* (irregularities in the structure similar to impurity or vacancy imperfections).

Crystals of the mineral fluorite, CaF_2, commonly exhibit a variety of colors; many, if not most, of these are caused by color centers. Transparent and clear fluorite specimens can be colored blue by radium irradiation. Undoubtedly, the development of imperfections and electron traps by the bombarding radiation imparts new light-absorbing properties to this mineral.

Some fluorite colors have been correlated with the size of the color centers. Small centers develop green, medium-sized centers develop blue, and larger centers produce a violet color. Why? The size of the electron trap or color center is related to the amount of energy holding the electron in the trap. Therefore, since each wavelength of light is associated with a different energy, the size of the color center will control the wavelength absorbed. One portion of the spectrum will have energy just equal to the amount required to cause an electron jump from the color center.

Many colors in minerals are the result of exposure to high-energy radiation from the widespread occurrence of naturally radioactive isotopes of uranium, thorium, and potassium. This radiation damages the structure and may lead to the development of color centers.

In some crystals color centers seem to be stable indefinitely; in others, the centers are unstable. Apparently, impurities help stabilize color centers. Color induced by the formation of color centers may change with time as the electronic environment of the color center is altered. The violet color of some natural fluorites may be a result of radioactive bombardment of blue fluorite.

Not all the colors observed in fluorite crystals are due to the development of color centers. Incorporation of transition metals or rare earths into a fluorite structure in place of some of the calcium will impart a color to the specimen. Lanthanides in fluorite usually give rise to a yellow color. Small amounts of Mn^{4+} will produce a violet, and Mn^{3+}, a pink fluorite. Most green fluorite contains ferrous iron, Fe^{2+}. Many blue fluorites contain a small quantity of Fe^{2+} plus Fe^{3+}. Is the blue color due to these impurities, or has an earlier irradiation produced blue color centers? Probably, the best test is to see if strong light or heat will bleach out the color by releasing electrons from traps. If so, the specimen probably contains color centers.

Halite is common table salt (sodium chloride), the name comes from the Greek for salt. It is normally colorless and transparent to light over a wide range of wavelengths. This transparency ends, however, in the ultraviolet at about 2000 angstrom units. Radiation with wavelengths shorter than this has sufficient energy to excite electrons in the crystal to higher energy states. A strongly irradiated halite crystal turns yellow, but exposure to the radiation of sunlight turns it blue. This blue is not easily bleached out but can be removed by heating. Many natural halite crystals that have been subjected to heavy X-ray bombardment by nearness to radioactive minerals exhibit a semi permanent blue to purplish-black color.

What is taking place in a halite crystal on an atomic scale? In a perfect sodium chloride crystal each Na^+ ion is surrounded by six Cl^- ions, and each Cl^- ion has six Na^+ ions as its nearest neighbors. However, this picture of a crystal is idealized. In nature, crystals have defects; every so often in a crystal an ion is missing. Half the missing ions will be positive ions, the other half negative, because the overall charge balance must be maintained. This type of defect that contributes to color centers is shown in Fig. 2.10. Some of the negative vacancies in the halite crystal that indicate a missing chloride ion may trap an electron that has been agitated by strong X-rays from outside the crystal. Such trapped electrons form color centers. When a halite crystal containing these trapped electron color centers is exposed to visible light the electron is excited and jumps from the vacancy in which it was trapped, thus destroying the color. Celestite, $SrSO_4$, is commonly blue, a color resulting from natural radioactive bombardment. Pure celestite, however, resists artificial coloring by irradiation. Impure celestite with some sodium ions (Na^+) substituting for strontium ions (Sr^{2+}) will develop radiation-induced colors. Every two sodium ions substituted in the structure may lead to one SO_4^{2-} vacancy that could become a color center electron trap. Other materials develop colors in response to different types of radiation. Colorless glass bottles usually become pink or violet

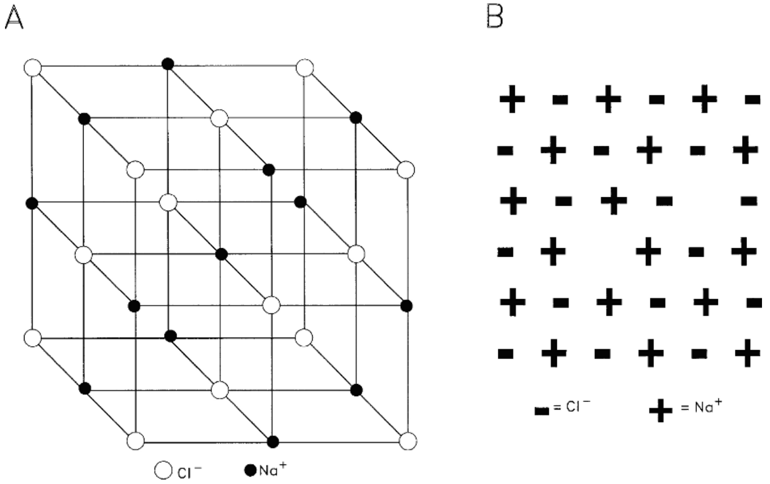


Fig. 2.10 **A** Structure of halite, NaCl. **B** Vacancies in halite crystals

from long exposure to the sun's radiation. In other materials, including halite, the sun's rays may have a bleaching effect. In each case, electrons are excited to jump to a different position by the energy contained in a given wavelength of electromagnetic radiation.

Band Theory in Metals. Unlike other causes of color which originate in the electronic structure of atoms or in crystal defects, the color of metals can be attributed to what is called band theory. In metals like gold, copper, and silver, and in alloys like brass, each metal atom contributes its outer electrons to a joint pool. These electrons can move freely throughout the metal, hence metals are good conductors of electricity and heat. These free electrons at the surface of a metal also give it the characteristic luster and high reflectivity. One aspect of this "sea of electrons" is that light cannot pass readily through the metal, so it is opaque.

Pleochroism is the characteristic of a mineral to produce different colors in different crystallographic directions. Alexandrite (a variety of chrysoberyl), when rotated, can exhibit red, orange, yellow, and green coloration. Amethyst has a weak dichromism, ranging from purple to gray-purple.

Reflectivity, Luster, and Luminescence. Reflectivity is a precise measure of the quantity of light reflected from a surface, usually recorded as a percentage of the incident light of a given wavelength that is reflected. Reflectivity varies with (1) the angle of refraction of the light as it enters the mineral, and (2) the absorption. The governing factor is absorption, since any light absorbed cannot be reflected. Reflectivity of minerals ranges from less than 5% (ice) to approximately 95% (native silver). Most common minerals have a reflectivity of less than 25%. Some light that we think of as purely reflected may be made up of rays that have traveled extensively in a mineral before returning to the air. A good example is snow. The small six-sided snow or ice crystals are minerals with a definite crystal structure. When light falls on a layer of snow, only 3 or 4% is reflected directly, but the random arrangement of billions of tiny crystal faces causes the reflections to be returned in a great variety of directions. Most of the light is refracted into the crystals and travels through them until it strikes their lower faces. The greater part will then be refracted deeper into the snow, but the angle made by the light with the lower faces of many snow crystals will cause reflection back into the mineral and upward toward the air. Light striking the billions of tiny, randomly arranged snow crystals bounces back and forth and in and out of the individual crystals, with most of it finally returning to the air. This gives the snow an appearance of high reflectivity. A thin layer of snow will not appear as white as a thicker layer because in the thin layer more of the light will escape into the ground rather than return and contribute to the twinkling effect.

Luster has been described historically in terms indicating the similarity of mineral luster to the luster of other common objects. A "pearly" luster simulates mother-of-pearl. The luster of glass is described as "vitreous"; "adamantine" luster comes from the Greek word for diamond. Most metals have the typical "metallic" luster.

The property we call luster is related to the manner and intensity of reflection of light from surface and near-surface atomic layers in a mineral. Some minerals have been named on the basis of luster. Galena (PbS) means “lead glance”. The nature of this optical property is determined by four factors:

1. chemical composition,
2. type of chemical bond (ionic, covalent, metallic),
3. smoothness of surface, and
4. size of the reflecting grains.

A reduction in the smoothness of the surface and a reduction in grain size are really the same, since both give smaller plane reflecting surfaces.

Considering the luster of minerals having reasonably smooth surfaces allows luster to be correlated with chemical composition and type of bonding. Ionic, covalent, and metallic bonds each provide a distinctly different type of electronic interaction with light waves. Many minerals, however, appear to have a combination of ionic and covalent, or of covalent and metallic bonds.

Minerals falling in the ionic-covalent group usually have a luster that is vitreous (at the ionic end) to adamantine (at the covalent end), and a comparatively low index of refraction (ratio of the sine of the angle of incidence to the sine of the angle of refraction) at the ionic end and a high index at the covalent end. In general, the more covalent the bond, the greater the absorption and the greater the index of refraction.

Covalent, adamantine minerals are often compounds combining an element that is a certain number of places to the left of the Group IV elements (C, Si, Ge, Sn) in the Periodic Table (Fig. 2.8) with an element an equal number of places to the right of Group IV. For example: sphalerite, ZnS, cinnabar, HgS, and greenockite, CdS.

Those minerals with covalent-metallic bonds contain transition elements with *d* orbital electrons or heavy metals with *s* orbital electrons not involved in bonding (e.g., lead). The electronic field of such minerals strongly interferes with the passage of light, and absorption is correspondingly large. The opacity and refractive index in this group depend on the number of loosely bonded electrons or weakly overlapping orbitals. A greater number of loosely held electrons results in a more metallic luster and a greater opacity to light. Opaque minerals have a metallic, black, or at least strongly colored streak (powder of the mineral on a porcelain plate), whereas transparent minerals usually have a white or weakly colored streak.

Whether or not a mineral has a metallic luster depends on the amount of energy necessary to remove an electron from the metal ion and allow it to become a “free” electron. If energy greater than that of visible light is required, the mineral has a luster that is not metallic; if smaller, it has a metallic luster.

Luminescence is a glow some minerals exhibit when they are heated or exposed to light rays. A mineral is said to *fluoresce* if it is luminescent only during the period of thermal or ultraviolet excitation and to *phosphoresce* if the luminescence continues for some time after the excitation has ceased.

Luminescence is illustrated in Fig. 2.11 by picturing the energy changes attending the absorption and emission of radiation. Each atom or molecule begins with its electrons in a stable or ground state, G. Fluorescence may be considered as

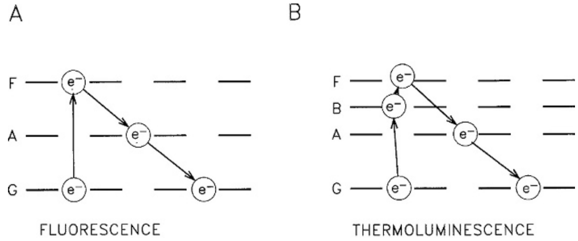


Fig. 2.11 **A** Fluorescence. **B** Thermoluminescence

absorption of radiation moving the electron energy level, F, followed by a drop of the electron to a lower energy state, A, by radiating with a wavelength longer than the stimulating radiation. In practice, fluorescence usually involves the absorption of radiation in the invisible ultraviolet portion of the electromagnetic spectrum, with the simultaneous emission of radiation of a longer wavelength in the region of visible light. The word "fluorescence" was first suggested to describe this mechanism in the brilliant blue luminescence of many specimens of fluorite found in England. The blue fluorescence in fluorites is caused by the lanthanide elements. They fluoresce by electron transitions involving unfilled *f* orbitals. Probably, no other mineral shows so many different fluorescent hues as fluorite.

As with some other light absorption phenomena, fluorescence is due to the presence of foreign ions acting as absorbers. In some minerals the activator or foreign ion is known. Manganese (+2) is the cause of fluorescence in calcite, $CaCO_3$, and willemite, Zn_2SiO_4; lead and molybdenum generate fluorescence in scheelite, $CaWO_4$. In some instances, a special combination of foreign ions is needed. The bright red fluorescence of halite from California dry lake deposits and from a salt spring in Idaho is due to cooperative activation by minute amounts of manganese and lead. Alone, neither element will generate fluorescence in halite. Apparently, Pb^{2+} acts as an absorber, Mn^{2+} as an emitter.

There are few minerals of which every specimen is fluorescent. Most minerals, however, have at least one occurrence of fluorescence when activator ions are incorporated into the crystal during its formation, producing fluorescence when it is exposed to radiation at one or more wavelengths. Fluorescent specimens of halite; gypsum, $CaSO_4{\cdot}2H_2O$; barite, $BaSO_4$; apatite, $Ca_5(PO_4)_3(F,Cl)$; and leucite, $KAlSi_2O_6$, have been found. The most interesting fluorescent mineral is hackmanite, $Na_4(S,Cl)Si_3Al_3O_{12}$, which changes color under the influence of different wavelengths of light. A purplish-pink when freshly exposed, hackmanite bleaches rapidly in sunlight, but the color returns when the strong light is removed. With ultraviolet stimulation, the mineral becomes an intense pink or purple. The source of these color changes in hackmanite is thought to be the chemical substitution of S^{2-} for Cl^-, resulting in the development of color centers.

In a few minerals the color is not a result of electronic properties of transition metals. For example, in lazurite (the main component of lapis lazuli), the sulfur atoms are in S_3^- groups. Transitions among the atoms in this grouping produce the deep-blue color.

The fluorescence characteristics of a mineral obtained in one locality will generally not be identical with those of the same mineral from other localities. Minor changes in the quantity or type of activator ion incorporated in the mineral structure will produce different fluorescent properties from locality to locality.

Chermette (1985), Fritsch (1985), and Fritsch and Rossman (1987, 1988 a, b) have presented extensive reviews of the physical and chemical basis for mineral color. Lehmann and Bambauer (1973) and Rossman (1994) explain the basis of the color in silvery minerals, particularly tin.

Chapter 3
Exploitation of Mineral and Rock Raw Materials

3.1 Introduction

Mineral deposits and rock types are unevenly distributed throughout the world and throughout the countries where they occur. To overcome this uneven distribution, trade or exchange began early in human society.

Those who exploited rock and mineral deposits in the ancient world were limited to extracting material from surface or near-surface deposits. The nature and quality of an exploitable deposit reside ultimately in the kind, amount, and properties of the minerals and rocks that comprise the deposit as well as the ease with which the desired material can be extracted.

The primary literature related to recovery/extraction of mineral raw materials in antiquity is very limited. Wilsdorf (1952) and Weisgerber (1976) have studied Corinthian clay tablets and vases for displays of mining and metallurgy; apparently only clay mining and ore smelting are depicted. R.J. Forbes (1963) *Studies in Ancient Technology* Volume VII is one of the major books (now quite dated) concerning ancient rock and mineral utilization. This volume has three long chapters: the first covers ancient geology, the second covers ancient mining and quarrying, and the third covers ancient mining techniques. A short chronological bibliography of ancient authors on geology and mining is also included. Williams and Heizer (1965) present a lengthy description of rock types and sources of stone used in prehistoric Mesoamerican sites. These authors cover early work on obsidian and the first efforts to understand the geologic context and sources of the rocks used in Olmec monuments in the area of the Gulf of Campeche.

Many individual rocks and minerals covered (and some not covered) in this present volume are discussed by Rosenfeld (1965). However, she allocates much of her short book to fundamentals such as crystallography and crystal chemistry in place of adequate references to specific cases of exploitation and utilization. The outdated but exceptional works of Oliver Davies (e.g., 1935 on Roman mines in Europe) need to be mentioned in any work on the ancient use of mineral raw materials. Finally, Kukal et al. (1989) examine many aspects of the prehistoric and historic relations between humans and their use of stones. Their book utilizes many illustrations to show ornaments, implements, weapons, dwellings, and temples over a long expanse of time.

G. Rapp, *Archaeomineralogy*, 2nd ed., Natural Science in Archaeology,
DOI 10.1007/978-3-540-78594-1_3,

Problems with nomenclature – establishing which ancient rock and mineral names can be correlated with modern usage – extend beyond puzzling about Pliny's terminology. Feldman (1973) has provided some correlations and ethnohistoric data on rock and mineral names used in studies of ancient Mesoamerica. Some names such as basalt, syenite, porphyry, **ophiolite**, and alabaster have their origins in ancient Egypt. Basalt appears to have the oldest roots, which can be traced back to a Pharaonic rock name in use as early as 2000 BCE. For a discussion of these name origins, see Harrell (1995).

3.2 Rock Classification and Properties

A rock is an aggregate of one or more specific minerals that occurs commonly enough to be given a name (e.g., granite, sandstone). Rocks are often referred to as "stone", a word that has many meanings. Within the archaeomineralogical context the usage should be restricted to "building stone" and "gemstone", but this book uses the word stone in the sense of each original author when referring to ancient or other texts that use the term "stone" whether or not the rock or mineral type is known.

The three major rock types are *igneous* (from the Latin *ignarious* "belonging to fire"), those that formed from molten **magma**; *sedimentary*, those formed from the consolidation of deposited **clastic** particles or formed by precipitation from solution; and *metamorphic* (from the Greek for *change of form*), those formed by major alteration of preexisting rocks by the action of high temperature and pressure.

Naming of rock types is based on component minerals (reflecting the chemical composition) and texture. In the field, it may be difficult to positively identify the component minerals, especially in fine-grained rocks, so names are generalized. When rock specimens are available for laboratory analyses, petrography can be used for positive identification and more specific names can be assigned.

The relative proportions of the constituent minerals in a rock determine its two most readily perceived properties – color and density. In igneous rocks the light-colored (high silica) minerals are of relatively low density (mostly 2.5–2.7), and the dark-colored (low silica) minerals are significantly denser (mostly 3.0–3.6). Rocks have no specific hardness, except for monomineralic rocks. However, the hardness of any rock is influenced by the minerals that make it up. For example, rocks such as granite, composed of quartz (hardness 7) and feldspar (hardness 6), are obviously harder than marble, composed of calcite (hardness 3).

3.3 Igneous Rocks

Igneous rocks, which result from the cooling and crystallization of molten magma, are divided into two major textural categories. Those that crystallize within the earth's crust are called intrusives, and those that solidify at the surface are called extrusives.

Intrusives cool slowly, deep within the earth, providing time for the crystals to grow large. These coarse-grained igneous rocks are also termed *plutonic*, because they formed deep in the earth – the realm of the ancient underworld god Pluto. *Extrusives* cool quickly when hot magma reaches the earth's surface, leaving little time for crystals to grow. As a result, extrusive rocks are very fine-grained. These rocks are also called *volcanic*, because they are the result of volcanic eruptions, named after Vulcan, the Roman god of fire. Granite is an example of an intrusive igneous rock, and basalt is an example of an extrusive igneous rock.

The dominant chemical constituent of igneous rocks is silica (SiO_2), and the silica content is fundamental in igneous rock classification. The high-silica igneous rocks are known as *acidic* (or felsic). The low-silica rocks are known as *basic* (or mafic). (Table 3.1).

Geologic nomenclature has hundreds of names for variations in igneous rocks, but the names in Table 3.1 should suffice for most archaeological work. The difference between granite and syenite is only in the percentage of quartz, with syenite having little or no quartz. Rhyolite is the fine-grained mineralogical equivalent of granite. Basalt is the fine-grained mineralogical equivalent of gabbro. Felsite is a general term for any light-colored, fine-grained igneous rock composed chiefly of quartz and feldspar.

Visually, one of the most apparent textural properties of rocks is grain size. Many rocks are so fine-grained that individual minerals cannot be distinguished, even with a hand lens; this texture is called **aphanitic**. Many igneous rocks contain relatively large crystals in a distinctly finer-grained, or glassy, groundmass. Rocks with this texture are called *porphyritic.* The large crystals in a porphyritic rock are called *phenocrysts.* Expanding gases in lavas often form cavities called *vesicles.* When subsequently filled with secondary minerals such as chalcedony, calcite, or **zeolites**, these vesicles are called *amygdules.*

Scoria is the name applied to very dark, highly **vesicular**, sometimes glassy, rock of basaltic composition. Coal clinker has the same appearance as scoria and is sometimes also called scoria. Another natural material resembling a scoriaceous rock is found at 75 sites spanning more than 3000 years on the Cape Bathurst Peninsula, Northwest Territories, Canada. The spontaneous combustion of local organic rich shales formed this material (Le Blanc 1991). In my experience, in the eastern Mediterranean region, a blackish product from the melting of kiln walls

Table 3.1 Common igneous rocks

Igneous rocks	High silica	Intermediate silica		Low silica	
Coarse grained	Granite Syenite	Granodiorite	Monzonite	Diorite	Gabbro
Fine grained	Rhyolite Felsite Phonolite	Dacite	Latite	Andesite	Basalt and diabase
Vitreous (Glassy)	Obsidian				Scoria

under **reducing** conditions has sometimes been mistaken for **slag**. Scoria has an intermediate density, appreciably less than slag. Melted kiln lining has a very low density but is frequently vesicular.

3.3.1 Extrusive Igneous Rocks

The term *pyroclastic* refers to rocks that form as particle deposition from explosive volcanic eruptions. *Pyroclastics* are the fragmented products of volcanoes. The name comes from the Latin word *pyro,* meaning "fire" and the Greek word *klastos,* meaning "broken". The most common pyroclastic rock of interest is called **tuff**, which is well-indurated ash composed of minerals, glass, and small rock fragments. To be classified as tuff, the material must be solidified. Tuffs have a grain size generally finer than 4 mm. Another useful pyroclastic is pumice, which is a light-colored, vesicular, high-silica rock commonly of rhyolitic composition, containing glass fragments called *shards.* Pumice is often porous enough to float and has been widely used as an abrasive. Volcanic ash is made up of unsolidified particles smaller than 2 mm in size. Pumice from archaeological excavations is now almost routinely traced to the volcano of origin and often to a dated eruption.

The Romans discovered that a finely ground mixture of lime and pumice or volcanic ash would make a cement that was markedly superior to lime mortar. It was strong, resisted attack by seawater, and would set under water as well as in air. The Romans mined their ash and pumice from a volcanic vent near the town of Pozzuoli, near Naples, and this cement came to be known as pozzolana (see Chap. 11).

In the middle of the second millennium BCE, the Aegean island of Thera witnessed an immense volcanic cataclysm forming a caldera 83 km^2 and 350 m deep. The ash layer covering the remnants of the island is more than 30 m thick. Pumice floated all over the Aegean and the eastern Mediterranean. Ash fell on settlements in Crete and Aegean Turkey. Thera lies just north of the island of Crete, home to the mid-second millennium BCE Minoans. It is possible that the Minoan Period eruption of Thera provided the geologic source of Plato's Atlantis legend.

The first Thera Congress in 1969 and the two congresses since then have provided a major impetus for archaeomineralogical studies of pumice and ash. In 1973, Rapp et al. published their identification of pumice from the Minoan eruption of Thera, recovered from a Greek mainland archaeological excavation. Since this site lies on a high ridge, the inhabitants must have carried the pumice, found washed up on the beach, to the site. For what purpose? Perhaps this was the first use of pumice as an abrasive to clean bronze vessels. The third Thera Congress, held in 1989, was published in 1990 in three volumes. See Hardy (1990a, b) Volume 1, for the archaeological context, and Volume 2 for the geologic context of the Thera eruption.

Felsite is a general term for any fine-grained, light-colored igneous rock composed chiefly of quartz and feldspar. Rhyolite is nearly the same as felsite but is specifically the fine-grained mineralogical equivalent of granite. Artifacts of rhyolite derived from two deposits in northern New Hampshire USA have been found in

Paleoindian, Archaic, and Woodland sites in Maine, New Hampshire, Massachusetts, Vermont, and easternmost Quebec (Pollock et al. 2008).

Trachytes are fine-grained igneous rocks composed largely of alkali feldspar. In Table 3.1 trachytes would lie between rhyolite and dacite. They are the extrusive equivalent of syenite. In central Italy trachyte was used for flagstone pavements and reused in Roman city walls (Renzulli et al. 1999). In Protohistoric times trachyte from near Padua, Italy, was exploited for the manufacture of grinding tools that were used in the **karst** plateau area that extends from Italy to Slovenia and Croatia (Antonelli et al. 2004).

The name "basalt" is one of the few rock names widely familiar to non-earth scientists. It is also one of the oldest names. Typical basalt is composed of plagioclase (Ca-rich), pyroxene, magnetite, and, frequently, olivine $[(Mg,Fe)_2\ SiO_4]$. Chemically, basalt is the equivalent of gabbro. Basalts are generally fine-grained, but some are medium-grained and some are glassy.

Basalt was the major rock type utilized by the prehistoric peoples of northwestern Chihuahua, Mexico, for implements including grindstones, mauls, mortars, and pestles (Gerald 1983). The second most common rock utilized was dacite, especially for stone axes. Small, smooth dacite pebbles were used to rub the surface of ceramic vessels to a glossy finish before decoration and firing. The third most common rock used was felsite.

As in Egypt, the Olmec culture of Mesoamerica carved colossal basalt heads more than 3 m tall. For a description of some of these monuments, see Stuart (1993). Basalt was also used widely for stone tools in the Lower Rhine and Meuse valleys, in the Netherlands and Germany. In Hawaii basalt was the main raw material, and basalt axe quarries were abundant (McCoy and Gould 1977).

In eastern Sicily, the production of basalt axes was long-lived, beginning in the Neolithic and reaching a climax in the Copper and Early Bronze ages. The axes from Serra Orlando, dating from the third millennium BCE to the Hellenistic Period, were made of basalt, serpentinite, tremolite-bearing rocks, and **pyroxenite**. The **lithology** and sources of these materials are given by Leighton et al. (1989).

Basaltic Roman rotary millstones are commonly found in ancient mines and iron-making centers. The millstones from the iron-making site at Les Martys, France, have been found in slag piles dated to the first century BCE. They are of two types. One type was made of basalt imported from Agde in southern France, and the other type was made of a phonolite imported from Orvieto in central Italy (Oliva et al. 1999).

Rapa Nui (Easter Island) is a string of volcanic sea mounts composed of basalt. The majority of artifacts such as adzes and hand axes found on Rapa Nui are basalt. The Moai statues were carved from a basaltic tuff. Basalt adzes have been traced to a Neolithic production site on the Penghu Islands, lying between mainland China and Taiwan (Rolett et al. 2007).

Andesites consist essentially of plagioclase and pyroxene, but many also contain biotite and hornblende. Andesites are the most abundant volcanic rocks of island arcs and active continental margins. For example, around the Pacific Ocean, andesites predominate in the Andes, Central America, northwestern United States, Japan, Indonesia, and the northwestern Pacific islands. They are also found in Wales and in parts of the eastern Mediterranean area. Unlike basalts, andesites are often porphyritic with phenocrysts of plagioclase and mafic minerals.

Vesicular andesite and basalt are ideal for grinding grain because the vesicles maintain a rough, hard surface that lessens the quantity of rock grit that gets into the final product. It has been the author's observation that most prehistoric and later querns from the eastern Mediterranean appear to be vesicular andesite. A wide-ranging article by Williams-Thorpe and Thorpe (1993) discusses Mediterranean millstones from the Neolithic to Roman Periods. Although the article focuses on geochemical sourcing of the igneous rock raw materials, the authors present a wealth of information on lithologies and on material sources from younger volcanics in Israel, Syria, Jordan, Egypt, Greece, and Turkey. Most Mediterranean millstones are made from hard, vesicular volcanic rocks. Most of these are younger than 30 million years, because most volcanic rocks older than 30 million years that are exposed at the earth's surface have been chemically altered, becoming softer in the process. Frequently, the vesicles of these older volcanic rocks have been filled (e.g., with zeolites) making them much less suitable for grinding. Some Cypriot millstones are nonvesicular ophiolite rocks. This article contains 97 references and is a must-read for anyone interested in eastern Mediterranean millstones and grindstones.

Basalt and andesite were common millstones. The Romans used these rocks in a flour mill in southern France (Lorenz and Wolfram 2007), and they were common throughout the Empire (Peacock 1989). Roman millstones found on Sardinia were mostly composed of grey vesicular lavas of basic to intermediate composition (basalts and andesites) (Williams-Thorpe and Thorpe 1989).

In ancient Pergamon there are numerous examples of andesite in structural use in temples, piers, floors, and columns. Andesite was also used in the temple of Athena, fortification walls in ancient Smyrna, and in the bouleterion and the gymnasium at ancient Assos.

Andesite was used widely as the raw material for axes in the Andean region of South America. In North America, a black glassy andesite that outcrops on San Antonio Mountain in New Mexico was used to make projectile points, knives, scrapers, and a large (24 × 6.5 × 3 cm) implement that may have been a hoe (Bryan and Butler 1940). This andesite, which broke with a smooth conchoidal fracture, was composed of plagioclase, augite, hypersthene (a pyroxene) phenocrysts, and a little magnetite, with glass as the largest single constituent. The sourcing of andesite artifacts has been accomplished using a variety of analytical methods including x-ray fluorescence (XRF) (Jones et al. 1997).

Other important extrusive igneous rocks include latite, dacite, and rhyolite. Latites, with the same mineral composition as monzonite, are quantitatively greatly subordinate to andesites in global abundance but are widely distributed on the continents. Dacite has the mineral composition of granodiorite. Rhyolite has the mineral composition of granite. Rapid quenching of dacitic and rhyolitic magmas produces rocks that consist wholly or almost wholly of glass – either obsidian or highly vesiculated pumice. Flow structure is conspicuous in many obsidians. For a thorough discussion of obsidian, see Chap. 4.

When reading the obsidian literature or dealing with related artifacts, it is necessary to become acquainted with *ignimbrite*, a related rock type. The term ignimbrite refers to deposits from very hot pyroclastic flows, sometimes also called ash-flow tuff or welded tuff. Most have a rhyolitic or dacitic composition and contain feldspar, quartz, and biotite, along with glass. Phonolites are too low in silica to contain quartz and are frequently porphyritic. Pitchstone is a glassy volcanic rock, distinguished from obsidian by its higher water content. It occurs as minor shallow intrusions and lava flows. Archaeologists have recorded pitchstone artifacts from 101 archaeological sites in Scotland and northern England, ranging in time from possibly Paleolithic to Bronze Age. Some pitchstone artifacts have been found as far as 300 km from their source (Williams-Thorpe and Thorpe 1984).

3.3.2 Intrusive Igneous Rocks

Wedepohl (1969) has estimated the relative abundance of intrusive (coarse-grained) igneous rocks in the earth's upper crust. His estimate is that 78% are of granite, granodiorite, and quartz monzonite composition. From this we see the preponderance of high-silica over low-silica, coarse-grained rocks. Granites contain both potassium and sodium feldspars and from 20–40% quartz. Other minerals common in granites are muscovite or biotite mica and one of the amphiboles, often **hornblende**. Syenites are composed mainly of feldspars; quartz is absent or only a very minor constituent. Diorites are low-silica, medium- to coarse-grained rocks in which plagioclase is the predominant mineral with hornblende and biotite (dark mica) as the chief mafic minerals. Monzonites are characterized by near-equal amounts of potassium feldspar and plagioclase. Peridotites are high-magnesium ultramafic rocks composed of olivine or its hydration product, serpentine [$Mg_3Si_2O_5(OH)_4$]. Serpentinite is an alteration product of a mafic igneous rock. It is important in archaeomineralogy because it is soft enough to be carved, with a hardness of approximately 3.5 (see Chap. 6). The name comes from the Latin *serpens* in reference to the snake-like patterns on some serpentine rocks.

Of the high-silica, coarse-grained, quartz-rich igneous rocks, granodiorites are quantitatively the most important. Monuments and constructions composed of these rocks are less subject to atmospheric weathering than low-silica igneous rocks. It has been the author's experience that many monuments, statues, and other artifacts that are called granites are really granodiorites or sometimes diorites.

The term "granitic" is also used in a textural sense, implying that the rock is granular, i.e., like a granite. Occasionally, the term "granitic rock" is used to refer to the whole range of coarse-grained quartz/feldspar rocks. Granitic rocks are quite hard and cohesive. They were used frequently for grindstones (Fig. 3.1). Quartz monzonite was used as a construction material at many ancient sites around the Mediterranean Sea including Ephesus on the Turkish Aegean coast (Birkle and Satir 1994).

Fig. 3.1 Granite grinder, Mine Dunquash, Egyptian Eastern Desert

Granites were used as building or monumental stone in nearly every country where good outcrops occurred. Granite columns are quite common in buildings of Roman Spain. Although many local granites were quarried for buildings, many granite building stones were imported from a number of other Mediterranean region sources. Williams-Thorpe and Potts (2002) studied 152 granite columns from Spain to determine their geologic provenance. Twenty-five columns were attributed to sources in western Turkey and the Italian Islands Elba/Giglio and Sardinia.

The granites of Aberdeen are the most famous of all building stones of Scotland. The Shap granite of Cumbria, England, with pink and white feldspar phenocrysts, was sought after as finishing stone. Finland is well known for the rapakivi granite– a hornblende-biotite granite that has a texture in which large crystals of potassium feldspar are rimmed by a sodic plagioclase feldspar in a finer-grained matrix. Rapakivi is Finnish for “crumbly rock”, a name given to this rock because when exposed to the atmosphere it crumbles into smaller pieces. Rapakivi granite is the material used in the stone churches in the Middle Ages in Åland in the Gulf of Bothnia between Sweden and Finland.

In India, granites were commonly used for the lower stories of Hindu temples and in cave temples. In Neolithic South India granites formed a significant percentage of querns and grindstones (Brumm et al. 2007).

In South America the famous Inca high mountain fortress at Machu Pichu was constructed largely of granite. In Italy the “Granito del foro” of architectural historians is a distinctive granodiorite (see Table 3.1) used in important monuments in ancient Rome. It was quarried from the famous Mons Claudianus deposits in the Egyptian Eastern Desert (Peacock et al. 1994). Many other granodiorites and quartz diorites from the Eastern Desert were exploited in ancient times. Granites and related quartz diorites also have been used as grindstones in the Bronze Age of Korea, where syenites were used for axe blades (Lee et al. 2006).

Gabbros are mafic intrusive rocks composed mainly of plagioclase and augite, sometimes with olivine. Gabbros are rarely porphyritic. In Croatia, six magmatic rock provinces provided the majority of the raw materials for Neolithic tool industries. The most common rock types found at Croatian sites are locally-derived gabbros and diabases (Paunovic 2001).

The Romans maintained a major gabbro quarry in Wadi Umm Wikala early in the first millennium CE. This site, named Ophites, was the next largest quarry in the Eastern Desert of Egypt after those of Mons Claudianus and Mons Porpyrites farther north. The Romans exported gabbro from this quarry for use as columns, basins, and wall and pavement tiles in Rome, Pompeii, Herculaneum, and elsewhere. Pliny described this rock which he said was named ophites (Sidebotham et al. 2001).

Rocks of mafic composition but intermediate in grain size between gabbros and basalts are called *dolerites*, especially in Great Britain. Local dolerite was used in Mesolithic and Neolithic axes in east central Sweden (Kars et al. 1992). There was an early Neolithic axe factory using dolerite rocks at Le Pinacle, Jersey, Channel Islands (Patton 1991). Dolerite axes are the most abundant lithologic type in Brittany. Most were produced at the great axe-manufacturing center at Plus-sulien (Le Roux 1971). In North America the term *diabase* means essentially the same thing as dolerite.

Tektites are small bodies of silicate glass formed by impact melting. They are normally dumbbell, spheroid, or tear-shaped. The term tektite comes from the Greek *tektos* meaning melted. Tektites have been found on every continent but always in restricted areas.

In addition to the utilization of igneous rocks themselves, many deposits of useful minerals such as metals result during the formation of igneous rocks. Following the solidification of igneous rocks from crystallization of the magma, associated metal-rich, hot water (hydrothermal) solutions have formed important metal deposits.

3.4 Sedimentary Rocks

Sedimentary rocks form at low temperatures and pressures near the earth's surface when sediment that was deposited by water, wind, or ice becomes lithified. Chemical sedimentary rocks form by precipitation from solution. Sedimentary rocks cover roughly three-quarters of the surface of the continents. Based on stratigraphic measurements, the percentages of the common sedimentary rocks are approximately: shale 45%, sandstone 25%, limestone 20%, and other 10%. However, geochemical and other calculations based on the products of weathering of igneous and metamorphic rocks indicate that shales could comprise up to 80%.

If one compares freshly deposited sands (for example, river or beach sands) with sandstone, the differences are obvious in terms of rock strength, coherence, and porosity. The term *diagenesis* is used for the many geologic processes involved in the post-depositional alteration of sediment into sedimentary rocks. Induration by cementation of the grains is perhaps the most significant diagenetic process. Diagenesis excludes those high-temperature and/or high-pressure regimes that form metamorphic rocks. Sedimentary rocks are inherently bedded. This is frequently visible because of variations in grain size and to a lesser extent because of variations in mineralogy.

The major sedimentary rocks that are used in buildings and monuments are listed in Table 3.2.

Geologic nomenclature has hundreds of names for the varieties of common sedimentary rocks. Because variations between sedimentary types are often gradational, all classifications of sedimentary rocks are somewhat arbitrary (Table 3.3). The pebbles or boulders in conglomerate are often very hard chert or quartz. The author has marveled at the ability of prehistoric societies to dress blocks of conglomerate cutting neatly across tough chert boulders, for example, at the Lion Gate at Mycenae in southwestern Greece. At the other end of the hardness scale, soft shale was used to carve beads because shaping and drilling it was easy.

Table 3.2 Major sedimentary rocks used in building and monument stone

Sandstones	Sandstones are composed of rounded or angular sand size particles cemented together by silica, iron oxide, or calcium carbonate. Sandstones are often made up mostly of quartz; they may be well cemented and cohesive or poorly cemented and friable.
Conglomerates	Conglomerates are coarse-grained clastic rocks composed of large rounded pebbles, cobbles, or boulders set in a fine-grained matrix of sand or silt cemented by silica, iron oxide, calcium carbonate, or hardened clay.
Limestones	Limestones are composed chiefly of calcium carbonate in the form of calcite and are formed by either **detrital**, biological, or chemical processes. Many are highly fossiliferous and clearly represent ancient shell banks or coral reefs. Chalk and travertine are also limestones.
Evaporites	Evaporites are sedimentary rocks composed primarily of the more soluble minerals such as halite, gypsum, and anhydrite, that are produced from saline solutions as a result of evaporation.

Table 3.3 Classification of major sedimentary rocks

Clastic	Chemical	Biogenic
Conglomerate	Limestone	Chalk
Sandstone	Dolomite	Some carbonates
Siltstone	Chert	Chert
Shale	Gypsum	Coal
	Anhydrite	Some iron formation
	Salt (halite)	
	Some iron formation	

Clastic particles are derived from preexisting rocks and transported some distance from their origin. There are three major types of clastic sediments: carbonate, **terrigenous**, and pyroclastic. *Carbonate* clastics are usually deposited in marine waters and consist primarily of skeletal grains, **oolites**, and some carbonate sand from the continents. Terrigenous clastics are the most common and are ultimately derived from outside the basin of deposition. Silicate minerals predominate in these sediments. *Pyroclastic* particles, such as volcanic ash, are derived directly from volcanic explosions.

3.4.1 Carbonate Sedimentary Rocks

Limestones are sedimentary rocks in which the carbonate minerals calcite and dolomite make up 50% or more of the rock. The balance is usually quartz, chert, and clay. Chert is sometimes a major constituent, occurring as nodules along certain bedding planes. These nodules may coalesce to form essentially continuous beds. The average limestone contains only about 5% quartz.

The name "limestone" covers a very broad range of sedimentary rocks. All are composed chiefly of calcium carbonate, but the method of formation varies and includes chemically precipitated, biogenic, and clastic rocks. For utility as a building or monumental stone, limestones range from friable and structurally weak to dense, compact rocks of great structural strength.

Limestone tools were used by the Paleolithic inhabitants at Choukoutien, China (Movius 1948), but limestone is too soft to have been widely used as a raw material for stone tools. The Great Pyramid of Cheops at Giza was constructed of **nummulitic** limestone. All the stone for Mayan structures appears to have come from local quarries. Most of the region of Mayan civilization is underlain by limestone, thus this rock was used for their extensive rock structures. Even much of their mortar consisted of *sascab*, which was made from crushed and burnt limestone that mimicked the properties of cement.

Dolomites are those varieties of limestone where more than half of the carbonate is the mineral dolomite. The name comes from the French geologist *de Dolomieu.* In terms of archaeomineralogy, dolomites were not good candidates for sources of lime plaster. Limestones are either mostly calcite or mostly dolomite, so ancient craftspeople seeking to make lime mortar would have soon identified the appropriate source rock.

Chalk is a porous, fine-grained, white, coccolith-rich limestone, usually of Cretaceous age. The name "Cretaceous" comes from the Latin word "creta", meaning chalk; the name was applied to this geologic time period because of the extensive English chalk beds of this age. Europe‘s tallest prehistoric mound, Silbury Hill in the British isles, is built of chalk. Chalk occurs widely in northwest Europe and extends eastward to Russia. It also covers areas in central North America. It is more than 98% calcite. The silica fraction of the original deposits has frequently been diagenetically converted to flint. Ancient authors often referred to chalk. Livy reported that those who sought election whitened their togas with chalk, and Plato said wells were dug to the chalk subsoil. Plato also indicated that in shipbuilding and house construction chalk was used to draw lines (much as we do today). Strabo at least twice referred to the city of Cameirus on the island of Rhodes as white with chalk.

Complete evaporation of seawater (in basins cut off from the sea) has concentrated soluble salts such as halite in deposits of high purity. These deposits, referred to as evaporates, include a great number of minerals. However, only gypsum, anhydrite, and halite are of any importance in archaeomineralogy. Gypsum in sedimentary deposits can form almost pure layers of considerable thickness. Deposits of anhydrite and gypsum are strictly chemical deposits. These minerals are not biogenic and only rarely form clastic deposits, although beds of gypsum and anhydrite occur in many water-laid formations around the world. They are more common than halite but much less abundant than limestone. Large evaporite deposits occur in the Zechstein Basin in northern Europe.

Evaporite deposition may also occur from saline pore waters in sediments exposed on arid **supratidal** flats and in **playas**. For example, gypsum and anhydrite are currently being deposited on the south side of the Persian Gulf where the rate of evaporation is high and seawater periodically floods extensive supratidal flats. At least some ancient evaporite deposits probably originated this way. Sodium carbonate, called soda ash from the ancient practice of obtaining sodium carbonate from seaweed ash, is a related sedimentary mineral.

Travertines (“Sinter” in German) are freshwater carbonate deposits found in caves, near the mouths of springs, as hot spring deposits, and as coatings on cliffs. Impure and porous varieties are called **calcareous tufa**. The principal mineral is calcite.

3.4.2 Terrigenous Sedimentary Rocks

Sandstones constitute a group of clastic rocks whose average grain size ranges from 1/16 to 2 mm. Sandstones are made up of a mixture of mineral grains and rock fragments that are derived from the weathering and erosion of rocks of all kinds, including older sediments. Their constituent mineralogy varies widely, but quartz predominates. The average sandstone contains about 65% quartz. In addition to quartz and feldspar, large **detrital** grains of muscovite, biotite, and chlorite are common (but minor) constituents. The mineral grains are cemented predominantly by silica (chalcedony, opal, or quartz), carbonates, or iron oxides.

Sandstone varies from poorly cemented rock with microfractures and joint planes to compact **orthoquartzites** of immense strength and durability. Highly compact quartzites are about as tough a lithic material as one can find. Late Pleistocene and Holocene flaked stone artifacts from one rock shelter in the Australian desert are dominantly a low grade orthoquartzite. (Smith 2006)

In ancient Egypt, sandstone was used for foundations, pillars, walls, and even as roofing. Pharaonic stone monuments at Luxor and Karnak Temples in Luxor were made from the so-called "Nubian Sandstone" from the Gebel el-Silsila area in southwest Egypt. These sandstones are still in use for repair and replacement as the monuments have suffered damage and weathering. Although there are distinct variations in the composition and texture of these rocks they are fine-grained and composed of quartz (the main component), rock fragments, clay minerals, feldspar, mica, and **heavy minerals**.

The main building stone of India is sandstone. Sandstone pebbles have been used as stone tools, but because sandstone is less well-cemented than quartzite and more friable than most igneous rocks, it is a vastly inferior stone for such purposes.

Arkose is a sandstone with a high percentage of feldspars (25%–60%). Greywacke is a dark gray, well-indurated sedimentary rock composed of quartz, feldspar, and dark rock fragments in a compact clayey matrix. The name was first used in 1789 as a German miner's term (graue Wacke) in the Harz Mountains for barren rock containing ore veins.

Beachrock is a cemented sedimentary rock lithified in the intertidal zone. The clastic particles range from sand to gravel sizes and frequently contain artifacts, especially in this author's experience, ranging in age from modern to Bronze Age. Beachrock has been used in the construction of ancient tombs (Mistardis 1963).

Conglomerates and breccia*s* are clastic rocks whose average grain size is greater than 2 mm. In conglomerates the coarse material is rounded, whereas in breccias the coarse material is angular. A matrix of finer-grained material of essentially the same mineral composition usually occupies the interstitial spaces in conglomerates and breccias. Silcrete is a conglomerate formed by the cementing of sand and fine gravel in a **duricrust** in arid environments. A fine-grained gray silcrete formed on sandstone and quartzite ridges in central Australia provided the most common stone artifact material in that part of the country.

Radiolarite is a comparatively hard, fine-grained, consolidated sediment composed of the skeletal remains of *radiolaria,* a marine pelagic organism. In the Middle and Late Neolithic of Hungary, radiolarite was exploited as a lithic raw material (Katalin 1998). Oolites are rocks that contain rounded, concretionary grains, commonly showing concentric banding. They are so named because of their resemblance to fish roe. They range in size with a maximum of about 2 mm in diameter. The important iron ores of Lorraine and Luxembourg are oolitic.

Argillaceous rocks are fine-grained sedimentary rocks such as clays, mud-stones, and shales. All natural clayey materials contain both non-clay minerals and material larger than clay sizes. Illite is often the dominant clay mineral, with chlorites, kaolinite, and montmorillonite present in varying amounts. The clay mineral content of shales varies from about 40% to almost 100%. The other major constituent of most shales is fine-grained quartz. Organic material and calcite may also occur.

Shale (*argile* in French, *Tonschiefer* in German) is the generic term for fine-grained, clastic sedimentary rocks. They are generally laminated parallel to the bedding, due to the parallel alignment of sheet silicates such as clay minerals (see Chap. 8). Siliceous shales, as the name implies, have a markedly high silica content. The average shale has about 59% silica, and siliceous shales range up to 85% silica. In siliceous shales, carbonates are very minor or absent. The high-silica content renders these rocks amenable for use as chipped or ground stone implements. Of the many shales found in Britain only one, a bituminous oil-shale, was worked in any quantity. When freshly quarried its texture and hardness approximated those of slate, and, because of its color, if smoothed and polished with beeswax it resembled jet. This shale had intermittent use in Neolithic and Bronze ages and became the basis of an industry from the Iron Age through the Roman Period. The products included armlets, whorls, beads, finger rings, and even furniture and statues (Lawson 1976).

Claystone is an indurated clay. If it has some fissility approximately parallel to bedding, then it is also referred to as shale. An **argillite** is a rock derived from shale or siltstone that has undergone a higher degree of induration than present in shales and siltstones. The name siltstone refers to a rock whose chief constituent is silt-sized grains.

3.4.3 Pyroclastic Sedimentary Rocks

Another group of clastic rocks is derived from explosive volcanism. Sometimes these are classified as igneous rocks, but, because they are deposited as sediments on land or in the water, they should be classified with the sedimentary rocks. Fisher and Schmincke (1984) give a complete description of these pyroclastic rocks.

3.5 Metamorphic Rocks

Metamorphic rocks are formed by major alteration of preexisting rocks as the result of high temperature, high pressure, and/or chemically active fluids. Sedimentary (and some igneous) rocks undergo mineralogical and textural changes in response to the imposed conditions. The degree of metamorphism varies with conditions, and specific mineral assemblages, referred to as “metamorphic facies” are associated with specific temperature/pressure conditions.

The bulk composition of the preexisting rocks and the temperature and pressure of the metamorphism control the mineral composition of metamorphic rocks (Table 3.4). There are a variety of names in the geologic literature to account for mineralogical or textural variation within the major metamorphic rock types. It should be noted that not all quartzites are of metamorphic origin. A quartz sandstone

Table 3.4 Types of metamorphic rocks

Through high-temperature (>>) and high-pressure (>>) transformation of sedimentary rocks.
Limestone >> Marble
Sandstone >> Quartzite
Shale >> Slate >> Phyllite >> Schist >> Gneiss

that is completely cemented with silica can fracture through (rather than around) the grains, emulating metamorphic quartzites.

Contact metamorphism results from the high temperature conditions in the area surrounding an igneous intrusion. Contact metamorphism of limestone produces marble. High-temperature contact metamorphism of basalts and andesites yields dense, dark **hornfels,** which has been used widely for stone axes and tools in Australia, New Guinea, Scotland, Wales, and elsewhere (Cummins 1983).

Regional metamorphism is geographically the most extensive and mineralogically the most varied form of metamorphism. It is usually associated with large-scale crustal deformation or mountain-building. Most regionally metamorphosed rocks have a characteristic laminated (or **schistose**) structure. The slaty cleavage of slates, the planar fissility of mica schists, and the somewhat irregular foliation of quartz-feldspar schists are all the result of regional metamorphism.

Slates and phyllites are fine-grained products of even finer-grained sedimentary rocks that have undergone regional metamorphism. The major mineral constituents of these rocks are muscovite, quartz, and chlorite. Slates represent the lowest metamorphic grade. The slaty cleavage that is typical of these rocks has long been utilized to obtain stone with parallel sides. Figure 3.2 exhibits this feature in a modern slate quarry. With increasing metamorphism, slates grade into phyllites, which have a similar mineralogy, but the muscovite is large enough to impart a silky sheen to the surface of the cleavage. With more intense metamorphism, phyllites grade into mica schists. With increasing metamorphism, feldspar forms. The highest grade of regional metamorphism leads to the formation of gneisses, which are composed mainly of coarse quartz and feldspar.

Fig. 3.2 Slate quarry, eastern United States

A number of slate cist graves dating to the first century BCE have been found in southwest China along the Min River (Tong 1982). An interesting, if minor, example of the use of slate, as well as hornfels, is for bracers, which are archer's wrist guards. Bracers are made of fine-grained rocks and are found in many parts of Europe in Early Bronze Age burials (Woodward et al. 2006). Slate, even today, is best known as a roofing material. The use of blue slate as a roofing material in England dates back to medieval times (Jope and Dunning 1954). The hardness and cohesion properties of slate can vary widely, depending on the silica content and the degree of metamorphism. A large slate blade was found in Massachusetts. Its length was over 22 cm and it measured over 7 cm at its widest point (Smith 1945).

Metamorphism contributes to making useful rock products by forming hard and durable quartzite from friable sand. Quartzite fractures conchoidally, allowing the same workability into sharp tools as chert and obsidian. Quartzite has been more widely used for chipped and groundstone tools than is commonly recognized (Figs. 3.3 and 3.4). Lower Paleolithic artifacts, from perhaps 260,000 years ago, have been recovered from the Diring Yuriakh site on the highest terrace of the ancient course of the Lena River in central Siberia. The oldest stratigraphic unit is composed of well-rounded gravel, mainly quartzite. It is not surprising that most of the 4000 artifacts recovered from excavations are cores and flakes of quartzite. Only a few were made from diabase or other siliceous rocks. Quartzite was the rock of choice for the tools used by Woodland Period peoples of the Appalachians to quarry and shape steatite for bowls and other objects. Paleolithic people in the Sahara used Nubian sandstone, a quartzite, for tools. Quartzite was also used in Pharaonic Egypt for statues and sarcophagi.

Marble can be found in thick deposits of wide areal extent that are relatively free of cracks and easy to quarry. It takes a high polish. The chief drawback of marble is its high susceptibility to disintegration under the action of acid rain. Even without modern pollution, rain is acidic, because CO_2 dissolves in atmospheric water to create a never-ending supply of carbonic acid in rain. Marble was the preferred statuary and monumental stone of the classical world, and in Egypt it was used for vases.

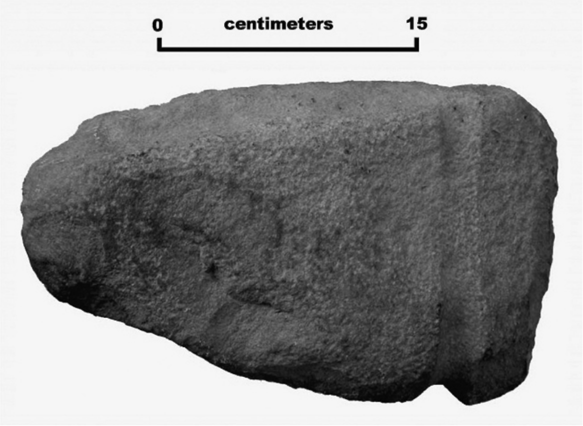


Fig. 3.3 Large hafted axe, quartzite, Boulder Lake Reservoir, St. Louis County, Minnesota, USA

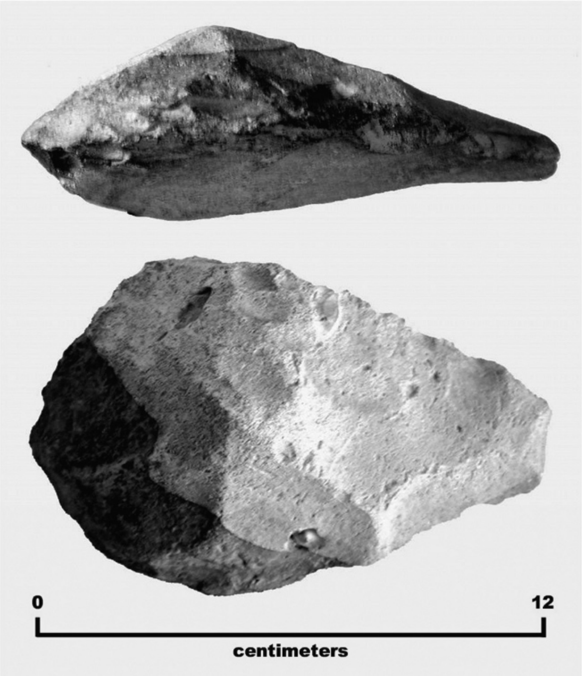


Fig. 3.4 Quartzite Acheulean hand axe

It was the favored stone for the great Moghul builders in India. Marble is plentiful in western Anatolia, Italy, Greece, and elsewhere in the Mediterranean area, so it was widely used in that region. Since the pioneering work of Craig and Craig (1972), determining the sources of Mediterranean region archaeological marbles has become a major field [see, for example, Herz 1992; Capedri and Venturelli 2004]. For an example of marble sourcing in the New World see Luke et al. (2006).

Soapstone (steatite) results from the metamorphism of mafic igneous rocks and some **dolomitic** rocks. The Predynastic and early Pharaonic Gebel el-Asr gneiss quarries of Egypt were the source of an **anorthosite** gneiss used in funerary vessels and a gabbro or diorite gneiss from which royal statues were carved, for example, the 4th Dynasty ruler Khafra.

Greenstone is a widely distributed metamorphosed basic igneous rock. In most publications the term “greenstone” refers to metamorphic rocks such as amphibolite, greenschist, or amphibolite schist. These hard and durable rocks were popular raw materials throughout the world for making stone axes. Greenstone axes have been recovered in France, Italy, Greece, Turkey, Iraq, and Syria. In northwestern Italy Neolithic polished stone axe blades were manufactured from “greenstone” eclogites, jadeites, pyroxenites, and other high pressure metamorphosed basic igneous rocks (D’Amico 2005). However, one needs to use some caution as the term is sometimes used to refer more generally to green rocks.

Numerous studies have reported a wide distribution of ancient axes in France made from Alpine metamorphic rocks (eclogites and jadeites) (Surmely et al. 2001). Eclogites are composed largely of an almandine-pyrope garnet and a sodic pyroxene and are the result of high pressure metamorphism. Jadeites, commonly consisting primarily of the pyroxene mineral jadeite, also are the result of high pressure metamorphism. From the Neolithic through the Middle Ages basic and ultrabasic metamorphic rocks of the greenschist **facies** have been quarried in the central Alps, in Italy, for use in a variety of fire-resistant objects such as stoves and cooking pots. These materials were called "pietra ollare". They had good thermal stability up to 1200°C and regular linear expansion up to about 700°C. These rocks were soft and easily workable with Mohs hardness ranging from 1 to 4. Also in Italy axes, adzes, and chisels were made from high pressure meta-**ophiolites** from the Early Neolithic to the Bronze Age (D'Amico and Starnini 2006).

Of more than 20,000 examples of stone axes recovered from prehistoric sites in Ireland, the raw material that accounted for over half was **porcellanite** (Mandal et al. 1997). Porcellanite axes are widely distributed throughout the Irish Neolithic with lesser representation in Britain. This porcellanite is the product of thermal metamorphism of a ferruginous **bauxitic** clay that was derived from weathering of basalt. For a thorough summary of the use of metamorphic and igneous rocks as stone axes and tools, see Cummins (1983).

3.6 Unconsolidated Deposits

3.6.1 Surface Deposits

Alluvium is a subaerial deposit of a river, both within the channel and beyond the banks of the channel. Coarser materials such as sands and gravels characterize channel deposits, whereas overbank deposits away from the channel are dominantly silt and clay particles (Table 3.5).

Humans have not only used alluvial terraces as habitation sites, but they have also exploited the local deposits for building materials and ceramic raw material. Sands, silts, clays, and clastic sediments in general have been useful raw materials for millennia. Silty clay is a common raw material used for pottery, tile, and other ceramics. Sands are found and recoverable from river channels, beaches, and dunes. Loose sand was used in antiquity as an abrasive and as a basic raw material for faience, glass, glaze, and brick. Sand that is composed almost exclusively of quartz has been the source of silica for the manufacture of glass since the beginning of glass technology. Pliny noted the production of glass from the sand of the Campanean littoral. Based on Pliny's text, Silvestri et al. (2006) studied experimentally the composition of the suggested raw materials and the resulting glass objects. Their studies showed that Campanian littoral sand could produce "Roman glass".

Sedimentary processes account for important concentrations of minerals in placer deposits (e.g., gold, cassiterite) and in the formation of secondary clay deposits. After the deposition of clastic or chemical sedimentary deposits, some elements are dissolved, transported, and redeposited in useful concentrations. This is the origin of many silicas (chert, chalcedony), manganese oxides, and hydrated iron oxides.

Table 3.5 Size categories of sedimentary particles

Size (mm)		Name	
	Gravel	Boulder	
256			
64		Cobble	
32		Pebble	Very large
16			Large
5			Medium
4			Small
2		Granule	
1	Sand	Very coarse sand	
1/2		Coarse sand	
1/4		Medium sand	
1/8		Fine sand	
1/16		Very fine sand	
1/32	Mud	Silt	Coarse
1/64			Medium
1/128			Fine
1/256			Very fine
1/512		Clay	Coarse
1/1024			Medium
1/2048			Fine
1/4096			Very fine

3.6.2 Placer Deposits

Placer deposits are surficial mineral deposits formed by gravity concentration of material that has weathered out of bedrock. Placers concentrate gold, cassiterite (tin oxide), other dense metallic minerals, and many precious stones (including diamond). Flowing water is the most effective separator of light from heavy materials, and the most common type of placer deposit is formed in alluvial systems where there is a break in the slope of the river course. Placer deposits form when the stream velocity is abruptly diminished and the heavier materials are dropped and concentrated in the bottom gravels. Dipping foliated rock or rocks that have irregular surfaces or "riffles" are most effective in trapping the heavy materials

One can judge what minerals will be concentrated in placer deposits by looking at their respective specific gravities as follows: quartz 2.65, feldspar 2.55–2.75, mafic silicates 2.9–3.4, corundum 4.0, magnetite 5.1, cassiterite 6.4–7.1, gold 19.3. In addition to having high density, the minerals recovered from placer deposits are those that are resistant to chemical and mechanical weathering.

Interestingly, the purity of placer gold is generally greater than the gold in the primary deposit from which it was derived. This results in part from the fact that surface waters dissolve the silver alloyed in the gold. The gold grains that collect in placer deposits vary considerably in size. Generally, large nuggets remain near the primary gold deposit and show little effect of transportation. Gold in larger stream channels is usually fine to medium-fine in size.

Placer deposits were major early sources of gold, cassiterite, and magnetite. For example, the Chalybes on the Black Sea coast exploited the magnetite found in the black placer sands as a source of iron ore. As elsewhere in the ancient world placers were mined in early China for gold and cassiterite and later for magnetite and probably for some durable precious stones.

The name placer (pronounced "plasser") may have come from the Spanish *plaza* (a place). Germans use the words *seife* or *erzseife* for placer-type mineral deposits. The British refer to placers simply as alluvial deposits. Geologists divide placers into four types: (1) *eluvial* placers develop directly from detrital deposits and therefore are found in the immediate vicinity of primary deposits; (2) *alluvial* placers, the most important type of placer deposit, develop as rivers carry the residues of decomposition downstream and the flow velocity of the water combined with the varying density and size of the mineral material leads to sorting and concentration by weight; (3) *beach* placers are formed when surf and tides sort the coastal deposits sometimes developing thick and extensive deposits of heavy minerals, and (4) *fossil* placers are geologically ancient placers that commonly are buried and lithified and later elevated to the surface. The use of the term "placer deposit" is ubiquitous in North America, but in many European descriptions they are designated simply as alluvial deposits. Some European writers designate as "placer deposits" only those that contain gold and use the term "alluvial deposits" for all others.

3.6.3 Residual Deposits

Residual deposits form from the weathering of rocks in situ. They may take the form of blanket or pocket deposits at the surface. Weathering begins the separation of the mineral constituents of a rock mass. The physically disintegrated or chemically dissolved rock material may remain in place and may be transformed by soil-forming processes or it may be subjected to removal by erosion and transportation. Deposition, which always follows erosion, results in a new combination of minerals. Sorting can lead to major concentrations of minerals or chemical elements that have the potential for exploitation.

Clay and some iron ore deposits are examples. Many iron ore deposits are residual deposits, which form when weathering occurs and the ferrous (Fe^{2+}) iron in the rock is **oxidized** to ferric (Fe^{3+}) iron. This is seen in the brown, yellow, and red colors of weathered rocks and soils. During the process of weathering, only a small portion of the iron is carried away in solution; most of the iron remains in iron oxide form, normally as limonite/goethite, $FeO(OH)$. Weathering often removes the more soluble minerals, and the ferric iron oxides and hydroxides remain as residual deposits. Such deposits are widespread chronologically and geographically in the geologic record.

These surface deposits are mostly small, usually only a few thousand tons. Many of the small surface deposits exploited by early (e.g., Roman) iron miners were these residual deposits. The iron ores of northern Spain are huge deposits of this type. Many deposits of ochre are residual deposits of goethite and hematite.

3.7 Outcrops, Mining, and Quarrying

Raw material resource studies are aided greatly by the use of maps. Geologists in all countries make many kinds of maps; geologic maps and surficial geology maps (sometimes called Quaternary maps) are the most important types for studying raw material resources. Bedrock geology maps (the kind you will get if you ask for a geologic map) present a generalized picture of the rock units mapped by the geologists. Surficial geology maps represent unconsolidated deposits above bedrock but do not include topsoil. The different map colors represent genetically and lithologically different deposits (e.g., fluvial, lacustrine, glacial, **eolian**). Soil scientists make maps of soil types at various scales. Their field methods are nearly identical to those used in geology. However, because soils exhibit more lateral variation than do geologic features or materials, an added emphasis is placed on close examination using coring and trenching. Topographic maps show contours of elevations, but they also contain considerable additional information. Surface water features (including swamps and springs), modern or abandoned quarries and mines, buildings, roads, other cultural features, and areas of vegetation are all recorded on United States Geological Survey topographic maps.

Geologists use the term *outcrop* for rock bodies that “crop out” at the surface of the earth. It seems a safe assumption that most rock and mineral products used by prehistoric cultures were gathered from outcrops. When they recognized a particularly high quality stone or ore deposit, early humans developed mining and quarrying techniques to maximize its exploitation. The miners often made use of natural vertical joints in the rock in their quarrying. Ore minerals disseminated throughout a host rock would have been difficult for early miners to exploit because of the energy required to break up the host rock. Therefore, many early mines were in vein deposits. Ore veins often followed fissures in the rock, concentrating the ore minerals and making extraction relatively easy. An example of early miners following veins is seen at the Chinflon in southern Spain (Rothenberg and Blanco-Freigeiro 1980).

Mining is the general term used for the separation of an ore from the ground, often implying underground efforts. Mining as we know it originated in the Neolithic in Europe and the Near East as a way to exploit flint deposits by digging vertical shafts and then moving outward to follow veins. However, Australian aborigines were using stone picks to retrieve chert from cave walls nearly 20,000 years ago (Gallus 1971), and humans have had the skills and tools to recover desired rock products from the earth for perhaps 100,000 years. Much of the earliest “mining” in the sense of using tools to assist in recovery of earth materials was carried out to recover pigments, particularly ochre but also specularite, manganese oxides, and other pigments that were colorful or glittered.

I have visited copper mines at Rudna Glava in Serbia where people of the Vinca culture 6500 years ago mined copper from 15-meter deep vertical shafts. The mining of copper ores/minerals in the Egyptian Sinai date to the Old Kingdom. Underground mines date back as far as 5400 years BP in Catalonia, Spain, where Neolithic miners exploited deposits for variscite ($AlPO_4 \cdot 2H_2O$) and turquoise for ornaments

(Costa et al. 1994). I also have visited underground Bronze Age copper mines in China and a first millennium BCE copper mining shaft on Cyprus. Underground flint mines that operated in England more than 5000 years ago in the Neolithic Period had shafts more than 4 m deep. Arnold and Bohor (1977) report on an underground mine in northern Yucatan dug by the Maya (about 800–1000 CE) to recover kaolinitic clays not readily available in the region.

Prehistoric northern Mexico had many mining districts. The earliest mining began in the Formative Period and targeted cinnabar. The largest and most varied mining complex in Mesoamerica was that near Chalchihuites, Zacatecas, Mexico. The Chalchihuites area had about 800 individual mines, the largest of which had interior chambers and tunnels stretching for more than 3 km. Mining here probably began somewhere between 200–500 CE and reached its peak before 800 CE. The minerals exploited were malachite, azurite, cinnabar, limonite, hematite, a weathered chert, and pyrite (Weigand 1994). The organization of the mining and the role of Teotihuacan at Chalchihuites are discussed at length in Schiavetti (1996).

It is not generally appreciated how many different gems and ornamental stones the indigenous peoples mined in the New World. Ball (1941) discusses the following: gems – diamond in Minas Gerais, Brazil; corundum (ruby and sapphire); emerald in Columbia, Venezuela, Ecuador, Bolivia, Peru, Brazil, and Panama; beryl by the Aztecs; tourmaline in California; turquoise, especially by the Pueblo Indians; garnet, also by the Pueblos; olivine by the Navajos; lapis lazuli in Peru, Bolivia, Ecuador, and Chile; sodalite in Peru, Bolivia, Ecuador, and Argentina; lazulite in Peru and Bolivia; fire opal by the Aztecs; the quartz gems amethyst, rock crystal, agate, jasper, chalcedony, and chrysoprase, all the way from Canada to Argentina; jade broadly from Canada to Brazil; actinolite (for axes) by the Hopi and the Zuni; pectolite in British Columbia and Alaska; serpentine by practically all the indigenous peoples; magnesite in California and British Columbia; galena in many localities in Canada and the United States; alabaster broadly where available from Canada to Argentina; hematite was mined across the Americas from Canada to Argentina; smithsonite in Peru; atacamite and brochantite in Chile, Peru, and Argentina; chrysocolla in South America; pyrite throughout the Americas wherever available; jet, widely in North America; mica, from Canada to Argentina; labradorite by the Eskimos; sunstone (andesine) in Arizona; moonstone in Mexico; amazonstone by the Aztecs, Mayas, and others; slate in British Columbia; variscite by the Pueblo people; calamine in Mexico; fluorite in the United States, Mexico, Bolivia, and Peru; amber in Mexico, United States, Canada, Peru, and Bolivia; steatite broadly across North and South America; catlinite in the United States; obsidian where it outcrops; and gypsum by the Eskimos and others from Canada to Argentina.

Often the most abundant evidence of early mining is the distinctive stone hammers left behind. Grooved hammers are known from Rudna Glava (observed by the author) in Serbia (Jovanovic 1982), Chinflon in southern Spain (Rothenberg and Blanco-Freijeiro 1980), the Mitterberg in Austria (Pittioni 1951), Chuquicamata, Chile (Weisgerber 1992), and prehistoric native copper pits observed by the author in the Lake Superior region. In some cases the evidence of ancient mining is limited to waste dumps. The surrounding (waste) rock in metal mining is called country rock or **gangue**. This material was routinely discarded at the mining site to prevent the major expenditure of energy required in transporting it to smelting or other metal-processing sites.

A worrying problem in Old World prehistoric metallurgy has been the dearth of copper slag dumps from the Bronze Age. Copper smelting generates large quantities of slag – a waste product. Perhaps later historic societies re-smelted or comminuted some of the earlier slags that retained recoverable copper. Perhaps insufficient intensive archaeological surveys have been conducted to locate these mounds. Prehistoric mining of iron ores to produce metallic iron began in Anatolia about 3000 years ago and in southern Africa about 2000 years ago. Iron ores were never smelted in the New World in prehistoric times.

Mining has always affected the landscape. Knapp (1999) calls attention to the way mining affects relationships between society and the landscape. The problem on Cyprus, as elsewhere, is the difficulty of finding the evidence of prehistoric mining, then dating the evidence. In his paper, Knapp also reviews the history of the research on prehistoric copper mining on Cyprus where production was primarily from copper and copper-iron sulfides (chalcopyrite, covellite, bornite, and chalcocite) occurring in mafic and ultramafic rocks. Schmidt et al. (1999) also present data on the long-lasting effect of mining on the environment, focusing on Roman mining in Spain.

Quarrying is the term used for "open pit" mining in which a rock product is exploited without additional processing. Examples are marble and granite. For more than five millennia, massive igneous, metamorphic, and sedimentary rocks have been quarried and transported hundreds of kilometers to serve as building and monumental stone.

The quarrying of large blocks of rock for building stone was not possible until copper and bronze tools were invented for working the softer rocks such as limestone. To quarry large blocks of stone, the rock must be free of closely spaced joints, cracks, or other planes of weakness. However, some well-spaced bedding and joint planes are necessary to permit breaking into blocks with flat surfaces. Blocks of rock were quarried by isolating a block on four sides by means of trenches cut in the rock and then detaching it from below by the action of wooden wedges wetted with water. In Egypt, quarrying probably had its roots in the cutting away of limestone to make tombs. Quarries are not easily eroded or removed from the landscape, unless replaced by even larger, later quarries, so many landscapes are dotted with ancient quarries. Ericson and Purdy (1984) present a broad coverage of prehistoric quarries.

Although indigenous North American peoples made extensive use of fluvial or glacial pebbles for lithic raw materials, they also quarried bedrock. Quarrying was the recovery method of choice where large blocks were required. In Dover, England, in the Medieval Period, blue slate was quarried extensively, chiefly for roof tiles as the English sought to reduce the fire danger of thatched roofs (Born 1988). Early prehistoric quarrying used fire-setting and quenching to fracture the rock. In samples from the Kopinkallio quartz quarry in southern Finland, operated about 9000–8500 BP, Kinnunen (1993) determined the maximum temperature reached in the rock to be about 480°C.

Ancient Egyptian limestone quarries in the Nile Valley occur in six separate geologic formations. Harrell (1992) determined that thin-section petrography and X-ray fluorescence spectrometry allowed him to ascertain the geographic provenance of the limestone used in ancient Egyptian sculptures and monuments. From Chephren's quarry in the extreme south of Egypt, the third and fourth millennium BCE Egyptians exploited plagioclase feldspar and amphibole gneiss boulders that had formed by spheroidal weathering. This rock material was used to create sculptures and thousands of vessels and funerary objects. Middleton and Bradley (1989) used four separate analytical techniques to provenance three major groups of Egyptian limestone sculpture to the raw material quarry. For more on ancient Egyptian quarries see Bloxam and Heldal (2007) and Harrell (1992, 2004a). A stela over 30 m long, the largest stone monument ever quarried in the ancient world, was quarried at Axum. In China the famous ancient quarry at Lotus Hill in Guangzhou dates back more than 2000 years.

Quarrying during the Roman Period was extensive throughout the Mediterranean area. Many of these quarries can be observed today. The author has visited many Roman quarries in Tunisia where the step-ledge technique can be seen. Perhaps the most famous Roman quarries in Tunisia are those at Smitthou, west of ancient Bulla Rhegia. The rock is a Jurassic low-grade marble, a recrystallized dolomitic limestone. In contrast to the carbonate rock, the major quarry near the northern tip of the Cap Bon Peninsula, northeast of Carthage, is cut into a bioclastic sandstone. This sandstone was used extensively by the Punic inhabitants of Carthage for harbor quay walls and buildings. A comprehensive volume on quarrying technology from the Bronze Age through the Byzantine is that by Waelkens et al. (1992). This book focuses on the eastern Mediterranean, with special emphasis on marble but with some reports on other stone. This publication also includes a wealth of information on provenance determination of stone material. Fant's (1988) study is devoted to ancient marble quarrying and the related subjects of statuary and trade.

There are abundant ancient quarry sites throughout the world beginning at least 20,000 years ago. Prehistoric lithic quarries in the New World are manifested by trenches following high-grade layers and the wholesale removal of ridge faces. Heizer and Treganza (1944) present a major contribution to our knowledge of prehistoric mines and quarries in California. The extensive treatise covers pigments, silica minerals, clays, rocks (including chalk and salt), and minerals such as mica, turquoise, galena, and malachite. For a Paleoindian site in Panama see Pearson (2003). The Inca quarry of Kachiqhata is located in two giant rockfalls at the base of a cliff of granite. The Inca quarried the rockfall rather than the rock face. The Inca quarries at Rumiqolqa are situated in a volcanic outcrop of flow-banded andesite that allowed extraction of slabs. For Inca quarrying see Protzen (1985).

Chapter 4
Lithic Materials

4.1 Introduction

Archaeologists use the word lithic (from the Greek *lithos* meaning stone or rock) for materials and artifacts made from rocks or minerals. Geologic nomenclature also makes extensive use of this Greek root, e.g., in lithification (the compaction and cementation of an unconsolidated sediment into a coherent, solid rock), lithology (the description of the characteristics of a rock, such as color, mineralogy, and grain size), and lithosphere (the solid portion of the earth, as contrasted to atmosphere and hydrosphere). Geologists have used the term lithic to describe volcanic tuffs rich in fragments of volcanic rocks, as contrasted to tuffs rich in unattached crystals and glassy particles (shards). Geologists have also used the term lithic to denote sandstones that contain less than 90–95% quartz plus chert and with more rock fragments than feldspars. A broad introduction to lithic resource studies, including terminology, sampling, provenance, geologic and chemical analyses and cultural resource management aspects, is given in Church (1994). This chapter focuses on lithics as the term is used by archaeologists, i.e., primarily on materials used for tools or weapons.

The required characteristics for the best chipped stone lithics are hardness, cohesiveness (lack of brittleness), and perfect conchoidal fracture. Conchoidal fracture resembles the surface of a shell and derives its name from the Latin *concha* (Greek *cogche*) meaning "mussel."

Ground stone techniques added another dimension to tool technology. A ground and polished **celt** can chop wood better than a flaked axe. Such tools were first shaped by flaking, then ground by rubbing on a slab of gritty rock such as sandstone and finally polished by rubbing with a finer-grained rock, using a fine sand as an abrasive.

Humans learned early that some kinds of rocks were far better than others for chipping into tools. These turned out to be high-silica rocks that broke with a conchoidal fracture. Hard siliceous materials are not easily weathered away nor mechanically decomposed during erosion so many prehistoric groups gathered their chipped stone and ground stone raw materials from river gravels. Local materials recovered from a creek drainage in Texas included quartzite, chert, petrified wood and ferruginous sandstone – all tough, high silica rocks. (Furman and Amick 2005) High-silica rocks not only break conchoidally, but are also extremely resistant to

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weathering, so are found in secondary deposits, often as conveniently sized boulders. In some regions these rocks were silicified wood.

The classification of Paleolithic cultures is based chiefly on the succession of stone industries. The earliest implements are crudely chipped boulders largely of basalt (including diabase) and quartzitic chert from the Early Pleistocene of Africa. As chipped/flaked stone tool technology improved, people used separate tools for cutting meat and whittling wood. In a Paleolithic site from southern Africa (Gabel 1965), the hammerstones were quartzite and gneiss; the querns were basalt and quartzite; and the hand rubbers were quartzite, basalt, diorite, and gneiss. Limestone tools have been found from the Paleolithic of Africa. Tools of this softness cannot have remained functional very long.

Lithic resources have been used since our hominid ancestors first threw stones and made stone tools (Fig. 4.1). Vermeersch et al. (1984) identified a 33,000-year-old chert mining site in the Nile Valley. Quartz (rock crystal) lithics were recovered at Paleolithic Choukoutien in northeastern China. The ancient Greeks and Romans had specific names for a very large number of common rocks and minerals. The Greek natural scientist Theophrastus published his *On Stones* in the fourth century BCE, and the last five books of Pliny's *Natural History* (first century CE) are devoted chiefly to the consideration of lithic materials. Pliny discusses about 150 separate rock and mineral species and indicates there were many more that he did not discuss. Pliny described the many varieties of "agate" in use at that time: *iaspachates* (agate jasper), *cerachates* (chalcedony), *smaragdachates* (green agate), *haemachates* (red agate), *leucachates* (also chalcedony), and *dendrachates* (moss agate).

Many names of common rocks and minerals have come down to us from these early times. Theophrastus used alabaster, agate, amethyst, azurite, crystal (quartz), lapis lazuli, malachite, and obsidian. For a highly detailed summary of mineral and

Fig. 4.1 Since Paleolithic times humans have utilized lithic resources to make tools

rock use in ancient Egypt, see Lucas (1989). There is a vast field of archaeological lithic materials. Here, we have concentrated on those rocks and minerals that those interested in archaeomineralogy are likely to encounter in Old World and New World contexts. The initial rock material for chipped stone tools is one that will flake in a manner that allows shaping by the removal of pieces by conchoidal fracturing (Fig. 4.2). Such rock material must be highly siliceous.

A study of the lithic industries of the Early Lower Paleolithic sites of Nolhac and Soleilhac, Central Massif, France, are presented in Bracco (1991). These industries utilized granite, basalt, quartz, and flint. Field investigations of the Early Paleolithic in Africa have uncovered large numbers of spheroidal and battered spheroidal stone artifacts. There appears to have been a greater variety of rock types selected for implement manufacture than at any other time. These minerals and rocks include quartz, chert, granite, basalt, dolerite, limestone, ironstone, sandstone, quartzite, and gneiss (Willoughby 1987). Stone toolmakers utilized a very wide range of available raw material resources. The Stone Age did not end because the world ran out of rocks.

In the mid to late fourth millennium BCE in Egypt, an influx of immigrants to the city of Gerza on the Nile, east of the Faiyum Basin, developed superior carving techniques for chert (Fig. 4.3), amethyst, carnelian, malachite, and imported lapis lazuli. For nearly a thousand years of the Old Kingdom and into the 12th Dynasty of the Middle Kingdom, the Egyptians mined turquoise at the Wadi Maghara in the Sinai. From the Twelfth through the 20th Dynasty, the Egyptians mined turquoise, chrysocolla, malachite, and azurite north of Wadi Maghara.

The Maori of New Zealand used a variety of lithic materials for distinct purposes, for example, obsidian for cutting, basalt for adzing. They also utilized quartzite boulders for chipped stone implements (Jones 1984). One of the earliest lithic assemblages from Japan is that from the Szudai site, of Paleolithic (early Würm) age (Bleed 1977). These lithics were primarily rhyolite and vein quartz.

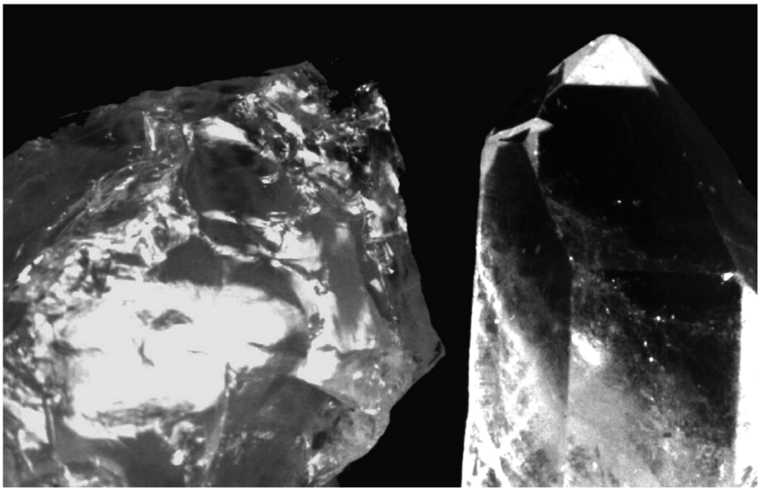

Fig. 4.2 Quartz, showing (*left*) conchoidal fracture and (*right*) crystal faces

Patay (1976) has presented a somewhat more restricted look at Chalcolithic stone tool resources in the Carpathian Basin. Takács-Biró has edited the papers from the First International Conference on Prehistoric Flint Mining and Lithic Raw Material Identification in the Carpathian Basin (1986), published by the Magyar Nemzeti Museum. In a wide-ranging book focusing on Late Neolithic flint procurement patterns of the Great Hungarian Plain, Biró (1998) covers what she considers 80 types of raw materials and discusses provenance, quality, circulation, cultural preferences, and means of identification. Major lithologic materials were obsidian, two distinct sources of flint, radiolarites, and quartzites of various qualities. Of significance in archaeomineralogy is that she shows that most of the raw materials needed analysis by X-ray spectroscopy or thin section petrography for positive lithologic identification. These analyzed materials now form a reference collection at the Hungarian National Museum in Budapest. Biró (1985) discusses the prehistoric utilization of **Neogene** rocks in the Carpathian Basin. For the western Carpathian region the great majority of geologic raw materials used during the Stone Age were of local origin. (Hovorka 2004) Obsidian and silex (high-silica) rocks, including quartzite and rhyolite, were of particular importance. Kozlowsky (1973) has documented the origin and distribution of the lithic raw materials used in the Paleolithic industries of the Carpathian region.

A word of caution about the name silex. It was used by Pliny for the mineral quartz but in recent times it has been used in France and elsewhere for flint and any high quartz rock. De Fourestier (1999) lists more thasn 50 compound mineral names [besides quartz and flint] that begin with silex: for example, silex granatus

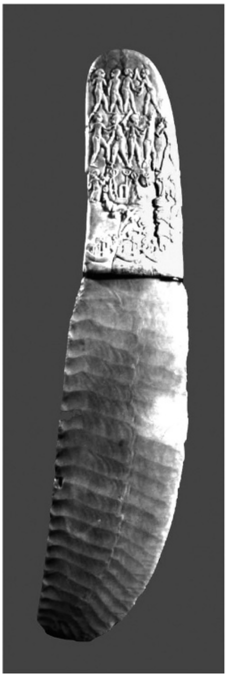

Fig. 4.3 Chert knife with carved ivory handle, Gerzean Period, Egypt

for garnet and silex resinita for obsidian. Silexite is the name for an igneous rock composed essentially of quartz [e.g. a quartz dike]. Many quartz lithics undoubtedly are a silexite because they are composed primarily of silica. Della Casa (2005) labels radiolarite and flint as silex.

At the Neolithic site of Çatal Höyük in Anatolia, none of the lithic raw materials were truly local. Volcanic and limestone rocks were brought from 100 km distant, and good obsidian from a little further afield. The nearest sources for chert and "flint" were south of the Taurus Mountains. Good "flint" is not available on the south Anatolian plateau. However, the brown, yellow, and red cherts that were available were little used (Mellaart 1967). The ceremonial "flint" dagger and similar objects from Çatal Höyük required long-distance trade or exchange.

A description of the general petrographic characteristics and possible raw material sources of the stone material at sites in the southern Urals is given by Zaykov et al. (1999). There, studies showed that various lithic types were made from chert, jasper, diabase, gabbro, **epidosites**, and dacites. All raw materials came from the region. Projectile points and drilling tools were made from a variety of high-silica rocks. Clastic rocks with grains of quartz were used as abrasives. Tools for metal foundry work were made from talcose rocks that have high heat resistance. Striking tools were produced from epidosites, high-silica sedimentary rocks, and jaspers. The distinctive prismatic jointing in the epidosites was used in the manufacture of hammers.

Nearly all excavation reports list and discuss lithic/stone artifacts. Most of the discussion concerns typology or chronology. Discussion of lithology (rock or mineral types) ranges normally from nonexistent to limited. Occasionally, greater efforts have been made. Unfortunately, the author has had a chance to check the lithologies from some eastern Mediterranean excavations where nonspecialists who apparently did not perform simple hydrochloric acid tests for marble and limestone or scratch tests for hardness made the assignments. There are also cases where discussions of the lithology are misleading. For example, Gatsov (1995), in discussing flint production in Bulgaria from the ninth to the sixth millennium BCE, says, "Local varieties of flint, like quartzite, dominate late Palaeolithic assemblages and continued in use through the Neolithic." Using flint and chert as synonymous may be understandable, but to include quartzite as a flint is certainly misleading.

In recent years, identifying the lithology of stone artifacts has been on the increase and apparently with much greater care. Of the 444 stone implements and weapons from Anyang, the last capital of China's Shang dynasty, studied by petrologists, 91% consisted of just eight lithologies, slate (61.5%), diabase (8%), marble (7%), limestone (3.6%), quartzite (3.6%), phyllite (3%), sandstone (2.5%), and jade (1.5%). Diabase and limestone were most often used for axes and adzes; slate was used for harvesting knives; weapons were made of slate and jade (Chang 1980).

In an in-depth study of the chipped stone raw materials at the well-known site of Black Mesa, Arizona, USA, Green (1985) and a geologist colleague determined the sources of the lithic materials listed below. They identified 38 types of raw materials from 29 sources. Their study illustrates the wide diversity of lithic raw materials that some prehistoric groups were able to utilize.

Baked siltstone: a local, Black Mesa white clinker, formed when fires that spread along coal seams thermally altered the siltstone. The baked siltstone occurs in layers a few centimeters thick.

Petrified wood: this material was secured from secondary deposits and from a bedrock source on the Mesa. This type of petrified wood differs considerably from that in the Petrified Forest National Monument area. The Black Mesa material is black or gray, coarse-grained, with quartz crystals and veins. It has a poor conchoidal fracture but is extremely tough, making it an ideal hammerstone material.

Sandstone: abundant on the Mesa, it was occasionally used as a chipped stone raw material. In some areas fires in coal seams **sinter** the sand grains converting the rock to a quartzite-like material.

Fused material: coal fires in some areas have caused siltstone to melt and become vesicular. It is only rarely suitable for knapping.

Quartzite and Vein Quartz: a gravel deposit along part of the western scarp of the Mesa provided cobbles and pebbles of quartz and chert. However, the small size of the chert pebbles suggests that this was not a significant source of chipped stone raw material.

Purple Conglomerate Sandstone: this stone was often used for ground stone manufacture. Its source outcrop was never located.

Silicified Siltstone: this stone apparently was imported from the Mesa Verde National Park area.

Creamy Opaque Silicified Claystone: this rock is available north of the Black Mesa area from the Morrison Formation. Prehistorically, this material comprised a significant percentage of the Black Mesa assemblage.

Gravels: within 60 km of Black Mesa, there are gravel outcrops containing chert, quartzite, petrified wood, jasper, and chalcedony.

Navajo Chert: within the larger region, there are chert-bearing limestone layers within the Navajo Sandstone Formation. The quality of the cherts varies considerably.

Owl Rock Chert and Purple-White Chert/Chalcedony: this knappable material comes from the Chinle Formation. The chert occurs in the Owl Rock member and is well represented in Black Mesa artifacts. The chalcedony sometimes grades into a purple chert.

Chinle Chert: this material comes from the Chinle Formation and is found in low frequencies on Black Mesa sites.

Volcanic Materials: obsidian and basalt were imported from considerable distances.

Oolitic and Fossiliferous Cherts: the source(s) of these easily identifiable raw materials has/have not been located.

Another site assemblage that is instructive of the spectrum of raw material from a major site is that from Spiro Mound, a Mississippian culture site along the lower Mississippi River drainage in the state of Oklahoma. The assemblage contained flint from quarries in Illinois, argillite beads, quartz as finished artifacts and natural crystals, galena nodules, mica, a serpentine spatula, hematite beads, turquoise beads, abundant native copper, and a large number of conch shells, both plain and decorated.

Although the earliest figurines date to a much earlier time, figurines become a major category of artifacts beginning with the Neolithic. Figurines were most often cult or ritual figures, vehicles of magic, representations of the deceased, or toys and items for entertainment. They were made of clay, bronze, precious metals, bone, ivory, and a variety of rocks and minerals. From the well-known Upper Paleolithic site of Mal'ta, Medvedev (1998) lists the following ornaments made from minerals: (1) small nephrite plates with natural and drilled holes, (2) pendants carved from nephrite with imitations of red deer incisors, (3) beads from pieces of schistose rock, (4) pendants made of calcite grooved at the center, and (5) bracelets made of platy coal. Most of the lithics described in Derev'anko and Medvedev's (1998) article on the Lower Paleolithic of Siberia and the Russian Far East were quartzite, but also included jasper, chalcedony, and slate.

The identification and classification of fine-grained lithics of volcanic origin present special problems for the archaeologist. Petrographic and geochemical analyses can overcome these problems and provide the data for firm identification and classification. Lithic debitage from the British Camp shell midden, San Juan Island, state of Washington, USA, had been classified for the past 100 years as basalt with a local source predicted. Petrographic and geochemical analyses have shown that these lithics are dacite rather than basalt, and that the source is the High Cascades, up to 200 km from the site (Bakewell 1996).

The number of geologists conducting research in archaeomineralogy has shown a steady increase since the middle of the twentieth century. This has been particularly true in the British Isles. Shotton and Hendry (1979) described the rise of petrography and trace-chemical analyses in studies of artifact obsidian, flint, sanukite, and soapstone. Shortly thereafter, Kemp and Harvey (1983) edited a wide-ranging book on archaeomineralogy with chapters on raw materials, building and sculptural stones, jade and obsidian artifacts, ceramics, and native metals and minerals. Seventeen chapters on the detailed petrography/petrology of stone axes from the British Isles are presented in McKlough and Cummins (1988).

The tiny drilled holes in beads and other objects during the Neolithic and later in quartz-based materials (hardness 7) have always prompted both admiration and puzzlement. Gwinnett and Gorelick (1979) undertook a series of experiments to determine the nature of ancient drilling technology. Using scanning electron microscopy, they show and correlate patterns from their experiments and from artifacts left by various drilling techniques.

I have read thousands of pages of articles on lithics recovered by archaeologists where no evidence of the lithology is given. However, Black and Wilson (1999) begin their abstract with, "Belyeas Cove on Washademoak Lake, Queens County, is the only primary bedrock source of chert in New Brunswick known to have been exploited by Native people." This is an attractive opening sentence. The authors go on to present a detailed study of the geology (14 pages) followed by two pages on the archaeology. Although they still say, as part of the summary, "Washademoak multicolored chert is a distinctive chert type associated with this source," they do not fall into the "quick to source on the basis of color" assertion that was common in North American archaeology for many decades. That the authors begin with a thorough review of the geology may be a fortunate trend. Earlier, in a comprehensive work on the mineralogy of Connecticut (USA) stone artifacts, Jackson (1940) identified flint, felsite, slate, basalt, coral, and possibly gabbro. Thus, we do have lithology data for some archaeological contexts.

It would take several volumes to discuss the chipped and ground stone industries of the world. Major volumes on regional lithic industries include:

Near East: Gebel and Kozlowski (1994)
North America: Butler and May (1984)
Central and South America: Hester and Shafer (1991)
Ural Mountains: Zaykov et al. (1999)

Some of these volumes, or chapters within volumes, do a creditable job with lithologies; others barely mention what the implements were made of.

4.2 Microcrystalline Quartz

There is much confusion in the literature concerning the origin of the terms "chert," "chalcedony," and "flint," their exact meaning, and the differences among them. In my view, chert is cryptocrystalline or microcrystalline quartz of roughly equidimensional crystals. Chalcedony is microcrystalline quartz with a fibrous structure that gives it its distinct greasy luster. I suggest the term "flint" should be reserved for the black, very dense, cohesive nodules that occur, for example, in the Cretaceous chalks of England. Readers will find, however, that the term "chert" has been applied to numerous materials. Chert and related high-silica rocks are quite widely distributed throughout the world. These high-silica rocks were among the first lithic materials utilized in the Paleolithic for scrapers, borers, adzes, axes, and projectile points. The compactness, cohesion, hardness, conchoidal fracture and durability of chert have made it the lithic material of choice across space and time. When there is not a local source exchange can provide the desired material. An example can be seen in the islands of the Kodiak Archipelago of the North Pacific where exchange with the mainland across 50 km of open water was necessary. (Fitzhugh 2004)

Few areas of lithic nomenclature are as confusing as the names for the fine-grained varieties of quartz (SiO_2). Quartz is important because rocks and minerals composed chiefly of quartz make up a large percentage of lithic artifacts. Quartz is one of the most stable of all minerals under sedimentary conditions and in the earth's surface environment. Chert has been used as a general term for fine-grained siliceous rock of chemical, biochemical, or biogenic origin. It is usually a very hard (quartz has a Mohs hardness of 7) compact material that fractures conchoidally when struck. Chert utilized as a lithic raw material has this conchoidal fracture, but many cherts have a splintery fracture. Grain size also has a significant effect on fracture properties. Chert is found in many colors: white (novaculite), gray, green, bluish, pink, red (jasper), yellow, honey-colored, brown, and black.

Fig. 4.4 Chert Levallois core from Wadi Barramiya, Egyptian Eastern Desert

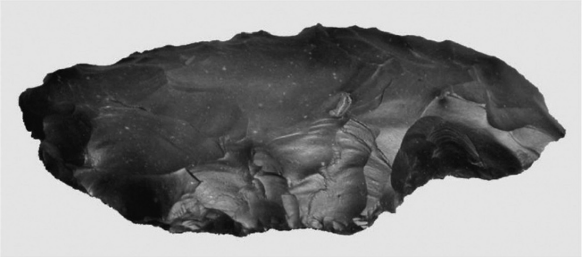

Fig. 4.5 Predynastic notched chert biface (shaft straightener?) from Bir Umm Tenedba, Egyptian Eastern Desert

Fig. 4.6 Predynastic chert blade from Tell Edfu, Upper Egypt

Chert is the most common raw material in the lithic technology of prehistoric peoples (see Figs. 4.4, 4.5, and 4.6). Many prehistoric groups learned that when raw chert was slowly heated and slowly cooled in sand, marked improvements in knapping properties resulted. Heating chert above about 375°C causes internal changes favorable for tool production. These thermal alterations increase the compressive strength, reduce the point **tensile strength**, and allow a more effective control of fracture for flaking. Purdy and Brooks (1971) suggest that this desirable alteration takes place when the melting point of impurities within the intercrystalline spaces is reached. This allows the microcrystals of quartz to be fitted closer with the impurities acting as fluxes. Rick (1978) presents an extensive experimental study of heat-altered cherts of the Lower Illinois Valley including point load tests. Point load strength is significant for the stone toolmaker, because a reduction in this characteristic means the toolmaker does not have to apply as much force to flake it.

In a highly recommended comprehensive monograph on chert and flint, archaeologist B.E. Luedtke (1992) opts for using *chert* as the general term for all rocks composed primarily of microcrystalline quartz. This book takes a slightly different approach. For example, chalcedony is distinguished from chert because it has a different fibrous structure that is easy to recognize under the petrographic microscope. However, chert often contains chalcedony.

In many limestones (and dolomites) silica is segregated into chert (or flint) nodules. These nodular masses vary from small disks a few centimeters across to much larger flat or tubular bodies. In most limestones, including the Cretaceous chalks of England and France, the nodules are elongated and concentrated parallel to certain bedding planes. Although most chert nodules are fine-grained, dense silica, some contain calcareous fossils, other carbonates, and iron oxide. Several types of fossils may be present in cherts, and carbonized plant fragments are not uncommon. The author has noted many lithics made from oolitic cherts. In some, the oolites are clearly outlined, and their nuclei are often fragments of bryozoans. Occasionally, the oolites are composed of the same cryptocrystalline silica as the cement, and they almost disappear under crossed **nicols** in a polarizing microscope. Cherts may have the texture and fracture of unglazed porcelain. In Europe important chert deposits occur in southern Scotland, south Wales, southeastern England, and the **radiolarian** cherts of the Alps and Apennines (Weisgerber 1999).

Siderite ($FeCO_3$) can occur intimately interbedded with cherty iron carbonates, clay ironstones, and iron oxides. In the Lake Superior region of North America, these rocks are thick and widespread and produce occurrences of jasper that provided good lithic material for early societies in the region. Chert occurs as bedded deposits, discontinuous lenses and nodules usually interstratified with chalk, limestone or dolomite.

A well-known American geologist in the middle 1900s, Kirk Bryan (1950), presented a broad discussion of “flint” quarries and tool manufacture. He began with a historical look, referring to the work of W.H. Holmes in the 1890s on lithic (quartzite) production. In describing a lithic quarry about 50 km northwest of Amarillo, Texas, Bryan called the chalcedony recovered from a dolomite formation a flint. Although Bryan was a geomorphologist and Quaternary geologist, this paper is largely about manufacturing technique.

Chert can be almost any color and can accommodate a wide variety of impurities that affect its workability in lithic manufacture. Carbonaceous cherts are frequently dark in color with a fair conchoidal structure and a vitreous luster. Their color is often attributed to a high content of organic matter, but this is not always true. One type of carbonaceous chert (called *silexites* in French) is very impure and develops in fossiliferous, coarse-grained clastic limestones. The very fine-grained, very dark-colored nodules found in chalk deposits represent a second type of carbonaceous chert. These are the classic flints.

Chert and related stone procurement areas and workshops are known throughout the ancient world. Some examples from Central and North America are described in Anderson (1978), Shafer and Hester (1983), Butler and May (1984), Ericson and Purdy (1984), Hester and Shafer (1984), Green (1985), Vehick (1985), Justice (1987), Sanders (1990), Arnold (1992), Gramly (1992b), Morrow et al. (1992), and Low (1996). An unusual aspect of informal flake tools at Chaco Canyon, New Mexico, USA, about 1000 CE, is that the chert was imported from 75 km away (Cameron 2001). Examples from Europe include: from Upper Paleolithic Greece, Adam (1989); from the British Isles, Clough and Cummins (1988); from Finland, Kinnunen et al. (1985), and from the late Paleolithic or early Mesolithic of Zemono, Slovenia (Petru 2005).

Cherts come in a wide variety of textures including spherulitic, **botryoidal**, and banded. Mineral impurities in cherts are largely confined to clay minerals, calcite, and hematite. Black cherts (flint) usually contain organic matter formed from the remains of soft parts of organisms. Chemical analyses are needed to identify many of the impurities. Some cherts contain recognizable fossils and a few contain feldspars and other minerals. Radiolarian cherts are relatively enriched in clay minerals, while nodular cherts contain a higher average percentage of calcite. The chief varieties of chert of interest in archaeology are listed below.

Flint: this term should be used primarily for the gray to black nodular chert found in chalk and **marly** limestone. It is very fine-grained and tough often with directional properties of value in flint knapping. Impurities are usually less than 1%, chiefly sponge spicules and calcite. The black color is derived largely from included organic matter. The best flints of Europe occur in chalk beds. In contrast to picking up flint pebbles, mining for flint undoubtedly started when toolmakers realized that flint dug from the soft chalk beds made better tools – because most eroded pebbles had been weathered by long exposure. Remains of ancient underground flint mining exist not only in England, but also in the Netherlands and in Belgium.

By the Neolithic, Europeans were sinking shafts into chalk and limestone to recover high-grade flint in Cissbury, Sussex, Grimes Graves, and Norfolk, England; at Spiennes, Belgium; at Grand Pressigny and south Auvergne, France; and in Sweden. Note that the French call flint *silex.* Lech and Lech (1984) describe research on prehistoric flint exploitation in Poland, focusing on the mine at Wierzbica "Zele." A detailed summary of research on flint and chert artifact materials from Finland is given in Kinnunen et al. (1985).

Although there was no evidence for either deep mining or quarrying flint at Grimes Graves, Norfolk, England, during the Middle Bronze Age, 210 out of 900 kg recovered can be firmly dated to this period (Longworth et al. 1991). Neolithic flint mining occurred earlier at this locality. The authors discuss the value of flint tools versus bronze tools during the Bronze Age in Great Britain. Neolithic flint miners in the British Isles exploited more than 20 high-quality deposits (Holgate 1991), sometimes digging deep shafts in the chalk. Carved chalk cups have been recovered which could have been filled with animal fat and used as lamps when working in dark recesses. The flint was fashioned into chipped stone knives and sickles as well as ground stone axes. Ashton et al. (1994) described flint assemblages (flakes, cores, and bifaces) from the Lower Paleolithic site at Barnham, Suffolk, England. Flint quarries in the Rohri Hills supplied lithic material to the Harappan city of Mohenjo-Daro (Biagi and Cremaschi 1991).

Jasper is a very common and widespread red chert; it is usually fine-grained and dense with up to 20% iron oxide. Although jasper now uniformly refers to a red chert or red chalcedony the name originally was applied to a green stone.

The name comes from the Persian *jashp*, meaning precious stone. Jasper from the Eastern Desert has been used in Egypt since Predynastic times for beads, amulets, and scarabs. Jasper drills are reported by Biswas (1996) from the first half of the fourth millennium BCE. Jasper was used extensively for the production of stone tools along the eastern seaboard of North America. Geologic outcrops occur from Nova Scotia to Virginia. Those near Allentown, Pennsylvania, were the most intensively worked in prehistoric times. King and Hatch (1997) document many artifact sites and provide chemical data for characterization. One conclusion of the authors is that most of the jasper from Reading Prong, Pennsylvania, was used locally. For approximately 4500 years, jasper from inland desert areas was widely traded over distances greater than 175 km to coastal California (Cottrell 1985).

Jasper implements from sites around Tokyo and Kobe, Japan, were traced to procurement areas up to 600 km distant (Warashina 1992). Two sources, Saruhachi and Kasengan, have long been known. In the period 300–700 CE, jasper was used abundantly for cylindrical beads, small beads, and a variety of bracelets. At Kasengan the jasper occurs in thin layers of andesite.

Novaculite is a white microgranular quartz of uniform grain size and without lamination. It is not common so it is of special archaeological importance when found as an artifact. Novaculite is white because of its relatively high content of extracrystalline water. Prehistoric miners quarried a whole ridge of novaculite in Arkansas, USA, for fine-quality, white agate-like, lithic material interbedded with coarse, unsuitable novaculite. Broken stone hammers of a dark gray syenite or brown quartzite were discarded nearby (Jenny 1891).

Chalcedony is also microcrystalline quartz. Under a microscope its texture appears as radiating fibers in bundles. The distinctive fibrous, radiating texture of chalcedony is quite visible in a thin section. The radiating fibers of chalcedony average about 0.1 mm but range up to 1.0 mm. This texture is more porous than that of chert. Chalcedony has a greasier luster than chert and lacks significant impurities, so it tends to be whitish. Chalcedony fractures parallel to the fibers to give an uneven or splintery surface, making it much less valuable than most cherts as a chipped-stone lithic. Most chalcedony may have been originally opal. It can be a major constituent of cherts.

The name chalcedony comes from Chalcedon, an ancient maritime city on the Sea of Marmara in Turkey. However, the use of this name has changed over time. The *charchedonia* (or *carcedonius*) of Pliny, brought from North Africa by way of Carthage, most likely was not chalcedony. Tripoli is a related white, gray, pink, buff, red, or yellow, highly siliceous rock composed mainly of chalcedony. It is porous and therefore light in weight.

Knife River Flint is a chalcedony named after a source in west-central North Dakota, USA, and was quarried in that area. This material was distributed quite widely over a large region in the north-central USA. Knife River Flint is brown (sometimes called “root beer” or “coffee” colored) with dull to satiny luster, fine-grained texture, and high translucency. Sometimes this material will patinate to a milky white or cream surface color. It is hard and highly siliceous, with a smooth and waxy surface, and has excellent flaking and edge-retention properties after heat treatment. Chalcedony from the Tertiary era Chadron Formation of a four-state region centered in northwestern Nebraska, USA, was used from Paleoindian to Protohistoric times over a wide geographic area to manufacture lithic tools (Hoard et al. 1992). Variants of the material, based on color and texture of the artifacts, are known from numerous sites over a wide geographic area.

Agate is a translucent cryptocrystalline variety of quartz frequently mixed with some opal. It is characterized by variegated colors in bands, cloud-like, or moss-like forms, in virtually all colors. It is found in vugs or cavities of rocks. As a cryptocrystalline variety of quartz it breaks with a conchoidal fracture and has been used for chipped stone tools (Fig. 4.7).

All these materials are chemically precipitated silica. Most cherts are derived from the silica in limestones as the chert becomes segregated as nodules or discontinuous beds. Cherts are nearly ubiquitous throughout the world. An X-ray examination by Heaney and Post (1992) of 150 specimens of fine-grained quartz varieties from around the world revealed that from 10–80% of the silica in many samples is moganite, a little-known silica poly-morph. Large amounts of moganite were prevalent in cherts from arid, alkaline environments. This could be important in provenance studies.

In North America, the increased interest in technical studies on chert and related materials has led to the discovery of many prehistoric quarries and prompted basic geologic studies on the stratigraphic and geographic distribution of cherts in limestones (see, for example, Butler and May 1984). The most famous prehistoric chert quarry in eastern North America is the Dover Quarry in Tennessee. The quarry pits cover about 2 ha. Large chert nodules and tabular pieces were made into hoes, adzes, and ceremonial objects. Ceremonial swords reached a length of 69 cm (Butler and May 1984; Gramly 1992a). The Late Plains Archaic Schmitt chert mine in the Horseshoe Hills of Montana supplied lithic material from 3100 BCE on from the chert-bearing layers of the Madison Limestone Formation. Many hammerstones used to break up the bedrock have been found at the mine site(s) (Davis 1982).

The ancient Maya exploited a large chert- and chalcedony-bearing zone in northern Belize for the production of chipped stone artifacts (Hester and Shafer 1984; Cackler et al. 1999). The chert is found as nodules in limestone. Several lithic workshops are located in this zone. The occurrence of black chert and chalcedony artifacts at many archaeological sites in Belize has been of special interest. The

Fig. 4.7 Predynastic agate blade from Wadi Bezeh, Egyptian Eastern Desert

analyses of Cackler et al. (1999) indicate that the black coloration is caused by weathering phenomena and is not indicative of geographic source.

The Romans carved vases of great beauty from a stone they called “murrha”, modern spelling “murrhine”. These were mentioned by Pliny but their mineralogical composition is unknown. It seems likely that murrha was one of the fine-grained varieties of silica such as agate or sardonyx, or possibly opal or feldspar. There were attempts to duplicate this material (or materials) in glass or porcelain. The resulting product was transparent and contained pieces of colored glass.

4.3 Other Siliceous Rocks

The term porcellanite designates high-silica rocks that are less hard, dense, and vitreous than chert. The dull aspect that causes them to resemble unglazed porcelain is due to minute pore spaces. Most porcellaneous rocks consist chiefly of a mixture of silty clay with a large amount of opaline silica. Calcite may also be present. The major siliceous rocks that have found favor as exploitable raw materials, i.e., quartz (Fig. 4.8), quartzite, opal, felsite, rhyolite, and siliceous shale/slate, are discussed in Sect. 4.3. Obsidian is so important it has a section of its own (Sect. 4.4).

4.3.1 Quartzite

There are two major types of quartzite, based on genesis. Orthoquartzite is sedimentary rock composed largely of quartz sand cemented by nearly pure silica. Metaquartzite is metamorphosed sandstone characterized by peripheral growth of recrystallized quartz. Both types fracture across the quartz grains and both fracture conchoidally, making good knapping material (Fig. 4.9). Quartzite also was used in Pharaonic Egypt for statues and sarcophagi. Nubian sandstone, a quartzite, was used by Paleolithic people in the Sahara. “Hixton Silicified Sandstone,” an ortho-

Fig. 4.8 Predynastic quartz blade from Wadi Abu Wasil, Egyptian Eastern Desert

Fig. 4.9 Quartzite biface from upper Wadi Barramiya, Egyptian Eastern Desert

quartzite with opal-chalcedony cement from western Wisconsin, USA, has been widely used in lithic tool manufacture in the western Great Lakes region (Porter 1961). A large quartzite reduction industry in east-central Mississippi is recorded by McGahey et al. (1992). Using thin-section petrography, De Boutray (1981) distinguished separate types of quartzite used by the Paleoeskimos of northern Québec, Canada. Erbright (1979) points out that quartzite is a lithic material that has been badly neglected, at least in replicative and other experimental studies.

4.3.2 Opal

Opal ($SiO_2 \cdot nH_2O$) is a sub-microcrystalline aggregate of cristobalite crystallites with some water that has a low density of 2.1. The name comes from the Greek "opallis". Opal is chemically precipitated colloidal silica and occurs in some cherts. It forms in two ways: either during a late stage in volcanic rocks, filling vesicles and fractures, or in sedimentary rocks, mostly sandstones, filling cavities or desiccation cracks. The silica is deposited from groundwater as a gel. Over time, it dehydrates and hardens. Given enough time it will completely crystallize, first to cristobalite and ultimately to quartz (both SiO_2). Much agate found today may once have been opal. Hyalite is a colorless, misty-blue, or sky-blue transparent variety of opal. It usually forms botryoidal masses as well as strange and unusual forms.

The play of colors in precious opal stems from its microscopic structure, consisting of small spheres of silica of uniform size, arranged in regular arrays. The size of the spheres is in the order of magnitude of 400–700 nm, the wavelength of visible light. The size of the spheres and the regular geometry of the arrays cause diffraction of light. Areas of the world with significant valuable opal deposits include Hungary, Mexico, Central America, western United States, Brazil, and Australia. For a thorough chronological history of the use of opal, see Eckert (1997).

4.3.3 Felsite

A general term for any fine-grained, light-colored igneous rock composed chiefly of quartz and feldspar; felsite can be very hard and cohesive and breaks with a conchoidal fracture making it valuable as a lithic tool raw material. Hermes and Ritchie (1997) developed a nondestructive method of using energy-dispersive X-Ray fluorescence spectroscopy to determine the trace-element concentrations in archaeological felsites as a guide to provenance.

4.3.4 Rhyolite/Andesite

Rhyolite is nearly the same as felsite but is specifically the volcanic finegrained mineralogical equivalent of granite. Gramly (1984) reported a rhyolite source in northern New England (USA) that was exploited for stone tools at a slow rate for more than 7000 years. Stewart (1984) detailed the prolonged and widespread use by prehistoric groups of a rhyolite from a small geographic area in the Blue Ridge province of Maryland and Pennsylvania, USA.

In western Japan, sanukite, a variety of andesite, was exploited from four districts to manufacture a variety of implements (Warashina et al. 1978). Sanukite and obsidian were imported from some distance and found at sites ranging in age from Paleolithic to the Jomon Period of Japan, as reported by Togashi and Matsumoto (1991).

4.3.5 Siliceous Shale/Slate/Schist

As with quartzite, this material fractures conchoidally. Because it is composed chiefly of silica, it has a hardness approaching 7. It was widely used in North America, especially in northern Minnesota, for projectile points and other sharp tools (Harrison et al. 1995).

Slate was a common material in some regions for ceremonial picks crafted by grinding and polishing. A center for pick production was Ohio, but picks occur throughout northeastern USA and north into Ontario, Canada (Converse 1978). Halsey (1984) has argued that these objects functioned as blades of tomahawks. In eastern Canada, slate was crafted by grinding into bayonets. Some were decorated and reached lengths of more than 30 cm (Sanger 1973). Slate has been used for projectile points and ground stone tools during the Neolithic Period in Norway and Sweden. The earliest evidence for the use of ground slate cutting and thrusting tools in Scandinavia appears about 6000 BCE (Fitzhugh 1974).

At the Magdalanean site of Gönnersdorf (ca. 13,000 BP), the occupants apparently spent considerable time making engraved plaques from schist beds located about 500 m away. Over 500 of these schist plaques have been recovered from the site (Phillips 1980).

4.4 Obsidian

Obsidian is a natural volcanic glass that is found in rich deposits around some young volcanoes. It has been used for making flaked tools since the Paleolithic. Obsidian helped several ancient civilizations develop before the onset of metal tools. Among Neolithic societies obsidian was traded widely because it had more workability and a sharper edge compared with competing materials. Obsidian was extensively available in some regions, entirely absent in others. Obsidian was such a near-perfect lithic material that it was traded over great distances. In the early Holocene a site on the northern Tibetan Plateau utilized obsidian from a source 416 km away (Brantingham and Xing 2006). This is especially surprising considering the difficulty of travel in that terrain.

The name obsidian goes back as far as Pliny who described material from Ethiopia. Recent provenance studies have shown that artifact obsidian from the Middle Stone Age of Ethiopia came from as far away as 250 km. (Negash and Shackley 2006) High-silica volcanic rocks are typically very fine-grained or glassy. The molten material from which these rocks formed is so extremely viscous that crystal growth is impeded and noncrystalline rocks often form during rapid cooling. With its conchoidal fracture, obsidian is easily worked into very sharp projectile points and other implements, so has had wide usage since prehistoric times.

Obsidian is usually black but may be gray, brown, red, or green. The fracture surface of obsidian is perfectly conchoidal. Generally, obsidian is rhyolitic in composition and contains less than 1% H_2O. The atomic arrangement of obsidian is that of a glass. Compositionally, obsidian is high in silica. Volcanic glasses form with difficulty in mafic magmas, such as those with basaltic composition, which have less silica. Only the rare *palagonite*, *sideromelane*, *tachylite*, and *hyalomelan* are obsidians with basaltic composition. *Lassenite* is related to obsidian but with a trachytic composition.

In the East African Rift Valley volcanic belt, obsidian was exploited throughout the Paleolithic (Ambrose 1998). At many sites it was the preferred material (Leakey 1931; Robertshaw 1988). Obsidian was utilized at least as far back as Upper Paleolithic times in the Near East. It was found in level C of the Shanidar Cave in Iraq and dated to approximately 30,000 BP. Obsidian has been recovered from almost every Neolithic site in the eastern Mediterranean area.

Approximately 1000 western Mediterranean sites contain obsidian, dating from the early Neolithic (6000 BCE) (Pollmann 1993). The important Lipari obsidians are discussed by Cortese et al. (1986). Figure 4.10 shows the major obsidian deposits of Europe. Neolithic sites in Anatolia are particularly rich in obsidian artifacts. In Anatolia, rich obsidian deposits were formed from volcanism in the Tertiary and the Quaternary. These deposits are present around young volcanoes such as Suphan Mountain, Nemrut Mountain, Tendurek Mountain, and Agri Mountain in East Anatolia, and Hasan Dag Mountain and Erciyas Mountain in Central Anatolia. Obsidian deposits also occur near Rize, Erzincan, Erzurum, around Bingöl, and between Bolu and Ankara. Obsidian deposits also exist in Erivan (Yerevan), Armenia, and on the island of Melos, Greece. Eastern Mediterranean obsidian was used not only for making tools, but also for mirrors and decorative goods. Figures 4.10 and 4.11 show the

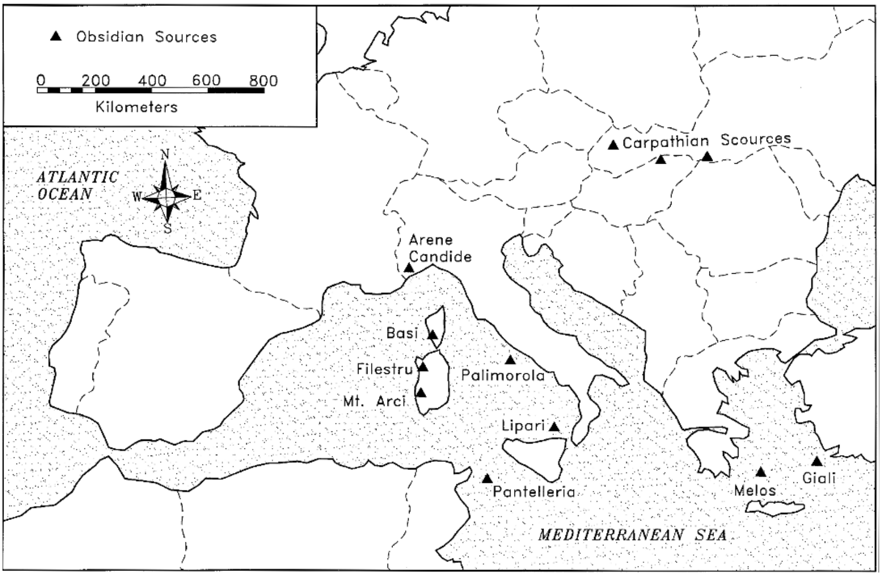

Fig. 4.10 Major obsidian deposits of Europe

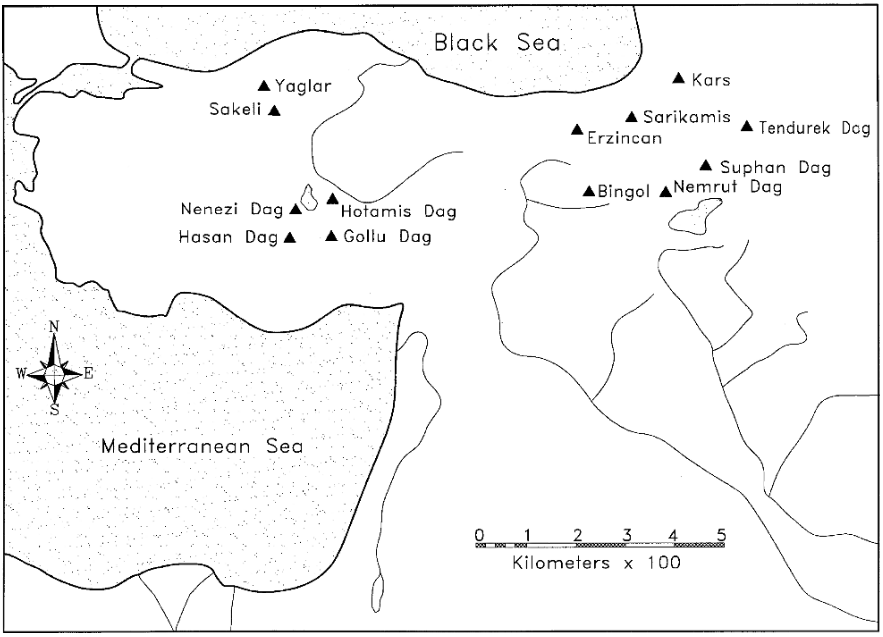

Fig. 4.11 Major obsidian deposits in Anatolia

major obsidian deposits of Europe and Anatolia, respectively. In Transcaucasia just east and northeast of Anatolia, there are major obsidian deposits at Dogubayatzit, Satanakar, Gutansar/Atis, Arteni, and in Georgia (Pernicka et al. 1996).

Obsidian was equally important in New World contexts. Indigenous miners in Central America even pursued high-quality obsidian at depth, developing underground mines. The Aztecs used obsidian extensively for projectile points, knives, razors, swords, mirrors, and ornaments. There are numerous high-grade obsidian deposits in western North America, such as Obsidian Cliff in Yellowstone National Park, Wyoming, and in the volcanic regions of Central America. The Obsidian Cliff source is one of the most famous obsidian localities in North America. This 180,000-year-old flow has been the source of obsidian for more than 10,000 years and has been widely traded. Archaeological survey has identified 59 separate quarries in the rhyolite plateau (Davis et al. 1992).

The major element composition of the Obsidian Cliff flows appears to be homogeneous, regardless of color. Hughes (1993) has investigated the trace-element variabilities in the flows. In the southwest USA, many obsidian deposits were exploited by the indigenous peoples. Figure 4.12 shows the major obsidian flows in this region. Glascock (1994) has reviewed recent work on obsidian in Mesoamerica. See also Sheets et al. (1990) for obsidian sources in southern Mesoamerica and the northern intermediate area. In South America, a quarry on the slopes of the Cotallalli volcano in the south-central Andes has supplied obsidian for a large region for at least 4500 years (Brooks et al. 1997).

The interest in obsidian and the success in provenancing archaeological obsidian have led to literally hundreds of studies since the 1960s. Some investigations have

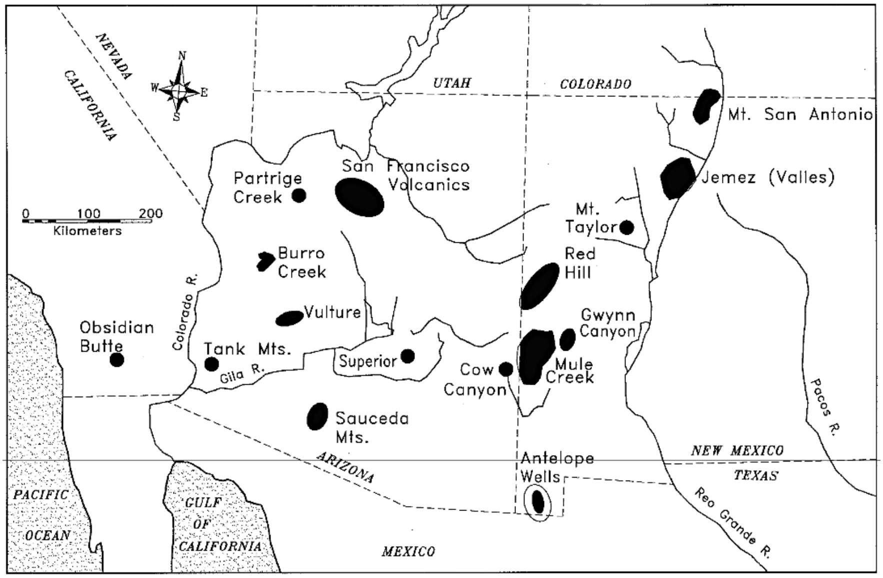

Fig. 4.12 Major obsidian deposits of the southwestern USA

focused on mapping obsidian flows, others on dating the flows, many on chemical provenancing, and some on obsidian artifacts. It would take a large volume to summarize these results. Some of the more important recent publications and the area(s) covered are: Bigazzi et al. (1992), Ecuadorian Andes; Glascock et al. (1998), Mesoamerica; Braswell et al. (1994), El Salvador; Brooks et al. (1997), southwestern Peru; Bellelli et al. (2006), northwester Patagonia (Argentina); Hughes (1993), Obsidian Cliffs, Oregon, USA; Althaus (1996), many parts of the world; Clark (1995), northwest Alaska; Fladmark (1984), British Columbia, Canada; Shackley (1995), American southwest; Davis et al. (1995), Obsidian Cliff, Wyoming USA; Pollman (1993), northwest Mediterranean region; Kardulias (1992), southern Greece; Oddone et al. (1997), Anatolia; Killikoglou et al. (1997), central Europe and the Aegean; Yellin (1995), Anatolia; Tykot (1997, 1998), Sardinia; Yellin et al. (1996), eastern Mediterranean/Anatolia; Bigazzi et al. (1994), eastern Anatolia; Ammerman et al. (1990), Italy; Hughes (1994), California, USA; Cobean et al. (1991), Mesoamerica; Randle et al. (1993), Italy and central Europe; Dahl et al. (1990), Mexico; Hughes and Lees (1991), Kansas USA; Cook (1995), Alaska; Ercan et al. (1990a, b), central Anatolia; Cauvin et al. (1992), Anatolia; Yegingil and Lunel (1991), Anatolia; Moore (1983), New Zealand; Weisler and Clague (1998), Oceanic islands of the southwest Pacific Ocean. Obsidian micro-blade tool use in Japan goes back at least to 20,000 BP in eastern Hokkaido (Sone et al. 1991).

Although it is focused on geochemical sourcing and obsidian hydration dating, there is a wealth of obsidian raw material information in the recent book edited by Shackley (1998). This volume covers progress in obsidian studies worldwide, including patterns of transport and exchange of lithic materials. The problems and methods of characterizing the large number of sites are discussed by a number of scholars. This author has never been convinced of the importance of obsidian hydration dating, but this volume successfully brings the scientific basis of this method to the fore.

4.5 Other Minerals and Rocks

Variscite is a green hydrated aluminum phosphate that was used in southwest Europe in the Neolithic and Aeneolithic for prestige objects such as collar beads up to 5 cm long. Some of the variscite was an intense emerald green. It is usually found as nodules having a hardness of 4. This material was included in what Pliny (NH 38) called “callute”. In archaeological contexts variscite beads are found with many other green beads made from steatite, jade, and serpentinite so caution is advised. (Dominguez-Bella 2004)

Picrolite, a hard, fibrous or columnar, and attractive variety of serpentine-blue rock native to southwestern Cyprus, was used for a variety of ground stone objects on Cyprus, including figurines. (Vagnetti 1991) Peltenberg (1991) suggests that the picrolite was derived from pebbles found in the Karyotis and Kouris Rivers in Cyprus. I have found picrolite pebbles in the Kouris River. (Rapp 2003) The use of picrolite dates back at least to the fourth millennium BCE.

In eastern North America (New Jersey, Pennsylvania, New York), one prehistoric group was designated the “Argillite culture” in the late 1800s, because the preponderance of lithic artifacts was made from local *argillite* rock. This group also exploited local *hornfels* sandstone and a siliceous oolite (Spier 1918). Jones (1984) presents in detail the use of "argillite" as a raw material for adze manufacturing by the Maori of South Island, New Zealand. However, as Jones reports, this use of argillite by New Zealand archaeologists is a misnomer. These "argillites" are **metasomatized** aphanitic inclusions in a serpentine-rich rock. These inclusions break with a conchoidal fracture.

The Middle Woodland Period peoples of eastern Pennsylvania (USA) made points of argillite (Turnbaugh 1970). These lithics had wide distribution but had a narrow range typologically and chronologically. This argillite was lightly metamorphosed, a little less than slate. It could be chipped into a quickly made, sharp point. The cutting edge remained sharp only temporarily. However, it could easily be rechipped. The source of this argillite includes known locations in Lebanon and Bucks Counties in Pennsylvania and near Trenton, New Jersey. Argillite was the dominant lithic material in assemblages from 18 sites in northern Tibet.

One of the principal knappable lithic materials indigenous to the Southern High Plains region of the USA is a *silicified dolomite.* This material was quarried but was also available from gravel deposits. The siliceous material is a colorful chert with some chalcedony. No more than 3% of the exposed dolomite formation is cherty, but where the chert was massive, it attracted many prehistoric miners (Wyckoff 1993).

The prehistoric peoples of Death Valley, California, quarried *basalt* for projectile points, knife blades, drills, and scrapers. Fist-sized cobbles of quartzite were utilized as hammerstones for pounding and trimming. Apparently, the basalt was too brittle for use as hammers, choppers, and the like. It should be noted that basalt was not the only material employed for smaller, chipped stonework. Chert, jasper, chalcedony, and a small amount of imported obsidian were also used in lithic production (Wallace 1962).

Igneous rocks have long been used as everything from hand axes (Fig. 4.13) to hammerstones (Figs. 4.14, 4.15, and 4.16). Hammerstones are used to batter other materials, so they need to be made of hard, durable, and relatively non-brittle rock.

Heavy stones, of course, make good anchors. Humans utilized available rock early in maritime pursuits. McCaslin (1980) reviews the use of stone anchors during the second millennium BCE in the eastern Mediterranean area, specifically Cyprus, southern Anatolia, the Aegean area, mainland Greece, Crete, Egypt, and Canaan.

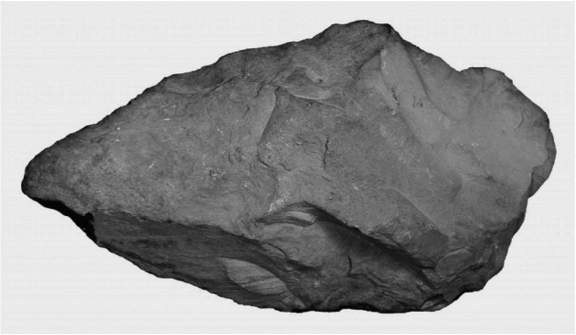

Fig. 4.13 Basalt hand axe from unnamed wadi near Mine Mueilha, Egyptian Eastern Desert

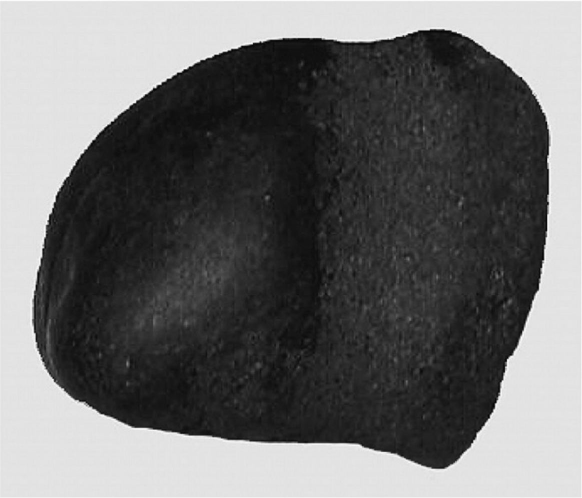

Fig. 4.14 Basalt hafted hammer from Lake Superior north shore, USA

Fig. 4.15 Hafted granite hammer from a mine near Bir al Alam, Egyptian Eastern Desert, Pharaonic Period

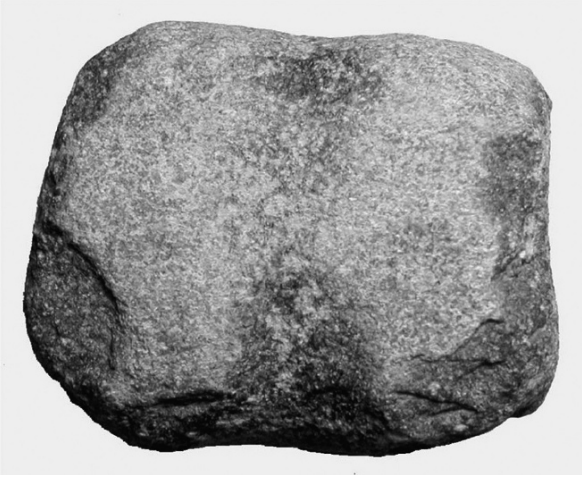

Fig. 4.16 Hafted granite hammer from Mine Dunquash, Egyptian Eastern Desert, Old Kingdom

Chapter 5
Gemstones, Seal Stones, and Ceremonial Stones

5.1 Introduction

Human beings have been fascinated by brightly colored minerals since prehistoric times. The earliest gemstones probably were found as small, polished pebbles lying in rivers and streams or in deposits of heavily weathered aggregates (Arem 1977). Initially, these objects may have been carried by hand or in small containers as highly prized personal possessions. Some were tied together or pierced for use as beads, and eventually adhesives were developed in order to secure the stones to metal settings. The art of gem carving dates at least back to the 7th millennium BCE in the Indus Valley.

Gemstones very early became associated with folklore and superstition. Without an understanding of mineral formation or chemical composition, people developed myths as a way to explain the colors of gemstones. According to ancient folklore of India, for example, gems were formed when the blood of a slain heavenly dragon fell to earth in droplets, crystallizing into stones of various colors (Jangl and Jangl 1989, p. 3). In some societies, individual gemstone colors were believed to have magical influence over the lives of humans. They could bring health or sickness, luck or misfortune, depending on the type of stone. In medieval Europe, gems were thought to reflect the morality and health of the wearer and certain stones were believed to lose their color as a result of the immoral behavior or death of the owner (Kunz 1971, p. 24). Some of these associations are provided in this chapter, but the treatment is not extensive.

Gemstones were also important cultural indicators of social rank, profession, and religious belief. In ancient Aztec society, only the gods, priests, and royalty were permitted to wear turquoise (Pogue 1915). The association of gemstones with the sacred is also found in the Old Testament, where the high priests of the temple wore a breastplate containing 12 stones representing the 12 tribes of Israel (Wright and Chadbourne 1970). In medieval times these 12 gems became affiliated with the 12 signs of the zodiac. The modern custom of birthstones is derived from this tradition.

Because highly valued stones were not always locally available, gemstones serve as a valuable indicator of trade patterns. A well-known example of this is found in the ancient use of lapis lazuli. Although Afghanistan was the only known source

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of this mineral during antiquity, lapis is found widely throughout the Old World (Herrmann 1968). The word lapis comes from the Latin for stone.

Throughout history, gemstones have been cut or shaped in order to enhance their beauty. In antiquity this often consisted of simply smoothing and rounding rough edges. However, ancient examples of carving can also be found. Even extremely hard substances such as rock crystal (quartz) were carved into elaborate objects including jewelry, sculptures, and vessels. The Babylonians carved seals into cylinder-shaped gems to use as ornaments and to make impressions in soft wax or clay for personal identification (Whitlock 1934). The Romans continued this practice by carving seals into ring stones (Zienkiewicz 1987).

The most popular materials for seal manufacture were quartz minerals (Fig. 5.1). Although quartz was more difficult to carve than softer stones, the resulting product was quite durable. Ancient craftsmen must have understood that a very hard material, such as emery (impure corundum, usually containing magnetite), was required to shape or engrave quartz (Collon 1989).

It should be noted that the enhancement of optical properties in gems was not well understood until relatively recently. Ancient craftsmen often polished gems or hollowed out the back in order to encourage the transmission of light through the stone (Osborne 1912), but faceting was not developed until the medieval era.

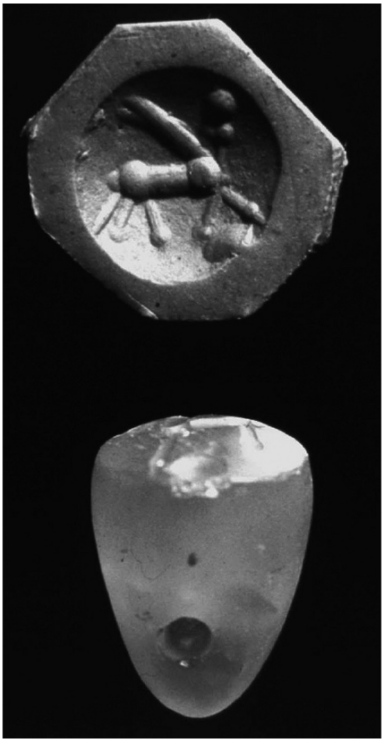

Fig. 5.1 Quartz seal from Tel Michal, Israel

Faceting gems required an intimate knowledge of hardness and cleavage, as well as great skill. One slip could destroy a valuable stone (Dickinson 1965).

In the Near East, faceting was used only to reveal the beauty of the stone's color. Any unnecessary cuts were viewed unfavorably since it was believed this would detract from the mystical powers of the stone (Woodward and Harding 1997). Conversely, European craftsmen began to develop intricate faceting that utilized the optimal proportions for optical brilliance of faceted gems. Great advances in diamond cutting took place during the fifteenth century (Bauer 1968, p. 239). It was not until after this evolution that the diamond began to gain the status and value as an object for personal adornment that it has in modern times.

As gemstones gained value and demand increased, new methods were developed to increase the value of more common stones and to artificially manufacture gems. Altered stones are found in the archaeological record from an early period (Nassau 1984). The ancient Romans valued darker chalcedony over the lighter variety, and they learned that burning light-colored chalcedony would cause it to darken as the heat chemically altered the iron oxide pigment. This had to be done carefully, without heating or cooling the stone too quickly to prevent fracturing (Nassau 1994). Methods for heat-treating gemstones became closely guarded trade secrets. One of the problems in dealing with the color of minerals in antiquity is that we do not know when early artisans discovered that the color of many minerals could be changed by heating (see Lehmann 1977). It is not possible to distinguish a naturally colored stone from a heat-treated stone with the naked eye, but laboratory analysis can reveal microscopic fractures that result from exposure to high temperatures in a kiln or hearth (Nassau 1994).

Imitation gems have been used since ancient times. The Romans made imitations from glass or paste, and, according to Pliny, they also knew how to impart artificial color to naturally occurring minerals. Few examples of these have survived in the archaeological record, but their use was likely widespread. During the Medieval Period, another imitation gem, known as a "doublet", became popular. If a craftsman had only a thin mineral fragment, he would glue this onto a less expensive material. The "gem" was shaped and mounted into a setting so that only the more valuable mineral was visible (Bauer 1968).

The following pages present the systematics of the minerals used in antiquity for gemstones, seal stones, and ceremonial stones. There is very little information on some of the gemstones listed because they may have been confused with other gemstones in antiquity. For example, classical Arab scholars identified chalcedony (عقيق أبيض), onyx (عقيق يماني), garnet, carnelian (عقيق أحمر), and agate all as forms of *acqeeq*. Archaeologists have perpetuated this problem by identifying all red stones as "ruby", blue stones as "sapphire", without mineralogical studies for confirmation. Therefore, some stones that may be present, but which have yet remained unidentified in the archaeological record, are listed in anticipation of future archaeomineralogic studies. A map of the gem deposits of the ancient Near East can be found in Forbes (1963, p. 236). In a recent article, Spiridonov (1998) has reviewed the gem deposits of the former Soviet Union.

5.2 Quartz Minerals (SiO_2)

5.2.1 Crystalline Varieties

Rock Crystal/Quartz. This quartz is colorless or transparent (Fig. 5.2). The name "quartz" may have originated from the Saxon word *querklufertz* meaning "cross-veined ore" (Blackburn and Dennen 1997). In the Middle Ages rock crystal was extracted in large quantities near St. Gotthard Pass in Italy. Objects made from rock crystal often were commissioned by the Church and the Italian courts. These took the form of crosses, caskets, vases, and pyxes. Quartz is one of the most common and widely distributed of all minerals. It was mined in Predynastic Egypt and eighth century Japan. Vessels and spheres have been carved from large crystals since ancient times. The use of the word crystal for fine glassware derives from this practice. Rock crystal artifacts are associated with ancient Greece, Rome, China, and Japan. The earliest lapidary centers, about 1500 CE, in India dealt mainly with quartz gems. According to Pliny, *crystallus* came from India, Asia Minor, Alabanda, Orthosia, Cyprus, the Alps, and an island in the Red Sea (*N.H.* 36.1–2, 198; 37.23–29, 56, 77, 116, 123, 127, 129, 132, 136, 197, 204). He may have been confusing rock crystal and diamond in some instances. Quartz was used in gems, beads, seal stones, inlaid "eyes," and decorative and ceremonial objects. In Egypt

Fig. 5.2 Ritual sprinkle in rock crystal from Kato Zakro, Greece

quartz objects were glazed until about 200 BCE (Singer et al. 1956). According to the Bible rock crystal was one of the gems used to decorate the foundations of the city of Jerusalem.

In the Greek play "Clouds" by Aristophanes there is mention of a stone used to concentrate the sun's rays enough to start fires. This must have been rock crystal. The early craftsmen of Rome secured rock crystal from the Swiss Alps and the island of Madagascar. These deposits produced huge crystals (over 100 kg) suitable for large carvings. The Chinese also made large carvings and spheres from crystals originating from a pegmatite in Myanmar.

Rock crystal was also used in North America for projectile points. Natural quartz crystals were used for ritual purposes by prehistoric peoples in California beginning about 6500 years BP (Beardsley 1954). A cross fashioned from a single quartz crystal was uncovered from a seventeenth century Franciscan mission site at Tallahassee, Florida (McEwan et al. 1997). Although the artifact shape combines Native American and Christian symbolism, the manufacturing techniques suggest the cross was fashioned by a Native American artisan.

Amethyst. Amethyst is characterized by various shades of purple or violet. The cause of color in amethyst is discussed in Cohen (1985, 1989). Its name is derived from Greek, meaning "not drunk." Amethyst crystals occur widely in hydrothermal veins formed at relatively low temperatures and pressures. The principal use of amethyst was for gem-stones, beads, and seal stones. Unfortunately, the name "amethyst" has also been applied to corundum and beryl in the literature.

Amethyst was mined in Egypt as early as the First Dynasty (2920–2770 BCE) (Lucas 1989). Amethyst from this region was also exploited by the Romans and was worn in ancient Israel by the high priests. Pliny lists *amethystus* sources as India, Arabia, Petra, Syria, Lesser Armenia, Egypt, and Cyprus (*N.H.* 37.91, 121–124, 125). Other varieties that he calls *sangenon* (*N.H.* 37.84, 130) and *socondios* (*N.H.* 37.122) also came from India. *Sapeno*s has also been identified as amethyst, but Pliny does not list its source (*N.H.* 37.122). *Tenites* from Egypt may have also been amethyst (*N.H.* 37.130). Pliny (*N.H.* 37.122) also uses the name *pharantis* as a type of amethyst. Catherine the Great of Russia was famed for her amethysts which came from mines in the Ural Mountains. In the "Old Testament" amethyst is the ninth stone that decorated the high priest's breastplate; but it should be noted that various translations of the Bible disagree on mineral names.

In ancient Europe amethyst and citrine were popular but relatively scarce. In India deposits were more abundant and have been exploited for thousands of years but these gemstones were much less popular. Amethyst is not represented in the Indian legend of the creation of gems. At archaeological sites in India contemporary with the Roman Empire amethyst is far less common than rock crystal, agate carnelian and related quartz minerals. The abundance of quartz gems in India stems from the extraordinary Mesozoic volcanic activity that formed the Deccan Trap. These basaltic rocks were often vesicular leading to later deposition of minerals from percolating water. For a review of the early mining and working of amethyst and citrine in the Indian subcontinent, see Francis (1986).

Citrine. Citrine's color varies from pale yellow, yellow, to yellow-brown or reddish-brown. Schmetzer (1988) has shown that color centers in citrine can be bleached with heating. It is transparent to translucent. The name originates from the French *citron* (lemon). It is often erroneously called "topaz." It was used as gems and seal stones. Citrine is much rarer in nature than amethyst. Amethyst but not citrine is noted in the Bible [as one of the gemstones used in decorating the high priest's breastplate].

In ancient times citrine was carried as a protection against snake venom. It was sometimes called "sunstone" because, as a result of its color, it was though capable of holding sunlight. Natural citrines are rare so today citrines are often heat treated amethyst or smoky quartz. Citrine can change color permanently if left in direct sunlight. It was first used in jewelry in Greece in the Hellenistic Period, from the 4th through the first century BCE. The first use by the Romans was in intaglios (a gem carved in negative relief) and cabochons in the first centuries CE.

Smoky Quartz. Smoky quartz varies from pale smoky-brown to almost black and from transparent to nearly opaque. It is also called *cairngorm* (after a locality in Scotland) or *morion* from Latin *mormorion.* This may be the mineral Pliny calls *chrysolithus*, which by his account came from India (*N.H.* 37.90, 91, 101, 126, 127). Another possibility is that smoky quartz is the mineral Pliny calls *capnias.* He does not list its source (*N.H.* 37.118, 128). It was used as a gemstone and seal stone. Smoky quartz crystals were used to decorate the breastplate of the high priest in Old Testament times.

Rose Quartz. This gemstone's name refers to its color, which varies from pale pink to deep rose red, occasionally with a purplish tinge. It sometimes exhibits distinct asterism. Maschmeyer and Lehmann (1983) have identified color centers in rose quartz. This could be the mineral Pliny calls *anteros* (*N.H.* 37.123). It was used as a gemstone and seal stone.

Tiger-Eye/Cat's Eye. This mineral can be found in many colors from yellow, yellow-brown, brown, reddish-brown, through bluish, grayish-green, or green, and it was used for both gems and seal stones.

Aventurine normally contains small inclusions. This material has also been called *sandastros.* According to Pliny, *sandastros* came from India and southern Arabia (*N.H.* 37.100–102). He also mentions a variety called *sandrisites* but does not list its source (*N.H.* 37.10). It was used for gems and seal stones.

5.2.2 Cryptocrystalline Varieties

Chalcedony can be white, grayish, blue, brown, or black. It has a waxy luster and is transparent to translucent. The name is derived from Chalcedon, an ancient city of Bithynia in Asia Minor. Ancient sources of this mineral were located in what is now India, Yemen, and Iraq. It also occurs in Egypt's Eastern Desert, Western Desert, Sinai, and other locations. It was used there as early as Predynastic times (Lucas 1989:392). Pliny's *capnias* may be chalcedony. He does not list its source

(*N.H.* 37.118, 128). Pliny's *enhygros* may also be chalcedony. Again, he does not list its source (*N.H.* 37.190). Its principal use was as a gemstone or seal stone, but it was used for engravings, stelae, and other objects where durability was important. Plasma (Green Chalcedony). Pliny's *iaspis* probably refers to plasma. He lists its sources as India, Cyprus, Persia, Phrygia, Cappadocia, Amisos, and Chalcedon (*N.H.* 37.90, 115–118, 119). It is found in various shades of green. The origin of the name is a Greek term applied to things formed or molded. It was used in making jewelry and seal stones. High quality chalcedony and chert from the Brule and Chadron formations were used by Native American throughout the central Great Plains in the United States. (Hoard et al. 1993)

Chrysoprase. The origin of the name is Greek for "gold leek." Chrysoprase is prized for its often jade-green color, although its color varies from olive-green to a pale sea green. The color of chrysoprase is due to the nickel incorporated in the quartz. Heflik et al. (1989) studied chrysoprase found in altered serpentinites that occur within a nickel deposit in lower Silesia. The authors were able to determine that the color was caused by tin and suggested the tin may by incorporated in the mineral as a distinct phase in bunsenite (NiO). Chrysoprase has been identified in ancient Egyptian artifacts, some of which have been dated to the Predynastic Period (Lucas 1989). It was used as a decorative stone during the European Middle Ages. The first significant deposit of it was found in Lower Silesia, Poland, in 1425 CE.

Carnelian. Carnelian is a translucent, red to reddish-brown stone. Its name derives from the Latin *carneus* meaning "fleshy." It is found abundantly as pebbles in the Eastern Desert of Egypt and was utilized from Predynastic times onward (Lucas 1989). In the Indo-Pakistani region, carnelian artifacts date from the seventh to sixth millennium BCE (Barthelemy de Saizieu and Casanova 1993). A major source was the Gujarat Province in India, but carnelian is also found as pebbles in riverbeds, particularly in Hindu Kush (de Saizieu and Casanova 1993). Inizan (1993) has recorded the use of carnelian in the third millennium BCE in the region from Mesopotamia to India, and the latter region may be the source of etched carnelian beads imported to Mesopotamia. Carnelian was used for beads by the early second millennium BCE (Higham and Bannanurag 1992). Carnelian was also used as gems, amulets, seal stones, and inlay for jewelry and furniture.

Sard. Sard takes its name from Sardis, the ancient capital of Lydia. Generally translucent, with a color varying from light to dark brown, sard was used in ancient Egypt from Predynastic times onward. Pliny affirms that this stone (which is almost identical to carnelian) occurs in Egypt (Lucas 1989). According to Pliny, *sarda* came from India, Arabia, Persia, Babylon, the Troad, Paros, Egypt, and Epirus (*N.H.* 37.80, 90, 91, 105–106, 116, 197). It was used both as a gemstone and as a seal stone.

Jasper. This gemstone normally is red and often opaque. Its name is derived from Latin *iaspis*, corresponding to the Persian *iashm* and *jashp*, and the Assyrian *ashpu.* Pliny's *haematitis* may correspond to red jasper. He lists its source as Arabia and Africa (*N.H.* 37.169). Jasper was used for lithics, beads, gems, and seal stones (Fig. 5.3). Because jasper can be found in very large masses, it has been carved into large objects such as vases and even pillars. Jasper has a dull luster but takes a high polish. It is widely distributed in veins, concretions, and replacements in

Fig. 5.3 Jasper seal stone from Vaphio, Greece

sedimentary and metamorphic rocks. For thousands of years black jasper was used to determine the gold content of gold-silver alloys. Rubbing the alloys on the stone produces a streak, the color of which indicates the gold content.

Jasper was plentiful in the Egyptian Eastern Desert (Lucas 1989). The use of red jasper in Egypt dates to Predynastic times, and during the Second Intermediate Period it was carved into scarabs. Seal rings, scarabs and scaraboids of jasper have been found on seventh century BCE Assyrian, Phoenician, Syrian, and Palestinian sites. Jasper projectile points were recovered from prehistoric sites on the east coast of the United Arab Emirates. (Diedrich 2006) During the Middle Ages, jasper was exported from the Krknoše and Jizerské Mountains of Bohemia to Europe as a decorative stone for altar pieces, components of tombs and wall facing.

Jasper has been used since prehistoric times in North America. An extensive and important deposit exploited by Paleoindians is located in southeastern Pennsylvania (Luedtke 1992). The Brook Run site is an Early Archaic jasper quarry in Virginia. This jasper occurs as large blocks of red-to-yellow brecciated material cemented by black chert. The quarrying formed a four-meter deep pit. (Monaghan et al. 2004) X-ray fluorescence (XRF) studies indicate that there were also other ancient sources of jasper in North America (King and Hatch 1997). A number of sources have been located in Japan based on XRF studies of ancient Japanese artifacts (Warashina 1992).

Heliotrope/Bloodstone. This relative of jasper is greenish, containing red spots of iron oxide. Its name originates from the Greek, meaning "sun turning." According to Pliny, *heliotropius* came from Ethiopia and Cyprus (*N.H.* 37.165, 113). In early Christian legends, the red spots were supposed to represent drops of the blood of Christ. In some cultures it was thought to control hemorrhaging or cure problems of the circulatory systems. For over 2000 years, bloodstone and jasper have been used as birthstones. Jewish people, Russians, and Italians selected jasper for the birthstone for March, while the Romans, Arabs, and Polish selected bloodstone. Bloodstones were used as gems and seal stones.

Agate. Agate is a varicolored microcrystalline quartz, often with irregular or concentric colored bands. Agate forms primarily from silica-rich igneous solutions. Many of the color variations in agate are caused by iron and manganese oxides. Note that the name *agate verdâtre* refers to the amphibole acti-nolite/nephrite and is not a quartz mineral.

The earliest evidence for working with agates comes from Mesopotamia, where ornaments and tools have been recovered. The best known is an axe head of agate with cuneiform writing on the side. It has been dated to the third millennium BCE (Hadley 1990). Agate was a preferred material for carving signets, stamps and cylinder seals throughout the ancient Near East. Theophrastus states that its name was taken from one of the principal sources for the stone, the "Achates" River. During the Classical Period, agate continued to be a popular stone for carved signet rings and for objects of art. The Greeks and Romans colorized agates by soaking first in sugar solution followed by acid treatment. The Roman emperor Nero was a collector of agate cups. Sources of agate mentioned in Pliny include Crete, India, Phrygia, Egypt, Cyprus, Persia, and various places in Greece.

In Biblical times agate was one of the 12 stones affixed to the breastplate of Aaron (Exodus 28:19). Agate occurs as pebbles in the Egyptian Eastern Desert. Agate was used throughout the ancient world, especially in Europe, the Near East, India, Japan, Tibet, Turkistan, and China. It was used by ancient Egyptians from the Predynastic Period and also by the ancient Sumerians for rings, beads, seal stones, scarabs and scaraboids, and small decorative objects. It has been reported that red agates and carnelian were heat-treated in India by about 2000 BCE, and similarly treated gems were found in Tutankhamen's tomb (1300 BCE) (Nassau 1994). Pliny's *cochlis* from Arabia may have also been a type of agate (*N.H.* 37.194).

In Predynastic India agate was found in river beds or quarried, and was fashioned into beads. Later production resulted in the founding of several important manufacturing sites including those in the Narmada River Valley, Gujarat, Pondicherry, and Cambay (Arkell 1936; Hawkins 1977). Another area, Tamil Nadu, functioned as an export and manufacturing center for agate trade with the Roman Empire (Warmington 1974).

The area of Idar-Oberstein in Germany may be the oldest gem-cutting center in the world. This region (then known as Hidera) supplied cut and polished agate to the Greeks and Romans. Idar-Oberstein remained an important center for agate carving and polishing during the Middle Ages (Wild 1991). In Roman Germany, agate was used to make small containers (Schmidt and Schröter 1990). A major "early" treatise on the properties and archaeology of agate is by Farrington and Laufer (1927). This remains a good reference for the long history of agate lore. Stone beads, including agate, from Cameroon, Africa, are described by Gauthier (1975). Agate was also used for beads in Tibet and Korea.

Onyx/Sardonyx/Banded Agate. This stone is a banded silica with comparatively regular successive layers of alternating colors. Onyx has alternating blackish and white bands, while the bands of sardonyx are alternating red or reddish-brown and white. The name takes its origin from Greek *onyx*, meaning “nail.” Onyx beads have been associated with Predynastic Egyptian graves. The earliest known use of sardonyx in ancient Egypt dates from the 19th Dynasty, but it became more common during the 22nd Dynasty and later (Lucas 1989). According to Pliny, *sarda* came from India, Arabia, Persia, Babylon, the Troad, Paros, Egypt, and Epirus (*N.H.* 37.80, 90, 91, 105–106, 116, 197). Sardonyx came from India and Arabia (*N.H.* 37.4, 85–89, 90, 197). It was used as a gemstone, for seal stones and small decorative objects. Roman soldiers wore sardonyx engraved with figures of Mars or Hercules to give them courage.

Prase. The color of this translucent gemstone is green, taking its name from the Greek word for “leek green.” Although *prasius* is mentioned by Pliny, he does not list any source where it might be found (*N.H.* 37.113). Prase was used for gems and seal stones.

Hornstone/Chert. This material is found in shades of gray or brown. The name originated as a mining term. Chert was mined in the Egyptian Eastern Desert, and occurs in roughly shaped bangles and pendants of the Predynastic and Early Dynastic Periods (Andrews 1991). In classical antiquity it was made into gems and seal stones.

5.3 Non-Quartz Silicates and Minerals

5.3.1 Coarse-Grained

Olivine (forsterite), Mg_2SiO_4, has a hardness of 7 and a density of 3.28. It is found in basic and ultrabasic rocks. The name olivine derives from its olive green color. Chrysolite/Peridot: Chrysolite is Greek for “gold frost”; peridot is a French word of unknown origin. Forsterite was named for Adolarius Jacob Forster (1739–1806), an English mineral collector and dealer. This mineral was often confused with emerald. Transparent to translucent, it is found in green, lemon-yellow, and white varieties. Pliny indicates a major source of peridot was the island of St. John, an Egyptian island located in the Red Sea. This source (now exhausted) was mentioned by Al-Biruni in the eleventh century (Sersen 1995). Peridot appeared in ancient Greece and Rome after Alexander the Great’s conquests (Spier 1989). Pliny’s *chrysoberyllus* (a pale-green stone approaching gold) may be a peridot. He does not list its source. (*N.H.* 37.76). Pliny also states that *topazus* comes from St. John’s Island and the Thebaid (*N.H.* 37.24, 107–109). Varieties of this stone were highly prized in antiquity and used as gemstones. It is mentioned in the Biblical book of Revelations as a precious stone. Large peridot crystals are found in the Mogok district of Myanmar.

Beryl, $Be_3Al_2Si_6O_{18}$, has a hardness of 7.5–8 and a density that varies from 2 to 2.9. It appears in several varieties. Common beryl is green and often opaque but may occur in gem forms as emerald (green), aquamarine (blue), or morganite (red). Beryl is highly weather resistant so is frequently recovered from weathered pegmatites.

Emerald, Cat's Eye Emerald. This stone occurs in various shades of green. The origin of the name is from Latin *smaragdus* and Greek *smaragdos*, probably originally derived from a Semitic word. In Greco-Roman sources this term was applied to various green minerals. It was often confused with peridot during antiquity. The earliest known emaerald mine was located in the Wai Sikait in the Egyptian Eastern Desert where mining likely began in the first century BCE. (Harrell 2004b) In Egypt, emeralds (often of poor quality) were used chiefly during the Ptolemaic Period. In earlier Egyptian jewelry, researchers have frequently confused green feldspar and other green-colored stones (Lucas 1989).

The sources for emeralds in antiquity were in Pakistan, Cleopatra's Mine in Egypt, and a small, Roman mine in the Austrian Alps. Emerald use appears in ancient Greece and Rome during the Hellenistic Period (Spier 1989). Pliny's *chrysoberyllus* (a pale-green stone approaching gold) may be an emerald, but no source of origin is listed (*N.H.* 37.76). Pliny also refers to *smaragdus* from Scythia and Egypt. However, he identifies 12 varieties, which may have included not only emeralds, but also malachite, green crystalline quartz, green chalcedony, green turquoise, zinc carbonate (smithsonite), and a green porphyry rock (*N.H.* 37.6, 8, 62–75, 112, 116, 118, 124, 197, 204). The use of emerald as a gemstone appears to have been introduced into Rome in the middle of the first century BCE following the eastern campaign of Pompey the Great. Pliny observed that emerald was a favorite gem of the wife of the emperor Gaius (Caligula) (*N.H.* 9.56–58).

Colombian emeralds were known to the natives before the Spanish arrived (Sinkankas 1988). The Spanish discovered a large supply in Colombia in the sixteenth century (Giuliani et al. 2000). A Mesoamerican figurine carved of emerald found near Guerrero, Mexico, has been dated to between 900 and 600 BCE. Although the source of the emerald has not been positively identified, it is thought to have come from emerald quarries in Colombia (Whittington et al. 1998).

Substitution of V^{3+} for Al^{3+} ions in beryl produces an emerald with a warm green or yellowish-green color in contrast to the blue-green resulting from the substitution of Cr^{3+} for Al^{3+}. A comparative study of the causes of color in green and blue beryls (from Brazil) is provided by Blak et al. (1982). Henn (1992) reviews the causes of color in green beryl. Color modification in beryl caused by irradiation or heating is described by Schmetzer et al. (1975), who include a detailed table of color modifications. Another review of the formation, properties, and colors in the beryl group of gems is provided by Hanni (1990). This review includes a good summary of the geologic conditions for the formation of beryl.

Aquamarine. This beryl has a pale-blue to blue-green color, resembling seawater, hence its Latin name (*aqua marina*). Caution should be exercised, because the name "aquamarine" has also been applied to corundum and topaz. Sri Lanka and Burma were major sources for aquamarine during antiquity. Pliny lists the sources of aquamarine as India and the Ural Mountains (*N.H.* 37.76–79). It was also found in the gravels of Sri Lanka and Burma (Sinkankas 1988). Aquamarine was used as gemstones as early as the Roman Republic when examples of earrings, rings, and cameos are found (Higgins 1980; Tait 1986). Aquamarine was thought to prevent seasickness and stomach disorders in Roman times. A famous example from the seventh century CE is the votive crown composed of gold, aquamarines, pearls, and rock crystal that belonged to the Visigothic king Recceswinth (Arbeiter et al. 1993; Jenkins 1993). Early Chinese artisans used large aquamarine crystals for figurines, seals, and engravings. Japanese carvers used the large crystals to carve **net-sukes**. Aquamarine has a density of 2.69–2.71 and can thereby be distinguished from similarly appearing topaz, which has a density of 3.49–3.57.

Golden Beryl has a golden color due to the presence of ferric iron. *Goshenite* is a colorless variety of the beryl group. *Moganite* has a pinkish tinge due to the presence of manganese. The name chrysoberyl comes from the Greek meaning golden beryl. The variety of chrysoberyl called Alexandrite was named for Czar Alexander II.

Topaz, $Al_2SiO_4(F,OH)_2$, has a hardness of 8 and a density that varies from 3.49–3.57. It is transparent to translucent. It occurs in a wide range of colors from colorless to white, gray, bluish, greenish, yellowish, yellow-brown, orange, purple, and pinkish to reddish. The colors in topaz are likely due to the presence of Cr^{3+}, Mn^{3+}, and the occurrence of color centers. Petrov (1978) has reviewed the causes for the colors found in topaz. The Greeks called this gemstone *topazion*, after the name of an island in the Red Sea, meaning "to seek." It is quite possible that the early usage of *topazion* did not refer to the mineral we know as topaz today. Green *topazion* was possibly peridot. The topaz of the biblical Old Testament may have been chrysolite (an olivine). The classic localities of Mursinka in the Ural Mountains and Schneckenstein in Germany were discovered in the seventeenth century. Topaz typically occurs in cavities in high-silica igneous rocks and often is associated with cassiterite (SnO_2).

Garnet. This group of silicates has a Mohs hardness between 6.5 and 7.5 and densities from 3.4–4.1. The name comes from the Latin related to pomegranate the red seeds of which resemble red garnet. The grossular variety has the chemical composition: $Ca_3Al_2(SiO_4)_3$. Other gem varieties are almandine, pyrope, rosolite, hessonite, andradite, and uvarovite. Garnets have a wide range of hue from colorless, through white, gray, yellow, yellowish-green, green, yellowish-brown, brown, pink, red, and black. Color is the most obvious feature of gem garnets. The garnet group of minerals shows one of the widest ranges of color in the mineral world. Only blue is missing. The color of garnets is due to several superimposed absorption mechanisms based on the incorporation of Fe^{2+}, Fe^{3+}, Mn^{2+}, Mn^{3+}, V^{3+}, and Cr^{3+}. Garnets are widely distributed in igneous and metamorphic rocks.

Principally used as a gemstone, the name "grossular" originates from Latin *grossularium* (gooseberry). Pliny's *chrysollectros* from Pontus may be hessonite (*N.H.* 37.127). During the Middle Ages, garnet was preferred as a gem-stone for decorating religious artifacts because of its deep blood-red color. The red gems that were a central feature of the cloisonné jewelry of the early Frankish kings were three kinds of garnet (Farges 1998). In Mesoamerica, garnet was used as a gemstone and for mosaic inlay.

Almandine garnet $Fe_3Al_2(SiO_4)_3$, is a deep red, brownish-red, or brownish-black stone. Pliny lists one source for this mineral as Alabanda, in Asia Minor (*N.H.* 36.62; 37.92). Garnet from the Egyptian Eastern Desert and the Sinai was used as early as

Predynastic times (Lucas 1989). It appeared in ancient Greece and Rome after Alexander the Great's conquest of the East (Spier 1989). Medieval Arab traders procured garnets (عقيق أحمر *acqeeq aahmar*) from Afghanistan (Sersen 1995). Garnets were also found in Sri Lanka, India, Bohemia, and Burma (Bauer 1968). The Romans sometimes hollowed out the underside of the garnets to make them more transparent (Bauer 1968). Almandine was used as a gemstone and for beads.

Pyrope garnet of the rhodolite variety $Mg_3Al_2(SiO_4)_3$, is pinkish-red, purplish-red, orange-red, or crimson to nearly black in color. Its name is derived from the Greek word for "fiery." Pliny refers to red stones by the general term *carbunculus.* He lists sources as India, North Africa, Caria, Ethiopia, Miletus, Orchomenos, Chios, Corinth, Troezen, Marseilles, and Lisbon (*N.H.* 37.91, 92–98, 103, 122, 123). His description may have included pyrope. However, pyrope garnet is found only in the foothills of the Central Mountains in Bohemia. Mining of Bohemian garnet is reported by Agricola. Pliny also mentions a fiery red to purple stone called *lychnis* which came from Orthosia and Caria (*N.H.* 37.103, 104). Garnets were used primarily as gemstones.

Sodalite, $Na_4Al_3Si3O_{12}Cl$ has a hardness of 5.5–6 and a density that varies from 2.14–2.4. Its name comes from the sodium in the mineral composition. Annersten and Hassib (1979) attribute the blue color of sodalite to the presence of colloidal particles of metallic sodium. This gemstone is usually blue, but may be colorless or appear in white, pink, yellowish, greenish, or reddish varieties. Pink sodalite usually fades when exposed to visible light. Hackmanite is a variety of sodalite. Sodalite forms in silica-poor granitic rocks and in some metamorphosed calcareous rocks. It is found in Germany, Romania, Burma, and Korea.

Feldspars. The feldspars are Na, Ca, K, and Al silicates with a hardness varying from 6 to 6.5 and densities from 2.55 to 2.76. The name comes from the Swedish for field plus spar in reference to finding feldspar in fields overlying granite. The feldspars are the most common minerals in the earth's crust and are major constituents of most igneous rocks. Feldspars are generally dull, cloudy and fairly opaque so they have not been widely sought after as ornamental "stones". They have, however, been found in archaeological contexts (Dittert 1968). The common feldspars are orthoclase, plagioclase, and microcline. Semiprecious stone varieties of feldspar include sunstone, moonstone and amazonstone. Indigenous Americans used all as gems: moonstone was used in Mexico, sunstone was used by the Apaches in Arizona, and amazonstone was used by the Aztecs, Mayas, Indians of Venezuela, Brazil, Trinidad, Wisconsin, and California.

Labradorite/Sunstone is named after its principal locality on the coast of Labrador. Labradorite can be colorless, white, or gray, and frequently exhibits an iridescent play of colors. Sunstone contains inclusions of hematite in parallel minute plate-like inclusions, giving it a spangled appearance.

Microcline feldspar varieties include amazonstone (amazonite), which is usually green, and perthite, which can be white, gray, yellowish, reddish, or green in color. The color is due to the presence of Pb^{2+} and OH^-. The name micrcline comes from Greek, meaning *little slanted*, which refers to the cleavage angle. The name plagioclase comes from the Greek for oblique fracture.

Amazonite is found principally in granites and pegmatites and occurs in the Egyptian Eastern Desert. Talismans of amazonite are known from Pharaonic Egypt and from tombs of kings in the region of ancient Ur (Chaldea) (Oostrooumov 1991). This gemstone was employed as early as the Neolithic Period in Egypt and was widely used in Dynastic times (Lucas 1989). Harrell and Osman (2007) have located two amazonite quarries in the Eastern Desert of Egypt. The most important one is located at Gebel Migif in Wadi Shait not far from the Red Sea. Amazonite was known to the ancient Egyptians as *neshmet.* It was made into beads, amulets, and inlays in Predynastic times through the Roman Periods.

Other Old World sources of this stone are the Ural Mountains and Kashmir. During the eighth century CE, beads of amazonite and cylinder seals were found in Neo-Assyrian contexts (Hawkins 1977). The Phoenicians made seals and scaraboids of amazonite. It was used in the New World by the Aztecs, Mayans, and the aborigines of Venezuela, Brazil, Trinidad, Wisconsin, and California. Pliny's *tanos* may have been amazonstone (*N.H.* 37.74).

Orthoclase varieties include adularia ("moonstone") and valencianite. The name orthoclase is taken from the Greek for *straight fracture.* This may be the mineral Pliny refers to as *astrion.* He lists its source as near the mouth of the Indus River in India (*N.H.* 37.132). Its color varies from colorless, to white, gray, yellow, reddish, and greenish, and may show a silvery or bluish iridescence. Moonstone shows an opalescent play of colors. It was used by various aboriginal groups in Mexico as a gemstone. Since microcline and orthoclase can look very much alike it seems certain that some orthoclase was called amazonite.

Zircon, $ZrSiO_4$, has a hardness of 7.5 and a density of 4.65. It is also known as cyrtolite. Zircon's ancient name was "jacinth" or "hyacinth." Zircon is widespread as an accessory mineral in silicic igneous rocks. Gem varieties have been recovered from gravel deposits. The high refractive index and dispersion results in a brilliancy approaching diamond. The variety hyacinth includes the clear and the transparent red, orange and yellow varieties. The name "zircon" is taken from Arabic *zarqun*, which, in turn, is derived from Persian *zargun* meaning "gold color." Pliny's *melichrysus* may refer to zircon. The source listed is India (*N.H.* 37.128). It was used as a gemstone.

Epidote/Pistacite, $Ca_2(Al,Fe)_3(SiO_4)_3(OH)$, has a hardness of 6 to 7 and a density that varies from 3.35 to 3.5. A chromium variety of this mineral is called tawmawite. These minerals have a wide range of color from yellowish-green, deep green, brownish-green, gray, grayish-white, greenish-black, and black. The colorless variety is rare. Epidote is the Greek word for "increase". Epidote minerals occur in a wide variety of rocks in France, Switzerland, Italy, Austria, Japan, and Korea. They were used as gemstones.

An epidote granite with pink feldspar and clear quartz has been used widely as a gemstone in modern times and given the name "unakite", from the Unakas mountains in North Carolina USA. It is the state stone of Virginia and is found in the Lake Superior region in glacial drift and in South Africa, China, and Brazil. Because of its especially pleasing color (pink and pistachio green) and lapidary qualities it might well have been exploited in more ancient times but I have not found any authentication of this.

Tourmaline is a very chemically complex silicate that occurs in several varieties as a result of chemical substitution. "The determination of the chemical composition of tourmaline is not a trivial matter" (Burns et al. 1994). It has a hardness of 7 to 7.5 and a density that varies from 3.03 to 3.25. Practically all gem tourmalines occur in rocks formed from the last stages of granite pegmatite crystallization. The color of tourmaline is due in part to charge transfer between Fe^{2+} and Fe^{3+} (Mattson and Rossman 1987). Rossman and Mattson (1986) present the manganese, iron, and titanium charge-transfer mechanisms that color some yellow-green and yellow-brown tourmalines. The pink-red color of some tourmalines may be due to Mn^{3+}. Greens are likely due to chromium and vanadium. The use of tourmaline as a gemstone is first documented in ancient Greece and Rome after Alexander the Great's conquest of the East (Spier 1989).

Elbaite, a lithium-bearing tourmaline with subvarieties achroite, indicolite, and rubellite, has the chemical composition $Na(Li,Al)_3Al_6(BO_3)_3Si_6O_{18}(OH)_4$. Elbaites are usually green, blue, red, or yellow, but may be white or colorless. The island of Elba is one area where deposits occur.

Dravite is a magnesium-containing tourmaline. Its color ranges from black, brownish-black, brown, greenish-black, emerald green, pale bluish-green, to dark red. Dravite can be found in the district of Drave, Austria. Pliny mentions a brown stone called *lyncurium*, which may refer to brown dravite. He does not list its source (*N.H.* 37.34, 52–53; 8.137). Dravite was used as a gemstone.

Dioptase, $CuSiO_2(OH)_2$, has a hardness of 5 and a density of 3.3. It varies in color from emerald green to deep bluish-green, and turquoise-blue. Its name origin is Greek meaning "to see through." It was used as a gemstone.

Chrysocolla, $(Cu,Al)_2H_2Si_2O_5(OH)_4{\cdot}nH_2O$, is a soft mineral with varying hardness of 2 through 4 and a density that varies from 2.01 to 2.4. Its color is usually blue, blue-green, or green, although it can be brown to black when impure. Its name is derived from the Greek meaning "gold glue". Pliny identifies *chrysocolla* as coming from Cyprus, Armenia, Macedonia, and Spain (*N.H.* 33.4, 86–93, 161; 35.30, 47, 48). It was used as a gemstone.

Diorite is not a mineral but an igneous rock. Its color can range from greenish-black to a speckled black and white. Although usually used for other more utilitarian purposes (see Chap. 11), its use for decorative objects is known. Diorite was obtained by the ancient Egyptians near Aswan. It was used during the Predynastic Period and earlier for beads and pendants (Andrews 1991).

Porphyry is a term applied to a variety of igneous rocks, with coarse-grained, colored crystals. The most famous source of this material is Egypt. A black variety with white crystals was used for pendants and beads as early as the Predynastic Period. The more famous purple variety found scattered use for amulets and pendants during the Predynastic Period, and for small vessels during the early dynasties (Andrews 1991). However, purple porphyry was not actively mined and heavily exploited until the Roman Period (see Chap. 11).

5.3.2 Fine-Grained

Jade. The name "jade" is the gem term used for two different minerals: jadeite and nephrite. For a mineralogical study of jade, see Wen and Jing (1996). When worked and polished, jadeite and nephrite can usually be distinguished by their appearance. The luster of nephrite is oily rather than vitreous while that of jadeite is the opposite. In addition, the apple-green or emerald-green varieties are jadeite. Jades have been worked into implements and ornaments since Neolithic times. The toughness and ability of jade to hold a sharp edge without chipping made it a useful tool and weapon. Jade was prized by Mesoamericans as far back as 3,500 years ago. The Maya sculpted green jades into ornaments and figurines. Among the earliest of Maya jades are ones of blue color, similar to the blue-green and blue jades preferred by the Olmec. Recent exploration has located new sources in Central America of the blue-green jade used by the Olmec. In addition to outcrops of jade related alluvial deposits were discovered. (Seitz et al. 2001) Many Mayan jades had a red pigment [cinnabar or hematite] rubbed into their designs. The Maya word for jade was *tun* = stone. They recognized differing qualities of jade as can be seen from the status contexts of offerings and burials. The Aztecs had several terms for different varieties of jade. (Hammond 1991) Blue-green jade artifacts contain slightly iron-enriched jadeite as well as some included titanite and albite. (Harlow 1991) Foshag (1957) provides a mineralogical basis for Guatemalan jade. Nephrite does not occur in Mesoamerican jades (Foshag 1955).

Nephrite is an actinolite amphibole with the chemical composition $Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$, a hardness of 5 to 6, and a density range (for actinolite) of 3.0–3.44. It is white to green to greenish-black in color with increasing iron content. Actinolite is named from the Greek word for "ray," and nephrite is named from the Latin *lapis nephriticus* (or "kidney stone"). One needs to be aware that nephrite is technically a compact variety of actinolite, and some scholars refer to the material as actinolite. The name nephrite also has been used for various mixtures of minerals. The extreme toughness and compactness of nephrite is due largely to the manner in which microscopic fibrous bundles are interwoven. Wen and Jing (1992) determined that the smaller the size of these bundles the higher quality the jade. Chinese scholars as early as the Han Dynasty had tests to distinguish true jade from pseudojade.

There are two distinct types of nephrite deposits: (1) ortho-nephrite jades associated with serpentinized ultrabasic igneous rocks, for example, those in British Columbia; and 2) para-nephrite jades associated with metasedimentary strata, for example, those found in the Eyre Peninsula, South Australia. Trace-element abundances in these two types show distinct differences. Ortho-nephrites have high levels of chromium, cobalt, and nickel. Para-nephrites are characterized by low trace-element levels. Earlier authors have distinguished serpentine and non-serpentine types with various names applied (Nichol 2000).

When thinking about jade many people think of China. Yet interest in the West concerning Chinese jade extends back only about 100 years. Laufer's classic study of Chinese jade was first published in 1912. (Laufer 1912 and 1974) Jade is one of

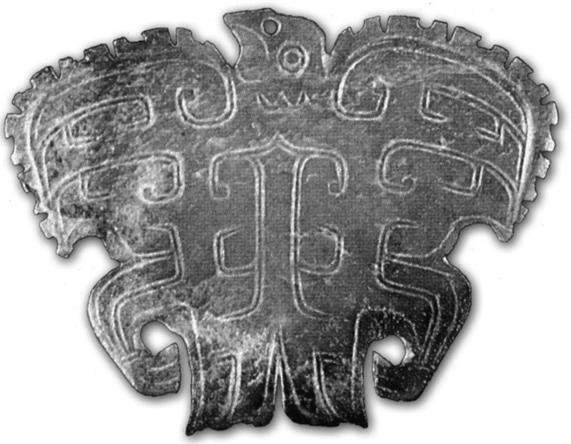

Fig. 5.4 Shang Dynasty nephrite jade artifact from China

the hallmarks of Chinese culture, particularly of the Shang Period [second millennium BCE]. From the tomb of Fu Hao at Anyang more than 590 jade carvings were recovered. (Chang 1980) (Fig. 5.4)

The ancient Chinese acquired nephrite from Burma and Turkistan. The Chinese word for their nephrite jade was *yu-shih.* Data on jadeite from Burma (Myanmar) are provided by Htein and Naing (1995). These authors include information on the chemical basis for the colors found in jade. Nephrite was employed for carvings, decorative and ceremonial objects, personal ornaments, and gems. Nephrite was the jade used in China from the Neolithic in the sixth millennium BCE through the Han dynasty. (Wen and Jing 1996) The earliest jade artifact is from Liaoning Province. Jing and Wen (1996 Fig. 1) have produced a map showing the studied Neolithic sites and modern sources of nephrite in China.

A number of ancient Egyptian artifacts have tentatively been identified as nephrite. The source is thought to be the Eastern Egyptian Desert (Lucas 1989). Neolithic and Bronze Age nephrite axes have been found in Italy, France, and other parts of Europe (D'Amico et al. 1995). The most prized stone of the precontact Maoris of New Zealand was nephrite, used for axes, knives, and chisels.

As mentioned above, geologically there are two types of nephrite deposits: one is associated with magnesian marbles and the other with serpentinized ultrabasic rocks. There are suitable rocks for the formation of nephrite in the serpentinized ultrabasic rocks in the western Balkans, including Bulgaria. Nephrite artifacts are spread throughout the Neolithic and Eneolithic [circa 7000–4000 BCE] in southwestern Bulgaria. These objects ar primarily small axes and chisels, ritual scepters, and zoomorphic amulets (Kostov 2005e). For a summary of the archaeomineralogy of nephrite jade during the Chalcolithic and Neolithic Periods in Bulgaria see Kostov (2007). For Early Neolithic nephrite use in the production of small axes from the Karanovo site in Bulgaria see Kostov (2005b). The nephrite deposits at Jordanów Slaski, Poland are among the largest in Europe. They have been worked off and on since the Neolithic for the manufacture of jewellery and ornaments. This was an important source for the carvers of Prague in the sixteenth and seventeenth centuries. Modern exploitation occurs exclusively within the contact alteration zone along faulted margins between serpentinite and diorite/gabbro rocks. (Nichol 2001). Early European explorers recorded the use of nephrite by aboriginals in British Columbia and Alaska. The source was determined to be the Columbia River Basin and the Kobuk River in Alaska (Desautels 1986).

Using electron microprobe analyses Hung et al. (2007) have mapped the distribution of nephrite atifacts from deposits on Taiwan, including the Fengtian deposit, and elsewhere in Southeast Asia. Artifacts dating from 3000 BCE to 1000 CE were exchanged throughout a large region including the Philippines, Thailand, Malaysia, and Vietnam. Jade carving developed in India with the advent of the Mughal emperors, who brought knowledge of the craft from east central Asia and Iran.

Jadeite is a pyroxene with the chemical composition $Na(Al,Fe)Si_2O_6$, a hardness of 6–7, and a density of 3.25. It is usually light to dark green, but it may also be dull white. Massive material is pale green to emerald green, greenish-white, gray, mauve, or white. It may be stained by iron oxides to various shades of brown, red, orange, or yellow. Its name is derived from Spanish "piedra de yjada" (stone of the side). Jadeites come in colors ranging from white through pink, lilac, red, brown, orange, green, blue, to black. The colors are derived primarily from trace elements incorporated in the mineral structure. For example, in white jadeite all the iron is ferric while in black jadeite one-half is ferrous. The highest quality green Bumese jadeite has up to 0.3 per cent chromium (Harder 1995).

The Aztecs, Mayas, and other precontact peoples of Mexico and Central America carved green jadeite for ornaments and amulets. Only the Montagua Valley of Guatemala has been established definitively as a source for Precolumbian jadeite in the New World. There is considerable speculation and research directed at the identification of other Mesoamerican sources, but none have yet been confirmed. Researchers have suggested other possible sources in Costa Rica (Soto n.d.) and Mexico (Fig. 5.5). Olmec knowledge of jadeite extends back to the Early Preclassic Period, in the second millennium BCE. Jadeite celts, ornaments, and gems have been recovered from workshop sites on the island of Antiqua, West Indies. These are dated to circa 250–500 CE. (Harlow 2006) Guatemala is a reasonable source for these jades.

In the Old World, Neolithic and Bronze Age jadeite axes have been found in Italy, France, and other parts of Europe. Evidence suggests that the source of this material was the western Alps (D'Amico et al. 1995). In China, jadeite artifacts dating from the eleventh century BCE and later have been found. Sources may have been in China's Shanxi and Yunnan provinces, and from Tibet (Whitlock 1934) and Burma (Desautels 1986). Jadeite has been used in carvings, decorative and ceremonial objects, personal ornaments, and gems.

Chloromelanite is impure jadeite. It is dark green or blackish in color. Its name comes from the Greek word for "green-black." It is commonly found in Mesoamerica where it was used for gems, carvings, decorative and ceremonial objects, and personal ornaments. It was also found in the form of tools in Mesoamerica, New Guinea, and Neolithic sites in Europe (Bishop et al. 1985).

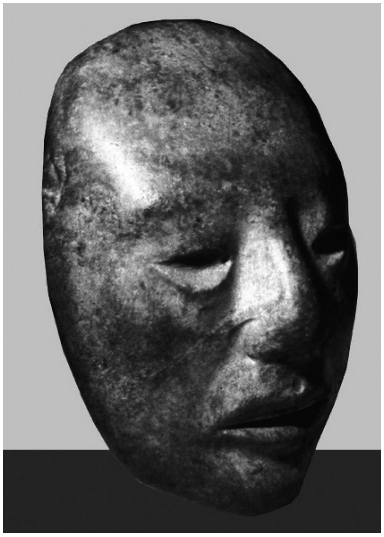

Fig. 5.5 Mayan jadeite mask

Opal, $SiO_2 \cdot nH_2O$, has a hardness varying from 5.5 to 6.5 and a density range of 1.99–2.25. In its purest form, opal is milky-white to colorless. However, through admixture of pigmenting material it can be almost any color, including yellow, brown, orange, green, and blue, usually in pale shades. The principal gem variety, termed *precious opal*, shows a rich internal play of colors by reflected light and has a pearly opalescence as it is viewed from different angles. The name "opal" may have derived from Sanskrit *upala* meaning precious stone.

The use of precious opal appeared in ancient Greece and Rome after Alexander the Great's quest of the East (Spier 1989). For the Romans, opal ranked second only to emerald among noble gems. From the fifth century BCE on, many of the opals from ancient Europe came from Slovakia near Dubnik. Pliny described the opals from this area, over 1000 km from Rome. Unfortunately, these opals became known as "Hungarian" (possibly because of a second site of production in northern Hungary). Production from Slovakia continued through the Middle Ages. In the Medieval Period, opal gained a reputation as a "lucky" gemstone.

Mexican opal was taken back to Europe by explorers as early as 1520. The ancient cultures of Mexico had access to many deposits of precious opal including those of Queretaro. It is found in Aztec carvings, including a carving of the last Aztec emperor Cuahtemoc composed of a black rhyolite densely embedded with tiny red, green, and gold opals. The Aztecs also used opal for mosaics and other purposes. Ordinary opal was frequently used in the New World for projectile points.

Opal was also obtained in ancient times from India, Egypt, Arabia, and other sources in the Mediterranean region. According to Pliny, *opalus* came from India (37.80–84, 129–130). Another variety he identifies as *paederos* came from Egypt, Arabia, Pontus, Galatia, Thasos, Cyprus, and India (*N.H.* 37.84, 123, 129–130). *Tenites* from Egypt may have also been opal (*N.H.* 37.130). In the Old World precious opal was used for engraved gems.

Fire opal gets its “fire” from the diffraction of light where units of silica (SiO_2) are arranged in a geometric pattern of the proper size to diffract light entering the material. Fire opal first came from Europe centuries ago, with Hungary providing the best material. The orderly arrangement of spherules of cristobalite in opal also can impart color. “Cacholong” is a milky white or bluish white opal resembling mother-of-pearl. It is found in Austria, Czech Republic, Iceland, Greenland, Mongolia, and Uzbekistan. Unfotunately, this name also has been given to similar-looking chalcedony. De Fourestier (1999) reports the name also has been used for nephrite.

Lapis Lazuli/Lazurite, $(Na,Ca)_8(Al,Si)_{12}O_{24}[(SO_4),Cl_2,(OH)_2]$, has a hardness of 5–5.5 and a density of approximately 2.42. It is known for its blue color, which can vary from deep blue, indigo blue, azure blue, and violet blue to greenish-blue. The color varies with the nature of the sulfur radicals in its structure (Leithner 1975). Its name is derived from the Latin word for “stone” and Persian *lazhward* (اللازورد) meaning blue color. In the fifth century CE, the mineral was introduced into Europe with the name *ultramarinum*, which became “ultramarine.” A word of caution: the word “lapis” comes from the Latin for “stone” so has been used as a part of many variety names, e.g., *lapis indicus* is nephrite. Both Pliny and Agricola use the name *sapphiris* for lazurite.

The only proven ancient source of lapis lazuli in the Old World is Badakshan, Afghanistan, although there are unsubstantiated suggestions that there may have been an ancient source in Iran (Von Rosen 1998). There has been some discussion about a possible source at Latium, Italy (see Stevenson et al. 1974; Hogarth and Griffin 1975). Badakshan is mentioned in Chinese writings as early as the sixth century CE. Lapis from Badakshan is almost always associated with pyrite. For a good discussion of lazurite, its sources, geology, and exploitation see Kostov (2005c). New sources of lazurite have been identified at Lake Baikal in Siberia, in Spain, and in Chile.

Lapis lazuli found its way to the Indo-Pakistani region by Neolithic times (Barthelemy and Casanova 1993). The mines of Badakshan were described by Marco Polo, who visited them in the thirteenth century (Bauer 1968; Leithner 1975). Necklaces of lapis lazuli have been found in the Caucasus. Importation of lapis began as early as the 3rd Dynasty at Ur for cylinder seals and beads. It found its way into Egypt by Predynastic times. Biswas (1996) reports the use of imported lapis lazuli in ancient India in the seventh, sixth, and fourth millennia BCE. Gems and seals were carved of lapis lazuli, and it was also used for beads, small decorative objects, and paint pigments.

Talc, $Mg_3Si_4O_{10}(OH)_2$, is the softest mineral with a hardness of 1. It has a density range of 2.58–2.83. Its name is taken from the Arabic *talq* (الطلق). It is the major constituent *of steatite* (*soapstone*), a rock whose hardness ranges from 3 to 4 because of other constituents. Talc is usually pale green to dark green or greenish-gray, but white, silvery white, gray, and brownish colors are also found. According to Pliny, *steatitis* came from Siphnos (*N.H.* 37.186; 36.159). Decorative objects, small carvings, and beads were made from steatite. The ancient Egyptians glazed steatite beads with a sodium or potassium-calcium silicate as early as the Badarian Period (4000 BCE) (Andrews 1991). The steatite was heated to between 800 and 1000°C (Vandiver and Kingery 1986). Heating dehydrates and hardens steatite up to Mohs hardness 5 to 7 – hard enough to cut glass (Aldred 1978).

Muscovite, [$KAl_2(AlSi_3)O_{10}(OH)_2$], has a hardness of 2.5 parallel to its cleavage sheets and 4.0 perpendicular to the sheets. Its density can vary from 2.77 to 2.88. It has a pearly luster and is colorless to yellow or pale brown. It was used in ancient Egypt for beads during the Predynastic Period. Its use expanded to pendants and attachments during the Middle Kingdom, particularly by the Kerma culture in ancient Nubia (Andrews 1991).

Slate is a fine-grained metamorphosed shale. Slate is highly siliceous and occurs in a wide range of colors, including gray, black, green, purple, red and brown. It cleaves in sheets. The ancient Egyptians of the Early Dynastic Period manufactured rings and bangles of green slate from the Eastern Desert (Andrews 1991).

5.3.3 Glassy

Obsidian is a volcanic glass whose color is usually brown or black. According to Pliny, obsidian *obsianus* was named for Obsius who discovered the material in Ethiopia. This widely distributed material was prized in prehistoric times in Europe, Asia, and North America. Although used most commonly for tools because it produced a sharp cutting edge, it was also used to manufacture decorative and ceremonial objects, statues, beads, and gems. The ancient Egyptians used obsidian as early as Predynastic times. It was not locally available and so was imported, probably from Abyssinia (Lucas 1989). Obsidian from El Chayal, Guatemala, was used by the Maya. In North America, “Apache tears” were valued obsidian ornaments. Pliny lists sources for *obsianus lapis* as Ethiopia, India, Italy, and Spain (*N.H.* 36.196–197; 37.177). Obsidian is treated more extensively in Chap. 4.

5.4 Carbonate and Sulfate Minerals

5.4.1 Coarse-Grained

Calcite, $CaCO_3$, has a hardness of 3 and a density of 2.71. Its crystals are colorless or white when pure. However, impurities often produce various shades of gray, yellow, brown, red, green, blue, and black. Its name comes from Latin *calx* (“lime”). Calcite has perfect rhombohedral cleavage and large calcite crystal masses will cleave into clear gem-like rhombs. These were admired far back into antiquity and have been recovered in excavations worldwide. A transparent, colorless form of crystalline calcite known as “Icelandic Spar” is found in the Egyptian Eastern Desert. Small beads of this material are known dating from the New Kingdom and Third Intermediate Period (Andrews 1991). Calcite crystals were recovered from German silver mines as far back as classical times.

Large-grained calcite (i.e., “marble”) was also used worldwide in the manufacture of seal stones, vessels, figurines, and small art objects. Marble is opaque and can have almost any coloring depending on the presence and amounts of other constituents. The ancient Egyptians obtained marble from the Eastern Desert. They used it mainly for statues and decorative objects, but large marble bangles are known from the Early Dynastic Period (Andrews 1991).

5.4.2 Fine-Grained

Calcite, $CaCO_3$, The fine-grained varieties of calcite usually are referred to as limestone. The appearance of limestone varies widely depending on the presence and amounts of other minor constituents. Limestone occurs in various shades of white, cream, yellow, buff, pink, gray and black. A black variety found in the Egyptian Eastern Desert was carved into beads and pendants from the Badarian Period. Pink limestone from the Western Desert was used for beads and amulets during the Old Kingdom and Early Dynastic Period (Andrews 1991).

Aragonite, $CaCO_3$, has a hardness of 3.5 and a density of 2.94.

Pearl. The chief mineral component of pearl is aragonite ($CaCO_3$). The name aragonite is derived from Aragon, Spain. The color of pearls varies with the type of mollusk species and its water environment. Pearls are characterized by their translucence and luster with an intricate play of surface color. The iridescence is a result of the refraction of light through many layers. Pearls can be found in white, yellowish-white, pinkish-white, bluish-white, reddish, or blackish-gray. The name originates from Latin *perma*, a type of shellfish. *Mother-of-Pearl* is a concretion formed by a mollusk as the bivalve mollusk’s shell. The highest quality pearls are produced from the genus *Pinctada.*

Pearl-oysters and pearl-mussels are found on the Red Sea coast of Egypt, in the Persian Gulf, and off the coast of Sri Lanka (Ceylon). Perhaps the earliest use of pearl in Europe dates to the Paleolithic, when it was used with mussel shells as jewelry. Although pearls have long been a valued gem, they generally were not used in Egypt until Ptolemaic times (Lucas 1989). Pliny lists a number of sources for *margarites* including the seas around India, Arabia, Sri Lanka, the Persian Gulf and the Red Sea (*N.H.* 37.12, 14–17, 62; 9.106–123). In Southeast Asia, mother-of-pearl was used widely as an inlay to decorate jewelry, boxes, weapons, and furniture. Saltwater pearls were also harvested from the northwestern Pacific Ocean and the waters around Japan. Pearls were highly prized on the Arabian Peninsula where there was a highly developed pearl diving and trading industry. The general name for the pearl in Arabic is *lulu* (لولوة), but this term was often qualified by an elaborate nomenclature based on shape, size and color. In the Old World, pearls were used medicinally and were made into beads or gemstones. Mother-of-pearl was used in mosaics during the Roman Empire; the interior of Nero’s palace, *Domus Aurea* in Rome, was inlaid with mother-of-pearl. This practice continued, as can be seen in the famous Ravenna mosaics in the church of St. Apollinare of the late Roman Empire, in which mother-of-pearl was also employed.

Freshwater pearls were collected by Native Americans. They have been found in the ancient burial mounds of the Hopewell people in Ohio. Conversely, aboriginal peoples of Australia regard pearls as a nuisance since they occasionally cracked their teeth on them while dining on north coast oysters (Ward 1985). Freshwater pearls have also been found in rivers in the British Isles and continental Europe.

Although the technique for growing cultured pearls was not developed by the Japanese until the early twentieth century, the Chinese developed a method for making "pearl" Buddhas as early as the twelfth century. A tiny carving or metal casting of a Buddha was cemented to the inside of a freshwater mussel until it was coated with nacre (Ward 1985). These were used as amulets and decorations.

Azurite, $Cu_3(CO_3)_2(OH)_2$, has a hardness from 3.5 to 4 and a density of 3.77. It is found in shades of light to dark blue. Pliny states that *cyanus* (azurite crystals) came from Scythia, Cyprus, and Egypt. *Lapis Armenius* came from Armenia and Spain (*N.H.* 35.47).

Malachite, $Cu_2CO_3(OH)_2$, has a hardness between 3.5 to 4 and a density of 4.05. It is bright green to dark or blackish-green in color. Its name is derived from the Greek *mallow* (green). In the New World, the deposits exploited between 200–800 CE near Chalchihuites, Mexico, included malachite (Weigand 1994). Malachite was used in the Old World at least as early as the fifth millennium BCE. Malachite occurs in Sinai, Egypt. It was rarely used for jewelry by the Egyptians, although a few Predynastic beads and several later ornaments are known (Lucas 1989). Pliny does not list a source for *molochitis* (*N.H.* 37.114). He mentions a number of other materials that could have been malachite. Pliny identifies *chrysocolla* as coming from Cyprus, Armenia, Macedonia, and Spain (*N.H.* 33.4, 86–93, 161; 35.30, 47, 48). He also mentions *chalcosmaragdus* from Cyprus (37.74). Cosmetics and paint pigment were made from malachite, and it was carved into beads, gems, and decorative objects.

Gypsum, $CaSO_4 \cdot 2H_2O$, has a hardness of 2 and a density of 2.32. The name comes from the Greek word for plaster. Alabaster is a compact, fine-grained variety of gypsum. It is found in white, cream, or variegated colors. Its ancient name was originally given to several materials from which ointment vases called "alabastra" were made (from *alabastron*), but its name may ultimately derive from a town in Egypt. Alabaster occurs abundantly in the Eastern Desert of Egypt and at El-Amarna. Jewelry and furniture inlaid with alabaster were found in the tomb of Tutankhamen. Beads are known from the 18th Dynasty and later (Lucas 1989). Cylinder seals, carvings, statues, and small decorative objects were carved from alabaster. It was also used for beads and jewelry inlay.

5.5 Oxide Minerals

Hematite, Fe_2O_3, varies in hardness from 5 to 6 and has a density of 5.26. It is steel gray to iron-black and sometimes appears rusty or iridescent; thin fragments can appear deep blood red. Massive and earthy material is dull brownish-red to bright red. It takes its name from Greek *haimatitis* (blood red). Hematite has been collected by humans since prehistoric times. Cylinder seals of hematite have been associated with Babylonian contexts. Hematite was also found in Egyptian tombs. In classical times, it was popular for carved intaglios (Bauer 1968). Hematite was mined in the Eastern Desert of Egypt during the Roman Period (Lucas 1989). Pliny states *tha*t *haematitus* came from Arabia and Africa (*N.H.* 37.169). It was used as beads, charms, paint pigment, and mortuary offerings. See Chap. 9 for the use of hematite as a pigment.

Limonite is a common rock name for material that is mostly the mineral goethite [FeO(OH)]. Brownish-yellow in color, limonite takes its name from the Greek word for "meadow." Its hardness varies. Pliny's *xuthos* from India may have been limonite (*N.H.* 37.128, 169). Goethite crystal beads are known from southwestern United States. One was a crystal **pseudomorphous** after pyrite and retained the pyrite crystal morphology (Breternitz 1964).

Ilmenite, $FeTiO_3$, has a hardness that ranges from 5 to 6 and a density of 4.72. It is iron-black in color. Its name is derived from a source in the Ilmen Mountains, Russia. Other sources are found in Mesoamerica, where the indigenous people used it to make small mirrors ca. 1500 BCE on the Gulf Coast and in the southern Highlands.

Turquoise, $CuAl_6(PO_4)_4(OH)_8{\cdot}4H_2O$, has a hardness between 5 and 6 and a density range of 2.6–2.8. It is usually turquoise, but the color can vary from bright blue, massive pale blue to sky blue, bluish-green to apple green to greenish-gray Turquoise is one of the oldest known talismanic and curative gems, prized by many cultures worldwide. Its name originates from the French word for "Turkish." The famous Persian mines were located near Nishapu in the province of Khorasan.

Turquoise was used in ancient Egypt prior to the First Dynasty. Turquoise mines operated in the Sinai Peninsula by the fourth millennium BCE. Pliny mentions different green stones that may have been turquoise (*N.H.* 37.74, 110–112) but there seems to have been some confusion between lapis lazuli and turquoise. Turquoise (الفيروز *al-fayruz*) is mentioned by the Arab mineralogist ibn-Mansur in 1300 CE (Bauer 1968). Kostov et al. (2007) have identified turquoise beads from the multiperiod prehistoric Orlovo site in Southern Bulgaria. A Bulgarian turquoise source is located at the Spahievo lead-zinc deposit.

Turquoise has been used in China for more than 3000 years, at least back to the late Shang at Anyang (Wang 1986). Tang Dynasty (618–907 CE) turquoise objects are known from ancient China (Laufer 1913). Carvings are known from the Yin Dynasty (1300 BCE) (Fuquan 1986). In Siberia it has been used since the Bronze Age (Laufer 1913). Turquoise is also mentioned in ancient Tibetan texts (Laufer 1913). The use of turquoise in ancient India in the sixth, fourth, and third millennia BCE is reported by Biswas (1996). Turquoise was carved and made into decorative objects, beads, gems, and seals.

Turquoise mines in the southwestern United States have been worked since prehistoric times. Here, there are a number of turquoise deposits. Perhaps the most exploited is near Chaco Canyon, New Mexico, USA. Over 56,000 pieces of turquoise were recovered from two burials at Pueblo Bonito. Much additional turquoise has been recovered from other sites in Chaco Canyon dating to the period 900–1150 CE (Mathien 2001). Turquoise was a major commodity in Mexico from the late first millennium BCE through modern times. Cortez reported that Aztec chieftains wore turquoise stones in their lower lips. There were numerous turquoise mines in northern Mexico (Weigand 1994).

In Precolumbian Mesoamerica, worked turquoise artifacts are abundant throughout its prehistory beginning in the early Preclassic (ca. 2000–1000 BCE). Its possession signified the status of nobility. Through neutron activation analysis it has been established that much of the turquoise found in Mesoamerica had its origin in the American southwest and the northern part of Mexico (Harbottle and Weigand 1992). It was used in jewelry and as inlay in ceremonial shields and mosaics. Perhaps the most famous artifact of Mesoamerican turquoise is the turquoise-covered mask of Quetzalcoatl made between the fourteenth and fifteenth century, and now in the Museum of Mankind in London (Lehman 1906). For a more extensive treatment of turquoise mosaics, see Saville (1922) and Carmichael (1970).

Spinel, $MgAl_2O_4$, has a hardness between 7.5 and 8 and a density of 3.58. Spinel varies in color from red, blue, green, brown, to black. Its name is from the Latin *spinella* (little thorn). It was probably mined early in antiquity, but the distinction between spinel and ruby was not made until Arab scholars learned to use specific gravity to distinguish spinel from ruby in the eleventh century, and even after this was probably not widely applied (Sersen 1995). In Europe, this distinction was made during the nineteenth century. Until recently, this mineral was often confused with ruby. Arab scholars identified this stone as originating in Afghanistan as early as the tenth century. Pliny refers to red stones by the general term *carbunculus.* This may have included red spinel. He lists sources as India, North Africa, Caria, Ethiopia, Miletus, Orchomenos, Chios, Corinth, Troezen, Marseilles, and Lisbon (*N.H.* 37.91, 92–98, 103, 122, 123). Spinel was used as a gemstone.

Corundum, Al_2O_3, with a hardness of 9 is one of the hardest minerals known. It has a density of 4.05 and is found in several varieties. It occurs widespread in crystalline limestone and dolomite, schists and gneisses, and granitic igneous rocks. The name corundum comes from the Tamil word *kurundum.* Ruby and sapphire are the gem varieties of this mineral.

Ruby. Red in color, ruby takes its name from the Latin *rubeus* (red). The red color arises from the replacement of some Al^{3+} atoms by Cr^{3+}. According to medieval Arab scholars, this stone (*yaaqut*, ياقوت) was mined in Sri Lanka (Sersen 1995). Pliny refers to red stones by the general term *carbunculus.* He lists sources as India, North Africa, Caria, Ethiopia, Miletus, Orchomenos, Chios, Corinth, Troezen, Marseilles, and Lisbon (*N.H.* 37.91, 92–98, 103, 122, 123). It was used as a gemstone and possibly as a cutting or engraving tool. Although ruby is mentioned in some translations of the Old Testament, there is no evidence that this mineral was known to the ancient Hebrews.

Sapphire. This variety is found in blue and yellow colors. Its name is an ancient term of uncertain origin, possibly related to Hebraic *sappir* and Sanskrit *sanipruja.* Pliny's *chrysolithus* from India may have been yellow sapphire (*N.H.* 37.90, 91, 101, 126, 127). *Leucochrysus* may have also been yellow corundum. Pliny does not list its source. Another candidate is a honey-gold stone called *melichrysus* which also came from India (*N.H.* 37.128). According to *Pliny*, *hyacinthus* (blue corundum, named for the hyacinth flower) came from Ethiopia. India may have been its original source (*N.H.* 36.198; 37.122, 125, 126). *Nilos* may have also referred to blue corundum. Pliny listed its source as India, Galatia and Egypt (*N.H.* 37.114). Sapphire was used as a gemstone beginning in the early first millennium BCE and possibly was used early as a cutting or engraving tool because of its extreme hardness.

Sapphire occurs in many igneous and some metamorphic rocks as a primary constituent. Many gem sapphires have been recovered from gravels and placer deposits. Sapphire is dichroic; in other words, the color changes with the angle from which it is viewed. The color is due to small amounts of iron and titanium substituting for the aluminum. Very minute, regularly arranged inclusions of rutile (TiO_2) are responsible for the asterism of star sapphire.

Rutile, TiO_2, has a hardness between 6 and 6.5 and a density of 4.23. It is found in many colors, ranging from red to reddish-brown, yellow, orange-yellow, bluish, grayish-black, to black. A rare greenish rutile also occurs. Its name originates from Latin *rutilus* (red). Pliny refers to red stones by the general term *carbunculus.* This may have included red rutile. Rutile occurs widespread in metamorphic and igneous rocks, and is found in placers, because it is resistant to weathering. It was used as a gemstone.

5.6 Organic Gems

Amber is not a mineral but a fossil resin exuded by the conifer *Pinites succinifer.* It has variable C/H/O ratios and a hardness of 2.5–3.0. Its varieties are succinite and retinite. In modern times geologists have used the term *resinite* as a field term for amber-like material. In Germany amber is called *Bernstein* [stone that burns]. In Egypt the name is *sekal.* Sicilian amber (simetite) has been exploited for many centuries. Much of this amber is similar to Baltic amber (succinite). The geologic age of simetite is Tertiary, produced by trees in the family *Leguminosae.* (Beck et al. 2003) A material related to amber is "copal", found in Mexico, Central and South America, Africa, and India. It is a resin produced by secretions from hymenaea trees. It is not as hard as amber but has been used in ornaments since the Paleolithic. In East Africa it is used to make beads.. This material hardens to a plastic-like polymer that is resistant to decay. (Armstrong 1993) The Maya regarded it as sacred. It also was used as a binder for cinnabar painted on jade as a pigment. Copal from Central America is found in three colors: gold/golden, white, and black.

Amber is easily shaped, even with primitive tools, so it came early to the scene in the Paleolithic as a material to make ornaments. Artifact amber is quite susceptible to weathering and to poor conservation techniques. Many early finds may no longer exist. The color of amber ranges from golden yellow through orange, red, brown, green and violet to black. It can be transparent to opaque. For a discussion of the color of ambers, especially blue amber, see Schlee (1984). Amber's name is taken from Arabic *acnbar* (العنبر, i.e. ambergris). Amber had a supposed medicinal value in antiquity, was made into lacquer, and was used for beads and pipe stems.

The exploitation of amber goes back over 10,000 years in Europe. By the Bronze Age amber was traded throughout Europe, including the British Isles. The best amber is found around the shores of the Baltic Sea; however, it has also been found in Poland, Sicily, and Romania. Deposits found in Mexico have been used since Precolumbian times. Schlee (1980) presents a broad overview of European and New World amber deposits and exploitation. Amber artifacts found in graves along the Baltic Sea coast date back 5000 years (Rice 1987). Amber artifacts found in central Russia, western Norway, and Finland suggest trade as early as 3000 BCE.

Ornaments found in 6th Dynasty (3200 BCE) Egyptian tombs have been labeled "amber" (Rice 1987). Although there are several early references to amber artifacts in Egypt dating as early as 3500 BCE, the analyses of Lucas (1989) show that these were other resins. Some of these may be true resins derived from coniferous trees in the Levant. Fossilized amber was probably not known in Egypt until the later periods (Andrews 1991). A number of resinous artifacts have been found in Egypt dating back to the Badarian Period, but not all of these are true amber. Resinous objects that easily dissolve in acetone or alcohol are not amber. In Mesopotamia, amber is found as early as the mid-third millennium BCE (Harding and Hughes-Brock 1974).

The Phoenicians traded bronze for amber with the Ligurians between the thirteenth and sixth centuries BCE. The Etruscans traded in amber as early as 1500 BCE (Rice 1987). A large hoard of amber found in Hallstatt, Austria, during the nineteenth century, was dated to the Early Iron Age. Homer wrote about amber beads in the *Odyssey.* Amber has long been recognized as an important indicator of Mycenaean trade and exchange. Most amber found in the Aegean area and Italy came from the Baltic region. The earliest true amber from Greece was from Mycenae and Pylos at the end of the Middle Helladic Period (ca. 1900–1600 BCE). By the end of the Late Helladic (ca. 1500–1100 BCE), amber artifacts are found in Crete, other Aegean islands, Cyprus, and Syria (Harding and Hughes-Brock 1974).

The Romans prized amber because it was supposed to cure gastric ailments, headaches, and toothache as well as relieve stress and shyness. They traded for amber with Germanic tribes and, by the time of Emperor Nero, sent expeditions to the Baltic for amber. The Roman poet Ovid in his "Metamorphoses" repeats a Greek legend of the origin of amber. The importance of amber in the Greek world is shown by the Atlantis legend in Plato's "Timeas", where the story has it that amber was mined in great quantities at the capital city of Atlantis. The Greeks were aware that amber could hold a negative electric charge, hence its name *electron* [electrum]. Amber was described by Pliny, the Arab scholar Al-Biruni (eleventh century CE), and by the Chinese scholar T'ao Hung-Ching (d. 532 CE). Pliny identifies different varieties of amber including *electrum* from Scythia; *sucinum* from an island "in the northern ocean," the Gulf of Sidra, Italy, and Sicily; and *chryselectrum*, for which he does not list a source (*N.H.* 37.50–52). Pliny's *lyncurium* may also refer to a variety of amber (*N.H.* 37.34, 52–53; 8.137). The name Lyncurium came from Theophastus but he was referring to a group of non organic minerals.

Coal. Coal is an organic sedimentary rock resulting from the accumulation of plant material. Beds of hard coal have closely spaced vertical jointing known as "cleat," with a less-developed jointing at right angles and a hardness between 3 and 4. The varieties of coal called cannel coal and jet were used for gemstones and decorative artifacts. The color varies from brownish-black to deep velvety black. There is solid evidence that humans used coal os a fuel as far back as 30,000 BP at a Paleolithic site in Silesia where coal outcrops at the surface near the site (Klíama 1956).

Jet was just one of a range of black lithic materials used in ancient times for jewelry. Jet is a lustrous black substance that is easily worked and will take a high polish. Jet has sometimes been called Black Amber. Like amber, it sometimes was burned and the fumes inhaled to alleviate edema, colds, female disorders, and hysteria. Hunter et al. (1993) investigated a wide range of analytical techniques and recommended techniques including Fourier transform infrared (FTIR) spectroscopy and X-radiography to resolve questions of identification. The word "jet" is taken from Greek *gagates* (Gagas), a town and river of Lycia in Asia Minor. According to Pliny, jet was procured from Pamphylia and Lycia (*N.H.* 36.141–142). There appears to have been a marked increase in the use of jet-like materials in the last few centuries of the third millennium BCE (Sheridan and Davis 2002).

Jet occurs as sporadic lenticular masses and is "derived from pieces of drifted wood buried in isolation which did not pass through a peat phase and thus were not coalified, but underwent decomposition and retained their cellular structure" (Ashurst and Dimes 1998). *Cannel* is from Scots dialect for "candle" (Ashurst and Dimes 1998). Deposits found in England have been exploited since prehistoric times, especially the Bronze Age (Shepherd 1981). The earliest use of jet in the British Isles dates to the first half of the 4th millennium BCE. Britain's only significant source of quality jet is at Whitby in North Yorkshire. The other European deposits of importance are in the Asturias in northern Spain, in the Poseidon slate of the Swabian and Frankish Alps in Germany, in the Upper Chalk formations of southern France, on the Dutch island of Bornholm, and in Poland. Lesser deposits have been found in the Czech Republic, Slovakia, Italy, and Portugal, as well as in Canada, the USA, India and Russia. (Muller 1980) Jet beads have been found in female burials of the Iron Age in the southern Ural Mountains (Morgunova and Khokhlova 2006).

Lignite, Kimmeridge coal, black shale, and cannel coal have all been erroneously called jet. Distinguishing between jet, cannel coal, lignite, and torbanite can be very difficult, and special analytical techniques may be required (Watts and Pollard 1999). Cannel coal is dense, lusterless, blackish, and typically shows conchoidal fracture surfaces. It is composed largely of spore and pollen remains, resin, and fragmented leaf cuticles (Ashurst and Dimes 1998). As a gemstone, hard coal was used mainly for beads and small, carved objects. Coal is more rarely found as larger, carved objects such as the Coal Seat at Osborne House in the Isle of Wight, and there is at least one example of the use of cannel coal as decorative inlay in the floor of Lichfield Cathedral in Britain (Ashurst and Dimes 1998).

In the second millennium BCE, jet from the great deposit at Whitby in the British Isles was traded far and wide. Jet amulets have been recovered in a third century

BCE Carthaginian necropolis in Spain. The Romans traded jet throughout the region from Britain to Germany. From early CE times through the Medieval Period jet was employed extensively for religious items in Western Europe.

5.7 Other Gem Minerals

Diamond. With a hardness of 10, diamond is the hardest mineral on the Mohs scale. It has a density of 3.51. It can be colorless, but is also found in white to blue-white, gray, various shades of yellow, brown, orange, pink, red, lavender blue, green, and black. Diamond's name originates from Greek *adamas* (invincible). From that name we get *adamantine* luster. Pliny stated that there were as many as six stones called *adamas.* However, it is unlikely that all of these were mineralogical diamonds (*N.H.* 37.55–61, 200, 204). Pliny also states that diamond splinters were much sought after by engravers of gems. Although diamond is listed in the Bible as the third stone in the second row of the breastplate of the high priest, this is not possible. The gem likely was rock crystal or possibly a highly translucent jade.

Diamonds in India were known from at least the seventh century BCE (Iyer 1942). According to Bauer (1968), most of the diamonds remained in India until the tenth century CE, when invaders plundered the area. Europeans were not aware of India's diamonds until Marco Polo visited the area in the thirteenth century. Because diamond forms in a rare igneous rock called kimberlite, its occurrences are limited. It is highly resistant to weathering, so is found in alluvial deposits. Diamonds were used for cutting tools, as a form of wealth, and for ornaments and gems. Diamond drilling in gemmology dates back to the period 700–1000 CE or possibly earlier. (Gorelick and Gwinnett 1988).

Fluorite (**Fluorspar**) (CaF_2) has a hardness of 4 and perfect octahedral cleavage. It has a density of 3.18. Fluorspar can be colorless, but is also found in shades of purple, blue, green, yellow, white, pink, crimson to brownish-red, brown, and bluish-black. Its name origin is from Latin for "to flow." Beads of fluorspar have been found in the ancient ruins of Tiahuanaco, near Lake Titicaca, on the high Bolivian plateau (Bauer 1968). Predynastic Egyptian beads of fluorspar are known (Lucas 1989). According to Pliny, *murrina* came from Carmania (Parthia) (*N.H.* 33.5; 36.1, 198; 37.18–22, 30). It is geologically widely distributed and was used as a gemstone.

Apatite, $Ca_5(PO_4)_3(F,OH)$, has a hardness of 5 and a density of 3.2. It can be colorless, white, gray, yellow, yellowish-green, pale to very dark blue, violet-blue, violet, purple, or various shades of red and brown. It has found minor use as a gemstone.

Chrysoberyl, $BeAl_2O_4$, has a hardness of 8.5 and a density of 3.75. It is found in two varieties, *alexandrite* and *cat's eye.* It has an extensive color range and can be found in various shades of yellowish-green, yellow, gray, brown, blue-green, and emerald green. Green varieties of this mineral often appear purplish-red under artificial light. Its name is taken from the Greek word for "golden" and the mineral beryl, in allusion to its color and beryllium content. This may be the mineral Pliny calls *chrysoprasus*; however, he lists no source where it is found (*N.H.* 37.77, 109, 113). It was used as a gemstone.

5.7.1 Sulfide Minerals

Marcasite, FeS_2, has a hardness between 6 and 6.5 and a density of 4.92. It is pale brass-yellow to tin-white. The name is derived from an Arabic or Moorish word (مرقشيشا) applied to pyrite and other substances. Mineral deposits exploited between 200–800 CE near Chalchihuites, Mexico, included marcasite (Weigand 1994).

Pyrite, FeS_2, also has a hardness of between 6 and 6.5. Its density is 5.02. It is pale brass-yellow. Pyrite's name is derived from the Greek word for fire (*pyrite*). There is evidence that pyrite had been used as early as the Upper Paleolithic in Denmark and the Netherlands with flint as a fire-starter. (Stapert and Johansen 1999) According to Pliny, *pyrites* came from Cyprus. However, he identifies its principal use as medicinal (*N.H.* 36.137–138; 37.144). Dioscorides describes pyrite as an ore of copper but acknowledges it sometimes contains no copper. Large, polished plates of this mineral were used by the Incas as mirrors. Mineral deposits exploited between 200–800 CE near Chalchihuites included pyrite (Weigand 1994). Pyrite artifacts were found at the Cenote of Sacrifice at Chichen Itza, Yucatan, Mexico (Moholy-Nagy and Ladd 1992). It occurs as the most abundant and widespread sulfide mineral in rocks of all ages. The ancient Chinese extracted sulfur from pyrite.

Cinnabar, HgS, has a hardness between 2 and 2.5 and a density of 8.1. Scarlet, brownish-red, brown, black, and lead-gray varieties have been found. The Latin word *cinnabaris*, derived from Persian *zinjifrah* (زنجفر), meaning "dragon's blood," gives this mineral its name. Mineral deposits around Chalchihuites (Mexico) exploited between 200–800 CE included cinnabar (Weigand 1994). Pliny lists ancient sources as Spain, Ethiopia, and Carmania (*N.H.* 33.115–117; 35.30). Cinnabar was used for beads, small, carved decorative objects, and as a paint pigment.

Galena, PbS, is lead-gray in color and has a hardness of 2.5. It has a density of 7.58. Its name is taken from Latin for "lead ore." Galena has been used in North America for over 8000 years (Walthall 1981). The earliest archaeological evidence for use of galena in North America dates from the Early Archaic Period. There is a large amount of archaeological evidence for galena use associated with the Copena Culture. In various contexts it was used for beads, charms, carvings, ornamental surfaces, for paint pigment, and as mortuary goods. Early Egyptians used powdered galena as a cosmetic, for eye shadow. Galena is found primarily in hydrothermal ore deposits in limestones. Important deposits occur in the USA, England, France, Germany, Austria, and Romania.

Stibnite, Sb_2S_3, was called *stibi* by the ancient Greeks but the "stibic stone" of the Bible may refer to powdered galena and the use of the term antimony in Isaiah in the Revised Standard version may refer to stibnite.

Chapter 6
Soft Stones and Other Carvable Materials

6.1 Introduction

Humans have been carving stone since the Paleolithic. Figure 6.1 shows a famous early example. Throughout the Mediterranean world, the carving of stone vessels dates from the Neolithic Period and continued through the Greco-Roman era. However, the apex of carving was reached in the late Predynastic Periods of Egypt and Mesopotamia and in the Early Bronze Age of Greece. Various soft stones were employed, the most popular being limestone, basalt, alabaster, serpentine, marble, slate, chlorite, selenite, steatite, and gypsum. The repertory of shapes and sizes was enormous. Professional carvers produced every thing from huge amphorae to small, delicate alabaster and amulets. At times the selection of lithologies for the manufacture of a class of objects is puzzling. The inhabitants of Kodiak Island, Alaska, from 500 to 1750 CE, used local diorite and granite for lamps rather than the available softer soapstone, slate, and limestone.

A visit to the exhibits of any of the world's major archaeological museums will show painted limestone, greywacke, quartzite, schist, and igneous rock statues from ancient Egypt as well as Near Eastern cylinder seals of hematite, apatite, steatite, chalcedony, lapis lazuli, and shell material. Soft stones such as sandstone, travertine, and marly limestones have also been used as decorative or finishing material on buildings through antiquity.

Quite often softstone is a combination of mineral species. The Semail Ophiolite in the al Hajjai Mountains of southeast Arabia is considered to be the primary source of carved softstone artifacts found at Iron Age archaeological sites along the Arabian Gulf coast. Provenance studies (Ruge et al. 2007) to source softstone artifacts from the United Arab Emirates showed the source materials and the artifacts to be composed of serpentine, steatite, soapstone [not further identified] and chlorite. Rocks from the ancient quarries were more mineralogically varied and included the talc-related minerals birnesite, bemenite, talc, clinochrysotile, antigorite, and dolomite.

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Fig. 6.1 The "Venus à la Corne," Gravettan Period, Laussel, France

6.2 Serpentinite

Serpentinites consist of combinations of the morphologic varieties of serpentine, $Mg_3Si_2O_5(OH)_4$, with a hardness of 2.5–3.5. The fibrous form, *chrysotile*, tends to develop as an interlacing network of microveinlets enclosing cores of cryptocrystalline serpentine in which relict grains of olivine may survive. The variety *antigorite* is formed in sheared serpentinite. The name comes from the locality at Antigoro, Italy. Antigorite is sheet-like and often flaky. Other secondary minerals that occur in serpentinites are talc, actinolite, and a magnesium carbonate. Serpentinite occurs very widely as the alteration product of mafic igneous rocks. In the Alpine chains of Europe, the Urals, and the Appalachian Mountains of the USA, large bodies of peridotite, a rock composed of olivine and pyroxene, are found as pods and elongate sheets metamorphosed to serpentinite. This stone was called *serpentium* in classical times because of its markings that resembled those of snakes (Pliny *N.H.* 36.9.55). One source of serpentine was from a quarry near Larissa, in Thessaly. In this period, serpentinite was also quarried near Tinos, Greece. In the Italian Alps and Apennines, basal layers of serpentine grade upward to basalts and diabases, and then to radiolarian cherts.

Serpentinite has been highly prized for carving for over three millennia, especially by the Minoans in Crete. However, recent unpublished studies by the author have shown that many of the green carved stone bowls are composed more of talc and chlorite than serpentine. The name chlorite comes from the Greek word for green.

Serpentinite has been used since antiquity in the Old World for stone bowls, vases, carved figures, and occasionally for molds. For example, at the 7th millennium BCE settlement of Nea Nikomedia, Greece, several small toads carved of serpentine were excavated (Rodden 1962). A serpentine sculpture of a human-headed bison was recovered from Mesopotamia and dated to the Second Dynasty of Lagash, ca. 2100 BCE (Harper 1997). Serpentinite was used for vases and ceremonial mace heads in ancient Egypt. Vases carved of serpentine were also found at Minoan Crete. Cretan artisans made use of serpentine and chlorite in a huge repertory of shapes. Stone vases, jars, ladles, lamps, amphorae, pithoi, tables, goblets, rhytons, and bowls were excavated from tombs in the region of Mesara and Mochlos, and the early palace at Phaistos and at the palace of Knossos. A number of ritual vases from between the eighteenth and seventeenth centuries BCE are carved in relief with scenes that suggested their ritual use. In some cases the surfaces of these vases were then covered in gold leaf. Pebble mosaics dating between the sixth and the fourth centuries BCE have been found in Greece, Asia Minor, and Sicily. These mosaics were frequently constructed of marble, serpentine, and alabaster. During the Middle Ages, serpentine was quarried from Monte Ferraro near Florence and from Crevole in Chianti (Penny 1993).

The term greenstone has been used to describe many different green rock and mineral species including a metamorphosed diorite used for beads and ornaments. Greenstone is thus a generic term, most often applied to low-grade metamorphic rocks derived from mafic or ultramafic igneous rocks. When sufficiently hard [6 or more] and cohesive they are easily shaped but hold their shape and edge as axe heads and celts. (Liu 2000) Hard greenstone axe blades from prehistoric Malta have been described by Skeates (2002) but the rock type was not further specified. Numerous greenstone axes of Chalcolithic and Bronze Age were found on archaeological sites and in collections from Serra Orlando in eastern Sicily. The abundance of artifacts suggests wide-scale production and trade of these tools, dating from the third millennium BCE up to the Hellenistic Period. Petrologic analyses of the serpentinite rocks indicate that their source is the Calabro-Peloritani Arc in northeastern Sicily (Leighton et al. 1989).

White serpentine was carved into mortars for medical use and into boxes and vessels during the Roman Period (Pliny *N.H.* 36.60, 158; 37.73, 144). Pliny recognized two types, one soft and white, the other hard and dark with markings resembling snakes. He noted that small columns could also be constructed of serpentine. When carved into an amulet, serpentine was believed to afford protection from delirium or a coma (*N.H.* 36.55–56, 158). Saxon and Norman arches in Cornwall used a type of serpentinite (Ashurst and Dimes 1998:51). The tomb of Cosimo di Medici, built in

Florence between 1465 and 1467 by Andrea del Verrocchio, is carved from marble, serpentinite, and porphyry. Another rock from the basic and ultrabasic greenschist facies, used in central and eastern Italy, is called “pietra ollare”. These rocks are magnesite-bearing talc-schists that contain carvable soapstone, used for two millennia for stoves and cooking utensils. It was mentioned by Pliny as coming from an area near Como. The typical refractory pietra ollare was composed mainly of talc, chlorite, and carbonates although other mineral assemblages with serpentine, amphibole or olivine occur. (Santi et al. 2005).

Serpentine was used throughout North America because it was easily worked. Several prehistoric quarry sites have been located in the eastern United States. A combination of analyses, including thin section petrography and atomic absorption spectrometry, have been employed to obtain a geochemical “fingerprint” for serpentinite tools and smoking pipes in order to trace them to their quarry source (Turnbaugh et al. 1984). In Alabama, 578 greenstone artifacts, predominantly celts were excavated from the Mississippian era Moundville site. These tools were manufactured from local outcrops in the nearby Hatchet Creek Valley (Gall 1995). The geologic source of greenstone artifacts from Arkansas (Gall et al. 2002) and Alabama USA (Gall and Steponaitis 2001) have been traced to the Hillabee Metavolcanic Complex of eastern Alabama. These rocks have been called a metabasite [a term coined by Finnish geologists to denote metamorphosed mafic rock].

From the Middle Formative Period in Mesoamerica, important Olmec sites are located along what appears to have been part of a large trade network to obtain raw materials for luxury goods. The Olmec sometimes obtained serpentine from remote areas, suggesting that this was a highly valued raw material. At the Mesoamerican site of La Venta, serpentine flagstones, figurines, and celts made up ritual offerings buried under the plazas of Group A, thought to have been built between 1100 and 1000 BCE (Drucker et al. 1959). Winged pendants of serpentinite have been found at two archaeological sites in the Venezuelan Andes. The area has no local sources for this raw material, suggesting that the indigenous people obtained the stone from the Antilles or from the Sierra Nevada de Santa Marta Colombia through trade (Wagner and Schubert 1972). In the Far East, early prehistoric inhabitants of the tropical coast of Thailand carved serpentine, marble, talc, and jade into bracelets (Higham and Bannanurag 1992).

Sepiolite is an alteration product of serpentine. It can be found in deposits in Turkey, Greece, France, the Czech Republic, and the United States. At the third millennium site of Maikop in the northern Caucasus (Russia), a necklace of sepiolite beads was found in a mound burial on a male skeleton (Nekhaev 1992). Meerschaum may have been exploited in the Roman Period (Ball 1950). Its use as a carving material has been documented since the late 1600s from the sepiolite deposit at Vallecas, Spain. (Sariiz and Isik 1995). Since the nineteenth century, sepiolite has been used primarily to make Meerschaum pipes. High quality meerschaum nodules occur in Pliocene-age conglomerates associated with dolomite, magnesite, opal, and lizardite in Eskiseher Province, Turkey. Virtually all meerschaum in Turkey comes from Eskiseher where exploitation began in the eighteenth century. The sepiolite nodules are from 8–10 cm in diameter but some range up to 25 cm. Some have magnesite cores. The name meerschaum is from the German for "sea froth" in reference to its low density and color.

6.3 Steatite and Soapstone

Steatite is a fine-grained, compact rock consisting chiefly of the mineral talc (hardness 1) but usually containing many other harder mineral constituents including chlorite, mica, tremolite, quartz, and magnetite. This has led to great difficulty in sourcing steatite artifacts to their geologic origin. (Jones et al. 2007) Talc occurs widespread as a common mineral of secondary origin formed primarily by the hydrothermal alteration of basaltic or gabbroic rocks. Large steatite outcrops are found in England, France, Italy, Austria, Germany, Switzerland, India, China, and the USA. Because of its softness and cohesion, it has been used since antiquity to carve ornaments and molds for casting. When fired to temperatures between 800 and 1000°C, steatite undergoes mineralogical changes that increase the hardness from 3–4 to greater than 5. Bar-Yosef Mayer et al. (2004) in studying Chalcolithic beads from the Levant found that heating talc to over 900°C altered the mineral composition to enstatite and the high-temperature silica mineral cristobalite which accounts for the increased hardness.

The names steatite and soapstone are used interchangeably. Some geologists draw a small distinction between steatite composed mainly of talc and soapstone (often with a more greasy feel) composed of talc, chlorite, serpentine, and often dark mica. Some material called steatite or soapstone is primarily composed of the soft mineral **pyrophyllite**, which gives the rock similar properties. Steatite occurs as lenses in metamorphosed dolomites, schists, or gneisses, or as large pods in **ultrabasic** intrusives. Major deposits occur in metamorphosed masses in the Alps and Pyrenees, in the Italian Piedmont, in the **shield** areas of Russia, Scandinavia, South Africa, India, Pakistan, Iran, and in parts of China, Japan, the United States, and Canada. Steatite and serpentinite often occur together as rock masses on the border of ophiolites.

Steatite has high latent heat retention. Vikings quarried large blocks of steatite to set around their fires. At night the steatite radiated back the absorbed heat. This property also accounts for ancient steatite cookware and steatite molds for casting copper or bronze objects. Nearly all of the North and Central American prehistoric peoples used steatite for pots, bowls, and pipes. The Inuit and others used steatite for lamps. Steatite outcrops are common in many locations throughout the Appalachian Mountains, Georgia, Tennessee, North and South Carolina, Alabama, Florida, and the northeastern United States (Bushnell 1940; Fowler 1975). Steatite also has excellent thermal shock properties, enough to go from sub-freezing conditions to the heat of a campfire. (Adams 2006) Interest in steatite artifacts in the United States started early in the twentieth century (Holmes 1912). Steatite has been used extensively in prehistoric North America during the last 4000 years for effigies, figurines, beads, gorgets, sucking tubes, pipes, mortars, and utilitarian and decorative stone bowls. Steatite bowls are characteristic of the Terminal Woodland Period in the eastern United States, where steatite also was a pottery temper. In California, it was used especially for figurines, beads, effigies, and pipes. Steatite vessels in eastern North America are widely distributed, from southeastern Canada to Louisiana, in the time horizon 1800–800 BCE. Steatite outcrops are concentrated along the eastern flank of the Appalachian Mountains. Truncer (2004) provides a map of steatite quarries and outcrops in the eastern United States.

Carved steatite tubes and pipes, some with incised figures, were recovered from the Coal Draw site in north central Wyoming. The large number of intact and broken specimens suggested to the excavators that the tubes had been used as sucking tubes by shamans. Since the pipes contained no residue, it was hypothesized that they may have been deposited as grave goods during late prehistoric or protohistoric times (Frison and VanNorman 1993). In northwestern Wyoming, small- and medium-sized bowls of a truncated ovoid shape with flat bases were made from steatite (Wedel 1954). Fine bowls representing seated human figures, human heads, and zoomorphic shapes were made from high-quality local steatite by prehistoric peoples along the middle and lower reaches of the Fraser River and the Strait of Georgia area in southwestern British Columbia and northwestern Washington (Duff 1956). Steatite quarries in Pennsylvania are suggested as the source of steatite vessels found at habitation sites in Delaware. The Shawnee later utilized these quarries around 1750 CE (Crozier 1939). Steatite artifacts were found associated with tools found at a quarry near Westfield, Massachusetts (USA), and dated to the Old Algonkian Culture. Two pipe forms and more than 26 pot forms ranging from 15–30 cm in length were recovered, suggesting that artifacts were at least partially finished before they were transported from the site (Fowler 1943).

About 7500 years ago, Montagnais-Naskapi Indians of southern Labrador made plummets, possibly used as fishing sinkers, of steatite. These plummets were also found at Late Maritime Archaic sites (4000–3500 BCE) in southern and central Labrador and in Newfoundland. The Dorset Eskimos of central Labrador used steatite for lamps, cooking vessels, and amulets about 4000 years ago (Allen et al. 1978). During the Dorset tradition (550 BCE–150 CE) in the Arctic, it was carved into human and animal shapes, and it was also used extensively for posts and lamps (Allen et al. 1978; Maxwell 1985). A steatite spindle whorl found at the Viking site of L'Anse aux Meadows indicates that Europeans also made use of the local steatite quarries. The most likely source of these artifacts is the local quarries in Labrador, at Freestone Harbour and Moores Island near Okak, and large outcrops at Fleur de Lys Island in Newfoundland. Crushed steatite was used as a temper in some early eastern North American ceramics. Heavy steatite bowls were widely traded in the northeastern United States. In the southeastern United States, steatite was used for atlatl weights, net sinkers, ornaments, and cooking vessels during Preceramic Periods.

Steatite was employed for carving beads, small statuary, cylinder seals, scarabs, amulets, bowls, vases, and other utensils in the Old World. The Harappan civilization in the Indus Valley made extensive use of steatite. Seals, beads, figurines, and decorative objects were carved from it, and steatite was used for making microbeads (Hegde et al. 1982). Glazed steatite bead working was one of the specialized crafts practiced at the site of Harappa from the earliest period of the site (ca. 3300 BCE) and continued until the latest prehistoric phase (ca. 1700 BCE) (Kenoyer 1997). Steatite was even carved into a wig at Harappa (Meadow 2002).

One of the most important uses for this material was in the manufacture of vases. Steatite artifacts excavated at the Iranian site of Tepe Yahya dating to the third millennium BCE (ca. 2600–2500) suggest that this locale may have been a production and distribution center for vases and vessels, plaques, and other small objects of steatite and chlorite (Asthana 1982). Holes in serpentinized zones surveyed near the site may be evidence of ancient mining practices. X-ray diffraction analyses by Kohl et al. (1979) suggest that, in addition to Tepe Yahya, there may have been other locations for the production of soft stone luxury goods at Bismaya, Mari, Tarut, Failaka, and the Arabian Peninsula using separate lithic sources. Steatite was a favored raw material for the production of cylinder seals in Mesopotamia, and it was employed in Egypt for seals, amulets, and scarabs.

Early Cycladic artisans carved vessels of steatite, chlorite schist, and other soft stones into beakers, bowls, **pyxides**, pans, and lids. Some of these have elaborately carved exterior decoration (Getz-Gentle 1996). While these vessels are found distributed throughout the Cyclades, the primary center for production of these sculptures is believed to have been the island of Naxos. Many carved seals resembling those of the Near East have been recovered from early tombs in Crete. Some of these early Cretan seals were made of soft, easily cut stones, such as steatite, serpentine, and chlorite.

Theophrastus mentions a "Siphnian stone" that could be turned on a lathe and carved into vessels. He also mentions a silver-colored "Magnesian stone" that could also be turned on a lathe. The latter was probably a variety of steatite containing talc, which sometimes takes on a pearly or silvery luster (Moore 1978). Pliny also knew of this "Siphnian stone" (*Siphnius Lapis*) and observes that when heated it turned black and hard (*N.H.* 36.159). He recognized another form of steatite (*steatitis*), which likewise came from the island of Siphnos. He records that it is a green, soft stone that is easily turned on a lathe. In the Classical Period, steatite was obtained from quarries on Siphnos and Como in Italy. The Romans used steatite mainly to produce cooking utensils and tableware, but they also formed it into roof tiles and drains. Its "soapy" feel was apparently a property noticed by the ancients, since Pliny mentions that varieties of steatite were named after the fat found in various animals.

During the Byzantine Period, steatite plaques carved in low relief with religious scenes or representations of saints were produced, predominantly from the ninth through fifteenth centuries CE. Examples of these may be seen in collections in the Louvre (Paris), Fiesole (Italy), and in the Hermitage (St. Petersburg) (Durand 1988). Small icons, crosses and pectorals were frequently carved of this material, such as those found in Tarnovo (Tarnovgrad, Bulgaria) and churches in Salonika (Totev 1992).

Fragments of steatite figurines recently recovered from a prehistoric site in western Igbomina (Nigeria) are related to approximately 1000 previously recovered

Esie steatite figures from north central Yorubaland, suggesting that this was a large center for the manufacture of steatite objects (Usman 1995).

6.3.1 Asbestos

Asbestos can be any of several minerals that readily separate into long fibers. Chrysotile, the fibrous form of the mineral serpentine, is the best-known type and accounts for about 95% of all asbestos in commercial use. It is a hydrous magnesium silicate with the chemical composition $Mg_3Si_2O_5(OH)_4$. The raw material, called *amiantus* by Pliny the Elder, may have been chrysotile. Pliny notes that asbestos was found in the Arcadian Mountains of Greece and had an iron-like color (*N.H.* 37.146). He adds that this substance was similar in appearance to alum. It was valued in antiquity because of its resistance to fire, and because it supposedly afforded protection from all magical spells, particularly those of the Magi. Pliny states that this "earth-flax" may be separated into threads and spun. It was woven into capes and clothing (*N.H.* 36, 19, 31, § 139).

Dioscorides reported reusable handkerchiefs sold to theater patrons were cleansed and whitened with fire. He also described an asbestos quarry on Mount Olympus in Cyprus. Strabo identified the first Greek asbestos quarry on the island of Evvoia. Some medieval alchemists believed that asbestos grew as hair on fire-resistant salamanders thus leading to the name salamandra for asbestos. Marco Polo visited a Chinese asbestos mine and debunked the salamander legend.

Asbestos was exploited in central Asia and the mountains of Tajikistan. The Abbasid Arabs wove this material into a fabric used for fireproof uniforms and for lantern wicks (Bilkadi 1995). In North America, archaeologists discovered a belt fragment of braided asbestos from the pueblo Awatovi in north-central Arizona (Stubbs 1959).

6.4 Alabaster and Gypsum

The name alabaster comes from the Greek word *alabastros*, a stone from which ointment vases were made. It is a fine-grained, cohesive variety of the mineral gypsum, usually with a whitish to pinkish color. It is quite soft, with a Mohs hardness of 2, making it softer than a fingernail (2.5). Because thin pieces are translucent, it was used to make lamps. Its aesthetic quality also caused it to be selected for the manufacture of small objects such as statuettes, vases, bowls, flasks, and boxes (Fig. 6.2). When properly worked, alabaster gains a silky or waxy sheen that is very lustrous.

From early dynastic times the Egyptians used alabaster as a subsidiary building material for lining passages and rooms. Some alabaster sculpture, such as the Berlin Museum alabaster baboon in the round inscribed with the name Narmer, can likewise be dated to this early period (Lange and Hirmer 1956). It was also carved

Fig. 6.2 Alabaster flask, Late Bronze Age

Fig. 6.3 Eighteenth Dynasty alabaster bowl from the tomb of Tutankhamun, Valley of the Kings, Egypt

into translucent cups and offering tables. By the Middle Kingdom, alabaster was quarried at Hatnub and used to carve colossal statues such as those of Amenemhet III, seen by Herodotus (Histories II.149). The use of alabaster by the ancient Egyptians was known to Theophrastus and Pliny. Alabaster was popular in ancient Egypt for funerary vessels to contain the viscera of mummies and with the Etruscans for vases, urns, and ornaments (Fig. 6.3). During the Middle Kingdom it was used to make sarcophagi. Most New Kingdom stone vessels were alabaster (both true alabaster and calcite). Some of the finest objects from the tomb of Tutankhamen were made of alabaster (Fig. 6.3). Some Egyptian material called alabaster is actually fine-grained calcite that has a hardness of 3. Various types of alabaster were a popular medium for carving vases, bowls, and statuary in Mesopotamia from the Protodynastic Period onward. The most famous alabaster quarries in Egypt are located at Hatnub, although smaller sources between Helwan and Asyut were exploited in Pharaonic times.

A famous alabaster vase from Uruk depicts a ritual scene before a goddess. At Tell Brak, alabaster heads were recovered from the Eye Temple dating to the Uruk Period (ca. 4000–2900 BCE) (Mallowan 1947; Oates 1985). In Assyrian palaces a principal use of alabaster was for the production of panels depicting scenes of war, hunting, and ritual ceremonies. Some of the most famous of these were found in the palace of Sargon II at Khorsabad (ca. 705 BCE). White alabaster was used for monumental statuary in Mesopotamia, some of which was quarried near Mosul and used by Assurnasirpal in 879 BCE. In 645 BCE the great wall relief of a lion hunt was produced for King Ashurbanipal at the site of Nineveh.

In ed-Dur, a pre-Islamic site in the lower Arabian Gulf, flat alabaster fragments 1 cm thick were discovered in the remains of two private houses. These fragments appear to have been used as windowpanes to enhance natural light. Such alabaster plates were used in Yemen as late as 1928 and can still be seen today in mosques (Potts 1996). Phoenician tombs found at Almuñécar, Trayamar, and Villaricos in Spain, included alabaster wine jars among their funerary goods. Alabaster was also a preferred raw material for small flasks and boxes that contained perfumes, oils, and unguents during the Greco-Roman Period. Pliny (*N.H.* 36.12, 60) considered alabaster the best

Fig. 6.4 Persian Period alabaster bottle, Tel Michal, Israel

medium in which to keep unguents fresh (Fig. 6.4). Since Pre-Roman times, some of the finest alabaster has come from the quarries around Volterra and Castellina, Italy. During the Hellenistic Period, tessellated pavements using alabaster and other stones became increasingly popular, especially in public buildings and baths.

Medieval artisans employed alabaster as a substitute for marble. It was extensively used in the production of statuary throughout Europe (Paatz 1956; Tavender 1959). One of the major uses of alabaster was for altar carvings, and more than 3000 such pieces are still extant throughout Denmark, Germany, France, Holland, Spain, Italy, and England. By the fourteenth century, gypsum alabaster, which is easy to carve and gild, was being used in Western Europe (Penny 1993). Calcite alabaster (often called "banded alabaster" or "onyx") was also employed. Alabaster quarries near Derby and Nottinghamshire in England provided raw material for such varied uses as gravestones, tables, paving stones, chimney pieces, candlesticks, plates, and bowls (Firman 1984). Other European quarries are found in Catalonia, France, Germany, and the Netherlands (Penny 1993).

Gypsum. Gypsum is hydrous calcium sulfate ($CaSO_4 \cdot 2H_2O$). The term is both a mineral name and a rock name. Mineral varieties include selenite, a transparent cleavable form, and alabaster, which is massive and finely crystalline, pure white, or slightly tinted, and translucent. The name comes from the Greek for moon-like in reference to its reflective properties. Gypsum is a common mineral widely distributed in sedimentary rocks, often as thick beds. The Minoans used large gypsum blocks as building stone.

Gypsum is an ancient name derived from the Greek word for plaster. Gypsum has been widely used as a plaster. It is the raw material for plaster of Paris. When heated to about 175°C, gypsum loses three-quarters of its water. On cooling, the hemihydrate (plaster of Paris) can be mixed with water and spread, cast, or molded. It then sets to a dense, rocklike mass of intergrown, needlelike crystals. The Egyptians used this hemihydrate on the walls of tombs. This material has been used in many countries and in every period since that time.

Gypsum was used as a mortar from the Early Bronze Age. It was similarly employed in this manner to bond wood in ancient tombs of central Germany. During the Bronze Age, gypsum was used for ornamental construction within the palaces of Crete, mainland Greece, and on the islands of Zakynthos and Kephallenia (Gale et al. 1988). About 2000 BCE, the ancient Minoans built a sandstone-paved road extending from the southern to the northern coast of the island of Crete. The mortar used to affix the sandstone pavement was a clay/gypsum mixture. The ceremonial chair in the so-called throne room in the palace of Knossos is carved from gypsum, and the later palace at Mycenae has a floor bordered with gypsum. Large sheets of gypsum were used to cover the lower parts of the interior walls of the palaces and houses. In the Greco-Roman Period, public and private statues were carved from this material. Pausanias mentions that he saw a painted gypsum statue of Dionysus in the home of a private individual (*Description of Greece* 9.32.1). Like alabaster, gypsum can be cut into thin slabs and used as a light-diffusing medium, and sheets of selenite have been found from the Roman Period. In the Medieval Period, such "windows" were often pierced and fragments of colored glass were inserted into the apertures.

The floor of the Great Bath, located on the citadel at Mohenjo Daro, is built of two layers of brick cemented by a mortar of gypsum. During the first century CE, construction of roads in India also made use of gypsum and other adhesives (Forbes, in Singer et al. 1954). Gypsum was mixed with glue to make *gesso*, a fluid, white material applied to smooth surfaces as a ground for artistic paintings or for gilding. Carved wooden sculptures of seated Kuanyin from the Song Dynasty in China were covered with gesso before they were painted or gilded. Tempera painting on a gesso ground was especially popular in the Middle Ages.

In North America, gypsum crystals were often found on archaeological sites along the Missouri River near South Dakota. Although their use has not been ascertained, these crystals were located near house sites, and ethnographic analogy suggests they may have been ground into a fine powder and used for cleaning and polishing projectile points, or perhaps to polish quill work (Porter 1962).

6.5 Limestone and Marble

Limestone and marble, made up exclusively or mostly of the mineral calcite [hardness 3], are easy to sculpt if the material has enough cohesiveness. The Venus of Willendorf statuette (Fig. 6.5) was carved from an oolitic limestone.

The very much larger limestone head (Fig. 6.6) is from first century BCE Turkey.

Because it takes a high polish, marble was one of the preferred raw materials for decorative stone, statues, and portrait busts during antiquity. It can be found in deposits of wide aerial extent that are relatively free of cracks and easy to quarry. The use of marble in the minor arts was varied. However, it was principally employed in antiquity to finish temple fronts, and the exterior of civic buildings and for the production of monuments, columns, and reliefs, interior embellishment, statuary, busts, stelae, furniture, tabletops, and novelties.

Marble was employed during the Neolithic Period to carve stone vessels and lamps. The Egyptians and Mesopotamian civilizations used white marble for sculpture and

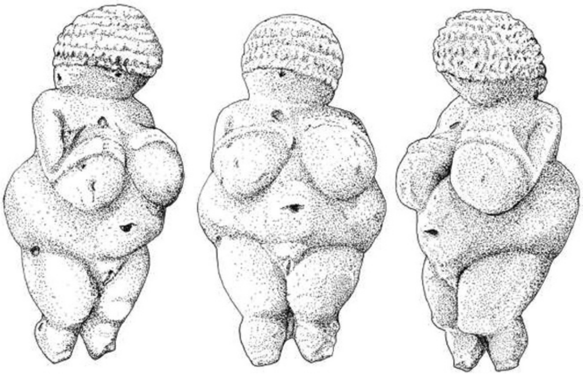

Fig. 6.5 Three views of the Venus Willendorf (Austria), carved from a non-local oolitic limestone about 22,000–24,000 BP, it was tinted with ochre

Fig. 6.6 Limestone sculpture from Nemrut Mountain, Turkey, a first century BCE site of Antiochus I

wall carvings. However, the greatest use for marble in the minor arts occurred during the Bronze Age. From the Early Cycladic Bronze Age (ca. 3200–2700), specialists in the Cyclades carved marble bowls in a wide variety of shapes, the most popular being spherical, hemispherical, conical, and cylindrical (Getz-Gentle 1996; Fig. 6.7). These are often found deposited as grave goods, and chests have also been recovered from Early Cycladic tombs. This art form spread throughout the Mediterranean to Minoan Crete and the Greek mainland. An extensive industry in stone bowl carving also developed in Predynastic Egypt. A three-volume publication by El-Khouli (1978) is a definitive reference for this Egyptian stone bowl industry. Pliny notes the use of marble to carve vessels, particularly those for cooling liquids. A dark red marble from Cape Taenarum known as *rosso antico* was used at both Knossos and Mycenae for carved decorations (Dodge 1988). Several different types of marbles are famous from antiquity, and most continue to be used today.

Exploitation of marble quarries began in Asia Minor and the Cyclades around the seventh century BCE, and advanced in the following centuries. Until the Hellenistic Period, white marbles were preferred. These include Parian marble, a pure-white, semitransparent variety quarried from Mt. Marpessa on the Cycladic island of Paros. It was especially popular in the Classical Greek Period and was used in all the major Greek temples either for statuary or as a subsidiary raw material in their construction. Marble was also quarried at Proconnesus on the island of Marmara in Turkey. Proconnesus marble was the most widely used for buildings and sarcophagi. Pentelic marble, from Mount Pentelicus in Attica about 16 km northeast of Athens, is the famous marble selected by Phidias, Praxiteles, and other Greek sculptors of the fifth and fourth centuries BCE for production of what are perhaps the best-recognized statues of antiquity. White marble was also obtained from Mount Hymettus in Greece. Pure white marble was not only used for freestanding statuary, but also as a veneer, to

Fig. 6.7 Cycladic marble statuette, Greece

construct colonnades, and for exterior carving that was painted. In some cases statues called acroliths were produced, in which the body of an individual would be carved of wood (frequently gilded) and the head, hands, and feet were made of marble.

Polychrome marbles were also employed, but these were reserved for the interior of buildings (Kozelj 1988). Exploitation of colored marble began during the Hellenistic Period, when it was used as a decorative stone in Ptolemaic Egypt where both onyx and purple porphyry are also found (Dodge 1988). Variegated marbles were quarried at Numidia, and the islands of Chios, Ceos, and Teos. Green marble was imported from the quarries at Euboea, red and grey marble from Chios, and pink and white from Teos (Kozelj 1988). During the Roman Period, colored or variegated marbles increased in popularity, and frequently various types of marbles were used in the same work: one for the face and body, and others for drapery or adornment. Colored marbles were also utilized in interior decoration and for carving small objects. The popularity of variegated marble continued into the Renaissance when it was used in various combinations in statuary. It was employed in the minor arts to fashion tabletops, veneers, parts of furniture, altar pieces, and decorative vessels.

Principal sources for high-grade marble required for freestanding Roman statuary were found at Paros, Pendeli, and Dokimeion (Turkey). In Italy, quarries were exploited at Luni and Carrara. Pure white Carrara marble from the north central region of Tuscany (Italy) was used extensively in Roman times. This marble is noted for its purity, grain size, and color, which make it a coveted ornamental and statuary stone. It was first quarried in the first century BCE and was used by Julius Caesar and his successor, Octavian, to replace older brick buildings. The Romans exported this stone throughout the Empire. Carrara marble continued to be one of the preferred raw materials during the Renaissance. The “David” by Michelangelo is but one example of a Renaissance statue carved from Carrara marble. Secondary sources for statuary marble during the Roman Imperial Period were Thasos, Naxos, Ephesus, Aphrodisias, and other quarries in the Maeander Valley (Menderes of modern Turkey) and possibly Algeria (Claridge 1988). In addition to statuary, marble was employed to construct columns, doorsills, sarcophagi, and to build parts of city walls (Pliny, *N.H.* 36.46). Two monographs by J. Ward Perkins (1951, 1980) present details concerning the Roman marble trade during the Roman Imperial Period. By the third century CE, the imperial monopoly of the trade in marble declined. However, the quarries continued to be worked on a smaller scale (Dodge 1988) and materials were exported until the time of the Arab conquest. Islamic art made use of marble for carved screens, sometimes inserting variegated marbles to make patterns of inlay, a technique that reached its apex in the sixteenth century Ottoman carvings. In addition to the well-known “classical” marbles, marble suitable for carving statues and related objects can be found in Spain, Portugal, France, Germany, Norway, Sweden, Austria, Hungary, and Russia.

During the Middle Ages, marble was quarried from Monte Pisano. Marble quarries at Seravezza in Tuscany were the source of a deep violet to pink marble used to carve statues of the Medici grand dukes (Penny 1993). An extensive database of isotope analyses from all the major marble quarries in the classical lands of the eastern Mediterranean (Italy, Greece, Turkey, and Tunisia) has been assembled by Herz (1992), among others. In most cases these data allow sourcing of Mediterranean area marbles. In addition to sourcing, these databases can be used to detect forgeries, and to associate broken and separated pieces of statues, epigraphy, and monuments.

Marble was also carved in the Far East, although much less frequently than jade. During the sixth through eighth centuries CE, in west central Hopei (near modern Beijing), a center developed where small marble statues of Buddha were produced (Penny 1993). During the Ming dynasty, life-sized figures of marble were set along the roads to imperial tombs. The use of white marble was also popular in India, especially in the areas near Rajasthan and Gujarat. During the tenth and eleventh centuries CE, it was used in Jain temple sculptures and in tomb construction. One of the most famous uses of marble to cover an entire building surface is in the Taj Mahal, India, built between 1632 and 1647 by the Moghul emperor Shah Jahan to commemorate his wife, Mumtaz Mahal. The Moghul emperors also preferred marble for their statues.

6.6 Catlinite

Catlinite is an easily carved argillite. The name comes from the American painter, George Catlin, who visited the rock source in southwestern Minnesota in 1836. Native Americans had been quarrying the rock as early as 900 CE. Some archaeologists have called any red argillites catlinite. However, the name should be reserved for rock of a specific mineral composition. Other argillites and related rocks that were used for pipes should be called pipestone. Sigstad (1970) has developed a field test for catlinite.

Although the best-known catlinite quarry is in southwestern Minnesota, there are similar deposits in Wisconsin, Ohio, Arizona, South Dakota, and Kansas (Berg 1938; Gunderson 1982). The trade in catlinite extended from the Atlantic to the Pacific and north into Canada. Pipes found in Hopewellian mounds in Erie County, Ohio, have been sourced to Wisconsin pipestone (Fredrickson 1981). Catlinite pipes, beads, and ornaments were found among the historic Iroquois of New York (Wray 1957). Pipes and other objects carved of this stone have been found throughout the Northern Great Plains (Morey 1983). The Minnesota Geological Survey worked at the Pipestone National Monument during 1980–1981. Their work resulted in the identification of three sites in the southern mine area and five sites in the northern mine area that have the highest potential for easily obtainable resources with minimum extraction effort (Morey 1983).

6.7 Other Carved Stone

Porphyry. Porphyry from Mons Porphyrites quarries in the Red Sea mountains (present day Gebel Dukhan) was one of the most valued stones used for building decoration and for sculpture throughout the Roman Empire. Also called “imperial porphyry” by Pliny, this red-to-purple porphyry was used for columns, baths, vases, and boxes (*N.H.* 36.57, 88). Delbrueck (1932) has produced an extensive monograph on the use of porphyry in the ancient world. His chapter on the written sources by author, inscriptions, ostraka, and papyri is of particular importance. The Egyptians employed porphyry to carve sphinxes and statues. In 1994, a previously unknown black porphyry quarry was discovered nearby (Peacock and Maxfield 1995). The Romans imported green porphyry from Sparta, rosso antico from Cape Taenarum, and breccia from a region that extended from northwest Turkey to Rome. Other porphyry came from Chalcis and Scyros. During the Middle Ages, porphyry was used throughout Europe for statuary, columns, altar pieces, furniture or parts of furniture, and as a finishing stone. In Sicily, this material was particularly favored by dynastic rulers to fashion their tombs. In Istanbul (ancient Constantinople), porphyry sarcophagi are found in the Church of the Holy Apostles, the burial site of many Eastern emperors (Deér 1959).

Mica. Muscovite mica is a sheet silicate mineral with perfect two-dimensional cleavage. It is colorless and transparent in thin sheets. It has a vitreous to pearly luster. Muscovite is common rock-forming mineral and form large sheets [more than a meter across] in granite pegmatites. Its low hardness [2–2.5] makes it very easy to carve (Fig. 6.8). The term for mica throughout Chinese history was *cloud mother.* A treatise in 1070 states, “Mica grows between earth and rocks. It is like plates in layers which can be separated, bright and smooth. The separate laminae look like the wings of a cicada.”

Fig. 6.8 Hopewell (100–400) mica bird claw. The Hopewell obtained mica from western North Carolina, USA

6.8 Sedimentary Rocks

Greywacke. Greywacke from the Wadi Hammamat was employed for the manufacture of ceremonial palettes during the Egyptian Predynastic and Protodynastic Periods (Petrie 1953). Andesite and greywacke were used to make stone vessels during these periods. The archaeologist George Reisner recovered six greywacke statue groups of the Old Kingdom Pharaoh Menkaure representing him standing between a nome goddess and Hathor (Romano 1976; Müller 1988). It was also used during the New Kingdom for statues. In the Late Egyptian Period, greywacke was used in the manufacture of statues and sarcophagi.

Limestone. Many ancient Hindu temples and their sculptures in India are carved in limestone. Buddhist cave temples in China are carved from limestone formations. In the early first millennium CE in Britain, amulets, spindle whorls, and bowls were carved from shale.

Sandstone. Sandstone is easy to dress and, therefore, has been used as a decorative stone in many parts of the world. The colossal statues of Ramesses II at Abu Simbel were carved in a sandstone cliff. At Petra in Jordan, the major structures were carved into a calcareous sandstone. While sandstone is acid-resistant if free of carbonate cement, it is also subject to deterioration due to subsurface salt crystallization. Xeidakis and Samaras (1996) cite an example of this degeneration in their study of the buildings of ancient Abdera in northern Greece. From the seventh century BCE, the builders at this site used local soft **molassic** sandstone to finish parts of buildings. The authors found that decay took place under the surface of the sandstone from sea spray and ground water uptake. In her article on materials and facades in the historical buildings of Bologna, Italy, Rossi Manaresi (1994) discusses the evolution of exterior architectural decoration in that city. She identifies selenite and sandstone as predominant raw materials during the eleventh through thirteenth centuries. By the fifteenth century, the demand had shifted to imported limestones and marbles.

Slate. In the late Egyptian Predynastic and Protodynastic Periods, ceremonial stone palettes were carved of slate. The most famous of these is the palette believed to recount the unification of Upper and Lower Egypt by the First Dynasty king, Narmer. By the Second Egyptian Dynasty, slate was carved into statuettes (Schweitzer 1948). In Britain, Bronze Age people used slate as a cooking surface. Pliny recognized two words for siliceous slate, *basanites* and *cos* (although the latter may have been emery or a slaty mica-schist). Both were used for whetstones and grindstones (*N.H.* 36.147, 164–65, 187, 188; 37.98.109). The Romans started the fashion of using slate as roof tiles, usually dressed to an elongated hexagonal shape.

Early and Middle Woodland peoples in Ohio made slate into gorgets and pendants with two drilled holes. (Converse 1978; Hart 1982) Slate was also worked in ancient Mesoamerica during the Classic Maya Period. Slate artifacts and debitage were discovered at more than 36 sites, suggesting that this material was fashioned into implements for trade with other Maya centers. At the site of Pacbitun (Belize), the large concentration of excavated raw material suggests that this may have been the location of a slate workshop and storage area (Healy et al. 1995). Another use for slate was as a backing for mirrors.

Chalcedony. In addition to its use as a gemstone known as prase, dark green chalcedony was used by the Romans for small cups and cylinders (Pliny, *N.H.* 37.113). Small statuettes were also fashioned from this stone. Examples include the translucent blue chalcedony statue of Heracles dating to the Roman Imperial Period now in the Princeton Museum of Art, the busts of the Emperor Trajan, and the bust of a Roman woman (now in the Metropolitan Museum of New York) (Jucker 1984; Penny 1993; Padgett 1995). Roman grave chambers dating between the second and the fourth centuries CE were discovered in the village of Weiden (near present-day Cologne, Germany). Among the finds were amber, a portrait bust in marble, and a small chalcedony statuette of the goddess Fortuna (Zwierlein-Diehl 1985).

Rock Crystal. In ancient Egypt, rock crystal (quartz) was used for seals, amulets, inlay, vessels, and figures such as the small Predynastic rock crystal lion thought to be a gaming piece, now in the Cairo Museum. Numerous carved vessels have been found in Early Dynastic tombs (ca. 2850–2650 BCE). During the Hellenistic Period, small rock crystal flasks and figurines were prevalent (El-Khouli 1978).

In the ancient Near East, freestanding rock crystal figures were rare. However, fragmentary rock crystal vessels have been found in several areas. During the Sassanian Period (226–651 CE), artisans experimented with new styles of carving, the most famous of which is the relief portrait medallion of a Sassanian king in the center of the polychrome Cup of Solomon (Ghirshman 1962).

The Minoans also made extensive use of rock crystal. Insets for walls and gaming boards have been found at Knossos. Vessels from Knossos and other sites, as well as the large number of extant armlets, pommels, and pendants, indicate that rock crystal was used for a wide variety of luxury goods. These may have been exported throughout the Mediterranean world. A duck-shaped bowl, now in the Athens National Archaeological Museum, in which the turned head of the bird forms the handle, is believed to have been a Cretan export to Mycenae (Bühler 1973). Statuettes, goblets, and vases carved from rock crystal were highly prized by the Romans. Carving in this medium was known to the Arabs, and the art continued to be practiced in the Near East from where it was passed to western Europe and China (Penny 1993).

Rock crystal was widely used during the Middle Ages for a variety of objects. Centers of production were in the Rhine-Meuse region, Freiburg, Waldkirch, the Saar-Nahe region, Catalonia, Venice, France, and the modern Czech Republic. Rock crystal was carved into reliquaries, crosses, gaming-boards, and panels that formed part of portable altars. The largest such panel is the fourteenth century Veronica Reliquary, now in the Vatican at the Basilica of St. Peter. Engraved reliquary cylinders and vessels, beakers, pitchers, cups, candlesticks, and bases of knives, forks, and spoons were also fashioned from rock crystal (Hahnloser 1985). In the fifteenth century, Italian carvers set rock crystal caskets and boxes within a gold framework. Plaques backed with gold were produced in Florence, Rome, Venice, and Verona during the early sixteenth century. Crystal vessels became increasingly popular in Italy during the 16th century (Kris 1929). The name quartz is likely a short form of the Saxon word *querkluftertz* from cross cutting veins of quartz in ore bodies.

Intrusive Rocks. Because of their durability, granitic rocks have been widely used since antiquity in the Near East, the Mediterranean, Europe, China, Japan, and India. Various types of granites have been used to construct obelisks, columns, pillars, statuary, fountain basins, and sarcophagi. It was also used in slabs to finish the exterior of buildings and for pavements and floors. Granite was used for statues, stelae, and columns in Pharaonic Egypt. Many obelisks were carved from Aswan granite. A black and white diorite was frequently used for the manufacture of canopic jars. Greenish-gray granodiorite was used in Pharaonic and Roman times for slabs, columns, vases, and mosaic tile.

The Akkadian kingdom of Lagash (ca. 2340–2000 BCE) produced diorite statues of kings and carved reliefs depicting royal victories (Spycket 1981). More than 20 statues of Gudea, its most famous ruler, have been found at Telloh. These sculptures are mostly made of black, highly polished diorite. The famous “Code of Hammurabi” now in the Louvre was also carved of a fine-grained diorite. Sidon, a city on the coast of Lebanon, has been a rich source of stone anthropoid sarcophagi manufactured between the sixth and fourth centuries BCE. In 1855, the huge diorite mummy case of a fifth century BCE king of Sidon was discovered at Magharat Abloun (Kleemann 1958).

Schist and Gneiss. Although stone carvers in the India-Pakistan region in the first millennium CE used a wide variety of rocks including schists, steatite, claystone, phyllite, slate, mudstone, and limestone, they preferred a homogeneous mica schist (Marshall 1960). Gneiss was used to carve the famous seated figure of Khafre that can now be viewed in the Cairo Museum. Gneiss was employed to carve both statues and amulets.

Breccia. Breccia was used in the Minoan world for column bases, such as those seen at Knossos and Kato Zakro, and for the production of vases. Breccia was also used in the production of late Predynastic Egypt stone vases. During the Renaissance it was used for window embrasures, columns, and as a decorative finishing stone.

6.9 Volcanic Rocks

Basalt. Volcanic rocks were a favorite material for Pharaonic sculptors (Fig. 6.9). Basalt was widely used for lithic tools, millstones, querns, and, in Egypt at least, statues. The earliest stone vessels made in Egypt were Neolithic basalt vases. About 22% of all Egyptian Predynastic stone vessels were made from basalt. One of the sources of the raw material was the Haddadin basalt outcrops west of Cairo. Quarrying of the Haddadin basalt for vessels spanned at least 900 years (Mallory-Greenough et al. 1999). Basalt is widely distributed in Egypt, and it was used as early as the Old Kingdom for pavement material in the necropolis that stretches from Giza to Saqqara. The basalt may have come from the Fayum where one can still observe the ancient quarry. During Pharaonic times, basalt was used in vessels, statues, and sarcophagi. The Greeks and Romans also carved sarcophagi from basalt. The Buddhist rock temples of western India are carved into the Deccan Trap – a basalt. In Mesoamerica in the first millennium BCE, the inhabitants carved monolithic statues and sarcophagi from basalt.

Andesite. A large fortress and temple precinct complex excavated at the site of Sarmizegethusa in the Carpathians contained the remains of a carved circular andesite sun disk and a large sanctuary with 104 andesite blocks forming its exterior circle (Hoddinott 1981). Phrygian sculptures carved from andesite were found in tombs of the eighth and seventh centuries BCE near present day Ankara. Andesite

Fig. 6.9 Twelfth Dynasty igneous rock statue of Sesostris III, Egypt

orthostats with relief carvings of animals in profile were also recovered (Akurgal 1955). Reliefs from Gordion and Ankara depicting the mother goddess Kybele standing in the niche of a miniature temple (a naïskos) were also carved in andesite (Akurgal 1961).

Vesicular andesite has been used extensively throughout the world as grinding stones for grains such as wheat and corn. In South America, andesite quarries are found 35 km southeast of Cuzco; stone extracted from the quarries was used to build statuary (Protzen 1985). The name andesite comes from the Andes Mountains of South America. In prehistoric Ecuador, utilitarian metates and bowls, as well as decorative statuary, were carved from andesite (Saville 1910). Probably the best-known sculpture from the site of Tiahuanaco (Bolivia) is the so-called Gateway of the Sun. It stands 3 m high, 3.75 m in width, weighs about 10 tons, and is cut from a single block of andesite (Kubler 1984). The prehistoric cultures of the Mesoamerican Central and Southern Highlands used basalt and andesite to carve monumental statuary as well (Nicholson 1971). The Precolumbian Maya site at Retalhuleu, in the Highland area near the Pacific coast of Guatemala, is best known for its monumental stone sculptures weighing between one and nearly twenty tons. Several hundred plain and worked monuments are made from local andesite (Thompson 1943; Graham et al. 1978). Quiriguá, the site of a Precolumbian Southern Lowland Maya city on the Motagua River flood plain in Guatemala, included sandstone and rhyolite monuments, stelae, altars, and zoomorphic sculptured boulders (Sharer 1978, 1990). The colossal sculptures from Teotihuacán, Mexico, are carved from an andesite outcropping about 2.5 km south of the site (Heizer and Williams 1956).

Tuff. In the second century CE, the Romans used volcanic tuff to carve statues. The famous megalithic Moai statues on Easter Island in the Pacific Ocean are sculpted from tuff (Shadmon 1996).

6.10 Miscellaneous Rocks

Fine-grained rocks that readily take polish, such as some schists and amphiboles and alabaster and marble, have been ground into charm stones dating to about 4000 BCE that were used as mortuary items in several parts of California (Chartkoff and Chartkoff 1984). Prehistoric pipe bowls in North America were also made from steatite, limestone, shale, hematite, and even granite. Comparative petrographic, mineralogic, and chemical studies confirm that the stone from the Pieta statue, dating from the beginning of the fifteenth century and recently discovered in Bern, is identical to the Golden Palaner marly chert from Prague. These results support the postulate that the Pieta comes from a Czech workshop (Konta 1993).

In South America, the Sambaquí cultures on the south and southeast coasts of Brazil produced a series of zoolithic sculptures from hard stones, such as diabase, basalt and diorite, between 4000 BCE and 1 CE (Prous 1976). The anthropomorphic figure known as the Raimondi Stele found at Chavín de Huántar is also carved from diorite (Kelemen 1969). At Tenochtitlán, the Aztecs carved ceremonial vessels from such hard stones as greenstone, diorite, chalcedony, and rock crystal (McGuire 1982). In West Africa, stone sculptures were carved from steatite, granite, gneiss, basalt, limestone, and sandstone (Allison 1968).

From the variety of rocks used for carving, including many considered very hard rocks, it can be seen that sculptors were able to utilize local or regional material in nearly all cases.

Chapter 7
Metals and Related Minerals and Ores

7.1 Introduction

Although there are 70 metallic chemical elements, only 8 (gold, copper, lead, iron, silver, tin, arsenic and mercury) were recognized and used in their metallic state before the eighteenth century CE. Only two – gold and copper – were sufficiently available in their uncombined native state to be of importance to ancient societies. In the Old World, gold and copper metallurgy originated in the Near East more than 7000 years ago. The first uncontested use of metallic copper dates to the late eighth millennium BCE at an aceramic Neolithic site in southeastern Turkey where beads made of native copper have been found. The name copper is derived from the Greek name of Cyprus [Kyprios]. In the last few decades, individuals and teams from many countries have begun to locate ancient mines of the Old World (e.g., Wagner et al. 1983, 1984; Gerwien 1984).

The word *ore* is derived from an Anglo-Saxon word meaning a lump of metal. It is applied to an aggregate of minerals from which one or more metals can be extracted *at a profit.* Therefore, what may be an ore at one time and place may not be an ore at another time or place. The desired ore mineral most often has to be separated from the surrounding "worthless" rock that is called *gangue.*

The upper crust of the earth is about 5% iron, but only 0.02% copper, 0.004% zinc, 0.002% lead, 0.001% tin, 0.000.001% silver, and 0.000.000.1% gold. Put another way, we can look at the average concentration of metallic elements in the earth's upper crust and see what enrichment is necessary to form an exploitable deposit. For iron, the enrichment must lead to a concentration five times the original. For the other important metals of antiquity, the concentration factors are:

Copper:	about 140 times
Zinc:	about 850 times
Lead:	about 2000 times
Tin:	more than 2000 times
Silver:	more than 5000 times
Gold:	more than 10,000 times

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A broad understanding of the geologic processes that concentrate these elements to the degree necessary for an ore deposit is of great value in understanding the context in which early humans utilized raw materials. Scattered throughout this book are short descriptions of geologic processes that form ore deposits, placers, and the rocks suitable for providing products useful for mankind.

Although gold was always found in the native state, other metals such as copper, lead, zinc, silver, arsenic, mercury, and cobalt were primarily concentrated in sulfide deposits. Oxidation later converted many of these metal sulfides to oxides, oxyhydroxides, carbonates, and sulfates.

The complex picture of the early smelting of lead ores, including the recovery of silver contained in the lead minerals, remains to be completed. Gale and Stos-Gale (1981) have argued that, because lead melts at a relatively low temperature (below 800°C), the smelting of galena (PbS) may have occurred early in the Bronze Age. They suggest that the appearance of quantities of silver artifacts in the fourth millennium BCE coincides with, or somewhat predates, the evidence for the start of copper smelting. Their paper includes maps of early metal smelting sites in the eastern Mediterranean region, Aegean ore deposits, ore deposits on the island of Siphnos, and the lead mines at Lavrion.

Before the arrival of Europeans in the sixteenth century, the indigenous peoples of the southwestern United States did not use metal for tools or weapons. However, in South America, there was a fairly advanced metallurgical **alloying** of copper, gold, silver, and even platinum (unknown in Europe). In Mexico and Central America, copper, gold, and silver were utilized. In the New World, the word “metallurgy” refers to “Andean metallurgy,” for it is this area alone that developed sophisticated technologies that later moved north and flourished from Panama to Mexico. The Andes Mountains contain some of the richest gold, copper, tin, and silver mines in the world. Unlike the Old World focus on copper, metallurgy in Andean societies focused on gold, beginning in the middle of the second millennium BCE.

Metal ore smelting normally requires the use of a **flux** to lower the melting point (extraction temperature) of the ore mineral or the fluidity of the slag. The slags formed in primitive copper and iron ore smelting consisted largely of fayalite (an olivine) with the composition Fe_2SiO_4, which has a melting point of 1170°C. Limestone found at ancient smelting sites cannot have been used as the flux, because the lime would not lower the melting point or fluidity of a fayalite slag.

Analyses of ice cores present another method of assessing metal production in antiquity. Atmospheric pollution from lead and copper production over the past 4000 years is locked in the well-preserved and well-dated ice layers in Greenland and elsewhere. Ferrari et al. (1999) have reviewed the research of the last 20 years on this topic and note the ice core evidence for the enhanced production of copper during the Roman Empire in Europe and the Song Empire in China.

Readers interested in the history of metals will come across references to the development of *niello* by many societies around the world. The term niello comes from the Latin for “black work”. Niello has been considered to be a combination of sulfur with copper, silver, or lead, heated to form a paste that is pressed into grooves to present a black contrast to copper or bronze. Recent laboratory analyses

(Thomas 2005) suggest that the black material in Mycenean bronze daggers may be black patinated bronze, not a black inlaid sulfide paste. The author argues that the black material is essentially identical with Japanese "shakudo", which is a mixture of gold and copper (usually 4% gold and 96% copper) that develops a dark purplish-black surface when treated with a suitable solution (normally containing copper sulfate). It is similar to decorative alloys used in ancient Egypt, Greece, and Rome.

The high luster of solidified lead sulfide smelt attracted ancient artisans from Egypt, Greece, Rome, and South America. Ancient Egyptians and the Myceneans of Greece developed a similar product in the second millennium BCE. The Romans called this material *aes Corinthium* "Corinthian bronze" (Giumlia-Mair 1996). Pliny mentions this material and the process for producing it. The Japanese developed and have used this material since the eighth century CE. Niello is based on contrasting a gold color with a black to black-violet inlay. After much discussion of conflicting views, Jacobson and Weitzman (1992) agree that Corinthian bronze is essentially identical to the *tumbaga* of Precolumbian South America and that it can be characterized by a mixture of precious metals (especially gold and silver with copper).

Although archaeometallurgy has only a small number of practitioners, most of our knowledge of the early use of metallic minerals comes from their studies. There is a substantial amount of information on metal raw materials in Tylecote (1962, 1986). Archaeometallurgists obtain most of their data from analyzing metal artifacts. This often does not indicate which specific ore minerals were the raw materials. However, concerning copper alloy raw materials see Rapp (1989).

Before discussing individual metals and ore minerals, it is worth noting some of the major general references. Many of these have a much broader coverage than mineral and rock raw materials but contain either a good overview or a good review of the sources of specific minerals or rocks or their utilization. Three volumes of *Der Anschnitt* are particularly valuable regarding archaeometallurgy and archaeomineralogy. These are Wagner and Weisgerber (1988), Hauptmann et al. (1989), and Rehren et al. (1998). Other volumes in archaeometallurgy that contain extensive material on archaeomineralogy are Craddock (1980), Wertime and Muhly (1980), and Maddin (1988). An annotated bibliography of the history of metal mining and metallurgy is available in Molloy (1986). Craddock (1995) presents a good overview of archaeometallurgy and related archaeomineralogy of early metal production. Although now somewhat dated, information on copper, lead, and zinc deposits of the former USSR are presented in Smirnov (1977). An important compendium of metal deposit information is the Pergamon Press series of annotated *Bibliographies of Mineral Deposits* by J.D. Ridge (e.g., Africa, Asia, and Australia 1976; northern Europe 1984).

For early metallurgy and related raw material use in various parts of the world, see:

Southeast Europe: Jovanovic (1971, 1982); Wertime and Muhly (1980); Gale and Stos-Gale (1981); Muhly et al. (1982); Glumac and Todd (1987, 1991); Pernicka (1987); Rothenberg (1990); Zwicker (1990); Geselowitz (1991); Glumac (1991); Stos-Gale (1993); McGeehan-Liritzis (1996); and Pernicka et al. (1997).

Western Europe: Tylecote (1986); Museo Nacional de Arqueologia Maritima y el Centro Nacional de Investigaciones Arqueologicas Submarinas (1987); Salkfield (1987); Bodega Barona (1991); and Hoffman (1991).

North America: Drier and du Temple (1961).

South and Central America: Lechtman (1980); Craig and West (1994); Scott and Meyers (1994); West (1994); and Burger and Gordon (1998).

Near East: Craddock (1980); de Jesus (1980); Wagner et al. (1983/1984); Moorey (1985); Muhly (1986); and Hauptmann and Weisgerber (1989).

Russia: Chernykh (1991).

Far East: Imai (1978); Chikwendu and Umeji (1979); Murowchick (1989); and Biswas (1996).

Africa: Sutton (1983).

A now dated but useful field survey of Roman mines in Europe by Davies (1935) should be consulted by anyone interested in early metal mining. The most comprehensive recent account of early metal mining and production is Craddock (1995). The mining of gold, copper, tin, and iron ores began in southern Africa about 2000 years ago. Miller (1995) has provided a thorough review of the mining history in Africa (south of 15 degrees south latitude).

The early exploitation of gold and silver in India is attested in the "Vedic" literature, which mentions rivers, indicating the gold was likely from placers. Archaeological evidence puts the use of gold back to the Harappan Period, and it appears gold recovery can be traced to the Neolithic in southern India. Lead was mined in India prior to the Indus Civilization. Iron in ancient India appears to have been a byproduct of copper smelting with a date of origin about the same as for the eastern Mediterranean region: the end of the second millennium BCE.

7.2 Gold (Au)

The name gold is from Old English and common to many Teutonic dialects, but the chemical symbol for gold is Au, derived from the Latin *aurum.* Gold was one of the first metals to be used by humans, primarily because it occurs naturally in the native, uncombined state. Gold is widely distributed throughout the world in lode and alluvial deposits. Because of its high density, gold concentrates in placer deposits. The first gold recovered and used was certainly shiny nuggets found in active or fossil streambeds. Anyone at all familiar with ancient Egypt is conscious of the Egyptian's use of gold since pre-Pharaonic times. Although the value of gold in early Pharaonic Egypt was not quantified, it was used by the Pharaohs to reward persons deemed worthy. By New Kingdom times it was used as a means of valuation. The Egyptians prized gold for its eternal sheen. There were 16 Akkadian words for gold. This suggests that at least some of these terms reflect different colors due to mineral additives or alloying (Lindsay 1970:214). Gold dust found along the African coast is called *tibir.*

Gold is widely distributed throughout the earth's crust in small amounts most commonly associated with high silica (SiO_2) igneous rocks and quartz veins. Its exceptionally high density (19.3 g/cm3, over six times that of the average rock) causes it to concentrate in placer deposits (see Chap. 3). Its melting point of 1063°C means it can be melted and cast, and its chemical status as a noble metal keeps it free of unsightly corrosion. Gold and silver are commonly found associated in mineral deposits. Gold is about one-tenth as abundant as silver in the earth's crust. Native gold normally contains some silver; if the silver content reaches 20%, it is called *electrum.* The atomic radii of gold and silver are both approximately 1.44 Å, so they are easily dissolved in one another. The earliest electrum used was probably natural, although, by Greek and Roman times, artificial electrum was in use. In his discussion of the origin of electrum coinage, Wallace (1987) points out that the early coins from Lydia and Ionia were struck only from electrum and that this natural alloy came from the Tmolos watershed, which includes the Pactolos and Hermos Rivers.

Gold forms a complete series of solid solutions with silver, copper, nickel, palladium, and platinum. Many of these alloys occur in nature. Electrum is widely distributed and may contain up to 50% silver. Native gold may contain copper up to a maximum of 20%. Mertie (1940) and others have noted that "pure" gold is not found in nature but always contains some silver and copper and, frequently, some iron.

Most scholars believe the first gold recovered came from placer deposits. There are approximately 900 occurrences of gold in Europe's Bohemian Massif. Of these, about half are placer deposits. These placers have been exploited for at least 3000 years. Most placer gold is in the form of fine dust, but larger lumps, called nuggets, are found. Normal placer gold ranges in size from submicroscopic to the size of a pea. The most common size for placer gold is that of sand. The purity of naturally occurring gold is usually expressed in parts per thousand (ppt, 1000 is pure gold). Placer gold varies from 500 to 999 ppt, whereas gold in veins varies from 500 to about 850 ppt. Most placer gold is above 800. The purity of the gold also increases with the distance it is transported from the source. This suggests that some silver has been dissolved from the gold during transport. Both the roundness of edges and the flattening of gold particles show a rapid increase in the first 5 km transport from the source **lode**. The most productive fossil placer in the world has been the Witwatersrand of South Africa. These deposits were formed over 2.5 billion years ago within fluvial fans in shallow water.

Ancient Egypt had gold and electrum in abundance. In the southern Eastern Desert at Barramiya and elsewhere, in the Wadi Allaqi region 90 km south of Aswan, and from Nubia to the south, there was gold in quartz veins as well as placer gold. The gold deposits in quartz veins ran down the length of Egypt's Eastern Desert into Nubia. In Pharaonic and later periods, the Egyptians secured at least some of their gold from Nubia. Diodorus in his *History* (3, 12) gives an account of gold mining in Nubia. The gold-bearing region between the Nile and the Red Sea is shown in Fig. 7.1.

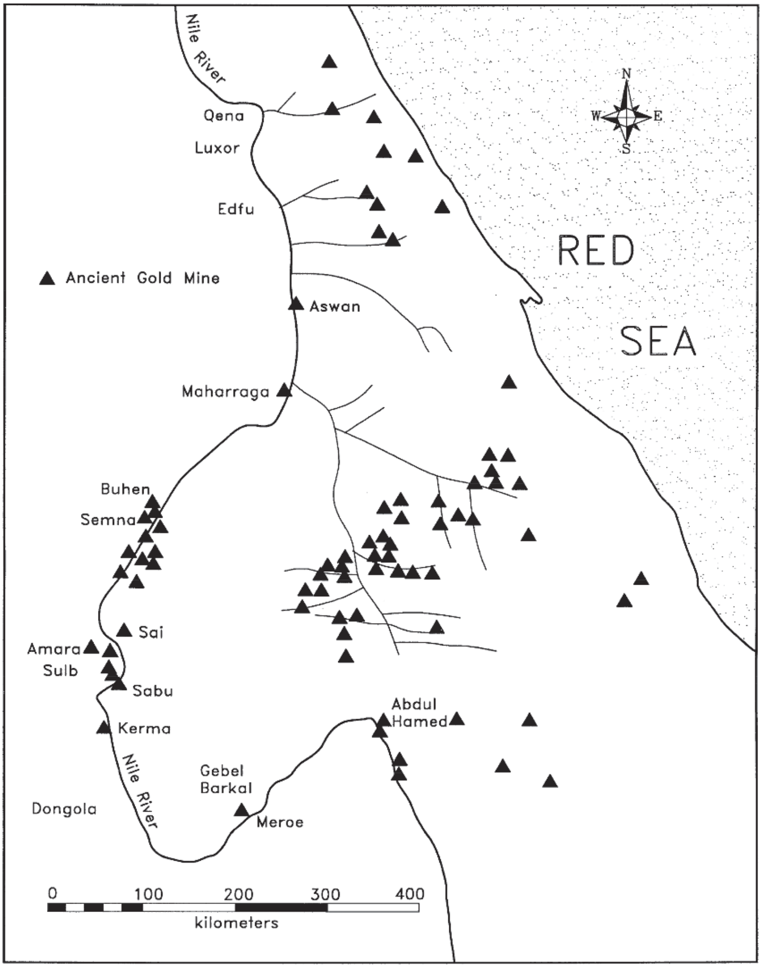

Fig. 7.1 Map showing known locations of gold deposits in Egypt and Nubia

Some of the world's oldest gold workings were uncovered near Varua, Bulgaria. This is the indigenous area of the Thracians, later noted for their exceptional gold work. Ancient Thrace included modern Bulgaria, the northern part of European Turkey, and bits of Greece, Serbia, and the Republic of Macedonia. Its boundaries were the Danube River on the north, the Aegean Sea on the south, the Black Seas and Sea of Marmara on the east, and the Vardar River on the west. The Thracians likely made extensive use of placer gold. The Strymon River on the border between Thrace and Macedonia is well known as a source of placer gold. The Thracians remained relatively obscure until archaeology in the early twentieth century brought their culture to light.

Deposits in the Taurus Mountains of Anatolia were extensively mined in the Early Bronze Age, and deposits in Greece were worked throughout the Bronze Age. However, no geologic or archaeological evidence for the source of the gold was uncovered until 1980 when a German and Greek team discovered the occurrence of gold and ancient mining on the island of Siphnos (Wagner 1980; Pernicka et al. 1982). In Europe, significant gold deposits are found in the Carpathian region, in southwestern France, in Brittany, and in the British Isles, especially in Ireland. In Britain the gold is widely distributed (Fig. 7.2) and was used commonly in the Bronze Age for ornaments.

Lehrberger (1995) indicates that the abundance of gold deposits in Europe, over 1000 low-grade deposits, would have allowed wide gold utilization since Neolithic times. Although traces of prehistoric gold mines in Bohemia and Bavaria have been destroyed by later mining and shifts in water courses, the small, but very rich, gold deposits were exploited in the first millennium BCE. The famous Bodenmais gold deposit in eastern Bavaria was active in the Middle Ages. Evidence remains

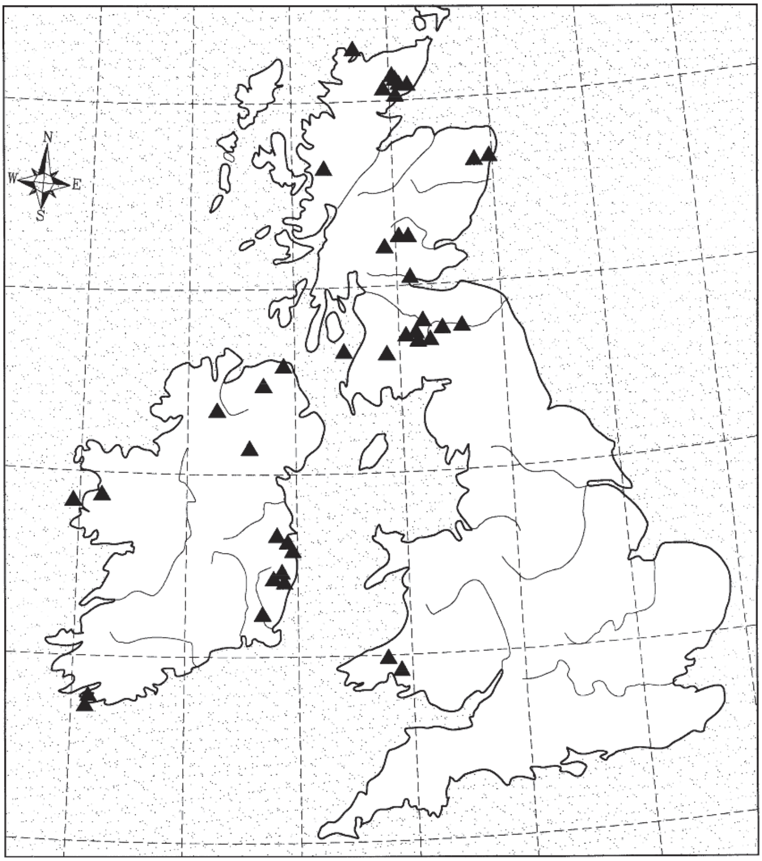

Fig. 7.2 Native gold deposits in the British Isles

for Roman and Medieval production in the region. Gold ore mills dating from the thirteenth century CE have been identified (Lehrberger et al. 1997). These authors describe in detail the gold mineralization in this region. The gold deposits of the Tauern Mountains in the eastern Austrian Alps have been worked for over 3000 years, first as placer deposits. These deposits were worked extensively by the Romans.

Probably the maximum production of early gold was the exploitation of Iberian deposits by the Romans. Pliny (NH 33) discussed Roman mining in Spain, and Davies (1935) brought things up to the twentieth century. Lewis and Jones (1970) have added new detail about Roman gold mining in northwest Spain, pointing out that much of the recoverable gold there was alluvial or placer gold. When the Visigoths controlled most of the Iberian Peninsula in the middle of the first millennium CE, they made high quality gold jewelry from gold recovered in the south of the peninsula (Guerra and Calligaro 2007).

Gold was recovered from many European countries, but was most abundant in Ireland, Britain, western France, and the Carpathian region. In Ireland, gold was the most common material used for ornaments during the Bronze Age. The Romans had extensive gold mining operations in southwestern Great Britain (Wales) at Dolaucothi, near Pumsaint (Jones and Lewis 1972). These mines were technically advanced. They were opencast, and used deep mining techniques in the exploitation of gold-bearing veins. Dumps of quartz gangue can still be observed. Nearby placer deposits had likely been worked earlier. The Leadhills-Wanlockhead district of Scotland produced gold for more than 400 years. Gold recovery from placers in the district was quite profitable in the early years, especially in the 1500s. Figure 7.2 shows the gold deposits of the British Isles.

Perhaps the most famous ancient gold district in Europe is in western Transylvania between the Aries River in the north and the Mures River in the south. Herodotus mentioned the gold jewelry worn by the inhabitants along the Mures River. The name of the River Aries may be derived from the early name for gold, *auries* or *aurum.* This river certainly contained placer gold. The Romans constructed many tunnels in the region to extract the lode gold. Some of the earliest gold objects in the world have been recovered from Necropoli in northeastern Bulgaria (Kostov 2005d).

In a very detailed study, Tamain and Ratz (1982) have described the gold ores of the west-central Massif in France in their geologic and archaeological context. The Limousin area in the southwestern part of the Central Massif of France has a long history of metals exploitation, especially gold and tin. Gold mining is attested from the fifth century BCE (Cauuet 1994). The gold was extracted primarily from veins, but there was also placer production. Mining continued through the sixth and seventh centuries CE and into the High Middle Ages. A comprehensive review of gold in prehistoric Europe is available in Morteani and Northover (1995). This book contains six articles on gold deposits and/or gold mining.

In the Greek legend of the "Golden Fleece," ancient placer miners extracted alluvial gold by shoveling the gravels into **sluice** boxes hollowed out of tree trunks. A lining of sheepskins trapped the gold particles. The coarse gold was shaken out, but the fine gold adhered to the wet wool. The fleece was then hung out to dry so the gold could be beaten out. Jason and the Argonauts set sail in search of this Golden

Fig. 7.3 Gold mask from Bronze Age Mycenae, Greece

Fleece (Fig. 7.3). The Romans exploited the gold deposits of Galicia (Bodega Barahona 1991), but, when Rome fell, the recovery of gold from these deposits declined rapidly.

In the New World, the use of gold came much later but reached great volumes and great artistic heights south of the Rio Grande River, in Central America, and northern South America. Indeed, stories of the abundance of gold objects were the driving force behind the Spanish conquest. Since the sixteenth century CE, northwestern South America (largely Colombia) has been a major source of gold. Precontact inhabitants had a wealth of gold objects as jewelry, religious objects, and tools (Von Hagen 1977). This led the early European explorers in a search for “El Dorado”. The Sican culture, a pre-Inca society that existed in northern Peru during the period 700–1400 CE, produced a wide variety of gold alloy ceremonial objects such as masks and knives (Shimada and Griffin 1994). The first metalworking in the Andes may have been practiced by early settlers in the Lake Titicaca basin (Peru) nearly 4000 years BP. These craftsmen fashioned objects from hammered native gold (Aldenderfer et al. 2008).

Placer gold was apparently available throughout much of ancient China but seems to have received little attention until the Late Shang Period. It was used to add color to other materials such as bronze. Although gold had been worked in China during the Shang Dynasty (ca. 1700–1100 BCE), it played only a minor role until the ensuing Zhou Dynasty. By 23 CE in the Han Dynasty, the Imperial treasury contained over 6.3 million oz. of gold (Louis 1994), which would be the rough equivalent of the amount held by the Roman Empire at the same time. Thus, Marco Polo’s account of the wealth of China's Imperial court in the late thirteenth century may be accurate. A detailed, if somewhat dated, look at gold in early China is presented in Andersson (1935). Bunker (1993) has reviewed the use of gold in ancient China.

7.3 Silver (Ag)

The name silver comes from the Teutonic languages. Because the Latin name of silver was *argentum* (chemical symbol Ag), native silver has often been called "argent". Silver occurs in the native (metallic) state, but throughout history most of it has been recovered as a by-product from the smelting of lead ores through **cupellation**. Silver is harder than gold but softer than copper. In ancient times there was far less sulfur in the atmosphere, so silver ornamentation kept its luster longer. But notice the blackened silver head in Fig. 7.4.

Mining of lead/silver ores began at least as early as the third millennium BCE (Fig. 7.4). Remains of a third millennium underground shaft in a lead/silver mine on the Aegean island of Siphnos have been reported by Wagner and Gentner (1979). Wertime (1973a) reports fifth millennium BCE silver from Beycesultan in Anatolia and Tepe Sialk in Iran, and a cupel button from third millennium BCE Mahmutler in Anatolia.

Silver was used in Egypt before 5000 BCE, but was comparatively rare until the 18th Dynasty. Silver objects such as beads and amulets dating from the Predynastic Period have been found. Although no native silver or silver ores occur in Egypt, textual evidence suggests that the Egyptians considered silver more valuable than gold until the end of the Middle Kingdom when it became more readily available

Fig. 7.4 Silver and gold rhyton from Shaft Grave IV, Mycenae, Greece

through trade (Lucas 1989). Silver was widely used in the ancient world to produce engraved signet rings (Fig. 7.5).

One of the most widespread and important uses of silver was for minting coins. Wagner (1982) presents a map of silver and gold mines in the Aegean area as well as important mints for silver coins in the region. Silver coins were the impetus for Scandinavian trade with the Arabs in the ninth and tenth centuries CE, which ultimately encouraged Norse settlement in European Russia (Gabriel 1999).

During classical times the silver mines at Laurion in Greece were a major source in the eastern Mediterranean. For a detailed picture of the archaeomineralogy of Lavrion, see Conophagos (1980). For a good description of the ancient silver mines at Lavrion, based on the works of Boeckh, Ardaillon, and Xenophon, see Kounas (1972).

Wagner et al. (1980) describe the Early Bronze Age lead/silver mining on the Aegean island of Siphnos where the ores were complex lead-antimony-silver minerals. The finding of litharge at this location indicates that cupellation was used as a method to extract silver. Radiocarbon and thermoluminesence dating indicate that mining started at Siphnos at least by Early Cycladic I.

In Italy, rich silver ores were available to early metalsmiths at Montieri, southwest of Siena. The Carthaginians worked the silver mines of Spain (Diodorus 5.38.2), but it was the Romans who exploited the Spanish lead/silver mines on a grand scale. These rich silver mines opened by Hannibal were acquired by the Romans after the Second Punic War. There are numerous lead/silver deposits in Spain; the richest ores exploited by the Romans were located in the Sierra Morena. The Romans also exploited deposits of lead minerals in Asia Minor, and the Danube provinces. Of all

Fig. 7.5 Woman seated in front of altar. Fifth to fourth century BCE, silver signet ring, Tel Michal, Israel

the parts of the later Roman Empire, Gaul yielded the greatest quantity of silver. The foremost silver producer in fifteenth century France was at Pampailly. The ore at this mine was galena (Benoit and Deroin 1994). Most of the silver in galena was contained as minute inclusions of argentite (Ag_2S). In Scandinavia the Gundestrup cauldron, a large silver vessel (69 cm in diameter, 42 cm in height) dating from the first or second century BCE, was found near the hamlet of Gundestrup in Denmark.

Shortly after Columbus came to the Americas, the great silver deposits of Central and South America were discovered. These have remained the major source of the world's silver supply. The ancient Peruvians mined and smelted lead/silver ores but artifacts are rare (see Lechtman 1980). Most silver has always been produced as a by-product of lead, copper, and zinc mining. Exploitation of the large silver deposits in the New World south of the Rio Grande River during the sixteenth century radically changed the monetary climate in Europe. In North America, native silver has been found in some Mound Builder (Hopewell) sites. On his second expedition to the New World in 1494, Columbus established the town of La Isabella on the north coast of Hispaniola. Archaeological excavation has recovered assaying crucibles and liquid mercury for extraction of gold from powdered ore. Also recovered was about 90 kg of argentiferous galena, indicating attempts to recover silver by cupellation (Thibodeau et al. 2007). Silver also occurs as argentite (Ag_2S), which is named after the Latin word for silver, *argentum.* It is sometimes called silver glance. In West Mexico during the Late Postclassic Period (1300–1521 CE), argentite and silver sulfosalts were mined as a source of silver (Hosler and Macfarlane 1996).

Although most of the silver recovered throughout history has come from lead ores, some exploitable native silver deposits do exist. Among the most noteworthy of these is the one at Kongsberg in southern Norway, which has been worked for several centuries. The deposits are found in narrow veins in mica schist and gneiss. Native silver can occur abundantly in association with silver-bearing galena. One such occurrence is at Andreasberg in the Harz Mountains. Seams of native silver have also been found in the cobalt ore veins in Saxony. Volume 17, 1986, of the *Mineralogical Record* has an extensive coverage of silver deposits and silver mining in Germany.

Silver was virtually unknown in dynastic China until the Late Zhou (Warring States Period, 475–221 BCE), where it was used as a colorful inlay in bronze. Native silver is not common in China, so silver was obtained from silver-bearing galena through the cupellation process. Precise descriptions of this process are not found in Chinese texts until the Tang Dynasty (618–906 CE) (Bunker 1994). This limited early Chinese interest, and silver is conspicuously lacking in Chinese Bronze Age sites. The earliest known silver artifact is a nose ring from Gansu Province dating to about 1600 BCE.

7.4 Native Copper (Cu)

Native copper occurs primarily in three geologic environments: (1) in mafic igneous rocks, both extrusive and intrusive, (2) in the oxidized zones of copper sulfide deposits, and (3) in clastic sediments associated with mafic igneous rocks and glacial till.

Native copper is mined from lode deposits; from river, shoreline, and **lag deposits** of rounded nuggets; and from glacial till. Subject only to minor surface alteration, native copper is nearly indestructible in the surface geologic environment.

In Precolumbian North America, most of the native copper available at or near the surface was derived from mafic igneous rocks. North of the Rio Grande River, prehistoric people did not smelt, melt, cast, or alloy metals, relying instead on the abundant native copper. Large deposits of native copper occur in the basaltic lavas and related sedimentary rocks of the Lake Superior region; these are by far the most extensive native copper deposits in the world. Other primary deposits in North America include those of the Appalachian belt, and in southeast Alaska, the Yukon Territory (especially the Coppermine River area), British Columbia (especially Victoria Island), the Northwest Territories, Labrador, and Cap d'Or, Nova Scotia.

Masses and sheets of native copper in the Keweenaw Peninsula of Michigan occur at the surface throughout a zone 5 km wide and nearly 150 km long. Outcrops are also common on Isle Royale and Michipicoten Island in Lake Superior. In prehistoric times, nuggets in a wide range of sizes must have been abundant in streams and along the Michigan shores of Lake Superior. Supplies available at the surface did not always exceed demand, however, as shown by the thousands of shallow pits dug to recover near-surface pockets of metallic copper. During the Archaic Period, inhabitants of the western Great Lakes area made a broad range of native copper implements (Fig. 7.6).

Fig. 7.6 Archaic copper tools from the Lake Superior region, USA

Native copper also occurs widely as a secondary alteration mineral within the oxidized zones of copper sulfide deposits. Strong oxidation occurs in these deposits because the abundant pyrite dissolves in water to form sulfuric acid and ferric sulfate. This oxidized zone is always close to the ground surface and is often visible at the surface. In the sulfide copper ores of western North America, native copper is a common but minor constituent of the oxidized zone. One of the largest native copper deposits of this type is located in the Santa Rita district of New Mexico where millions of pounds of native copper were mined in the early days of mining.

The copper deposits of the southwestern United States have been important economically as large low-grade copper sulfide deposits. The oxidized zones near the surface sometimes include native copper, but little has been published about the native copper occurrences and their accessibility at the surface. In Arizona, native copper occurs in the enriched zone at San Manuel, and native copper has been found in most of the deposits of the Banner district. Anthony et al. (1995) detail the many known occurrences of native copper in Arizona. They consider it to be "very abundant in Arizona, usually in small amounts in the oxidized portions of copper deposits". Bullock (1981) lists the native copper occurrences in Utah by county and by mine or mining district.

A sourcing study of North American native copper artifacts showed that arsenic is the best element to use for distinguishing between primary native copper from mafic volcanic rocks and secondary native copper from oxidized copper sulfide deposits (Rapp et al. 2000). In this study, the secondary native copper contained much lower concentrations of arsenic. Native copper is widely, but not abundantly, found in the oxide zones of copper sulfide deposits in Mexico (Panczner 1987). Despite the information available from the geologic literature about copper deposits within reach of Aegean Bronze Age metalsmiths by direct exploitation or trade, we have insufficient data on these deposits to understand their chemical and mineral composition (for sourcing) or their size and surface expression (for assessing their availability for Bronze Age exploitation).

Masses of "float copper" transported and deposited by glacial action have been found in the glacial drift in Michigan, Wisconsin, Iowa, Illinois, Indiana, Ohio, New York, and Minnesota. When discovered, such loose nuggets undoubtedly were fashioned into artifacts by copper-using cultures.

Watson (1923) has detailed the occurrence of native copper in the Appalachian region in basaltic flows. The main Blue Ridge outcrop belt extends from central Virginia through Maryland into Pennsylvania (South Mountain). A second belt occurs in the piedmont of Virginia and North Carolina. Native copper is the chief ore mineral of both belts. Copper mining in the state of Maryland began before the Revolutionary War (Parre 1964).

In southeastern Alaska, native copper occurs in placers in Chititu Creek, a tributary of the Nizine River about nine miles southeast of McCarthy. Copper nuggets are still quite abundant in the stream gravels. The native copper in this region weathered out of the Nizine Greenstone belt, and is found in many streams in addition to Chititu Creek. An almost unlimited copper supply would have been available to the indigenous peoples if they had recognized the native copper in the gravels. The placer copper occurs with native silver and gold, and many of the copper nuggets contain silver (Moffit and Capps 1911). Moffit and Capps note a strong similarity between the native copper from the greenstone and the amygdaloidal copper from the Lake Superior region. This is not surprising since the greenstone is probably altered mafic lavas. A good, if somewhat dated, review of the dispersal of native copper artifacts in the Late Archaic of North America is given in Fogel (1963). Patterson (1971) provides an in-depth look at what deposits of native copper, silver, and gold would have been accessible to early metallurgists. He discusses the mineralogy and economic geology of relevant mineral deposits, considers the total amount of ores available, regional variations in native metal abundances (including the Lake Superior region native copper anomaly), and how these data affected early developments in metallurgy.

Outside of North America, well-known native copper deposits include Monte Catini on the west coast of Italy near Livorno and the ancient Etruscan city of Volterra. The native copper in these locations occurs in a diabase. For Europe and eastern Asia, where native copper is much less abundant than in North America, there is nevertheless an extensive, but scattered, literature on early copper. In China, copper was found at the Neolithic site of Banpo dating to about 6000 BCE (An 1983). Smirnov (1977) indicates that there are small occurrences of native copper in Azerbaidzhan (Azerbaijan) and Kazakhstan. Very often the various authors do not attempt to distinguish native copper from smelted copper. Rapp (1989) and Rapp et al. (2000) have shown that native copper often can be distinguished from smelted copper by trace-element analysis. Many of the native copper deposits of the Old World, for example, those of the Ergani-Maden area in southeastern Turkey, have been entirely removed by large-scale modern mining.

Small amounts of native copper were utilized in Predynastic Egypt and as far back as the seventh millennium BCE in Anatolia and India. The copper mines of the Sinai probably propelled ancient Egypt into metallurgy. Heaps of slag still mark ancient sites in Wadis Nasb, Kharg, and Malba. According to the Harris Papyrus now in the British Museum, the last Pharaoh to mine actively in the Sinai was Ramesses III in the 20th Dynasty. The mines were especially active during the reign of Snefru of the 4th Dynasty.

The early use of copper in Anatolia has been well described by J.D. Muhly in numerous papers. For early India, see Biswas (1996). Two of the problems for archaeomineralogy are: (1) to determine the copper mineral(s) exploited, and (2) to determine the chronology and geography of the first copper extraction by smelting. The very earliest copper was undoubtedly native copper, but it appears that recovery of copper from malachite was accomplished at an early date. Although Rapp (1989; Rapp et al. 2000) has indicated that native copper can frequently be distinguished from smelted copper by trace-element analysis, the lack of such analyses on the valuable early copper specimens in museums leaves the question open. It can safely be said that native copper in Europe, the Near East, and northern Africa is nowhere near as abundant as in North America, particularly in the Lake Superior region.

Archaeological evidence for early copper mining in India is scanty. What evidence there is points to pits in surficial deposits of rich **gossan** ore using typical fire then water to shatter the rock. A native copper bead from India dates to earlier than 6000 BCE (Shrivastava 2006). Tin bronze did not take hold in India until the Medieval Period.

7.5 Other Copper Minerals

After the early exploitation of the supply of native copper, metalsmiths in all parts of the world except North America had to turn to extraction of copper from complex copper minerals. The smelting of copper ores goes back six millennia in the Old World. Over a considerable span of time ancient metalsmiths discovered the rewards of pyrotechnology applied to metalliferous rocks. Our knowledge of the origins of copper alloy metallurgy (combining copper with one or more other metals) is primarily indirect, and is derived from analyses and interpretations of the composition and structure of artifacts, slags, and ores. Slags retain residues of the ores that were smelted and sometimes give us the only hard evidence of the minerals that were processed. The Servette copper mine in the western Italian Alps has huge slag dumps. The local copper ore was chalcopyrite ($CuFeS_2$). It appears that Romans may have exploited this deposit, and it may have been mined even earlier by the Celtic inhabitants, the Salasses. Pliny noted that these people mined a good kind of copper ore he called “Sallustianum”. Tumiati et al. (2005) have established that some of the slags date back to at least 890–980 CE. Unfortunately, archaeology (particularly Old World archaeology) has focused on the excavation of temples, graves, and habitation sites. Relatively few examples of Chalcolithic or Early Bronze Age metallurgical or mining sites are known and most of these have provided only scant evidence of ores or technology.

It is only since the time of John Dalton, about 200 years ago, that the concept of chemical elements has been used in any scientific or technical sense. Therefore, the development of alloy metallurgy must have come about without any clear understanding of elements and compounds. Ancient metalsmiths must have been fully conscious of the results of smelting a mix of different “ores,” but they must have marveled at the results of smelting both metallic-looking and nonmetallic-looking stones.

Although copper deposits are widespread, some countries have none and other countries have none that could have been exploited by miners from the Bronze Age through the first millennium CE. The author spent many months in the field in the 1970s assessing the evidence for ancient copper mining in Greece, Turkey, Serbia, Cyprus, and Egypt. Greece had no mineable deposits, Turkey had many, and evidence indicates that Cyprus had major copper production by the Late Bronze Age.

Rudna Glava is an abandoned modern open pit magnetite mine in northeastern Serbia. The author visited the mine and studied the area with Borislav Jovanovic and others in the 1970s. From ceramic and radiocarbon dating, early mining for the copper carbonates malachite and azurite began in the Chalcolithic and continued through the Bronze Age. Numerous mining tools have been recovered. Maggi and Pearce (2005) have presented new radiocarbon dates to show that copper mining at Monte Loreta in Liguria, northwest Italy, began about 3500 BCE, making this the earliest copper mining in western Europe. The prehistoric miners exploited natural fissures of copper ore. The authors did not identify the copper ore mineral(s).

Jackson (1980) notes that there are 74 copper mines of proven or probable Early Bronze Age in southwest Ireland. Nearly all are mines of modest dimensions in the famous Old Red Sandstone. Figure 7.7 shows copper mining areas in the British Isles. It must be stressed that modern exploitation does not imply anything about the potential for ancient mining. Each site must be investigated to establish both the geologic and the archaeological contexts. A study conducted over a 30-year period on North American native copper sources (Rapp et al. 2000) and an investigation of early Anatolian copper mining (Wagner et al. 1983/1984) clearly show the need for this.

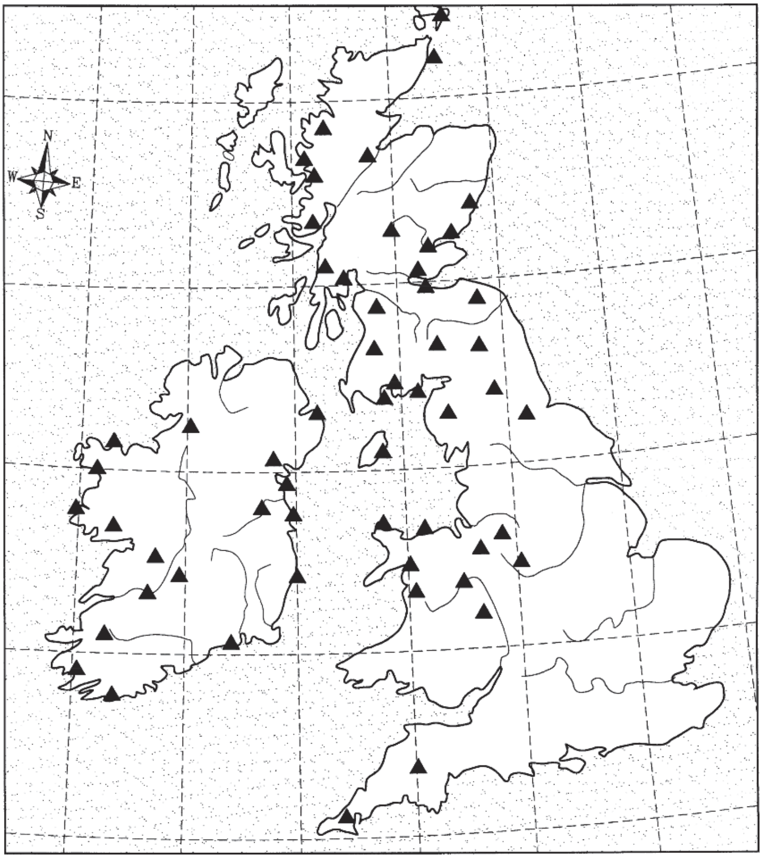

Fig. 7.7 Copper deposits in the British Isles

Copper ores developed at the base of gossans were called by the German name *fahlerze* (pale ore), and now are commonly called fahl ores. In some environments, lead/silver ores are also found at the base of gossans, often accompanied by the mineral jarosite [$KFe_3(SO_4)_2(OH)_6$]. An example of this is at Lavrion in Greece, but there are other occurrences in France, Germany, Spain (see Williams 1950), and the Czech Republic. Pre-Roman mining at Rio Tinto, Spain, extracted silver and copper. The silver ores were jarositic in composition because they came from gossans.

It is likely that the earliest copper smelting was conducted well below the melting temperature of copper (1083°C). A variety of scenarios may be proposed to account for the initial discovery that copper metal can be separated from nonmetallic-looking minerals such as malachite and azurite. For example, bright green malachite or bright blue azurite might have been applied as decoration on the surface of pottery by Chalcolithic artisans. If the pottery was then fired in a reducing atmosphere, copper beads would have formed. Malachite and azurite, which are carbonate minerals, begin to decompose below 400°C, and early pottery was fired at temperatures above 600°C. Once ancient metallurgists learned how to smelt the more difficult copper sulfide ores, perhaps soon after 2000 BCE in the eastern Mediterranean, they turned to the much more abundant copper iron sulfide, chalcopyrite. The technology for smelting copper sulfide minerals probably had a profound effect on economics and trade relationships in the early phases of the Bronze Age. Oxide zone copper deposits, which undoubtedly provided the first raw material for copper smelting, are not normally as rich or as extensive as sulfide zone copper deposits. As the Bronze Age developed, oxide zone deposits were depleted, and sulfide copper, available beneath the oxide zone and in regions where erosion exposed primary copper ores, would have been the only secure source for copper.

The earliest copper "alloys" contain appreciable quantities of arsenic and lead, sometimes nickel or antimony, and occasionally silver, bismuth, or tin. A primary question is whether the arsenic, lead, and tin were added deliberately or were the result of impure raw materials. If the early arsenical coppers were deliberate, then what prompted the initial effort(s) to smelt "mixed" ores? Was it random experimentation with metallic-looking stones, or was it the result of perceptive understanding of the smelting products of naturally complex ores? Zwicker et al. (1980) point out that arsenic in a copper ore can be dissolved in the copper during smelting. The Sican culture, 700–1400 CE, introduced bronze metallurgy in northern Peru with their extensive production of arsenical copper (Shimada and Griffin 1994).

For most of the region from Europe and the Mediterranean throughout the Near East to the Indian subcontinent, the first copper alloys were predominantly arsenic bronzes containing more than 1% arsenic. The name arsenic comes from the Greek word for strong because of its potent chemical properties. In the British Bronze Age the earliest bronzes were made with arsenic (McKerrell and Tylecote 1972). Renfrew (1967) states that tin bronze is rare in the Greek Aegean Early Bronze Age. In Crete in EB I–II, arsenic was more common than tin as an alloying element (Branigan 1974). In central Italy, excavations near a number of copper deposits about 20 km south of Sienna have revealed an Etruscan bronze metallurgy of the seventh and sixth centuries BCE (Warden et al. 1982).

Much has been written, both speculation and with field and analytical evidence, about the sources of the key elements (copper, tin, and arsenic) for the early development of bronze metallurgy in the eastern Mediterranean region (Rapp 1999). There are abundant likely sources for copper and arsenic, but the question of tin sources remains unanswered. In the eastern Mediterranean region, tin bronzes predominated only at Troy. In the Araba of southern Israel, copper mining and smelting was underway at Timna by the Chalcolithic (fourth millennium BCE) (Rothenberg 1978). In addition to malachite, they used siliceous copper minerals including chrysocolla and paratacamite. Malachite is still in evidence at the ancient workings. Shalev (1994) has argued that the first smelting in Israel and Jordan should be dated to the Early Bronze Age rather than the Chalcolithic. Eaton and McKerrell (1976) have summarized the data for the eastern Mediterranean and Near East. Agrawal (1971) has republished data from this broad region. In many areas tin bronze was not common until the Middle Bronze Age. Lead, nickel, antimony, and silver were found in addition to arsenic and tin in copper alloys in amounts greater than 1%. Lead was used frequently as an alloying element.

Although it was neither the earliest nor the largest supplier in the region, Cyprus has long been known as a source of copper. Because there is no evidence that substantial quantities of native copper or the easily smelted copper oxides and copper carbonates were ever available in Cyprus, significant bronze production did not begin until the Late Bronze Age when smelting technology could accommodate the massive sulfide ores of Cyprus. Raber (1987) has located and dated 49 metallurgical and related sites in the Polis region of western Cyprus, dating from the eighth century BCE to the fifteenth century CE.

One of the most important sources of early copper in the eastern Mediterranean is the Feinan district of southern Jordan. The area produced copper at least since the Early Bronze Age. By EB III, the region had the largest copper production in the Near East (Levy et al. 1999). Wagner et al. (1983/1984) and (Weisgerber 2006) investigated early mining and smelting sites in northwestern Anatolia. One focus of the Wagner inquiry was to study ore and slag samples to determine whether raw materials from this region were the sources for bronze artifacts found at Troy and other archaeological sites. Their analyses indicated that Early Bronze Age metal artifacts found in the Troad were predominantly produced from ores of other regions.

Based on radiocarbon dates, Kaptan (1980) presented evidence of copper ore mining and smelting (slags) during the third millennium in the region of the city of Tokat, Turkey (central Black Sea area). Zaykov et al. (1999) have shown that Bronze Age settlements in the southern Urals utilized nine types of copper ores. Many of the copper deposits were oxidized sulfide ores in which malachite and azurite were the dominant minerals.

Early alloys of copper and arsenic have been found not only in the Mediterranean region, but also in the Andes of South America. From her work in Peru, covering the Late Intermediate Period (900–1476 CE), Lechtman (1991) has provided insights into the raw materials used. The copper ores were identified as chalcopyrite, copper oxides, copper carbonates, and copper chloride. The arsenic minerals, however, remain somewhat in question. Lechtman believes the arsenic minerals were most likely enargite and arsenopyrite. Arsenic compounds have been known since the first millennium BCE. Aristotle refers to sandarach (As_2S_3) in the fourth century BCE. In the first century CE, Pliny stated that sandarach is found in gold and silver mines. In the early first millennium CE, inhabitants of the north coast of Puerto Rico were alloying copper, gold, and silver in a ratio of 55 Cu/40 Au/5 Ag (Siegel and Severin 1993).

The most interesting questions involve the early arsenical coppers. Analyses from dozens of early metallurgical centers have shown that arsenic bronzes were fairly common in the Chalcolithic and early Bronze Age. The most intriguing question is how the metalsmith discovered the technology of alloying arsenic with copper. The "problem" of early copper-arsenic alloys is widespread. For example, see the article on the North Caucasus by Ravich and Ryndina (1995). The use of arsenic was not only widespread, it was intensive. In a fourth millennium BCE Near Eastern (Nahal Mishmar) hoard of copper objects, 24 of the 36 analyzed had an average arsenic content of 5.23% (Muhly 1977). An ancient copper mine from the southern Sinai contains the copper arsenides koutekite (Cu_5AsS_2) and domeykite (Cu_3As) associated with native copper. Ilani and Rosenfeld (1994) suggest that this mine might be the source for the high arsenic (2–12%) Chalcolithic copper hoard at Nahal Mishmar.

Unlike lead, there is no evidence that arsenic was ever used as a metal (and native arsenic is *very* rare), and arsenic has never been found as an ingot (such as copper and tin). Thus, arsenic must have become alloyed with copper because of the smelting of complex ores containing both copper and arsenic.

There seems to be a consensus among archaeometallurgists that the first copper minerals smelted were the hydroxycarbonates (malachite and azurite) and the oxides (cuprite and tenorite), yet the first alloys were arsenical. McKerrell and Tylecote (1972) and many others have suggested that the metallic-looking complex copper-arsenic sulfide mineral tennantite is the most likely source of the arsenic. However, tennantite would come from the lower unoxidized zone (along with many metallic-looking copper sulfides).

The most likely raw materials are arsenates from the oxidized zone of ore deposits. The following arsenates are all associated with malachite in the oxidized zone of copper deposits in Europe, the Near East (including the former USSR), and elsewhere: olivenite $Cu_2(AsO_4)(OH)$, clinoclase $Cu_3(AsO_4)(OH)_3$, tyrolite $CaCu_5(AsO_4)_2(CO_3)(OH)_4{\cdot}6H_2O$, mimetite $Pb_5(AsO_4)_3Cl$, adamite $Zn_2(AsO_4)_2{\cdot}(OH)$, erythrite $Co_3(AsO_4)_2{\cdot}8H_2O$, and annabergite $Ni_3(AsO_4)_2{\cdot}8H_2O$. Use of the last four could account for the occasional high Pb, Zn, Co, or Ni contents of arsenic bronzes. In addition to arsenic, there is the question of the related element, antimony, finding its way into second and first millennium BCE bronzes in the Far East. The percentages of antimony suggest that ores containing tetrahedrite ($Cu_{12}Sb_4S_{13}$) were used.

Bronze-making was a major industry during China's Shang Dynasty. The last capital of the Shang at Anyang was a particularly prolific site for bronze-making. For raw materials there were three copper mines and four tin mines within 100 km of Anyang, six copper and three tin mines within 200 km, and six additional copper and tin mines were located within 400 km (Chang 1980). In the analyses of the earliest Chinese bronzes presented by Barnard (1961), it was lead rather than arsenic that served as the alloying element. Lead provided the castability desired by the Chinese metalsmiths. Mei and Shell (1998) summarize the evidence for the beginning and early use of copper and bronze in Xinjiang Province, China. These authors also report preliminary results of research at the Nurasay site, the only Bronze Age copper mining and smelting site in Xinjiang. Of some importance is the possible smelting of arsenical copper ore. The copper ore at Nurasay is a sulfide ore. Radiocarbon dates indicate that copper/bronze came into use by 2000 BCE. The authors note that copper artifact and copper deposit distributions match very closely.

Based on the physical and chemical properties of ore minerals discussed in the ancient Chinese literature, Wang and Shen (1986) have concluded that thirteen species of copper-bearing minerals were exploited. These were native copper, three sulfides (chalcopyrite, chalcocite, and bornite), three sulfosalts (enargite, bournonite, and tetrahedrite), two sulfates (brochantite and chalcanthite), two oxides (tenorite and cuprite), and two carbonates (malachite and azurite).

In India signatures of ancient mining and processing of ores are present in almost all of the slags from Rajastan and Gujarat. The most common slag was produced during the smelting of copper ores (Grover 2004). Elsewhere in Southeast Asia, Thailand played a major role in early large-scale copper production. Ban Chiang has long been a focus of study (e.g., see Higham and Kijngam 1984). Bennett (1989) has detailed early copper exploitation in central Thailand. She indicates that both malachite and chrysocolla were the most likely early ores. From the sulfur content of slag analyses, Bennett surmises that sulfide ores (probably chalcopyrite or bornite) were also being smelted. To the north in Vietnam, bronze technology flourished at Dongson (Ha 1980).

In Mesoamerica, copper ore sources exploited during the Late Postclassic Period (1300–1521 CE) occur in west Mexico (Hosler and Macfarlane 1996). The minerals mined and smelted included copper carbonates and copper sulfides. Copper alloy metallurgy came late to sub-Saharan Africa, not much earlier than the introduction of iron smelting.

As indicated above, Chalcolithic and Early Bronze Age copper-based artifacts show appreciable amounts of arsenic, tin, antimony, and lead, often greater than 1%. Because of lead's low melting point (327°C) and the ease of smelting galena (below 800°C), lead was an easy metal for early metalsmiths to use. Galena deposits are available throughout the area where metalsmithing originated. The difficulty is determining whether lead was added deliberately to improve the resulting alloy or whether lead entered the metal because it was available as a component in the ore.

Although antimony is present occasionally in some early copper-based metals in amounts greater than 1% (thereby having an effect on the properties of the metal), it seems likely that antimony was always an accidental alloying element when it was a component of the sulfide ores. As an element, antimony was first described in 1450.

Nickel presents a greater problem. Cheng and Schwitter (1957) have shown that many Syrian, Sumerian, and Indian bronzes contain more than 1% nickel, and some contain more than 3%. They also found that the nickel composition was a function of the type of object, thus indicating deliberate choice. The question remains, how much of the choice was made before smelting and how much was based later on the working characteristics of the products of smelting various raw materials? Nickel is present in amounts greater than trace levels (>100 ppm) in many copper-based artifacts from most of the important metalworking regions in the Chalcolithic and Early Bronze Age.

Most ancient tin bronze contained about 10%–12% tin. Tin is a significant component in a few copper ores (e.g., Cornwall, England); however, except in rare cases, it is unlikely that tin in amounts greater than 0.10% was accidentally incorporated in smelted copper. Tin percentages between 0.10% and perhaps 1.5 or 2.0% most likely resulted from reuse of scrap metal.

Budd et al. (1992) argue that the traditional view that the earliest copper exploitation in the British Isles centered in southwest Ireland is fallacious. Following on the work of Case (1966), the authors propose that Early Bronze Age craftsmen exploited the oxidized zones of arsenic-bearing copper deposits. The oxidized ores would likely include olivenite (Cu_2AsO_4OH) and clinoclase [$Cu_3AsO_4(OH)_3$]. There are numerous studies showing that early smelted copper in Europe was arsenic-rich.

Copper ore deposits are widespread and exist in a great variety of mineralogies, complexities, and structures, but only a small number are credible as Chalcolithic and Early Bronze Age ore sources. Native copper was undoubtedly the initial source but deposits were not extensive enough to sustain increasing demand. Until contrary evidence is offered, we can assume that the earliest smelting utilized oxide ores.

7.5.1 The Copper Ore Minerals

Malachite [$Cu_2CO_3(OH)_2$]. This dark green copper carbonate hydrate has a hardness of 3.5–4.5 and was most likely the first mineral ever smelted. It also has been used since the Neolithic for carved beads and other ornaments. It occurs widely in the oxidized portions of copper ore deposits, especially in regions where limestone is present. One of the earliest examples of the mining and smelting of malachite is at Aibunar in southern Bulgaria, about 8 km northwest of Stara Zagora (Černych 1978). Large quantities of diagnostic pottery place the surrounding archaeological sites in the Eneolithic. Chalcolithic Period beads and related decorative objects from northwestern Bulgaria include malachite and azurite as well as cuprite, antigorite, spinel, carnelian, red jasper, agate, and a black lignite coal (Kostov 2005c).

El Gayar and Jones (1989) identified malachite from Old Kingdom copper smelting at the town of Buhen in Egypt. Because of the high proportion of gold in the copper ore, the authors believe the source of the ore was Kush (modern Sudan). Pharaonic Egyptians mined the copper ores malachite, azurite, and chalcocite contained in the sandstone formation at Timna, from approximately 1300–1100 BCE. In the second century CE, the Romans had a small mining operation there. The first copper "beads" from the Near East may have come from rare native copper nuggets but, just as likely, may have come from accidental smelting of malachite or azurite in the Neolithic campfires, or from the reduction of malachite or azurite "paint" on early pottery.

During the Pre-Pottery Neolithic B, people moved into the southern Sinai to exploit deposits of malachite, turquoise, and flint. The flint industries left behind a very large number of stone tools and flakes. Turquoise was mined in the Maghara area. Long-lived settlements were formed in the location of the malachite deposits. The malachite was used only for ornaments, pigments or cosmetics, as smelting in this region dates to the later Bronze Age (Rothenberg 1979).

Malachite and chrysocolla ores emplaced in a dolomite-limestone-shale host rock have been mined since the Early Bronze Age at Feinan in the Arabah Valley of southern Jordan. In the Chalcolithic, the miners extracted malachite and other copper minerals from sandstone at Feinan (Hauptman et al. 1992).

Azurite, $Cu_3(CO_3)_2(OH)_2$, is a deep blue complex copper hydroxycarbonate related to malachite, but less abundant. The name comes from the Persian word *lazhward* meaning blue. Azurite was an early, easily smelted ore of copper. It forms in the upper oxidized zone of copper sulfide deposits along with the more common malachite. Azurite has a long history of use and was used as a cosmetic by the Egyptians. However, once powdered, it absorbs moisture and over time will lose its blue color and become green. The deposit at Chessy, France, was worked in the Bronze Age and in Roman times.

Chrysocolla, $(Cu,Al)_2H_2Si_2O_5(OH)_4 \cdot nH_2O$, is a complex hydrated silicate of copper. It was named by Theophrastus by combining two Greek words for gold and glue, because it looked similar to a material used to solder gold. Sense (1966) has reported a prehistoric, possibly Hohokam, chrysocolla quarry at Ray, Arizona. The ancient miners removed over 180 tons of rock in quarrying the chrysocolla. Stone tools were recovered at the site.

Chalcopyrite, $CuFeS_2$, is the most widely occurring ore of copper. It is easily recognized by its brass-yellow color. Although pyrite is called "fools' gold", chalcopyrite has a much more golden color than pyrite. The development of copper sulfide metallurgy – more complex than copper oxide metallurgy – allowed the continued expansion of bronze-making in the ancient world. Sulfide ores in copper deposits lie below the oxidized ores, so ancient metallurgists may have been forced into sulfide smelting when the oxide ores were depleted.

Cupiferous Pyrite FeS_2. In two of the great ancient copper mining areas of antiquity, Cyprus and Spain, the primary copper mineral was cupiferous pyrite. The great copper-pyrite ore bodies of Rio Tinto in southern Spain have been exploited since Phoenician times. The ores are dominantly massive pyrite, containing between 2% and 12% copper. These deposits are capped by a gossan more than 25 m thick. Another pyrite deposit that has been mined for copper (and lead) since at least the tenth century is the Rammelsberg deposit, which lies on the northern slope of the Harz Mountains in Germany.

7.6 Iron (Fe)

Iron has the chemical symbol Fe from the Latin *ferrum.* Iron is the fourth most-common element in the earth's crust. Because iron combines readily with oxygen, sulfur, and other anions, it is rarely found in the native state. Native iron does occur as minute pellets in basaltic rocks in many areas including Ireland, Scotland, France, Germany, Poland, Russia, Japan, Canada, and the United States. The only significant occurrence of large masses of native iron in basalts is on Disko Island, Greenland. Native iron is also found in carbonaceous sedimentary deposits in a few localities.

Both native iron and meteoric iron (see below) are quite rare, so the technique of smelting iron oxide ores had to be developed before iron became a widely used metal. For good summaries of the transition from the Bronze Age to the Iron Age, see Waldbaum (1978) and Wertime and Muhly (1980). Waldbaum's work was updated by Muhly et al. (1985). In 1999, Waldbaum reviewed the current status of our knowledge and provided a map of eastern Mediterranean and Near Eastern Bronze Age/Early Iron Age sites at which iron had been found.

True iron metallurgy originated in ancient Anatolia in Hittite and Mitanni kingdoms over 3000 years BP and separately in India at about the same time. Iron came to be used regularly in Europe by the middle of the first millennium BCE. Agricola in his 'De Re Metallica' describes the mining of metal ores in Europe. Much earlier in Saxony, two types of low-grade bog iron ore provided the raw material for Early Iron Age (and onward) iron production. The two types were distinguished by their manganese and barium contents. Slag compositions showed that both types of ores were inefficiently processed (Heimann et al. 1998).

Along with the question of iron usage in the Bronze Age of the eastern Mediterranean, we have the question of early steel. Smith et al. (1984) report on a Middle Bronze Age steel blade from Pella, Jordan. The metal contained 0.9% carbon that was distributed heterogeneously, calling into question whether the carbon was purposefully or accidentally incorporated. This blade marks the earliest known steel from the eastern Mediterranean region. The report by Williams and Maxwell-Hyslop (1976) on "Ancient steel from Egypt" is inconclusive because the carbon content is in the range 0.1–0.2%. However, even this low amount of carbon resulted in moderate, but workable, increases in hardness.

Perhaps the most famous early steel was "Damascus steel" used in Near and Middle Eastern sword-making circa 1100–1700 CE. These swords were noted for both sharpness and strength. The basis for Damascus steel is "Wootz steel" which originated in India about 500 CE and spread to Persia. The finished steel had a visible grain pattern, the result of alignment of Fe_3C particles in the steel. Damascus steel was not produced in Damascus, but rather in India, and ingots were shipped to Syria where the weapons were forged.

References to what iron ore deposits were exploited are scarce in the literature. Iron oxide minerals are almost ubiquitous at the earth's surface, so early iron metalsmiths did not have the resource problem faced by bronzesmiths. As stated earlier, iron makes up about 5% of the earth's crust, whereas copper is only 0.005% and tin is a scant 0.0005%.

Iron ores have a considerable range of compositions. Common impurities in iron ores include silica, calcium carbonate, phosphorus, manganese (especially in hematite), sulfur, alumina, titanium, and water. Ancient metalsmiths had to have an ore greater than about 60% Fe_2O_3 because the slag itself would have a 2:1 Fe/Si ratio. The best iron ore for smelting is not necessarily the ore with the highest iron content. Good iron ores are the ones low in lime, magnesia, alumina, and silica. The manganese oxide content does not matter, because it will go into the slag. All primitive slags contain at least 50% iron plus manganese oxides.

Although iron ore deposits are both widespread throughout the world and often of considerable extent, the exacting requirements for smelting, including a temperature not attainable by methods used in early copper, lead, tin, and zinc extraction, led to a relatively late iron metallurgy. Although some iron was smelted by about 1200 BCE, the technology was not widespread until 800 BCE. The earliest smelted iron may be from Alaça Höyük near the end of the third millennium BCE (Wertime 1973b). Iron is the only common metal that will dissolve carbon. Steel is an alloy of iron with small amounts of carbon. Since charcoal (carbon) was used to smelt iron, ancient metallurgists were unwittingly making low-grade steel for about two millennia. Steel came into use early in the first millennium CE and the blast furnace was fully employed by the fourteenth century CE. It was not until about 1700 that coal was used to reduce iron ore in Europe.

In terms of raw material for iron smelting, something needs to be said about sulfur. Cupiferous pyrite (FeS_2) and chalcopyrite ($CuFeS_2$) were smelted since the Bronze Age. This process produced a high-iron **matte** but, in terms of iron recovery, the matte was high in sulfur. Sulfur incorporated in iron is one of the most deleterious materials possible to the quality of the iron. The sulfur content of coal prevented its use in iron production in the Western World until the eighteenth century CE. In the late sixteenth and seventeenth centuries, English iron producers attempted to desulfurize coal.

Although iron was recovered far below its melting point (ca. 1536°C) by reduction of iron oxide using carbon, this iron was not liquid and was interspersed throughout the slag. By hammering when the material was hot, the iron particles could be “welded” together and the silicate particles could be largely removed.

Although they attributed the problem incorrectly to a variety of substances, by the seventeenth century, iron workers began to be aware of the deleterious effect that high-phosphorus iron ores (such as the bog ores of Sweden) had on the final product. By the late eighteenth century, German and Swedish chemists correctly identified the problem.

In Southeast Asia, a major Iron Age technology thrived from about 500 BCE at Dongson (Ha 1980). For a review of early iron production in India, see Agrawal and Kharakwal (1998). The development of iron production in Africa is given broad coverage by eleven authors in Haaland and Shinnie (1985). Beginning in the 1960s, archaeologists were able to date metallurgical sites in sub-Saharan Africa. Van der Merwe and Avery (1982) have pointed to the lack of evidence in sub-Saharan Africa of any metallurgical expertise prior to the appearance of iron. The most extensive evidence for early iron-working in Africa is found in central Nigeria. The Nok culture in this region is firmly dated to between the sixth century BCE and the early first millennium CE (Calvocoressi and David 1979).

The earliest blast furnaces for **cast iron** came into existence in northern Europe by the late eighth century CE, but the Chinese were making cast iron in the fourth century BCE by a lower-temperature, solid-state process that required comminution of the metal/slag product to extract the iron. There may be two reasons for the early Chinese technology. China had good **refractory** clays for construction of high temperature furnaces, and they added a high iron phosphate ("black earth") that probably reduced the melting point by about 200°C. By the fourth century CE, the Chinese were using coal in their iron production. An in-depth account of the development and production of iron in ancient China is given in Wagner (1993). Wagner (1999) reviews the earliest use of iron in China and suggests that, after the making of luxury weapons from meteoric iron during the Shang and early Zhou Dynasties, the technique of solid-state iron ore smelting came to China by the eighth century BCE from the west via Scythian nomads. New evidence shows that wrought **bloomery** iron was the first iron to be used in China.

Meteorites. Although most meteorites have a composition similar to rocks, many are composed of a combination of iron and nickel that is nearly rustproof and easily recognized as a metal. Meteoric iron is malleable and easily worked. It can be distinguished from smelted iron by its high (5%–26%) nickel content. Metallic meteorites were picked up and used by humans over 8000 years ago, long before the Iron Age in the Old World.

The prehistoric utilization of meteoric iron to fashion tools probably was worldwide, including the Arctic. Iron meteorites were prized in prehistoric America. The Aztecs made knives from iron meteorites. Ancient Sumerian texts mentioned meteoric iron and called it "fire from heaven". The association of iron meteorites with the heavens was common among most ancient peoples. In Egypt and the Near East, artifacts of meteoric iron are known from the end of the third millennium BCE. For a review of meteorite artifacts from the Near East, see Bjorkman (1973). LaPaz (1969) presents a record of meteorite utilization from the Paleolithic to the present.

Pringle (1997) reports on a number of archaeological investigations that recorded the use of meteoric iron by Arctic cultures. Pringle also mentions that some iron implements may have been made of pea-sized inclusions of **telluric iron** that occurs in the Disko Island basalts. Numerous examples record the use of meteoric iron by Hopewell people in eastern North America (see Grogan 1948; Prufer 1961; Hertzog 1965). Piaskowski (1982) discusses the use of early iron artifacts of meteoric (and non-meteoric) origin.

For a discussion of the means of distinguishing meteoric iron from man-made nickel-iron in ancient artifacts, see Knox (1987). It should be noted that there are nickel-rich iron ores, particularly **lateritic** ores. Such ores were smelted at Hellenistic Petres in northwest Greece (Photos et al. 1988).

7.7 Iron Minerals

By the time of Agricola, early mineralogists distinguished the following iron "ores:" hematite, magnetite, ochre, and *ferrugo* (limonite or rust). For a discussion on early iron ores, see Coghlan (1956). The iron deposits of the island of Elba in the Tuscan Archipelago have been worked for over 2000 years by the Etruscans, the Romans, and later by others.

Hematite, α-Fe_2O_3. A red iron oxide, this mineral (hardness 5–6.5; density 5.26) was used extensively throughout the world. The name comes from the Greek word for blood-red. While the streak (the color of the finely powdered mineral, so-called because of the diagnostic test used by geologists of drawing a mineral across a piece of unglazed porcelain and noting the streak) of hematite is red, the mineral itself can be black or, in the case of specular hematite, a metallic silvery color. Hematite is widely distributed in rocks of all ages and is the most abundant and important ore of iron. Hematite sometimes, as in the variety called specularite, has a lustrous gun-metal color and was fashioned into ornaments. Well-crystallized hematite is tough, hard, and heat-resistant.

Engraved cylinder seals of hematite have been found in the ruins of Babylon. The specular variety of hematite has long been valued as a gemstone. This material is so lustrous it can be used as a mirror. In Europe, the best hematite crystals are from the Swiss Alps and the island of Elba.

Most hematite can be ground to a good red ochre powder, a pigment that has been used throughout history. Red ochre was a widely used pigment in the ancient Near East. The ancient Egyptians had plentiful supplies of red ochre near Aswan and in the oases of the Western Desert. In North America, red ochre (either as lumps or as ground into a pigment) was used to accompany the dead in their burials. In central and eastern North America (an area roughly bounded by Minnesota; Ottawa, Canada; North Carolina; and Alabama), hematite was used in prehistoric times to make pendants, axes, celts, and edged tools. Celts are the most common and widespread hematite implements in this region. The hematite was recovered from glacial till and from bedrock quarries.

A cylindrical silver container with an attached probe was recovered from a noblewoman's grave in Judea dated to the third century CE. The composition of the tube was found to be a silver alloy with silver solder. Inside the silver tube was a red powder composed mostly of red hematite (50%) and malachite (35%), with lesser amounts of cassiterite (1%), galena (0.5%), and calcite (<0.1%). Hematite, malachite, and kaolinite are found locally in Judea. However, the cassiterite found in the medicine must have been imported. The authors suggest that the powder was mixed with a moist medium such as honey, animal fat, or beeswax. "Moist" remedies were traditionally kept in metal or ivory containers to keep the active ingredients effective. The probe was used as an applicator (Ilani et al. 1999). Similar powders have been found in bronze containers at Nea Paphos (Cyprus) and in a physician's box now in the Hecht Museum of Haifa University (Israel). On textual evidence, the compound was used by Roman physicians to stop hemorrhages in wounds and ulcerations and also used as a cleanser, desiccant, and emollient.

Red ochre has been used for decoration at least since Mousterian times (in France). It was used in the Upper Paleolithic in cave painting and since the Neolithic for painted pottery. Recent excavations in south-central Sicily recovered small jars of ochre from the first phase of the local Copper Age (Maniscalco 1989). Maniscalco believes this discovery provides evidence of contact between Sicily and Malta, where potters used ochre that may have been imported from Sicily. Red and yellow ochres used by aboriginal societies in southern and western Australia were found to have a diverse mineralogy, being mixtures of up to seven minerals (hematite, ankerite, calcite, dolomite, quartz, feldspar, and corundum) (Jercher et al. 1998).

Goethite/limonite, α-FeO(OH), has a hardness of 5.0–5.5 and a density range of 3.3–4.3. The name goethite is in honor of Goethe, the German poet. Goethite is a major ore of iron in some locations. Limonite is essentially a field term used by geologists for hydrous iron oxides of uncertain identity but largely goethite. Goethite is one of the most common and most widespread of minerals. It typically forms as a weathering product of iron-bearing minerals. Goethite is the gossan or "iron hat" that caps oxidized sulfide deposits. Goethite is common in near-surface sediments and soils as a secondary or concretionary material precipitated from circulating groundwater. The dearth of archaeological knowledge concerning iron ore mines of the European Iron Age probably stems from the wide occurrence of small, shallow deposits of limonitic and hematitic iron ores. The exploitation of such ores would have had little lasting effect on the landscape.

At the Nichoria excavation in southwestern Greece, goethite was found as small rod-shaped forms in Bronze Age contexts. This initially created quite a stir, because it was conjectured that these might have been pre-Iron Age oxidized iron nails. However, I found the rods to have a radial cross-sectional structure similar to other known goethite nodules rather than the concentric or structureless cross-section that would be consistent with a rusted metallic iron nail.

When yellow in color, goethite is called yellow ochre. Many yellow ochres also contain jarosite [$KFe_3(SO_4)_2(OH)_6$] or natrojarosite [$NaFe_3(SO_4)_2(OH)_6$]. Several types of ochre fragments were recovered from the Natufian layers of el-Wad Cave, Mount Carmel, Israel. Yellow ochre was available from local deposits and was apparently used to produce a red hematitic pigment, residues of which were found on basalt pestles in the cave (Weinstein-Evron and Ilani 1994). This would have required heating the goethite [FeO(OH)] of yellow ochre to convert it to red hematite (Fe_2O_3).

Magnetite, $Fe^{2+}Fe_2^{3+}O_4$, has a hardness of 5.5–6.5 and a density of 5.18. It is iron-black with a metallic luster and a black streak. It is magnetic enough to act as a natural magnet known as *lodestone.* It is common in small amounts in most igneous rocks, and is occasionally sufficiently concentrated in lode or placer deposits to be classed as an ore deposit. An early form of steel was made in India by reducing a mixture of powdered magnetite and hematite in small crucibles with wood or green leaves as a carburizer and with a calcareous flux (Hulme 1940).

The Latin name for lodestone was *adamas*, which was also the name given to the compass in the time of Edward III of England. A wide-ranging history of lodestone, now somewhat out of date, is presented by Still (1946). The Chinese were the first to use lodestone (magnetite) as a compass. The Mesoamerican Olmec "compass" was made of hematite (see Carlson 1975).

In parts of Europe, siderite ($FeCO_3$) was also exploited as an iron ore. It was called chalybite, a name derived from Chalybes, an ancient nation in Asia Minor famed for skill in iron-working.

7.8 Tin (Sn) Minerals

The chemical symbol for tin, Sn, is derived from its Latin name *stannum.* The word tin likely derives from the German *zinn.* Tin only occurs rarely and in very small quantities as a native metal. Its chief importance in antiquity was as a component (about 10%) with copper in bronze and with lead in pewter. Tin bronze is harder and has greater tensile strength than copper, important for weapons, and greater fluidity in the molten state, important for casting. Tin came into medical use in the Middle Ages as an agent for expelling intestinal worms, a remedy recommended by Paracelsus. Tin metal is relatively soft, but, with small amounts of other metals added to make an alloy, it becomes sufficiently durable for domestic use. However, even the alloys had low melting points (170–230°C) so were not suitable for cooking pots.

For a thorough review of our knowledge of tin in antiquity (through the early 1980s), see Penhallurick (1986). The scope of Penhallurick's book is basically worldwide. He covers Africa and Asia, but concentrates on Europe. A now somewhat dated overview of tin in the ancient world is available in Franklin et al. (1978). The literature is full of misinformation, or at least uncritical reporting, concerning ancient tin sources. For example, Wilson (1994:18) presents a map of "mines of the Middle East". On this map, tin mines are shown near Eskisehir and Erzincan, Turkey. I have visited this area, and there is no evidence for significant tin in regional geologic formations.

Cassiterite (SnO_2) (sometimes called stream tin or wood tin) has a hardness of 6.0–7.0 and density of 6.99. It is the only important ore of tin. Stannite (Cu_2FeSnS_4) is fairly widely distributed, but there is no evidence that it was exploited in the ancient world and it is not economically important in the modern world. The name cassiterite comes from the Greek word for tin, *kassiteros.* Cassiterite is found in granites, pegmatite dikes, and quartz veins. It is also found in high-temperature hydrothermal veins in or near granite. It is liberated from these primary deposits by disintegration of the host rock. Because of its high density and resistance to weathering, cassiterite becomes concentrated in gravel and placer deposits. The original recovery of cassiterite is likely to have been from such placer deposits. One can only wonder how early miners distinguished small grains of black cassiterite from those of magnetite, which is also black and has high specific gravity. Many placers are called "black sand" because of the predominance of magnetite. Cassiterite is sometimes also associated with gold in placer deposits, which may have been the reason it was first noticed. Tin becomes molten at 232°C and occasionally was used in its metallic form in the ancient Old World. For the geology and mineralogy of tin deposits, see Taylor (1979). For the metallogeny of tin, see Lehmann (1990). Bronze, an alloy of copper and tin, was developed more than 5000 years ago in the Near East. Perhaps the greatest unsolved mystery in Mediterranean and Near Eastern Bronze Age metallurgy is the source(s) of the tin.

Whereas copper deposits are widespread in the British Isles, tin deposits are limited to Cornwall in the far southwest corner of England. The plentiful placer deposits of cassiterite from Cornwall were certainly utilized in British Isles Bronze Age metallurgy, but it is still unknown how widely it was traded. Thorndycraft et al. (1999) used a combination of geochemistry, mineralogy, and particle size analysis to relate mine waste contaminated sediments to early alluvial tin on Dartmoor in the United Kingdom. A recent review of the earliest days of mining in Cornwall and a brief description of the regional geology and mineralogy are presented by Bancroft and Weller (1993). By Roman times, cassiterite from Iberia and Cornwall was available. Figure 7.8 is a map showing known cassiterite deposits in Europe, Asia, and North Africa.

In Mesoamerica, cassiterite occurs in Mexico's Zacatecas tin province (Hosler and Macfarlane 1996). In the Andes Mountains of South America, when tin bronze became a widely used alloy during the establishment of Inca hegemony (1476–1532 CE), the cassiterite source was the well-known deposits of northern Bolivia (Lechtman 1980).

Surface deposits of cassiterite, concentrated enough to be an ore available to Aegean Bronze Age metalsmiths, are found in the Iberian peninsula, the Czech Republic, Egypt, and Tajikistan (Fig. 7.8). Saxony and the adjacent part of Bohemia

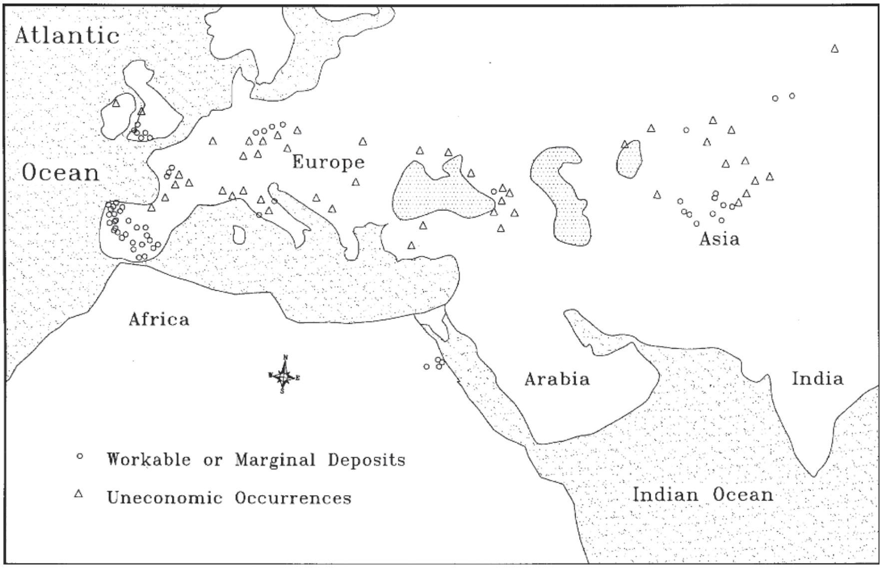

Fig. 7.8 Map showing known cassiterite deposits in Europe, Asia, and North Africa

contain several tin-producing districts, but there is little evidence of how early these were exploited. The first direct evidence for mining in the Erzgebirge dates to the close of the twelfth century. Penhallurick (1986) addresses the question by stating, "...but tin mining there must have been in the Erzebirge during the Bronze Age, for without it, the achievements of European metallurgists before the discovery of the Cornish ores cannot be explained." McGeehan-Liritzis and Taylor (1987) have suggested that Yugoslavian tin deposits may have been a Bronze Age source. However, until the basic geology of these deposits is understood in the light of requirements for Bronze Age exploitation, such suggestions are highly speculative.

A source of tin in the Taurus Mountains of Turkey for the Bronze Age of the eastern Mediterranean has been widely argued (Yener and Ozbal 1987; Yener et al. 1989). However, in the company of Yener, Ozbal, and others on the Yener team, the author was able to visit this deposit, enter the mine, study the local geology, and assess the potential of this deposit as a source of Bronze Age tin. No cassiterite was observed anywhere. Although the "mine" was occupied by Bronze Age peoples, it has much more the characteristics of a natural cave. For a summary of the history of the investigations of ancient mining in Turkey see Kaptan (1995).

The latest work on tin deposits in Egypt and the Czech Republic is reported in Rapp et al. (2000; Fig. 7.9). Until recently, many scholars have assumed that the Erzebirge, Czech Republic cassiterite deposits, could not have been exploited prior to the last two millennia. However, see Bouzek et al. (1989) and Taylor (1983). At the time of writing, the actual sources of the tin for eastern Mediterranean and Near Eastern Bronze Age metallurgy are not accurately known. For a brief summary of aspects of this problem, see Muhly (1985). Unlike the Eastern Mediterranean region the sources for tin [as well as copper] for the Bronze Age of China are well known (Chang 1980; Needham 1999). There are 28 copper and 16 tin deposits within a 350 km radius of the great Late Shang capital of Yinxu at Anyang.

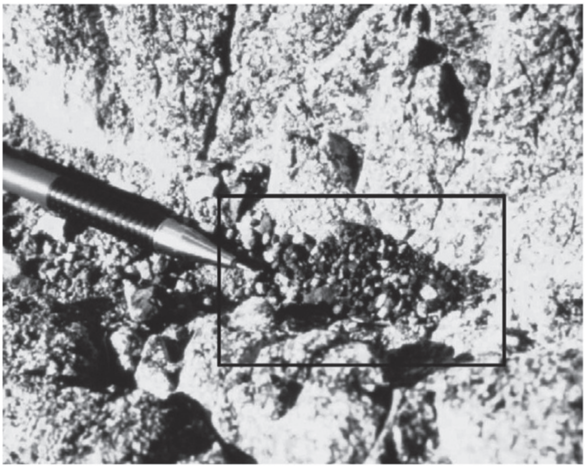

Fig. 7.9 Cassiterite in riffles, Mine Mueilha, Egyptian Eastern Desert

An independent and extensive bronze metallurgy developed in southeast Asia. The southeastern Asian tin belt is an elongate zone about 2800 km long north/south and 400 km wide. It extends from Myanmar (Burma) and Thailand to Malaysia and Indonesia (Fig. 7.10). Abundant cassiterite at or near the surface along with regional copper deposits allowed the early development of bronze metallurgy.

Additional tin deposits to the north in China led to the important evolution of the Shang bronze metallurgy centered in Henan Province in the area of Zhengzhou and Anyang (Fig. 7.11). The Chinese deposits are largely unrelated to the geology of the deposits to the south. For a comprehensive review of the geology of the southeastern Asian tin deposits, see Hutchinson (1988). At the onset of the Chinese Bronze Age in the early second millennium BCE, the metalsmiths were adding about 5% tin to the copper. By the late second millennium, the Shang had developed a highly sophisticated bronze technology centered on the ability

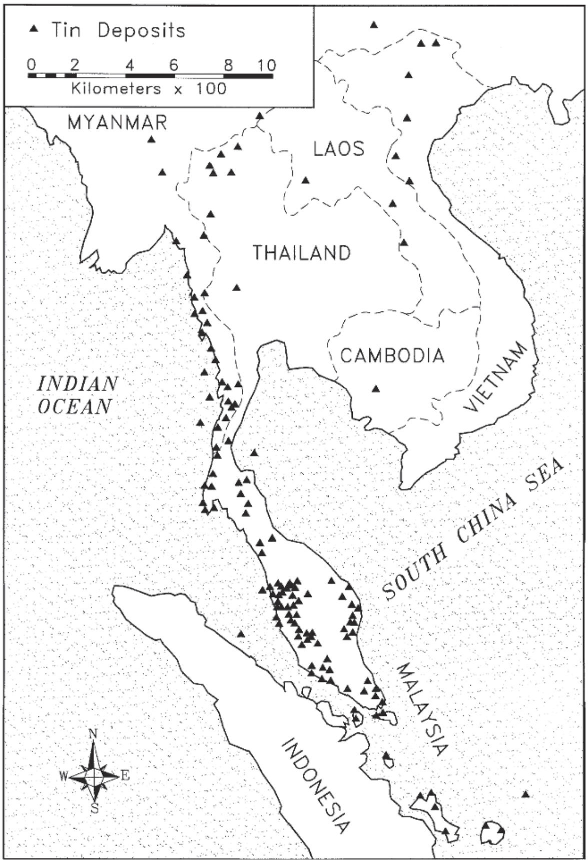

Fig. 7.10 Southeast Asian tin deposits

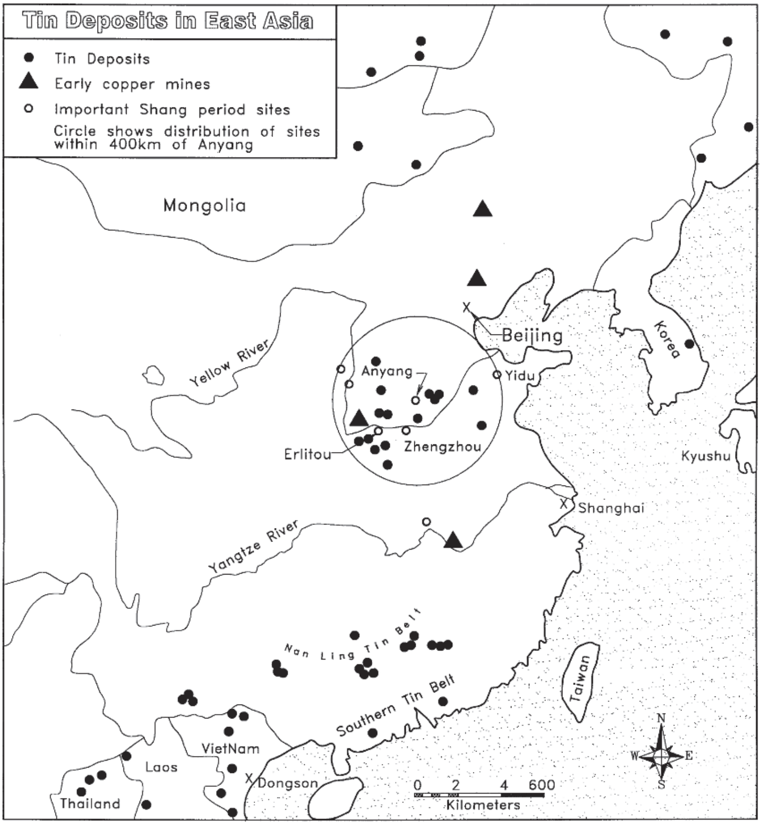

Fig. 7.11 Tin deposits in China and nearby areas

to cast large and intricate vessels. A single bronze vessel from Anyang dating to 1200 BCE weighed 875 kg. This metallurgy was based on a three-component bronze: copper, tin, and lead. Nothing remotely comparable to the Shang bronzes in total quantity is known elsewhere in the ancient world. The Chinese had mastered the separate skills of prospecting, mining, extraction, metallurgy, alloying, and casting.

In the territory of the former Soviet Union, Russian archaeologists believe that tin was first mined on the slopes of the Caucasus Mountains in the second to first centuries BCE. Later, in the fourth to ninth centuries CE, tin was recovered along the western slopes of the Urals (Levine and Bond 1994).

In Japan, with a relatively metal-poor geology, there are minor lode deposits on Honshu (Taylor 1979) and Kyushu (Fig. 7.12). Many of the lodes contain copper. Bronze was introduced into Japan from the Han Dynasty in China (Penhallurick 1986), and much of the early copper and tin undoubtedly came from China.

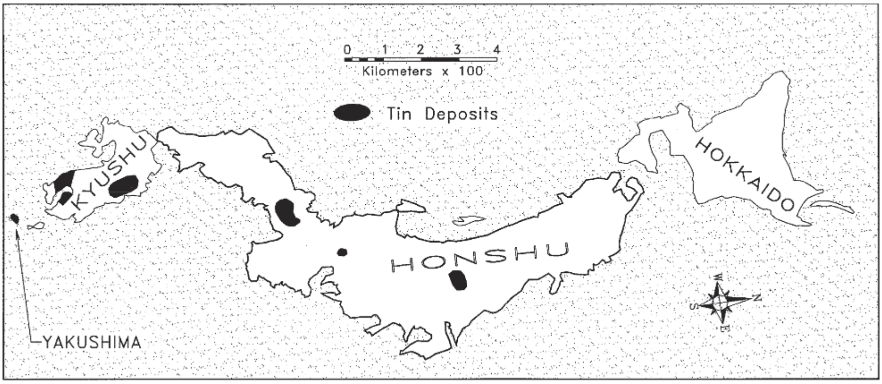

Fig. 7.12 Japanese tin deposits

7.9 Lead (Pb) Minerals

The name lead comes from an Old English word. Native lead metal occurs naturally as rounded masses and plates up to 60 kg but is *very* rare, and it is highly unlikely that native lead was utilized in ancient times. Unlike gold, silver and copper, native lead was not available; therefore, it had to be smelted from its ores, primarily lead sulfide (galena), lead carbonate (cerussite), and lead sulfate (anglesite). Lead becomes molten at 327°C, so it is easily cast. It may have been smelted as early as copper. It is known from the Old World as long ago as the sixth millennium BCE. Early use of metallic lead includes a necklace from the Early Bronze Age of Scotland (Hunter and Davis 1994), which has since weathered to pyromorphite [$Pb_5(PO_4)_3Cl$] and cerussite ($PbCO_3$). Cerussite has been frequently referred to as white lead spar. Note the confusion with white lead in Chap. 9.

At Çatal Höyük, galena beads date back to 6500 BCE (Sperl 1990). Lead has been recovered from a sixth millennium BCE level at Yarim Tepe in Iraq, two fourth millennium sites in Iran, and one in Egypt (Gale and Stos-Gale 1981). Because of its density, lead has been used for anchors at least since the early first millennium BCE. Lead mining at Rio Tinto, Spain, goes back to about 900 BCE, and at Lavrion, Greece, lead mining extends back at least to late prehistoric times. A lead seal was discovered from the Early Bronze Age at the site of Tsoungiza, Greece (Pullen 1994). Lead seals are rare (or rarely preserved), and this is the first one recovered from mainland Greece from this time period. The exploitation of the lead-zinc deposits of Belgium dates back to prehistoric times (Dejonghe 1998). The mineralogy of the deposits is generally galena, sphalerite, and pyrite. Bronze Age tombs near these deposits contained lead tools with high zinc contents.

The Romans used lead for a vast array of items including coffins and urns (Toller 1977), inscribed tablets (Tomlin 1988), pipes, coins, pewter, glass, glaze, and as standard weights. It was used as a preservative and as a sweetener in their wines. This toxic element then accumulated in their bodies and caused severe medical disorders.

Lead has been detected in bones from Roman archaeological sites (Aufderheide et al. 1992). For a comprehensive look at lead and lead poisoning in antiquity, see Nriagu (1983). This book has hundreds of references and a bibliography of ancient authors.

Lead-tin pewter has been used at least since Roman times. The amount of lead in good pewter does not exceed 10%. A dark, soft pewter, known as ley, contains up to 50% lead. If small amounts of copper are added, a hard pewter is formed, while small amounts of antimony lead to a silvery luster. The amount of lead in pewter tended to be related to the purpose of the object. The Chinese began making pewter in the Han Period. As was the case in the Mediterranean region the early Chinese obtained much of their silver from argentiferous galena.

Pliny notes that lead oxides were used as paints. Nriagu (1983) gives an extensive treatment of the use of lead oxides in antiquity. Three lead oxides were used in antiquity: minium (Pb_3O_4) is scarlet red, massicot (PbO) is yellow to reddish-yellow, and litharge (PbO) is red. Litharge (PbO), called red lead, has been widely used since ancient times as a red pigment, even though it is quite toxic (see Chap. 9). Natural litharge forms in the oxidized zone of lead ore deposits. By Roman times red lead was also being manufactured from other lead minerals such as cerussite (lead carbonate). As can be seen from many ancient texts, women in ancient Greece used white lead (lead carbonate) in cosmetics (e.g., in Plato's *Lysis*, Xenophon's *Economics*, Aristophanes' *Ecclesiazusae*). The mineral cerrusite has been frequently referred to as white lead ($PbCO_3$) or white lead spar.

Willies (1984, 1989) reports finding evidence of late first millennium BCE mining for lead and zinc at the Zwar Mines in Rajasthan, India. The weathered zone included oxidized lead ores, anglesite ($PbSO_4$) and smithsonite ($ZnCO_3$), but the principal ores appear to have been sphalerite (ZnS) and galena (PbS).

There are numerous lead/zinc deposits in southwest China and lead/silver deposits in southeast China. Ancient Chinese texts occasionally referred to the mining of lead and silver. It should be noted that Chinese bronzes, beginning in the Late Shang and Early Zhou Dynasties, are ternary Cu/Sn/Pb rather than the binary Cu/Sn bronzes of the eastern Mediterranean and Near East regions. Nriagu (1983) devotes a chapter to detailing the lead resources in antiquity of more than 20 countries. The ancient Chinese used lead oxides as pharmaceuticals (Needham 1974) and to dry oil paints. During Zhou times, lead vessels and vases were cast in the same shapes as the bronzes.

Galena (PbS). Galena (*lead-glance*) has a hardness of 2.5 and density of 7.59. It is a very common metallic sulfide frequently associated with silver minerals. The Romans gave the name galena to this lead-ore mineral. It is easily recognized by its perfect cubic cleavage, high density, and silvery metallic color. It is one of the most widely distributed sulfide ore minerals. Galena was used in antiquity in the Old World as eye paint and as ornaments. In Pharaonic Egypt, galena was mined at Gebel Zeit from approximately 1000–1200 BCE. In a study of two of the mining sites, Castel et al. (1988, 1989) found that at site 1 it was possible to reconstruct the history of the ancient mining, because the mines have not been worked in modern times. At site 2 about 600 old workings were found. The galena was used to make **kohl**.

In North America, where no smelting occurred in antiquity, the brilliant silvery luster of galena nevertheless attracted the indigenous peoples, and it was used extensively in burial practices and for ornaments. Geologic sources of galena are numerous in the region from the southern Appalachians to the western Great Lakes area and from Virginia to northeastern Oklahoma. Galena was used by North American prehistoric peoples for perhaps 8000 years. The large archaeological site at Cahokia, Illinois, located near a major source, was a significant consumer and exporter (Walthall 1981). The earliest use here was during the Early Archaic. Of the 232 sites reported by Walthall (1981), 60% were mortuary sites with galena in a burial association.

Galena has been reported from over 200 prehistoric sites in eastern North America, but is rarely found in sites before Late Archaic. It is found at Late Archaic/Early Woodland Period(s) in the Great Lakes and Mississippi Valley regions. During the Middle Woodland, a large quantity of galena was moved through regional and long-distance exchange systems. Over 60 Mississippian sites, located from Illinois to the southern Appalachians, contained galena. These artifacts often exhibited ground facets. Galena has been recovered from archaeological sites throughout most of North America. It was valued for use in ceremonial objects because of its attractive silvery color and perfect cubic cleavage. The individual pieces varied from 30 g to 100 kg and from 5 to 15 cm in diameter (Walthall et al. 1980). At least one group made a gray paint from finely ground galena.

Galena is available at or near the surface in more than 20 states in the United States and also across Canada. The earliest significant exploitation in North America occurred in the second millennium BCE where small pieces were placed in burials with red ochre. The most extensive use of galena in North America occurred from about 300 BCE to about 400 CE when it was traded over distances greater than 1000 km.

The largest and most accessible deposits were found in the Upper Mississippi Valley (UMV) region near the border of Illinois, Wisconsin, and Iowa. Early exploitation of these deposits is well documented (Agnew 1955). Source assignments using atomic absorption (AA) spectrometry are provided by Walthall (1981) and Walthall et al. (1979, 1980), and lead isotope analyses by Farquhar and Fletcher (1984). These authors found that the galena from Archaic/Woodland sites in northeastern North America had various sources. Galena from five sites probably originated from a single vein near Rossie, New York. One galena source may have been a vein close to the Ottawa River, Ontario, and another in the southern part of the UMV region. Walthall and his associates traced galena to the UMV deposits and elsewhere in the eastern United States. In the United States, lead ore deposits in the Illinois/Kentucky region also contained fluorite (CaF_2) that was carved into figurines by prehistoric people.

7.10 Zinc (Zn) Minerals

The most common zinc ore is sphalerite (ZnS), also called zincblende or just blende. It has a hardness of 3.5–4.0 and a density of 3.9–4.1. Zinc carbonate, smithsonite ($ZnCO_3$), is less common than sphalerite, but it is much easier to smelt than sphalerite and may have been the first zinc mineral to be exploited. Large masses of smithsonite that are bright green, blue-green, and yellow, as well as nearly colorless, are frequently found in the upper oxidized zone of zinc deposits. In Europe the classic deposits are at Lavrion, Greece, and on the island of Sardinia. Zinc ores are found widespread throughout Germany, Austria, Italy, Belgium, France, and Spain. Two major European sources of zinc have been the Harz region and the Legenback quarry at Binnatal, Switzerland. The term zinc may come from the German word *zinken*, which means "nails". Zinc was used to make galvanized nails. The identification of zinc as an element was by Paracelsus in 1526.

Calamine [the German word is Galmei] is the historic name for zinc ore. In the eighteenth century it was discovered that what was thought to be one mineral was actually two: zinc carbonate [Smithsonite] and zinc silicate [hemimorphite]. These two minerals are very similar in appearance. Although still used as a mining term, calamine is no longer used in mineralogy. Calamine (smithsonite) deposits on Thasos, Greece, were exploited for lead and silver from the seventh century BCE. Agricola (1546) reported a white metal that condensed when lead and silver ores from the Harz Mountains were smelted. He called it "contrefey" because it was used to imitate gold. He did not recognize it as zinc. The name zinc was not coined until 1697.

Brass, an alloy of copper and zinc, has been known since classical times. Originally it was called "yellow copper". Although perhaps originally formed accidentally from zinc-containing copper ores, the Greeks learned to add "calamine" (either hemimorphite [$Zn_4Si_2O_7(OH)_2 \cdot H_2O$] or smithsonite [$ZnCO_3$]) along with their regular copper ores to produce yellow copper. There are numerous zinc-copper deposits in the eastern Mediterranean/Near Eastern areas. The Greeks called a "yellow copper ore" *orichalcum* from which they made brass. Vergil mentions *aurichalcum* in the Aeneid. It seems likely that it was the mineral aurichalcite [$(Zn,Cu)_5(CO_3)_2(OH)_6$], which occurs widely as a secondary mineral in oxidized copper-zinc deposits. In antiquity the zinc content of brass was never more than 28%.

The name sphalerite derives from a Greek word meaning "treacherous". The early name for ZnS, blende, also means "deceiving," apparently derived from the difficulty of identifying sphalerite in a host of copper ores. The mineral also has been called zincblende, schalenblende, and blackjack. When rich in iron, it is called marmatite. Sphalerite is found in a variety of colors: yellow, red, green, brown, and black, depending on the concentration of other metal **cations** in the structure. When it occurs as a transparent variety, it has been used as a gem.

The earliest evidence for the production of metallic zinc is from India and Persia. Zinc ore is difficult to smelt because zinc volatilizes at about the same temperature (1000°C) that is needed to smelt the ore. In Europe metallic zinc was not known until the first zinc smelting process in Bristol in the 1740s. India became known for the production of "bidri" ware, an inlaid zinc alloy treasured by the Muslim rulers in Bidar Province in the fourteenth century. The Romans were the first to produce brass on a major scale. The archaeometallurgy of brass is confused by the use of the name that is often used to refer to all copper-based alloys (e.g., in the King James 1611 CE version of the Bible). Brass accounted for approximately one-third of the copper alloys used during the Roman Imperial Period (Craddock 1978). Brass manufacture goes back at least to 400–450 BCE in the Magdalensberg, Austria area (Löhberg 1966).

Molten zinc is quite volatile, and in early smelting furnaces would have been volatilized. Carrying out the zinc ore reduction and copper alloying together in a closed system solved this problem. Theophilus described this process. For the antiquity of brass and the extraction of zinc minerals in India, see Biswas (1996), who reports a copper alloy artifact with 6% zinc from Lothal (2200–1500 BCE). This percentage of zinc could have come from smelting a zinc-bearing copper ore. Zinc ores were mined in the southern part of Rajasthan as early as the thirteenth century BCE.

7.11 Other Ore Minerals and Metals

Mercury/Cinnabar (HgS). The name mercury comes from the Roman god Mercury – named for its fluidity as is its other name: quicksilver. Mercury in the ancient (and modern) world comes primarily from the vermillion-colored cinnabar, which is found sparsely distributed in small veins near volcanic areas. Cinnabar has a hardness of 2.0–2.5 and a density of 2.1. Cinnabar deposits are found throughout the ancient world and have been exploited for centuries in Peru, Mesoamerica, Italy (Tuscany), Austria, Serbia, and Spain (Almaden). The Almaden mine has been producing for more than 2000 years. Mercury was an important metal in ancient China. It forms amalgams with most metals, especially with gold and silver. By the Warring States Period [fifth century BCE to the unification of China by the Qin Dynasty in 221 BCE] mercury/gold amalgams were used commonly for gold plating metal objects. After the amalgam was applied heating would volatilize the mercury leaving a gold gild. The same process was used for silver. Silvering mirrors goes back more than 1500 years in China.

Cinnabar was highly prized by the Maya as a pigment, probably because its color was symbolic of blood and blood sacrifice. Most of the cinnabar they used probably came from the Mayan highlands. Excavation of a Mayan site in Belize dating to the late ninth or early tenth century uncovered an offering vessel containing more than 100 g of hematite, 19 g of cinnabar, and other objects atop a pool of 132 g of mercury (Pendergast 1982). Two possible sources for the Belize mercury are in the Todos los Santos Formation of Guatemala or the Matapan Formation of western Honduras. This suggests that the mercury was acquired locally and not through long-distance trade. Native mercury is rare in geologic deposits, but it is not known whether the Mayans mined liquid mercury or smelted it from cinnabar. Cinnabar was the coloring used on the famous oracle bones of ancient China. Ancient artisans had great difficulty at times differentiating among the various red pigments. Pliny's account of them is quite garbled.

Pyrite (FeS_2). Pyrite has a hardness of 6.0–6.5 and a density of 5.01. The most common and widespread of all sulfide minerals, brass-colored pyrite frequently occurs as crystals and has long been called “fools’ gold”. An iron sulfide, it is easily distinguished from gold by its brittleness and hardness and from chalcopyrite by its paler color and greater hardness. It is ubiquitous in copper deposits and contributes to the formation of the gossan that marks most sulfide deposits.

As far back as the Mesolithic pyrite was used as a convenient and portable source to strike a fire. The name pyrite is derived from the Greek “*pyrites lithos*”, which means “stone which strikes fire”. The names pyrite and marcasite (also FeS_2) were used interchangeably for centuries until the development of crystallography in the early nineteenth century. Early writing on the use of pyrite and marcasite as gem material shows that a good deal of confusion existed for hundreds of years between these two species of iron sulfide. Pliny refers to pyrite as “fire-stone”. Galen and Avicenna likely confused the species. Agricola considered pyrite to be a species between a rock and a mineral.

Pyrite has been found in many archaeological contexts. The Maya used it to make mirrors. A unique piece of pressure-flaked pyrite was found in Alaska. The piece likely was used as an end scraper. When it fractured, a hole was drilled at one end and it was kept as an amulet (Potosky and Potosky 1947). The Aztecs used pyrite as inlays in mosaics and eyes in statues. The Inuit and others used it as a firestone because it gives off sparks when struck. It was also used to make amulets to ensure protection from danger or for good luck. The large copper deposits of Cyprus, exploited since the Late Bronze Age, are largely cupiferous pyrites. By the eleventh century CE, the Chinese were obtaining pure sulfur for gunpowder by roasting pyrite with coal briquettes.

Platinum (Pt). Native platinum has a hardness of 4.0–4.5 and a density of 21.4. The Precolumbian peoples of Ecuador and Colombia may have been the first to make use of relatively rare native platinum, beginning late in the first millennium BCE and continuing until about 800 CE. Native platinum melts at 1772°C, so they developed a sintering process to make platinum-gold alloys. This metallurgy had no parallel in the Old World. The major gold-producing region in Colombia was also the only placer deposit of platinum (Scott 1992). With its high density, platinum, when released from lode deposits, would concentrate in placers. Ogden (1977) has reviewed the occurrence of platinum alloys in Europe, including in ancient times. Occasionally gold placers have been found to contain platinum group elements (platinum, osmium, iridium, and ruthenium) in minerals such as sperrylite ($PtAS_2$) and in natural alloys

7.12 Oxidation of Metallic Ores

Near the earth’s surface, within the zone of weathering, metallic mineral deposits are altered by contact with water that contains free oxygen. Where sulfides are involved, alteration may extend to a considerable depth below the water level. In the upper zone of alteration, metal oxides and native metals are formed. At the lower depths, primary sulfide minerals are altered to secondary sulfide minerals that are

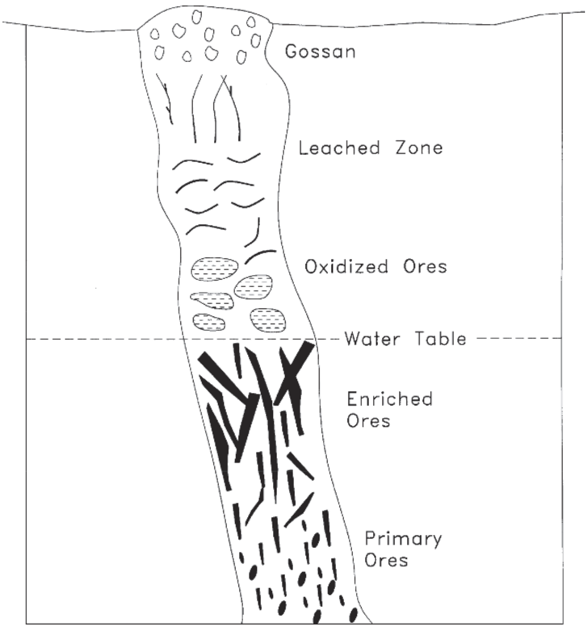

Fig. 7.13 A generalized cross-section illustrating the alteration of primary copper sulfides near the earth's surface

enriched in the metal (see Fig. 7.13). In deposits that contain sulfides but no pyrite, the changes are slow and may be inconspicuous.

Galena (PbS) changes slowly to anglesite ($PbSO_4$) and cerussite ($PbCO_3$); sphalerite (ZnS) is replaced by calamine [$Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$] and smithsonite ($ZnCO_3$); enargite ($Cu_3AsS_4$) may remain unoxidized. The presence of pyrite changes the whole trend of the oxidizing process. Pyrite (FeS_2) rapidly breaks down with the formation of sulfuric acid (H_2SO_4). The acid then attacks the sulfide minerals and forms a gossan at the surface of the deposit. Oxidation is speeded up and is more likely to go to completion. Chalcopyrite ($CuFeS_2$) changes to cuprite (Cu_2O), malachite [$Cu_2(OH)_2CO_3$], azurite [$Cu_3(OH)_2(CO_3)_2$] and native copper.

The cupiferous pyrite deposits of Rio Tinto in southern Spain are located in a region of sub-tropical climate with an annual rainfall of about 75 cm and a mature topography where erosion is minimal. These deposits have a heavy gossan of massive hematite (Fe_2O_3) from 15 to nearly 30 m thick. The depth of alteration is governed by the groundwater level. The lower limit of the gossan is sharp. Below this is a narrow zone of leached pyrite, then a zone of enriched sulfide with the upper zone containing 3–12% copper, primarily chalcocite (Cu_2S). The depth to unaltered ore varies from about 75–450 m.

Shales may also host copper deposits. For a description of the important Zechstein copper-bearing shales of Germany and Poland, see Harańczyk (1986). These deposits in Germany were exploited in the thirteenth century CE and may have been mined as early as the second millennium BCE.

Chapter 8
Ceramic Raw Materials

8.1 Introduction

This chapter is mostly about pottery. Pottery is only one of the large number of products known as ceramics. Other ceramics are covered briefly. Although pottery is composed of predominantly crystalline phases, glass (including glaze) is not. Glasses (including obsidian) are formed from the solidification of molten silicate – solidification that took place too rapidly for minerals to crystallize. Terracottas are thick, coarse, porous wares normally fired well below 900°C. Porcelain is a ternary mixture of clay, quartz, and feldspar. The latter acts as a flux that aids in the development of a glassy phase in the fired product.

Ceramic production has always been an empirical art. This is especially true of pottery making. The lack of any scientific basis in ancient pottery construction within a society led to a slow, trial-and-error process that often lasted for at least decades, if not much longer. Choosing raw materials was one of the most important aspects. The preparation of these materials before firing also had significant effects on the final product. However, at the heart of ceramic production is a pyrotechnology – how the raw materials change during firing.

The raw materials for pottery making can be divided into three categories: (1) clays, the dominant material, (2) temper (additives) used to control physical properties of the ceramic, and (3) minerals to impart a glaze, a color, or other desirable property.

Low-grade clays, those that do not make good pottery without refining or mixing, are available almost everywhere, so the manufacture of building brick and tile did not require much consideration of raw materials. Clays have two important functions in the production of ceramics. First, their plasticity is basic to shaping the material in its green (unfired) state. Second, clays fuse over a temperature range without the body losing its shape. The modern ceramics industry has benefited from a solid scientific foundation, but the production of ancient ceramics discussed in this book was an empirical art, practiced with a limited array of raw materials.

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8.2 Clays

The term clay has three meanings: (1) a rock term describing a natural, earthy, fine-grained material that develops plasticity when mixed with a limited amount of water, (2) a particle-size term for the smallest particles (less than 2 μm), and (3) the name of a group of sheetlike silicate minerals. Some clays have little or no plasticity, e.g., the so-called "flint clay," but, for the purpose of this book, the plasticity criteria will hold.

Clay minerals form as a product of weathering, as a product of **pedogenesis**, and as a deposited sediment. With rare exceptions, such as some kaolinite deposits, natural clay is not a single mineral but rather an aggregate of minerals and colloidal substances. All natural clays contain both non-clay minerals and material larger than clay sizes. The clay minerals are always exceedingly fine-grained, and X-ray diffraction (XRD) analyses are necessary to identify them. Some can be observed only with an electron microscope at magnifications greater than 5000. Clay mineral shapes may be sheetlike, lathlike, fiberlike, or hollow-tube shaped.

Common clays are found everywhere but high-grade clays, those that make good pottery without refining or mixing, are more restricted. China clays (pure kaolin) occur only in Britain, France, the Czech Republic, southern United States, and China.

One of the earliest uses of clay may be the famous "Venus" female figurines dating from about 32,000 BP (Zimmerman and Huxtable 1971). By the late Neolithic, other items made of clay included toys, models, loom weights, spindle whorls, and stamped items used to record economic transactions (Fig. 8.1). Since ancient times

Fig. 8.1 Clay head of a figurine, Iron Age, Tel Michal, Israel

clays have been used for writing tablets, figurines, pottery, crucibles, ornaments, tile, brick, plumbing fixtures, foundation blocks, adobe, and related building materials. In this chapter, the ceramic and related uses of clay are considered.

The primary raw materials for ancient ceramics were local clay-rich sediments and soils for the **paste** and coarse sedimentary particles, comminuted shells or **grog** for the temper. Clay deposits are of two general types: (1) primary deposits formed in situ by the weathering of bedrock such as granite or shale, and (2) secondary deposits formed by river (fluvial) or lake (lacustrine) deposition. These are often referred to as transported clays.

In soils, primary deposits of clay minerals form as part of the natural chemical weathering of the parent bedrock. In soils, clay particles (less than 0.002 mm) are mixed with larger particles and a variety of other chemical precipitates and biogenic material. Pedologists call a soil clay if it contains 35–30% clay. Clay minerals are low-temperature hydrous minerals stable at the earth's surface. Clays are the products of the chemical weathering of silicate rocks containing a significant amount of Al_2O_3. High-alumina minerals, particularly the feldspars, weather directly to clay.

Feldspar is the most abundant mineral in the earth's crust, so sufficient parent material is available nearly everywhere. Feldspars weather to kaolinite or smectite depending on environmental conditions. The residues of the most extreme weathering are quartz and alumina minerals such as gibbsite [$Al(OH)_3$]. For example, on the island of Hawaii, the basalts weather to smectite on the dry, leeward side of the island, and to gibbsite on the wet, windward side. Under intermediate conditions, kaolinite formation is favored. Because the decomposition of silicates is often not total, primary clays contain fragments of the parent material. These minerals are principally quartz, feldspar, and mica. The other major source of clays is through soil-forming processes. Soil clays tend to be impure mixtures of two or three clay minerals plus mica and chlorite as well as quartz silt and sand.

Secondary clays were transported and deposited by fluvial, eolian, lacustrine, glacial, and marine processes. Glacial clays are usually coarse and unsorted, with a high percentage of impurities. Lacustrine clays are often high in organic matter.

Fluvial and eolian clays are most often fairly well sorted and contain fewer impurities. Each of these geologic processes deposit clay of different grain sizes – and, therefore, different plasticities. In Italy, an argillite formation outcropping near Venosa has been used since ancient times as raw material for ceramics, including bricks. This argillite is mostly clayey silt containing calcite, quartz, and dolomite. To produce bricks with increased strength, the argillite was mixed with volcanoclastic material (Summa 1996).

Precise identification of clay minerals requires XRD methods. The clay minerals are not equally stable in all surface environments. This topic cannot be considered here, but see Krauskopf (1967:176–203). Many other sheet silicates are found mixed with these clay minerals in many deposits, but they all promote poor plasticity. The addition of fine-grained organic material and many varieties of plastic and aplastic tempers can improve plasticity, strength, and firing properties.

Clay is a very adaptable material. The earliest use of clay appears to be in the upper Paleolithic when cave dwellers drew designs in wet clay on cave walls. Next came the making of clay figurines, then clay as a building material. By the Neolithic, in many parts of the Old World, artisans discovered that fire hardened clay. Therefore, pottery making was just an extension of clay technology.

Some clays dug straight from the ground are suitable for potting, but others have to be mixed, usually because they are either not plastic enough or too plastic. Fortunately, many geologic and **pedologic** processes form a mixture of clays that prove suitable. The clay or clays needed vary widely by the product desired. Clays needed for low-fired terracotta, medium-fired pithoi or household jars, artistic cups for royalty, and high-fired specialty products like porcelain, all required different raw materials. Trial and error was the only means of determining the usefulness of any clay deposit. Some clays will melt at slightly over 1000°C, while others will stand 1400°C before melting.

Because of their small size and sheet structure, clays become plastic when mixed with a limited amount of water. This allows the mixture to be shaped and to retain the new shape. Whether or not a clayey raw material will make good pottery depends on which clay mineral predominates, the shape and the size distribution of non-clay minerals, the organic content, exchangeable ions present, and the size distribution in the whole mass. Many pottery clays also contain fine-grained quartz, which provides the refractory infrastructure during firing.

The clay minerals have the property of being able to exchange certain cations and anions in an aqueous solution. The commonest exchangeable cations are Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}, and H^{+}. Ion exchange is important because the physical properties of clay materials frequently depend on the exchangeable ions carried by the clay. In general, the plasticity of a clay (or soil) is different depending on whether Na^{+} or Ca^{2+} is the exchangeable cation.

Crude pottery is relatively simple to make. Many clayey soils and sediments can be fired to form simple, thick-walled vessels that can withstand moderate thermal and physical stress. Fired clay objects are known from the Upper Paleolithic of central Europe. The earliest known ceramics from North America are from Florida and date to about 1700 BCE. Through trial and error, early potters learned to select fundamentally different clays, calcareous versus noncalcareous, at the site. For example, Middle Cypriot potters at Alambra not only selected the end members, but used varying compositions to achieve desired results (Barlow and Idziak 1989). The red clay deposits from eastern Crete provide a good example of where the geochemical and mineralogic diversity among distinct deposits allows adequate provenance determination of ancient ceramics (Hein et al. 2004). Martineau et al. (2007) used chemical, petrographic, grain-size, and paleontological analyses to determine the nature and origin of raw materials used by the Neolithic potters of Chalain, Jura, France. Their results allow a reconstruction of the constraints and the reasons for changes and choices in pottery raw materials over time.

The major clay minerals and their important properties for pottery making are as follows:

Kaolinite: $(OH)_8 Al_4 Si_4 O_{10}$. Kaolinite is the most refractory of the clays and has excellent firing properties. It has the best high-temperature stability, it can be heated rapidly, and shrinks very little. It is the clay of fine china. Kaolinite forms equidimensional, flakelike crystals/particles. The particle size and shape – small hexagonal plates – give it good plasticity. It is the only clay that works well alone in pottery manufacture. It is a common and widespread product of the weathering of feldspars in igneous and metamorphic rocks. Kaolinite is formed in warm and wet tropical or subtropical regions where there is good drainage. Most kaolinite is derived from the weathering of feldspars, but it can also be derived from pyroxene and biotite in the weathering of granodiorites. Leaching removes sodium, potassium, calcium, magnesium and iron, leaving only hydrous alumino-silicate or kaolinite. Some kaolinite deposits, like those found in Cornwall, England, are the result of hydrothermal alteration of granite.

Kaolinite can also be found as a secondary clay. Secondary kaolinites usually benefit from sorting during transport and deposition, making these finer-grained and lower in impurities. In ancient sediments, kaolinite occurs in fluvial and near-shore deposits. Kaolinite is not usually found in alkaline or calcareous sediments.

The name kaolin (and related kaolinite) comes from the early Chinese mining area of Dazhou. Kaolin is a "corruption" of the Chinese "*kauling*" meaning "high ridge." For a discussion of the origin of the name and identification of the type locality, see Chen et al. (1997). Whether formed directly as a weathering product of feldspars, or as a sediment, kaolinite tends to be relatively free of iron oxides and as a result it fires to a nearly white color.

Halloysite: $(OH)_8Al_4\,Si_4O_{10}{\cdot}4H_2O$. Halloysite forms elongate and tubular crystals/particles. Although similar to kaolinite in composition, the thin platelets of halloysite curl, which leads to poor workability (e.g., cracking during forming and drying). Halloysite must be heated slowly to prevent fracture during firing. It is a common product of the alteration of feldspars and often occurs with kaolinite. Halloysite can form rapidly from volcanic ash in tropical environments. Halloysite is commonly associated with kaolinite in deposits formed by the weathering of pegmatites. The name halloysite was given to material from pockets in a limestone near Liége, Belgium.

Montmorillonite/Smectite: $(OH)_2(Al,Mg,Na)_2Si_4O_{10}$ [composition variable]. The montmorillonites are the expanding (swelling) clays that can take up large amounts of water between the sheets in their structure. Their ceramic properties include high plasticity, moderate refractoriness, and high shrinkage. Montmorillonites are formed by the weathering of mafic igneous rocks high in magnesium, iron, and calcium, such as basalts and volcanic ash. They form in reducing environments with low rainfall and relatively poor drainage. Smectites are finer-grained than kaolinites and therefore usually very plastic. They also form as soil clays.

The name montmorillonite is used currently both as a group name for clay minerals with an expanding structure and as a specific mineral name. Calcium montmorillonite is known as *fuller's earth.* This material has been used since prehistoric times in the washing of woolen cloth, because it has some detergent properties. In Roman times, pieces of cloth were trampled in a vat of fuller's earth (*creta fullonia*). Several rinses with clean water served to carry away dirt and grease from the wool (Robertson 1986).

Illite: $(OH)K_4\,Al_4(Si,Al)_8O_{20}$ [composition variable]. Illite has good plasticity, variable shrinkage, and low refractoriness. It is good for slips. Illites are the dominant clay minerals in shales and mudstones. They also form commonly in soils from the alteration of micas and other clay minerals and from colloidal silica. Illite is the only clay mineral containing appreciable amounts of potassium. In soil-forming processes, illite apparently can form from montmorillonite by exchanging all the exchangeable cations with potassium.

Illite forms small, poorly defined flakes, commonly grouped together in irregular aggregates. This type of clay has a luster that makes it sought after for pottery slips (e.g., Greek black figure ware). Illites are characteristic of offshore marine deposits. They are common in calcareous sediments. Grim et al. (1937) proposed the term illite as a general term, not as a specific clay-mineral name, for the mica-like clay minerals. The name was derived from an abbreviation for the state of Illinois.

The dominant clay mineral in most shales is illite, but montmorillonite is common in shales of Mesozoic or younger age. Kaolinite is common in some shales. Kulbicki (1954) concluded that diagenetic changes in the sediments of the Aquitaine Basin in France produced kaolinite and halloysite from nuclei of other clay minerals, and that montmorillonite formed from halloysite or formed together with halloysite from kaolinite. Therefore, we can see that most clay deposits are mixtures.

Soils developed under cool and damp climatic conditions with forest or grass cover provide an abundant surface accumulation of organic material. Kaolinite predominates in these soils, and illite is frequently present. In the soils of arid regions, montmorillonite and illite predominate. Illite is the dominant clay mineral in sediments accumulating in Lake Erie in North America (Cuthbert 1944). Sarmiento and Kirby (1962) reported kaolinite, illite, montmorillonite, and chlorite in the sediments of Lake Maracaibo in South America.

8.3 Pottery

Along with lithics, pottery fragments are the most widespread traces of human occupation. Most ceramic studies concentrate on the reconstruction of descriptive technologies in order to establish temporal sequences and cultural boundaries.

The first pottery dates back 8500 years and probably was a traded product well before 6000 BCE (Mellaart 1964). The development of European and Near Eastern pottery is a major story that cannot be repeated here. In North America, pottery developed much later, coincident with the transition to farming and settlements. The earliest ceramics probably come from the southeastern United States about 2000 BCE. In South America, pottery may have developed somewhat earlier, about 2500 BCE (Meggers and Evans 1966). By the late first millennium CE, Mayan potters had developed exceptional skill.

The Chinese, always inventive artisans with bronze and jade, were also excellent ceramists from the Neolithic onward. Nearly all of the eastern (populated) areas of China have almost unequaled resources of suitable raw materials for pottery production. The Chinese have long excelled in both low-fired earthenware and high-fired stoneware and porcelain. Neolithic earthenware from east central China is a gray or reddish-brown sandy pottery, a finegrained, very hard dark gray ware, or a unique fine-grained black pottery made into thin-walled vessels. During the Shang and Zhou Dynasties, the Chinese developed high-fired stonewares, began using kaolinite, and developed glazing. During the Zhou Dynasty, they made a high-fired and glazed product with kaolinitic clay that produced a finish that resembled jade. Lead glazes were introduced during the Han Dynasty; perhaps traders from the Middle East brought the use of lead to China. However, the Chinese were the first to make high-lead bronzes, so they may have introduced lead glazes independently because they were familiar with lead minerals.

The color of ceramic vessels depends on two variables. One is the content of iron, manganese, and organic matter in the raw clay. The other is the temperature and the atmosphere (oxidizing or reducing) of the firing.

Mineralogical and chemical characterization of ancient pottery is now commonplace (Blackman 1981; Noll 1981). Such studies can give direct evidence of temper materials and indirect evidence of the clay paste used. Blackman (1981) presents a quantitative picture of the influence of the temper on the chemical composition of a hypothetical parent clay body.

Although the three major clay groups (kaolinite, illite, and montmorillonite) have distinctly different chemical compositions, most ancient pottery was made from a mixture of these clay groups as well as other minerals present in the clay deposit exploited. Fred Matson (see Matson 1965) taught the author in the field in southwestern Greece how wide a variety of local soil and sedimentary clays can be made useful for household pottery. After analyzing a variety of ancient Egyptian painted ceramics for 8 years, Noll (1981) notes, "the ceramic material itself… is rather uniform." Noll found that two clay sources were used in ancient (and modern) Egyptian pottery. Lime-rich pottery utilized the marly clay of the Qena area that contained quartz, feldspar, hematite, and diopside. Lime-poor pottery made of Nile mud contained quartz, feldspars, mica, and hematite.

To understand the local raw material base for pottery making, one needs to know the local surficial geology and pedology. If sedimentary rocks are also potential sources, then knowing the bedrock geology is also essential. Although X-ray diffraction and chemical analyses are useful in ceramic studies, thin-section analysis utilizing a polarizing microscope is the best single method for determining the raw materials, especially tempers, and the technology of ceramic production. Books focusing on results of ceramic petrography include Freestone et al. (1982), Jones (1986), and Middleton and Freestone (1991).

8.4 Tempers

To reduce shrinkage of the final product and/or improve workability of the raw material, temper is added to the clayey material. By definition, temper is something the potter added to the clay to modify its properties. A wide variety of raw materials have been used as temper: quartz sand, shells, calcite, mica, crushed rock (limestone, sandstone, basalt), volcanic ash, organics (ranging from straw to dung), and grog (ground sherds). Coarse sediments for temper are normally available in nearby streams. Fossil shells make good temper because calcium carbonate has the same thermal expansion properties as the average pottery clay. The same is true for marble and limestone (also calcium carbonate). Figure 8.2 is a thin section of pottery showing the larger grains of temper against the fine-grained background of clay paste. The temper is predominantly quartz with one grain of feldspar in the upper right. Steatite-tempered pottery is known from the Neolithic of Yugoslavia (Kaiser 1989).

When determining whether temper has been added to a given clay, a problem arises for the archaeologist, because many natural clays contain quartz sand, shells, volcanic ash, and rock fragments. Four properties are used to suggest whether coarse material in pottery is naturally occurring or purposely added. These are identity, particle shape, size range, and ratio of coarse material to clay paste.

Volcanic by-products have been used as temper by many cultures. The Maya used volcanic ash for several centuries as temper in their utilitarian pottery in the limestone lowlands, well away from the volcanic highlands (Simmons and Brem 1979; Ford and Rose 1995). Volcanic sands have been used for temper in the pottery of the South Pacific since prehistoric time. Pottery from the island of Tonga has been a major provenance problem. The scarcity of volcanic sand on most of the inhabited islands in the Tongan group has prompted suggestions that either temper was imported from a volcanic island to the west or that the finished pottery was imported from Fiji. Although the mineralogy of the tempers is compatible with that of Tongan volcanic rocks, Tonga lacks deposits of the rounded and well-sorted sands found in the tempers. Recent discovery of beach placer sands derived from reworking of **tephra** deposits provides a satisfactory source. Using petrographic techniques, compositional analyses of temper sands in numerous ancient sherds

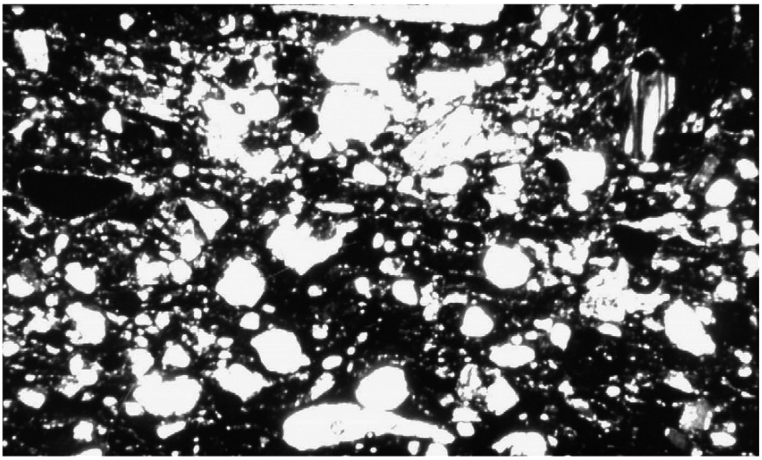

Fig. 8.2 Thin section of pottery from Big Rice Lake site, Minnesota, USA

from throughout the island group indicate that pottery making using local raw materials was once a widespread industry (Dye and Dickinson 1996).

One of the most thorough and inclusive case studies of the provenance of ceramic raw materials focused on the Bronze Age of the island of Cyprus. This study originated in efforts to reconstruct prehistoric production and exchange systems. The resulting monograph assesses the various analytical techniques used in sourcing Cypriot pottery and clays (Knapp and Cherry 1994). In this assessment the authors point out that sourcing pottery raw materials has proven exceedingly difficult.

An interesting example of temper comes from a Late Archaic to Early Woodland (4500–3000 BP) culture in the state of South Carolina. In addition to pottery that was sand-tempered, some pottery was fiber-tempered, visible as a secondary porosity. This fiber material was identified as Spanish moss (*Tillandsia usneoides*) (Smith and Trinkley 2006). Petrographic methods can readily identify tempers and frequently can determine their geographic/geologic source or sources. In the state of North Dakota, the grit temper of granodioritic composition was available from local glacial tills (Josephs 2005).

Although geographically limited in scope, the most wide-ranging and thorough look at the archaeomineralogy of tempers is provided by Dickinson (2006) who examined 2223 prehistoric sherds in thin section from sites across the southwest Pacific Ocean. These tempers included calcareous as well as terrigenous sands. Only the latter can be assigned a source from a specific island or island group. Petrographically the temper sands fell into three groups: (1) light mineral grains including quartz and feldspar; (2) heavy iron-magnesium minerals and opaque iron oxides; and (3) polycrystalline lithic fragments. In 106 cases temper had been imported; two-thirds of these involved distances of less than 200 km, and most of the others involved distances of 200–600 km. A few cases were recorded where temper analysis indicated imports from 1000 km or more. This volume includes 30 instructive thin-section photomicrographs in color.

8.5 Glazes

Glazes are vitreous (glassy) coatings melted on the surfaces of pottery to make them watertight. They may also be used to impart color and decoration to the pottery surface. All glazes by definition contain silica, and most have compositional ranges similar to other types of glass (see Sect. 8.7 on glass). Early glazes were derived from silica sands and glass frits (such as those found on glazed faience beads dating from the fourth millennium BCE in Egypt). From Egypt, Anatolia, and the Persian Gulf colored glazes were produced from the fifth millennium. These glazes all seem to have contained some antimony.

Glazes must contain a flux agent in order to lower the melting temperature of the silica. Without a flux agent, the melting temperature of the glaze would also melt and deform the ceramic body to which the glaze is applied. The range of effective firing temperatures is different for each type of flux agent. There are both "high" and "low" temperature range fluxes. The differentiation between these temperature ranges has a direct influence on color (high temperatures "burn off" certain colors) and compatibility with the ceramic body. Different clay mixtures will absorb the glaze at different rates, largely depending on how open or fine the texture of the vessel after the first firing. High-fired glazes usually contain feldspars, calcite, dolomite or wood ash. Low-fired glazes are usually alkaline in composition, containing sodium or potassium.

A number of compounds can be used as flux agents including lead, tin, sodium and potassium. These compounds have been derived from numerous mineralogical sources throughout history. The simplest and earliest fluxes were probably derived from wood ash adhered to the surface of ceramics fired in open pits. If fired at a sufficiently elevated temperature, the wood ash causes the surface of the clay to vitrify, thereby resulting in a glazed surface. Sodium and lead are the most common elements used as flux agents. Soluble salts (NaCl), saline water or natron can be the source of sodium fluxes for "salt" glazes. Salt glazing was known from the earliest times. This was one of the easiest ways to make a glaze flux. Other common fluxes are Na_2O and PbO, although K_2O and CaO are also used. Boron and lithium also can serve to make low temperature glazes.

The total reflectance spectrum and luminosity of a glaze provide a useful measure of its opacity and ability to conceal the underlying body color. Vendrell et al. (2000) showed that tin glazes contain SnO_2 particles with a diameter similar to the wavelength of visible light. These particles are responsible for the glaze opacification.

Lead fluxes (which were highly favored for their bright colors) have only recently fallen out of favor since they can cause lead toxicity if used for drinking or eating ware. In China before the first millennium BCE, lead was a common fluxing agent in glaze on pottery. The Assyrians used both lead and tin. Knowledge of lead glazes used in Dynastic Egypt and Mesopotamia was transmitted by the Romans to Italy, France, Germany, and England.

Glazes may also contain metal oxides as colorants, and various alumina (Al_2O_3) compounds, which help stabilize the glaze and bind it to the surface of the ceramic. The colors of glazes result from the presence of the transition elements iron, manganese, chromium, vanadium, cobalt, and copper. Iron is ubiquitous as hematite or limonite. Black manganese oxides are fairly abundant in small quantities at the earth's surface. Copper is also fairly widely distributed as oxide and hydroxycarbonate minerals. It is harder to determine the sources for vanadium, chromium, and cobalt, although the common vanadium minerals are highly colored and would attract artisans. By the fourteenth century CE, cobalt arsenide was the initial raw material for cobalt blue in the Near East and China. Coming initially from Persia it is likely the arsenide was roasted to provide cobalt oxide. Sodium was the low temperature fluxing agent in Egyptian alkaline glazes that provided a rich blue-green glaze when copper was the colorant. With a sodium glaze manganese gives a reddish purple color. If potassium replaces the sodium, the manganese imparts a bluish-purple color.

Ninth to tenth century CE Abbasid pottery from Iraq used traditional Mesopotamian alkali-lime glazes on calcareous clay earthenware. Some of these blue and white glazes used a mixture of cobalt pigment and lead oxide to produce the color (Wood et al. 2008). Cobalt alums from the western oases of Egypt were used in the second millennium BCE as a colorant to produce dark blue glazes (Shortland et al. 2006).

In their investigation of glazed steatite from ancient Egypt during the fourth to first millennium BCE, Tite and Bimson (1989) found two different glazes. The first was characterized by high copper and magnesium oxide and a high density of recrystallized forsterite (high Mg olivine). The second was characterized by lower copper and magnesium oxide and a low density of recrystallized forsterite. Laboratory replication of these glazes confirmed that the differences were the result of very different glazing methods rather than differences in the composition of the raw materials.

From the sixth to fourth centuries BCE, attic black "glaze" was produced by a fine suspension of an illitic clay applied to the surface. When the vase was fired in an oxidizing-reducing-oxidizing cycle, a thin black layer of polycrystalline black magnetite or wüstite (FeO) formed from iron oxide in the raw material (Maniatis et al. 1993). This technique does not meet the strict technical definition of "glaze," although it is frequently referred to as such. It would be more correct to refer to the decorative surface as a clay stain or "slip" design.

The use of lead oxide glazes was common at Byzantium, especially during the eighth and ninth centuries CE. The use of a white, tin-based glaze on red-bodied vessels was developed in Sicily about 1200 CE. During the thirteenth century, Spanish potters began to use a white tin-based glaze. To achieve a variety of lusters the potters of Andalusia used silver, sulfur, and ochre. During the Han Dynasty, stoneware vessels with feldspathic glazes (containing feldspar clays) were widespread. During the Song Dynasty, the Chinese introduced a stoneware glaze with a high iron content that broke into orange around the edges and rims. Ming Dynasty (1368–1644 CE) ceramists developed a thin copper oxide wash that turned bright red when fired in a reducing atmosphere.

8.6 Porcelain

Porcelain is quite different from ordinary pottery. It is made from pure kaolin mixed with a high feldspar-weathering product (called petuntze) and vitrified at about 1280°C. The feldspar provides both the alkali flux and additional silica for translucency. In its fired state porcelain is vitrified and translucent. Because of the very high temperature of firing, only three coloring oxides can be used with porcelain: iron oxide, copper oxide, and cobalt oxide.

Production of true porcelain began in southern China during the Eastern Han Period (25–221 CE) and began in northern China several hundred years later. The southern porcelain produced during various periods always had a lower Al_2O_3 content (<20%) than northern porcelain (>25%) due to raw material selection. The southern porcelain was made of petuntze, which is abundant in most southern

Chinese provinces (Guo 1987). In north China, a different, high-alumina, raw material was used in the development of porcelain. The basic constituents were kaolin with admixed quartz, mica, and carbonates. Both raw materials transformed into the dense porcelain at between 1200 and 1300°C.

Rich deposits of what is termed porcelain stone were discovered in the southern provinces of China in late Shang times. Chinese porcelain stone is a rock composed mainly of quartz and sericite (fine-grained hydromica). Porcelain stone sometimes also contained small amounts of feldspar and/or kaolinite. Throughout the long development of Chinese porcelain, the potters experimented with a variety of raw materials to achieve special effects. Without any knowledge of the chemical elements, potters learned which manganese and iron oxides would color porcelain glazes and that high phosphate raw materials encouraged bubbles in the glaze (see Scott and Kerr 1993).

Protoporcelain was produced as early as the Shang Dynasty (seventeenth to eleventh centuries BCE) in China. The earliest protoporcelain has a lead-free glaze and a fairly vitrified body, suggesting the use of high firing techniques. Protoporcelain requires suitable raw material as well as a high firing temperature. A recent paper by Chen et al. (1999) explores the potential of chemical composition in characterizing protoporcelain sources. Their results suggest a centralized source of production of protoporcelain during the Shang Dynasty, perhaps at Wucheng. No dramatic change occurred in making proto-porcelain during the following Zhou Dynasty (eleventh century to 221 BCE) (Medley 1976). Europeans did not develop a true form of porcelain until early in the eighteenth century (Kingery 1986b).

8.7 Glass

Glasses are solid, noncrystalline silicate bodies. The rapid solidification of a silicate melt forms glass. To understand the raw material requirements for glass, it is necessary to review the chemicals needed to make glass. Considering only ancient glass, the most important constituent is silica (SiO_2). Pure silica will make a glass, but only at exceedingly high temperatures. One of the most efficient and easily obtainable additives to reduce the temperature of fusion is Na_2O. A second compound that serves well as a flux is lead oxide (PbO). Potassium oxide (K_2O) and calcium oxide (CaO) also serve to reduce temperatures of fusion. Ancient glass found on archaeological sites may appear varicolored, because the inclusion of manganese imparts a lavender hue after long exposure to the sun. Over very long periods, glasses may crystallize, because they are unstable compared with an assemblage of crystalline minerals of the same total composition. This process is called devitrification. A good introduction to glass and other vitreous materials, especially colorants, is given by Biek and Bayley (1979). The compositions of ancient Egyptian, Roman, European, and Syrian glass are presented and discussed by Freestone (1991). Analysis of window glass found at Pompeii indicates it was composed of 69% silica, 17% soda, 7% lime, 3% alumina, and 1% iron oxide with traces of copper and manganese (Lindsay 1970:215). A broad exposition of the materials and technology of glass and glazing in ancient Mesopotamia is given in Moorey (1985). Silica sands and quartzite pebbles were used as starting materials in early glasses in Egypt (Shortland and Eremin 2006) with the soda coming from natron or plant ash. White glasses were colored by small particles of a calcium antimonate opacifier.

The initial use of glass was as small objects such as beads, seals, amulets, and glazes. Products with the structure of glass, including glazes, frits, and faience, go far back into history, certainly more than 10,000 years. Once pyrotechnology developed, manufacture of glass spread rapidly. The earliest pure glass, from Egypt, dates to about 7000 BCE. Shortland and Tite (2000) analyzed 19 blue glasses from Amarna, Egypt, dated to around 1350 BCE. The results indicate two distinct types of glass: one is cobalt-colored with a natron-based alkali made from local raw materials; the coloring agent in the other is copper with a plant ash alkali, following the Mesopotamian tradition. The latter glass may have been an import. The raw materials for Egyptian glass were a mineral soda and a lime-bearing siliceous sand, which combined to produce a silica-lime-soda glass (Freestone 2006). Such silica-lime-soda glasses also were produced in Late Bronze Age Mesopotamia. The soda flux tended to be some form of sodium carbonate or, in semi-arid environments, the ash from the plants *Salicornia* or *Salsola* (also known as salwort). Lead glasses came into use in the Medieval Period.

The beginning of glass making in China goes back at least to the Western Zhou Dynasty (eleventh to eighth centuries BCE) with beads found in a tomb. These greenish beads are likely to have been made by melting a mixture of a high-quartz clay and possibly some copper mineral or slag. The beads contain quartz grains surrounded by an alkali-silica glass (Brill and Martin 1991:157–158).

Determination of the raw materials used in making glass can be approached indirectly by analyzing the major oxide components of the glass. The basic ingredients are silica with added simple sodium, potassium, and calcium ionic minerals. These raw materials are available essentially everywhere. In addition to these basic constituents, most ancient glasses contain some Al_2O_3, Fe_2O_3, TiO_2 and MgO, plus a small amount of colorant. High-fired ceramic materials such as porcelain and Chinese celadon are most likely to contain higher percentages of Al_2O_3 than most glasses. Brill and Martin (1991) published dozens of analyses that indicate clearly that many early Chinese glasses were made from a mixture of lead-bearing and silica minerals. Some were soda-silica glass, and others were potash-silica glass. Some had a major amount of lime as a constituent. A related publication of analytical data on ancient glass is the projected three-volume *Chemical Analyses of Early Glasses* (Brill 1999). Volumes. 1 (*The Catalog*) and 2 (*The Tables*).

Glass came into its own about 2000 years ago in the hands of Roman artisans. Building on the technical traditions of the late first millennium BCE Greeks, the Romans established an empire-wide glass industry. Glass manufacture was a major industry of the Romans. After the fall of Rome, the Byzantines, Arabs, and the Venetians continued to manufacture glass. The Latin word for glass (*vitrum*) enters the language in the late first century BCE (Grose 1983, 1986). The rapid expansion in glass production was based on changes in manufacturing technology, not changes in raw materials.

The Romans were the first to truly master the control of color in glass using colorizers and decolorizers. Colorless glass was popular in the last first and second centuries CE. Pliny (NH XXXVI) mentions colorless glass mimicking rock crystal as closely as possible. Most Roman glasses were blue-green due to the iron content. To make a colorless glass, the Romans had to select the raw materials very carefully and/or add a decolorizer. Roman glasses were made from silica sand and natron ($Na_2CO_3 \cdot 10H_2O$) or trona ($Na_3H(CO_3)_2 \cdot 2H_2O$). If a decolorizer was required, antimony and manganese could be added to oxidize the iron. Tin-based opacifiers (lead stannate yellow and tin oxide white) were used in glass-making in Europe from the second century BCE. Tin-opacified glazes were introduced into the Islamic world in the ninth century CE (Tite et al. 2008).

In Roman Palestine glass was manufactured in two stages. The raw materials were first melted together, resulting in the production of large blocks. These were then broken into smaller chunks and shipped to factories where vessels were produced. The great glass slab found at Beth Shearim is an example of an unsuccessful first melting (Weinberg 1988:25). In a program of chemical analyses of the samples from the glass factory at Jalame in Palestine, Brill (1988) reports that the glass has a soda-lime-silica composition with only minor potassium and magnesium oxides. Brill suggests that this is evidence that natron was used as the alkali.

About 1680, on the slopes of the Riesengebirge in Germany, glass was decisively improved by the addition of chalk. The chalk glass was not only clearer than the compositions used previously, but the refraction was also changed, making the glass more sparkling and allowing thicker glass to retain its transparency.

Glass can be colored by adding small amounts of particular elements or compounds to the glass melt. These additives can enter the glass structure as ions, or they can be dispersed in the glass as small metallic particles. In both cases the metals develop an electronic structure in the glass that absorbs light of distinct wavelengths; sometimes causing striking colors (see Chap. 3). The best-known case of glass colored by dispersed metallic particles is that of gold ruby glass, known since the seventeenth century. The golden color of this glass results from finely divided gold particles. Silver particles in glass color it yellow. The red color of copper ruby glass may be due to copper or copper oxide. Some of the ions that have long been added to color glass are:

Ion	Color of glass
$Mn3^+$	Purple/violet
$Mn2^+$	Brown
$Fe3^+$	Green/brown
$Co2^+$	Blue
$Cu2^+$	Blue
$Cr3^+$	Green

The colorants in some seventh century Roman silica-soda-lime glasses were determined by Mirti et al. (2000). Iron determined the color of blue-green, green, and yellow-green transparent glasses. Copper was the main colorant in red, pale blue, and blue-green opaque fragments. Elemental copper acted as an **opacifier** in red glass. Calcium antimonate played this role in white, pale blue, and blue-green glasses.

Tektites are natural glasses formed when comets or asteroids hit the earth, melting part of the crust. An example of a worked tektite is given by Povenmire (1975).

8.8 Faience

Initially, the term "faience" meant a glazed ceramic originally made at Faenza, Italy. Later, the term became loosely applied to a variety of "glaze" "quartz frit" and "paste" based on quartz ceramics (rather than clay ceramics). The earliest faience from Egypt and the Near East dates back at least 6000 years. Its essential components were quartz or quartz sand with lime, potash, soda, and usually a copper colorant. When fired to 800–1000°C, the products were shiny, vitreous beads coated with a vitreous blue or green glaze. Noting the fact that copper is an essential ingredient in blue Egyptian faience, glazes, and frits, combined with the fact that ancient Egyptian dynastic artisans used tubular copper drills to excavate holes in stone, Stocks (1997) suggests that waste powder containing copper may have led to the use of copper colorant.

By the third millennium BCE, the Pharaonic Egyptians were forming faience and glazed tiles in molds. See Vandiver and Kingery (1986) for the development of Egyptian faience. Vandiver and Kingery call attention to the related developments of faience and glazed steatite. In the Late Bronze Age of the Near East, new colorants were applied to faience glazes. Chromite was used as a gray pigment that also served as a nucleating agent for spherulite crystallization of augite that gave the faience a uniquely sparkly appearance (Groot et al. 2006).

The Egyptian craftspeople learned to modify compositions to produce a particular color or hardness in their glazes and faience. Egypt had enough quartz sand for silica, limestone for lime, and soda niter for soda for raw materials. They had only to seek potash. What they accomplished was the development of the first artificial stone – to compete with hard-to-acquire lapis lazuli or turquoise. The latter was available in the southern Eastern Desert of Egypt, but the former had to be imported from Afghanistan. According to Hodges, faience appeared in Mesopotamia about 4000 BCE, long before it appeared in Egypt. Faience is found at sites in the lower Nile Valley and northern Iran dated to 3000 BCE, and in the Indus Valley dated to 2000 BCE. Near Eastern faience reached Europe via trade routes by 1500 BCE (Hodges 1970:65). By the time of the Zhou Dynasty in China, faience beads with cores of quartz or glass were being produced (Liu 2005).

The glaze on ancient faience can develop spontaneously if added alkali salts migrate to the surface and crystallize as the faience dries. If this material is fired, the salts will fuse and dissolve some of the underlying quartz, producing a glaze.

8.9 Fired-Brick, Tile, and Terracotta

Brick is a type of ceramic. During firing, the exterior of the brick tends to vitrify, while the interior remains soft and porous. The firing process may be described as follows: “Sandy clays, or mixtures of clay and quartz sand are required for the manufacture of bricks. During firing, water and carbon dioxide are driven off and aluminum silicate (mullite) and more quartz are formed. Sodium or potassium in the clay causes some melting. As the molten clay cools, glass is formed. With high temperatures there is an increase in the formation of glassy material lending greater hardness, density and durability. Primitive firing conditions produce an inconsistency which at best lends attractive and subtle variations in color and texture, and at worst results in highly distorted or soft underburnt material which will not weather well. Firing temperatures vary according to conditions and fuels, but a range of between 800°C and 1200°C is usual” (Ashurst and Ashurst 1988, p. 47).

In its earliest stages of development, fired-brick was probably very similar, if not identical, in composition to the sun-baked variety. The purposeful firing of these materials would have required developed pyrotechnology and the availability of fuel. Fired-brick technology eventually evolved apart from its earlier sun-dried ancestor. This may have been a response to increased efficiency of pyrotechnology and higher, more-controlled firing temperatures. Ironically, as temperature increases, so do problems with warping and shrinkage. Thus, mineralogical materials that may be acceptable for sun-dried mud-brick may not be appropriate for a high-fired ceramic. Vitruvius described examples of brick wall construction in Greece and Italy. Bricks were used for both public and private structures.

The earliest bricks were probably fired in a “clamp” rather than a draught kiln. “The principle was to construct a floor of fired bricks and a level site, with an arrangement of channels running across its length and breadth. These channels or flues were filled with fuel (wood, charcoal, furze and later coal).... The green bricks, with more fuel stacked between them, were built up on the floor of the clamp and spaced to allow the fire to penetrate beneath them. Finally, a thick layer of burnt bricks and clay matrix was spread over the stack and the clamp was fired. A clamp of this kind might burn for several weeks” (Ashurst and Ashurst 1988, p. 47).

The resulting bricks would have been crudely and unevenly fired. “The bricks produced are not uniformly burnt and whilst a large proportion is satisfactory, those on the outside are underburnt, and those near the fire-holes and in the heart of the kiln may be misshapen and cracked owing to the excessive heat” (Ashurst and Ashurst 1988:47). The clamp firing method was eventually surpassed by draught kilns that could achieve more controlled temperatures. Roman kilns were able to achieve a firing temperature of about 1000°C (Ashurst and Ashurst 1988, p. 48).

A variety of factors, including chemical composition, firing temperature, atmospheric conditions, and sand rolling, affect the color of brick. These factors work in combination to produce the final appearance and physical properties of the brick. For example, bricks containing iron oxides turn red in an oxidizing atmosphere at 900–1000°C. “Above this temperature, the colour may change to plum or purple or to brown or grey at 1200°C" (Ashurst and Ashurst 1988, pp. 48–49). It is also common for the color of the interior and exterior of the ceramic body to vary within a single brick unit. For example, "in a reducing atmosphere, in which the supply of oxygen is restricted or cut off, purple or blue bricks often with black cores are produced". (Ashurst and Ashurst 1988) Mineralogical compounds can affect color as follows:

Lime (high percentage) with iron traces: White
Lime (low percentage) with iron traces: Grey
Chalk (low percentage) with iron traces: Cream
Iron oxide (up to 2%): Buff
Iron oxide at 900°C in a reducing atmosphere: Brown
Iron oxide at 900°C in an oxidizing atmosphere: Bright salmon
Iron oxide at 1100°C in a reducing atmosphere: Red
Iron oxide (7–10%): Blue
Iron oxide (7%–10%) + manganese oxides: Black

In addition, the presence of vegetal matter will also produce black coloration, sealing carbon in a black core, especially when there is a sudden increase in temperature (Ashurst and Ashurst 1988). Using this type of information, the archaeologist may be able to infer information regarding the sources of clay materials used in the manufacture of brick and advances in pyrotechnology. Po River alluvial deposits, a clay and a subordinate sand, provided the raw material for bricks for Medieval Period buildings in Ferrara, northeast Italy. Brick makers preferred high CaO clays to promote vitrification. Analyses of brick composition showed excess sodium, so it is likely that sodium was added as a flux. The firing temperature appeared to be 800–1000°C (Bianchini et al. 2006).

Just as with pottery and decorative ceramics, the surface color of brick may be modified using colored glazes. Glazes may be achieved by adding "finely ground metallic oxides to sand sprinkled on the brick before burning, for example, manganese – brown, … cobalt and manganese – black, antimony – yellow, copper – green, cobalt – blue" (Ashurst and Ashurst 1988, p. 49). In regions where fuel was scarce, fired-brick was reserved for constructions where the unprotected material would be exposed to more severe atmospheric conditions (Lloyd in Singer et al. 1954, p. 465).

The manufacture of terracotta architectural units is closely related to brick and pottery manufacture. Terracotta is Italian for "baked earth". Terracotta had its origins in Greece in the seventh century BCE, but the golden age of terracotta was in Italy and Germany during the Renaissance. A wide variety of common clays were used to make terracotta. The iron content of most clays is sufficient to give terracotta a reddish, orangish, or brownish color. Without applying a glaze, terracotta is not waterproof. By the time of the Zhou Dynasty in China, faience beads with cores of quartz or glass were being produced (Liu 2005). Perhaps the most famous use of terracotta is the terracotta army buried with the Qin emperor in 210–209 BCE.

The ancient Greeks and Romans manufactured decorative wall reliefs, friezes, roof tiles, cornices, and gutters from coarse, fired clays (Singer et al. 1954/1956). The ancient Romans used terracotta pipes for plumbing systems and terracotta tiles for hypocausts (Singer et al. 1954/1956). The colors painted on a polychrome Etruscan terracotta slab representing a warrior were determined spectroscopically by Bordignon et al. (2007) to be from red ochre, azurite, yellow ochre, burnt umber, and carbon black. The authors suggest that the white pigment was a kaolin.

Eventually, the decorative effects of terracotta tiles and structural qualities of masonry units were combined by artisans. The result was the creation of architectural masonry units that mimicked the appearance of carved stone. The creation of these intricate architectural units required precise anticipation of clay shrinkage and a tightly controlled firing process. A few early examples of this have survived, including terracotta window tracery at Sutton Palace in England, dating from the sixteenth century (Ashurst and Ashurst 1988, p. 68).

Tiles may be affixed by any number of methods, but the most common technique is to embed the tile slab in a thin layer or “screed” of mortar. Tiles were frequently manufactured with ribbed or textured backs to create a bond with the mortar. Color was imparted to tiles with glazes and slips.

8.10 Refractory Ceramics

Prehistoric iron smelting placed enormous stress on the refractory material used to contain the iron smelt as well as the smelting tuyeres. Childs (1989) conducted a series of experiments on clay used for refractories at an Early Iron Age African iron-making site. She reports that modern sources were usually sandy clays collected from upper banks along the edges of swamps or on ridges above the swamps. Such (tropical) soils are in relatively early stages of breakdown. Another source of furnace materials was termite mounds. Childs determined that most of the source clays were effective up to 1500°C in an oxidizing atmosphere. A montmorillonite clay had poorer refractory properties. The addition of broken sherd fragments increased the refractoriness and structural stability of the briquettes tested.

Chapter 9
Pigments and Colorants

9.1 The Nature of Pigments and Colorants

When discussing almost any archaeological artifact, color is an important characteristic. Unfortunately, there is often confusion between what constitutes a colorant and what constitutes a pigment. These terms are often used interchangeably, but they have different meanings. Colorants are compounds that impart color to a substance. A colorant may be a pigment, a dye, or an ionized solution. Mineral colorants have definite chemical compositions, recognizable physical characteristics (see Chap. 2), and consistent chemical behavior. Organic colorants contain carbon with hydrogen, oxygen, nitrogen, and sulfur with other minor elements. They are derived from vegetable sources or made synthetically. Although a few organic colorants are stable and basically permanent, in general they tend to be fugitive. The key concept in determining a pigment versus a colorant is its solubility. Only insoluble materials such as minerals are pigments.

The term "pigment" comes from the Latin *pigmentum* meaning "drug". A pigment is a finely divided, insoluble material that is suspended in a medium and acts as a coloring agent (Matero 1993). The adequate dispersion of the pigment throughout the medium is important for achieving an intense and uniform color. Natural resins, glues, animal tallow, blood, casein, eggs, urine, oils, wax, and human saliva have all been used as a medium for pigments. Generally speaking, pigments are mechanically mixed with the medium and maintain their physical properties in the suspension. Pigments can be either organic or inorganic, naturally occurring or artificial.

Pigments must be distinguished from dyes. Dyes are soluble complex organics and cannot be used on their own to impart color to paints (Gettens and Stout 1966). For example, white or colorless particles (such as clay) can be dyed with organic matter (such as Indigo). The resulting substance is traditionally referred to as a **lake**. The pigment is the particle rather than the dye itself. The dye, however, is a colorant.

In pigments, color is based on the wavelengths absorbed as well as the size, shape, and texture of the grains. The degree of hydration in the pigment can influence color. Preparation of the pigment is also a factor in determining the final color of the preparation. For example, overgrinding may produce a less intense color.

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This can easily be seen in comparing finely ground **smalt** to coarse smalt. The coarse smalt is darker and has a much denser color than the fine smalt. Conversely, grinding may be inadequate to disperse the pigment evenly throughout the medium. This results in a weaker color. Before modern manufacturing methods, pigments were ground by hand with stone, mortar and pestle, or slab and muller.

Hiding power (also known as opacity) is the property of a pigment to obscure the surface it is covering (Gettens and Stout 1966). This characteristic is related to the opacity of the particle and its ability to absorb or reflect light. In white pigments, the measure of hiding power is the particle's ability to reflect all wavelengths of light. The hiding power of a mineral pigment is directly proportional to the refractive index of its grains; the higher the refractive index, the greater the hiding power. The difference between the refractive index and the surrounding medium of the pigment further influences this characteristic of the pigment and the medium.

An important characteristic of pigments is permanence. Permanence (also known as light-fastness) is the ability of a pigment to resist fading due to photochemical deterioration. Pigments with poor light-fastness are said to be "fugitive". Photochemical deterioration can produce by-products that remain on the surface. These can sometimes be identified through analytical methods (Corbeil and Helwig 1995). However, most mineral pigments are permanent.

Chemical stability refers to a pigment's level of reactivity to moisture, light, air, acidity, and alkalinity. There are very few pigments that are completely inert, and by-products of chemical reactions may be present in archaeological contexts (Gettens and Stout 1966). For example, white lead turns black when exposed to atmospheric acidity. An understanding of the chemical stability of mineral pigments and the possible types of reactivity to which they are susceptible is important when interpreting the archaeological record.

Pigments often have names that correspond to a precise chemical composition; therefore, it is important to avoid using epithets indiscriminately because they may be confused with a specific compound. For example, "lemon yellow" should be used only to describe barium chromate. This pigment is not likely to be found in an archaeological context since it was not synthesized until the late eighteenth century (Feller 1986).

A word of caution is merited regarding the use of traditional terminology. Historical references to pigments use traditional nomenclature. The traditional classifications of pigments are somewhat unscientific and are often based on the ancient geographical source of the material or on the processing method used, rather than on the geology or mineralogy. Correlating historical references with archaeological materials may shed light on geologic sources and materials. However, there are overlaps in the use of traditional terms. These terms are often confused, misapplied, or include more than one group of mineralogical and chemical compounds. In archaeomineralogy, pigments should be defined by specific chemical and mineralogical composition. Munsell produces a number of color charts designed for matching pigments and colorants.

Other types of colorants of interest in archaeomineralogy include those used in the manufacture of glass and ceramic glazes. There were three ways color was imparted to vitreous materials in antiquity. The first method was by the addition of relatively small amounts of the oxides of transition metals such as cobalt, copper, iron, nickel, and manganese that became part of the silicate network. Secondly, colloidal dispersions of insoluble particles were developed, such as those in gold ruby glasses (see Chap. 8). The third method introduced opalizing agents for translucent and opal effects (Newton and Davison 1989).

9.2 Historical Background

Pigments. Before artistic expression developed, early hominids must have simply picked up lumps of colored minerals out of curiosity. The use of these materials as pigments implicitly requires the ability to understand abstraction and symbolism and thus to create art. Thus, the first use of pigments may be inextricably intertwined with the question of when hominids became cognizant (Wreschner 1985).

Archaeological evidence suggests that the earliest pigments used by humans were ochres, clays, and charcoals from burned wood and bone. The range of colors included reds, browns, yellows, and blacks. These are the pigments found in the very earliest cave paintings. The famous cave paintings at Altamira, Spain, and Lascaux, France, were made 15,000 years ago using mineral pigments and charcoal. Earth pigments were being used at least 300,000 years ago (Upper Paleolithic), and L.S.B. Leakey stated that he found lumps of ochre at Olduvai in a context dating from more than 500,000 years ago (Wreschner 1985). Probably the first mineral pigment used was red ochre, in places as far apart as Africa, Europe, Australia, and Japan.

Pigments must have become important as exchange items almost from the beginning, as exclusive access to mineral deposits could have contributed to a group's economy. As humans organized into extended social units, minerals and the knowledge required to utilize them became part of a complex web of trade or exchange.

In many cultures, the use of pigments was important not only for decorative purposes, but also for ritual and medicinal uses. The attribution of magical and therapeutic properties to pigments may have originated in the associated symbolism of certain colors. The use of pigments in cosmetics was not simply a matter of vanity. Numerous ancient texts explained the ability of various mineralogical compounds to empower individuals against adversaries, ward off sickness, and cure disease. It is not surprising that, even today, cosmetics are sold in drug stores.

The artist's palette expanded as civilizations formed in the Fertile Crescent, Nile Valley, and ancient China. Colored stones including lapis lazuli, vermilion, and copper minerals such as azurite were utilized in bright wall paintings. Advances in pyrotechnology provided new ways to manufacture and alter pigments. Processing techniques became more sophisticated as artists learned to create artificial pigments such as Egyptian Blue.

Although some knowledge regarding pigment use in Egypt comes from ancient textual sources, this information is sketchy. Most of what is known regarding early pigment use is based on archaeological evidence. Early wall paintings at

Hierakonpolis show the use of yellow, red, green, white, and black. In Meidum and other Old Kingdom **mastabas**, this palette is completed with brown (hematite mixed with soot), gray (gypsum mixed with soot), and two blues (azurite and blue frit). During the 12th Dynasty, new green, red, and black colors are introduced, but only one blue (Egyptian blue) is now used. From the 18th Dynasty onward, yellow orpiment is introduced as well as more ochres and frits. A pink gypsum stained with madder is an acquisition of Roman Egypt (Forbes III 1965). A new white pigment on fifth and fourth century BCE Greek pottery has been shown to be alumina (Al_2O_3), probably the result of thermal decomposition of bauxite (Pérez and Esteve-Tébar 2004).

The application technique can be very important in how a pigment behaves. Certain techniques enhance the color of the pigment. Specifically, pigment grains reflect less light when surrounded with a "vehicle", and the color becomes more "saturated". "Paint reflects in proportion to the difference between refractive indices of the pigment and the surrounding medium. The higher the refractive index of the pigment and the lower that of the vehicle, the greater the light reflection, and with white pigments, the greater is the resulting whiteness and hiding power. There is also a close relationship between refractive index and color" (Laurie 1967). In other words, there is a direct relationship between the technique of application and the resulting optical effects. Therefore, the development of new and improved application techniques constitutes an important aspect in the history of pigment use. The ancient Egyptians used a **tempera** technique in which the pigment lay directly on top of the wall surface (Lucas 1989). The adequate hiding power of a pigment was crucial for the success of this technique.

The Greeks made a significant advance when they developed new techniques for creating fresco paintings (Forbes III 1965). In fresco painting, the paint is applied directly to wet lime plaster. As the plaster dries, the color chroma intensifies. This is because a significant amount of shrinkage takes place in the surface, causing the pigments to be drawn closer together over a smaller surface area. The reason that the Egyptians did not develop this technique may be because they used gypsum plaster, which does not exhibit a significant amount of shrinkage during the drying process. An early example of the Greek use of the fresco technique can be found at the Palace of Knossos, Crete. One of the pigments found at this site is Egyptian Blue, which was probably procured through trade. The Greeks also employed a technique known as "*fresco secco*", which entailed mixing the pigments with lime and water and applying the color to a dry ground (Laurie 1967).

Paints also could be applied to marble, limestone, wood, ivory, or metal. Wood panels and ships were painted using pigmented waxes known as "encaustic" paints (Pliny *N.H.* 35.3; 35.39; 35.61). Evidence suggests that the use of color on ancient Greek structures, statues, and stelae was a common practice. The Parthenon was reportedly painted with a polychrome scheme. This practice was apparently also known to the Romans, but, unfortunately, little archaeological evidence remains.

Documentation for pigment manufacture during the Roman Period has survived through the writings of Vitruvius and Pliny. Although Vitruvius sometimes confused pigment names and techniques, his writings and those of Pliny have generally agreed with archaeological evidence. The vivid frescoes and wall paintings at Pompeii contain pigments that Vitruvius described (Forbes III 1965). The frescoes at Pompeii have their roots in Etruscan wall painting, a technique in which paints were applied directly onto stone, or onto a thin layer of sand and lime. In the late Etruscan Period, this practice became more sophisticated and a true fresco technique evolved.

Béarat (1996) used a wide variety of analytical techniques to identify the pigments in Roman wall painting of the first to third centuries CE. The identified pigments were: ash, calcite, carbon black, celadonite, cinnabar, Egyptian Blue, **glauconite**, goethite, hematite, and red lead. Pigment mixtures were used to obtain colors such as brown, pink, and purple. Despite great turmoil, the traditions of pigment preparation survived the fall of the Roman Empire, and there were important advances in the manufacture and use of pigments before the Renaissance. Many of the ancient texts and recipes were preserved in medieval monasteries. The monks also pursued the study of alchemy, so the manufacture of pigments became associated with both alchemy and art (Fleming 1984).

By the eighth century CE, Arab civilization was in its golden age. Arab scientists were making significant advances in chemistry, which had an impact on the manufacture of pigments (Fleming 1984). Their many achievements included synthesizing cinnabar. Some researchers believe they were the first to do this. However, the Chinese have also been credited with this achievement, and it is interesting to note that the Arabs had well-established trade routes with China via the Silk Road. The technique for synthesizing cinnabar may have been brought to the west via Spain by the Moors (Gettens and Stout 1966).

Another major innovation was the European development of oils as a pigment vehicle. Oils enhanced the optical qualities and improved the chemical stability and permanence of certain pigments. Although oils were available in antiquity, these compounds apparently were not used as a vehicle for pigments. The drying properties of oils were described briefly by Galen in the second century CE. However, the connection between drying oils and pigments was not described extensively by Aetius until the sixth century CE. Gradually, artists began to understand which pigments were most compatible with oils, the required ratio of oil to pigment, and what other compounds could accelerate the film-forming oxidation process. The precise date of the perfection of this technique is not known. However, it is certain that oil paints were gaining popularity by the twelfth century, as the fine arts became an acceptable pursuit for the layman. By the fifteenth century, oil had become the vehicle of choice in fine art pigments.

Significant advances in the creation of new artificial pigments followed, but these are generally of little interest in archaeomineralogy. Many of these new pigments were lakes made with artificial dyes. Before the advent of modern chemistry, the production and manufacture of European pigments had been the domain of apothecaries. However, during the Renaissance, scientists became interested in formulating new compounds, some of which proved to be of use as pigments. Unfortunately, many of these did not have the permanence or stability of their ancient antecedents.

The nature of modern pigments is beyond the scope of this book. However, the reader may want to become familiar with these if faced with the task of establishing authenticity (Fleming et al. 1971). The presence of certain modern pigments in an archaeological object could expose fraud. There are a number of excellent sources on this topic including *Painting Materials* by Gettens and Stout (1966) and *The Particle Atlas* by McCrone and Delly (Vol. 2, 1973). A table of pigments used in antiquity is given in the Appendix A.

Colorants. The early use of colorants may have been accidental. Before methods for glazing were known, ceramics were painted with earth pigments. The presence of a fluxing agent in the paint or the accidental scattering of wood ash across the ceramic surface during firing could have unintentionally caused a reaction with the ceramic body, resulting in a vitrified and more durable colored finish. However, until pyrotechnology had advanced sufficiently to control kiln temperatures, the usefulness of this new technology would have been limited. If the flames touched the object, color could be burned off or blackened, thereby marring the aesthetic appeal of the ceramic surface. Eventually, advances in pyrotechnology allowed the production of decorative colored objects including glazed ceramics and glass. The understanding of oxidizing and reducing atmospheres in the kiln became especially important for imparting color.

Although the precise origin of glass made by humans is not known, by 3000 BCE glass objects were being produced in the eastern Mediterranean (Newton and Davison 1989). Early coloring agents may have been the result of natural contaminants found in quartz sand. The most common contaminant would have been iron. However, it was quickly discovered that the purposeful addition of naturally occurring compounds could impart various colors to glass. The earliest contexts in which manufactured glass have been found are Egyptian. Glass beads and small containers were sometimes colored blue or red in imitation of semi-precious stones (Newton and Davison 1989). These same colorants were found to produce similar results in enamels and glazes used on ceramics.

The increase in the range of available colorants may have been contemporaneous with the use of these same compounds in paint pigments. However, this is not known for certain. As previously mentioned, smalt may have been used by the ancient Egyptians in glass production, even though it was not known to have been used as a pigment until its rediscovery by fifteenth century Europeans.

The ancient Egyptians are known to have used cobalt (blue or violet), iron oxides (yellow), copper (red and bluish-green), and manganese (blue) as colorants in their glass and ceramic glazes. They also used antimony as an opacifier to produce “white” or opaque glass. The Romans used copper (red and blue) and cobalt (blue). They also discovered that ferrous iron, which produced yellows and ambers under oxidizing conditions, would produce blue in a reducing atmosphere. Iron oxides could also be used to produce a black glass, although an excess of any coloring agent may produce a similar effect (Newton and Davison 1989).

Soulier et al. (1996) report from their studies of the origin of cobalt blue pigments in French glass from the Bronze Age to the eighteenth century CE that the raw materials for four distinct chemical groups seem to have come from: group one – the mining district of Freiberg, Germany; group two – the mining district of Schneeberg, Germany; group three – no determination was possible from analytical data; group four – of those with Roman glass composition, some must have used (reused) ancient cobalt blue mosaic tesserae to color the glass.

The Chinese were among the most advanced in early pottery production. Glazes first appeared in China during the Shang dynasty (1300–1028 BCE) (Medley 1976). During the Zhou dynasty (1155–255 BCE), craftsmen used feldspar glazes to mimic the appearance of jade. The Han dynasty (206 BCE–220 CE) introduced lead glazes. During the Tang Dynasty, lead was used to enhance colorants to produce various shades of green, amber, and yellow. The use of an oxidizing atmosphere in the kiln produced the famous gray-green celadon glazes (Medley 1976).

The Medieval Period was a time of enormous advances in the use of glass colorants, making possible the creation of the elaborate stained glass that was used to adorn European cathedrals. Copper was still used for red, but it was discovered that manganese could be used for a pale rose-red or pink. Craftsmen also learned to use modifiers to alter the color. Manganese oxide yielded a purple-brown color, while manganese carbonate produced violet. The addition of iron to the manganese produced black. The firing temperature had to be controlled carefully, since glass colors fade above 1200°C (Newton and Davison 1989).

9.3 Iron Oxide Compounds

Iron oxides are the most universally employed pigments. They occur naturally in some form in nearly every region of the earth. Iron oxide pigments range in color from dull yellow to reds, purples, and browns. The **hue** depends primarily on the level of hydration in the mineral. Hue is also influenced by particle size, shape, and combination with other mineral compounds. The anhydrous varieties, such as Fe_2O_3, lean toward the purplish-red and maroon hues. Hydrated iron oxides, such as $Fe_2O_3{\cdot}nH_2O$, lean toward the warm reds and yellows. The color can be modified by heating the pigment and driving off water (Pomies and Menu 1999). Iron oxides are extremely stable compounds that are resistant to alkalis, acids (weak to moderate), and to bright light.

Table 9.1 summarizes traditional names for iron oxide compounds. Ancient references to iron oxide pigments are particularly problematic, and, as previously stated, it is best to avoid traditional terminology except when discussing historical texts. There has been considerable confusion in the archaeological literature regarding terms such as “ochre”, which has often been misused by archaeologists to refer to any type of red deposit. Furthermore, scientists have not been able to agree on the scientific delineation of traditional epithets used to describe iron oxides. For example, the difference between ochre and umber is a source of contention between some scholars (see Constantinou and Govett 1972; Robertson 1976).

A complete history of the use of iron oxide pigments would fill an entire book. Nevertheless, a brief synopsis of the historic use of iron oxides and their associated

Table 9.1 Compounds of iron oxides

Chemical composition	Source	Range of hues	Ancient name[a]	Geological name	Traditional trade names
Fe_2O_3, anhydrous iron oxide, silica and clay	Natural earth	Warm reds	Haematitis (L) Rubrica (L) Sinopis (G)	Hematite	Red ochre Iron oxide red Indian red
FeO(OH), hydrous iron oxide, silica and clay	Natural mixture	Warm yellows	Sil (L) Ochra (G)	Goethite, quartz, and clay	Yellow ochre Raw sienna
FeO(OH), partially hydrated iron oxide	Natural oxide partially hydrated	Reds		Goethite	Venetian red
FeO, anhydrous iron oxide	Calcined yellow ochre	Light warm reds		Goethite	Light red
FeO, anhydrous iron oxide	Calcined goethite	Reddish-browns			Burnt sienna
$Fe_2O_3+MnO_2+H_2O$ with silica and alumina	Brown earth	Browns			Raw umber
$Fe_2O_3+MnO_2$ with silica and alumina	Calcined brown earth	Warm reddish browns			Burnt umber
$FeO(OH)+H_2O$, hydrous iron oxide		Warm browns		Limonite	Brown ochre

[a] L, Latin; G, Greek.

cultural contexts will serve as an introduction to their use as pigments. The earliest use of iron oxides as pigments in Europe has been definitively documented to at least 13,000 BCE (Benbow 1989). Iron oxides are found in early cave paintings, including those at Lascaux Cave in France (Leroi-Gourham 1982). In North America, red iron oxides have been associated with Paleoindian cultural complexes (Tankersley et al. 1995). However, evidence suggests that these compounds were used even earlier. Indications of the mortuary use of iron oxides in Australia extend back 30,000 years (Peterson and Lampert 1985). These are only a few of the many examples of iron oxides associated with early prehistoric archaeological contexts.

Analyses of samples from Paleolithic cave paintings in the Pyrenees show that hematite was used for reds, and manganese oxide (with or without charcoal) was used for black. Potassium feldspar, sometimes with biotite, was used as an extender (Clottes 1993). All the paint included pigment for color and an organic binder for cohesion and fluidity.

The prehistoric use of red iron oxides in a ritual context is implied by their frequent association with funerary practices. This has led some scholars to suggest that red hues may have been especially important as symbols of life (Noll 1979). However, others have argued that there is no evidence for the assignment of a universal prehistoric meaning to the color red (Marshack 1981).

Red iron oxide has been associated with a number of indigenous North American cultures. In the Upper Great Lakes Region of Wisconsin, Michigan, Illinois, Iowa, Indiana, and Ohio, a Late Archaic and Early Woodland archaeological complex has become known as the "Red Ochre" culture. The most salient surviving feature of this culture is the powdered red iron oxide scattered over the interred bodies of the deceased (Ritzenthaler and Quimby 1962). This practice has also been correlated with the presence of specific types of artifacts, establishing the association between powdered ochre in funerary practices and a specific cultural complex (Faulkner 1962).

The Ancient Assyrians and Babylonians left textual evidence regarding the symbolism of iron oxide. Hematite in amulet form was regarded as a source of power over one's adversaries (Thompson 1925). It is probable that this association was also transferred to the use of the mineral as a powdered pigment. Ancient Assyrian texts prescribe the application of black iron oxides to the eyes, temples, throat, and other passages. The use of black iron oxide is also noted on bronze weaponry (Thompson 1925). The ancient Egyptians used iron oxide pigments in cosmetics (Lucas 1989) and paint. Iron oxides were also colorants in ancient Egyptian glass. Quartz sands containing iron compounds were used to produce various shades of green, yellow, and black glass (Lucas 1989).

The Egyptians' primary source of red and yellow pigments was iron oxides (Uda et al. 1993). Small amounts of arsenic compounds were added to iron oxides, apparently to improve the quality of the pigment (Goresy et al. 1986). This practice may reflect the availability and cost of these compounds. According to Lucas, red ochre was available near Aswan and in the western desert (Forbes III 1965). Yellow ochre occurs naturally in sandstones, shales, and in gossans of sulfide deposits. Conversely, arsenic pigments were most certainly imported from elsewhere (Goresy et al. 1986).

Evidence confirms that iron oxide pigments were used by many societies to decorate ceramics as early as the Neolithic Period. Later, the ancient Greeks advanced this art to a new level. Clay slips containing iron oxide compounds were used to produce the famous "black figure" ceramic ware. The technique, which was perfected by 500 BCE, involved highly advanced skills in pyrotechnology. Iron oxide slip normally fires to dark red in a kiln with an oxidizing atmosphere. The Greeks learned to produce a reducing atmosphere by limiting the amount of oxygen entering the kiln and by firing the kiln with green wood to yield carbon monoxide. Under these conditions, the painted and unpainted areas of the ceramic turn black. Oxygen was again briefly permitted to enter the kiln chamber at the end of the firing cycle, thus causing the unpainted areas to return to a red color (Flight 1989).

The Greek scholar Theophrastus (ca. 372–287 BCE) categorized pigments as being either earth, sand, or powder. He considered "ochre" and "ruddle" (sintered ochre) to be earth (*De Lapidibus* 8.53). Although Theophrastus probably grouped chemically and mineralogically different compounds together, "earth" pigments certainly included iron oxides. According to Theophrastus, the Hellenistic Greeks obtained ochre from Cappadocia (central Turkey), but the best ochre came from the island of Keos. Ochre was frequently associated with gold, silver, copper, and iron mines (*De Lapidibus* 8.51ff).

Another ancient Greek writer, Dioscorides (ca. 40–90 CE), recommended Egypt as the best source for red ochre (Lucas 1989). The shift from Cappadocian to Egyptian sources may reflect a change in trade routes and commercial influence. Perhaps this was the result of the growing political influence exerted by the city of Alexandria.

Pliny (23–79 CE) rated the red ochres of Egypt and Africa as "the most useful for builders" since "they are most thoroughly absorbed by plaster" (Pliny, *N.H.* 35.15). He noted the association of "red ochre" with iron mines. He also described methods of altering red ochre by burning "in new earthen pots with lids stopped with clay. The more completely it is calcined in the furnaces the better its quality" (*N.H.* 35.16). An example of the use of red ochre in northern Jordan during the Byzantine Period is shown in Fig. 9.1.

Despite the detailed information offered by Pliny, it is obvious that he often confused iron and lead pigments. He identified the compound called "ceruse" as being "manufactured from lead and vinegar". Pliny further stated that this compound could be made by "calcinating yellow ochre which is as hard as marble and quenching it with vinegar" (*N.H.* 35.19–20). This example again emphasizes that the ancients identified pigments based on subjective characteristics, including color. "Ochre" or "ceruse" could consist of a number of similarly colored, yet chemically different, mineralogical compounds. Note that the modern use of the word ceruse is for the compound $(PbCO_3)_2 \cdot Pb(OH)_2$, which is used chiefly in paints and putty. The name of the mineral cerussite, $PbCO_3$, is derived from the ancient Greek word for lead carbonate, which became *cerussa* in Latin.

According to the Roman architect Vitruvius (ca. first century CE), yellow ochre could be found in many places throughout Italy. However, the previously favored

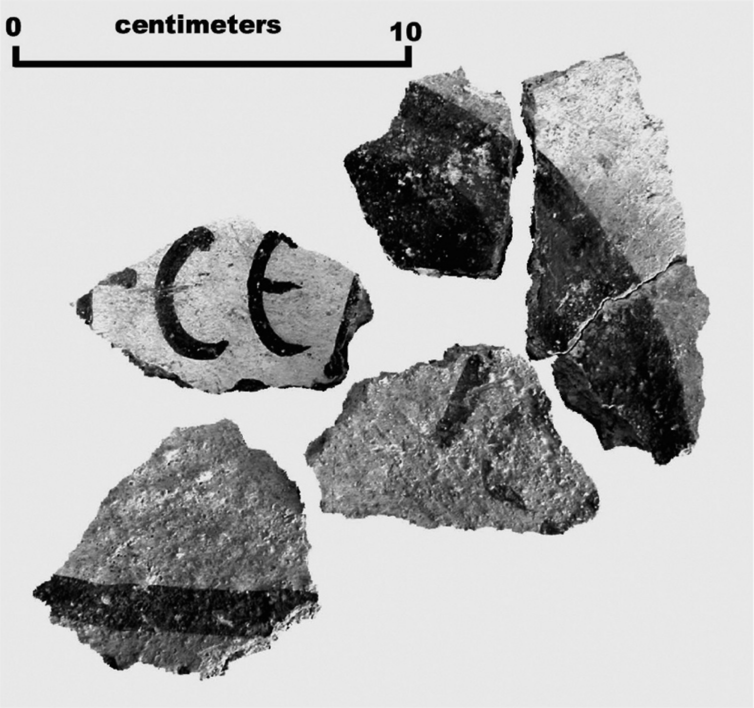

Fig. 9.1 Fragments of painted wall plaster from Umm el-Jimal, Jordan, Byzantine Period

source, the Attic silver mines, was exhausted by the time he wrote his architectural treatise. Vitruvius identified the best "red earths" as coming from Egypt and Spain (*De Architectura* 7).

Medieval treatises focused less on the sources of iron oxide and more on recipes and methods of preparation. Despite the discovery of other red mineral pigments and dyes, the use of iron oxide pigments and colorants continued through the Medieval Period into the Renaissance and modern times. For a discussion of 300,000 years of the use of ochre as a pigment, see Schmandt-Besserat (1980).

In some gem-quality New Zealand jades the development of the attractive flecking is due to agglomerations of colloidally dispersed magnetite or chromite. Darker samples were, as could be expected, higher in total iron (Wilkins et al. 2003). The challenge for the archaeomineralogist is successful identification and characterization of iron oxide pigment and colorants, particularly where they have survived only in trace amounts. Evidence of iron oxide pigments on many prehistoric artifacts has been obliterated by weathering, careless handling, or even cleaning (Faulkner 1962). It is therefore vital to handle objects sparingly and to plan decisions regarding artifact processing and analysis before excavation and recovery.

9.4 Manganese Compounds

The use of manganese oxide pigments extends back into prehistory. They are found in early cave paintings, including those at Lascaux Cave in France (Leroi-Gourhan 1982). Manganese oxides are a significant component in the group of pigments known as umbers (see Table 9.1). Manganese oxide occurs in mineral form as pyrolusite and its **dimorph**, ramsdellite (MnO_2). Pyrolusite has been identified on ancient Egyptian tomb paintings (Lucas 1989). The ancient Egyptians also used manganese oxide for eye paint. Manganese oxides have been used in pottery decoration since prehistory. Eventually, their application was extended to glazes and glass. The purple-black glass of ancient Egypt owed its color to manganese (Lucas 1989).

9.5 Copper Compounds

General. A number of different copper compounds were used as colorants in red glass. Copper oxides were used by the ancient Egyptians in a reducing furnace atmosphere as early as the 18th Dynasty. Pliny described a Roman manufactured glass called "*haematinum*" presumably named for its color rather than the copper used in its coloration. The use of copper compounds for red glass production continued throughout the Medieval Period. It was not until the sixteenth century that gold colloids were used for red glass production (Newton and Davison 1989).

An as-yet unidentified blue copper compound has been discovered on the 2000-year-old human remains found in a peat bog in Cheshire, England. There is speculation that this pigment may be the "*vitrum*" referred to by Pliny. Pliny reported that the ancient Britons painted themselves blue before going into battle, presumably to make themselves look wild, thereby frightening the enemy (Bahn 1991).

Verdigris. Verdigris, $Cu(C_2H_3O_2)_2 \cdot 2Cu(OH)_2$, is an artificial green copper pigment. It is a green corrosion coating on copper or bronze, forming a copper carbonate when exposed to air or a copper chloride in seawater. The name originated in the Middle Ages and means "green of Greece". Pliny gives the following description of its manufacture: "… it is scraped off the stone from which copper is smelted, or by drilling holes in white copper and hanging it up in casks over strong vinegar which is stopped with a lid;… Some people put the actual vessels, made of white copper, into vinegar in earthenware jars, and nine days later scrape them. Others cover the vessels with grape-skins and scrape them after the same interval, others sprinkle copper filings with vinegar and several times a day turn them over with spattles until the copper is completely dissolved. Others prefer to grind copper fillings mixed with vinegar in copper mortars. But the quickest result is obtained by adding the vinegar shavings of coronet copper" (*N.H.* 34.26). Pliny here confuses verdigris with naturally occurring copper carbonate, a chemically different compound. Verdigris is a source of frustration for modern conservators. It is highly corrosive, especially when in contact with paper and parchment. The result is that it frequently eats away the page of the manuscripts on which it has been used (Banik 1990).

Chrysocolla. Chrysocolla, $CuSiO_3 \cdot nH_2O$, is a common secondary mineral from the oxidation zone of copper deposits. It occurs in the Sinai and the Eastern Desert of Egypt. It was occasionally used in antiquity as a cosmetic for greenish-blue eye paint (Lucas 1989). In Europe it was exploited from deposits in the Carpathian and Harz Mountains.

Malachite. Malachite, $CuCO_3 \cdot Cu(OH)_2$, was used commonly for cosmetic purposes as an eye paint by the ancient Egyptians. Evidence for the use of malachite exists from the Badarian Predynastic Period until at least the 18th Dynasty (Lucas 1989). There has been some speculation regarding the role malachite may have played in the development of glazed steatite. Malachite may have been used as an ingredient in the production of "Egyptian Blue". The use of malachite as a pigment spread to Japan in the mid-sixth century CE (Yamasaki and Emoto 1979).

Azurite. Azurite, $2CuCO_3 \cdot Cu(OH)_2$, has been called "mountain blue" and "copper blue". It has poor light-fastness, a marked tendency for the prominent blue to fade over time, so its use as a pigment has been somewhat limited. It is found in the Sinai and the Eastern Desert of Egypt. It was used as a paint pigment by the Egyptians as early as the 4th Dynasty (Lucas 1989). Pliny mentions a blue pigment from Armenia, probably azurite, which was used "in medicine to give nourishment to the hair, and especially the eyelashes" (*N.H.* 35:28). However, "Egyptian Blue" was favored throughout the Classical Period, and the use of azurite as a pigment was not widespread in the west until the Middle Ages, when its principal European source was Hungary (Roy 1993). Azurite has been identified in central China wall paintings of the Song and Ming dynasties, and on precolumbian kiva murals in the American Southwest (Roy 1993).

Azurite is also known on Japanese sculpture and wall paintings of the seventh and eighth centuries CE (Roy 1993). The use of azurite as a pigment also spread to Japan in the mid-sixth century. However, the use of azurite ceased in Japan between the ninth and eleventh centuries. The reason for this is not known, but azurite pigment reappeared in Japan after the twelfth and thirteenth centuries CE (Yamasaki and Emoto 1979).

9.6 Lead Compounds

Massicot. According to Gettens and Stout (1966), the term "massicot" (PbO) is sometimes used interchangeably with "litharge", but structurally they are dimorphs. Artificial massicot is the unfused monoxide of lead made by roasting white lead. It also is a fairly soft natural mineral (H = 2) that occurs as an oxidation product of galena and other lead minerals. Massicot is found in France, Germany, Italy, the Czech Republic, Romania, and Greece. It is yellow to reddish-yellow.

Litharge. Litharge, PbO, is a "fused and crystalline oxide which is formed from the direct oxidation of molten metallic lead" (Gettens and Stout 1966). It is more orange in appearance than massicot. As a naturally occurring mineral it is found at Laurion, Greece, and in other oxidized lead deposits throughout the world.

White Lead/Flake White. White lead, $2PbCO_3 \cdot Pb(OH)_2$, is one of the oldest synthetically produced pigments and also one of the most important white pigments that was used until the nineteenth century. White pigments in the Greek and Roman worlds frequently were mixtures of hydrocerussite (white lead) and cerussite ($PbCO_3$). Although cerussite was readily available, hydrocerussite did not occur in the region. Greek and Roman ladies covered their faces with powdered white lead, a popular cosmetic of the day (Forbes III 1965). Theophrastus, Pliny, and Vitruvius all described the preparation of white lead from metallic lead and vinegar.

According to Needham, the same method probably was used in China as early as 300 BCE (Roy 1993). This has been disputed by Wai, who believes that a very different method was used. According to an early Song dynasty document, the lead was heated in a pot and water was added (Wai and Liu 1991). This would then be massicot, a chemically different compound (PbO) from white lead. There are also numerous medieval recipes for making white lead.

The manufacture of white lead was one of several advances in painting techniques reportedly spread to Japan along with Buddhism in the mid-sixth century. Ancient Japanese texts credit the introduction of white lead to a Buddhist monk named Kanjo in 692 CE. He was rewarded for his efforts by the Empress Jito (Yamasaki and Emoto 1979).

White lead is notorious for its tendency to convert to alteration products when exposed to certain environmental conditions. For example, white lead exposed to the sulfur of airborne pollutants will turn black. White lead tends to turn into brown PbO_2 when used on **intonaco** plaster (Giovannoni et al. 1990).

Minium/Red Lead. Red lead, $PbO_2 \cdot 2PbO$, is generally made by heating litharge to a temperature of about 480°C. Chinese texts as early as the fifth century BCE refer to the manufacture of lead pigments from lead. Some Chinese texts exhibit confusion between red lead and cinnabar. However, it is clear that these pigments were being artificially produced. Red lead is found on wall paintings in central China (fifth to ninth centuries CE) and Buddhist wall paintings in Afghanistan (sixth century CE). In Japan, red lead is found on wall paintings of the Horyuji Temple (seventh to eighth centuries CE) (Feller 1986).

Red lead may have been known in Mesopotamia, but the only evidence appears in ancient cuneiform texts. The Persian alchemist al-Razi (ninth to tenth century CE) described artificially prepared oxides of lead. Theophrastus did not mention red lead (Feller 1986). Pliny referred to red lead as "*secondarium minium*" but seems to have confused it with cinnabar (*N.H.* 33.40). His confusion is understandable, since red lead was often mixed with cinnabar. Dioscorides and Pliny also referred to red lead as "false sandarach (realgar)". Vitruvius referred to red lead as "sandarach" further confusing pigments that are chemically different. Roman women used red lead as a cosmetic (Forbes III 1965). Red lead is also mentioned in numerous medieval treatises and was used on manuscripts and textiles in the west and Near East.

Lead Antimonate Yellow/Naples Yellow. Lead antimonate yellow, $Pb_3(SbO_4)_2$ (also referred to as Naples Yellow), is one of the earliest artificial pigments. It was used as a colorant for glass in ancient Egypt as early as the 18th Dynasty. Lead antimonate yellow pigments have also been found in association with Mesopotamian sites at Tell al-Rimah and Nuzi. Lead antimonate has been identified in glazes from Mesopotamia, Assyria, and Babylon (Feller 1986). The Romans also used antimony compounds as both colorants and opacifiers. Lead antimony was available as a by-product of the silver-refining industry (Mass et al. 1997).

Galena. The ancient Egyptians used galena (PbS) for a silvery-black eye paint. Galena continued to be used as a cosmetic into the Classical Period.

9.7 Carbon Compounds

Graphite. Graphite, a sheet-like soft mineral composed of carbon, has been used since antiquity chiefly as a writing material without the aid of either vehicle or medium. However, there are rare examples of its use as a pigment. The use of graphite pigments on Neolithic pottery was discovered at Sitagroi, in northern Greece. Ancient artisans of this region used graphite pigments to produce a highly reflective decorated surface (Gardner 1979). The name graphite is from the Greek *to write*. Its use in pencils dates to the mid 1600s when it was thought to be a soft black form of lead, hence the name "lead pencil". Prior to this use of graphite, metallic silver was used on many surfaces because inscribed lines of silver would darken as they tarnished by the formation of silver sulfide. Graphite also was used as a lubricant in antiquity.

Carbon Black. Carbon black refers to any carbon pigment that is manufactured by burning organic material. Depending on the source of the organic material, carbon black is often known by a number of different names including: "ivory" or "bone" black (made from charred bones),"vine" and "charcoal" black (usually made from charred twigs, vines, or wood but can be other types of charred vegetation), and "lamp" black (made from carbonized mineral oil, tar, pitch, or resin collected from brick oven chambers or other incendiary devices) (Gettens and Stout 1966). A burned vegetal matter combined with hematite was identified among pigments found at Herod's palace in Jericho (Ilani and Porat 1993).

Asphaltum/Bitumen. Hydrocarbons have been used since antiquity for a variety of uses, including colorants. These compounds are naturally occurring fossilized organic remains. Asphaltum is readily available near the Dead Sea. Pliny states that in "early days people used to stain statues with bitumen" (*N.H.* 34.9).

9.8 Sulfide Compounds

Orpiment. The mineral orpiment, As_2S_3, is a soft (H = 1.5–2), naturally occurring yellow pigment. It was used as a cosmetic by the Akkadians (Forbes III 1965). Its principal sources in antiquity were Hungary, Macedonia, Asia Minor, and possibly

Central Asia (Gettens and Stout 1966). Pliny notes the medicinal uses of orpiment (*N.H.* 34.56). The name comes from the Latin *auripigmentum* meaning golden paint. The orpiment used in ancient Egypt likely came from Persia.

Realgar. The mineral realgar, AsS, is a soft (H = 1.5–2), naturally occurring red-orange pigment. The name comes from the Persian *rahj al ghar.* It was used as a cosmetic by the Akkadians (Forbes III 1965). Pliny notes the medicinal uses of realgar and its occurrence in gold and silver mines (*N.H.* 34.55). Both orpiment and realgar pigments break down on exposure to light. Orpiment whitens to arsenolite (As_2O_3), and realgar changes to yellow to orange pararealgar. A pot of realgar was found in fourth century BCE ruins at Corinth, Greece. In Chinese alchemy, realgar (but not orpiment) had some importance.

There is a related mineral called pararealgar, AsS, which is thought to be a light-induced phase inversion of realgar. There is some concern among art conservators regarding its presence on paintings since it is not known if it was an original or altered color (Corbeil and Helwig 1995).

Cinnabar/Vermillion. Cinnabar (HgS) has been used as a red pigment since about 1500 BCE. It has been called “vermillion”, derived from the Latin “vermes”, an insect that was used to prepare a red dye. Theophrastus reported two types of cinnabar, likely true cinnabar plus red lead. Pliny knew about cinnabar but confused the issue by calling it “minium”. He knew the Roman supply came from Spain, likely the mines of Almaden. Ancient China also had an adequate supply of cinnabar. Mercury sulfide (cinnabar) was extracted from silver mines during antiquity. Red in color, cinnabar was apparently used from the earliest periods. Cinnabar is sensitive to light, and the color blackens over time. Cinnabar has been found in a funerary setting at a 5000-year-old site in Spain. It has also been discovered on human remains found in Peru dating from about 900–1000 CE (Martin-Gil et al. 1995). According to Pliny, the Romans regarded cinnabar with great importance and sacred associations. He quotes Verrius who “gives a list of writers of unquestionable authority who say that on holidays it was custom for the statue of Jupiter himself to be colored with cinnabar, as well as the bodies of persons going in triumphal procession” (*N.H.* 33:36). Roman women used cinnabar as a cosmetic. Cinnabar was called “minium” by Vitruvius, not to be confused with the lead oxide of the same name. In addition to Spain and Peru, cinnabar was mined in Mexico, Egypt, Greece, and China.

Stibnite. Stibnite (Sb_2S_3), sometimes called *antimonite*, is a fairly soft (H = 2) mineral often used as a pigment and colorant in antiquity. It is lead-gray to dark gray. It is known to have been used as an eye paint in ancient Egypt and into the Classical Period (Forbes III 1965). The Romans may have also used roasted stibnite as a glass colorant and opacifier (Mass et al. 1997).

9.9 Carbonates

Calcium Carbonate. Calcium carbonate, $CaCO_3$, occurs in a wide variety of mineral settings including calcite veins, limestone, chalk, mollusk shells, and coral. The name calcite comes from the Latin word *calx* for lime. In a Bronze Age Greek tomb, an offering of face powder consisting of calcium carbonate and lead was discovered (Diamandopoulos et al. 1994). Roman women used red chalk as a cosmetic. Chalk was identified among pigments found at Herod's palace in Jericho (Ilani and Porat 1993). Calcite was identified as a lake pigment on a Greek marble basin (fourth century BCE) that is now in the Getty Museum (Wallert 1995). Crushed oyster shells have been used in Japan since the fifteenth century. Japan seems to be the only place where oyster shell has been used as a pigment (Yamasaki and Emoto 1979). Named primarily from their geographic sources, calcite pigments have been called Spanish White, Paris White, Chinese White, and Troy White.

Bone White. Bone white, $Ca_3(PO_4)_2$, is a grayish-white, gritty material made by burning animal bones. "In medieval times it was used on paper or parchment to give it tooth or abrasive quality to receive the streak of silver point" (Gettens and Stout 1966).

Magnesium Carbonates. Huntite, $Mg_3(CO_3)_4$, a very soft mineral, may have been used as a white pigment by the Egyptians, although this could also have been a mixture of calcite and dolomite. This pigment has been found on a number of wooden objects (Riederer 1974).

9.10 Silicates

Green Earth/Terra Verte. Green earth, also known as *terra verte*, is principally celadonite and glauconite (both mica group minerals). As the name implies, it is used to produce the color green. The Egyptians seem to have preferred copper pigments for green, and there is no evidence for its use in the Dynastic Periods. Vitruvius mentions green earth as "*creta viridis*" in his architectural treatise. According to Pliny, the Romans used an inexpensive green earth pigment called "Appian" to counterfeit malachite (*N.H.* 35.29). This may have been a reference to green earth. Green earth was discovered among jars of pigments in a shop of ancient Pompeii. It was also used in medieval paintings (Feller 1986). Glauconite pigments have been discovered on Japanese tomb paintings of the Kofun Period (third to seventh centuries CE) (Yamasaki and Emoto 1979).

Clays. Some of the earliest natural pigments and colorants included various clays. A wide range of earth tones is available in clays, depending on chemical composition and impurities. Clays were used in paintings, cosmetics, and pottery "slip" glazes. Many light-colored clays make excellent pigments for use in lakes, since they will easily absorb organic dyes. Clays were given numerous traditional and trade designations such as white and red bole, china clay, and pipe clay (all of which are kaolinite). A pink pigment made from heated kaolinite was popular during the Classical Period of Greece. This pigment was identified at Herod's palace in Jericho (Ilani and Porat 1993). In Japan, clays were the predominant white pigments used in painting from the Protohistoric (Kofun) Period (third to seventh centuries CE) until the fifteenth to sixteenth centuries (Yamasaki and Emoto 1979).

Maya Blue. Maya Blue is a bluish-green pigment that has been found associated with Mayan artifacts in Central America. Its use appears to have extended into the Colonial Period (Tagle et al. 1990). Maya Blue is a mixture of minerals and indigo – a blue dye obtained from various plants. The mineral constituents are palygorskite (formerly called attapulgite) and sepiolite (also called meerschaum). The pigment is notable not only for its association with specific archaeological contexts, but also for its unique physical properties. Maya Blue is known to have survived the extremely harsh environmental conditions of the rain forest. It is also remarkably resistant to alkalis and all but hot concentrated acids (Gettens and Stout 1966).

Maya Blue appears to have had special cultural significance for the Maya beyond its decorative qualities. According to the sixteenth century bishop and explorer Diego de Landa, the Maya painted their victims before sacrificing them on a stone altar. Maya Blue was employed extensively on ceremonial objects and temple murals (Arnold and Bohor 1975).

There has been considerable debate regarding the precise nature of Maya Blue. Most scientists now agree that this pigment has a substantial clay component. However, there is no consensus regarding the source of the pigment's blue color. There are two theories regarding the source of color in Maya Blue. Some scientists have suggested that Maya Blue is a lake consisting of an indigo-stained attapulgite clay. However, the marked stability of Maya Blue is inconsistent with the notorious instability of modern manufactured lakes, and, until recently, there was some question regarding the availability of attapulgite clay to the Maya (Arnold and Bohor 1975). However, possible sources of attapulgite have now been identified in Guatemala and the northern Yucatan Peninsula (Folan 1969).

Research has been conducted regarding the possible effects of heat processing as a possible explanation for the apparent stability of Maya Blue. It has been suggested that heating indigo-stained attapulgite at moderate temperatures for several days will result in a relatively stable compound (Van Olphen 1966; Littmann 1982).

An alternative theory regarding the color source in Maya Blue is that the pigment derives its color from iron. This possibility was presented early in the Maya Blue debate by Gettens and Stout (1966). However, this theory has been disregarded because of the low concentrations of metallic impurities found in Maya Blue. Nevertheless, some scientists have continued to explore the possible role of metal compounds in Maya Blue (Jose-Yacaman et al. 1996).

Lapis Lazuli/Natural Ultramarine. Although lapis lazuli, the mineral lazurite, also known as ultramarine, $(Na,Ca)_8(AlSiO_4)_6(SO_4,S,Cl)_2$, was available to the ancient Egyptians, there is no evidence that it was used as a blue pigment until much later. Lapis was expensive, and its application as a pigment required processing by **levigation** of the powdered material. The resulting yield would have been very low, making lapis far too expensive to utilize in this manner (Lucas 1989).

The earliest known use of natural ultramarine as a paint pigment is found in wall paintings at the cave temples of Bamiyan in Afghanistan (sixth to seventh century CE). Ultramarine is also known from Chinese paintings of the tenth to eleventh centuries and from Indian murals as early as the eleventh century. In Europe, ultramarine found favor in illuminated manuscripts of the fourteenth to mid-fifteenth centuries (Roy 1993). The use of ultramarine was rendered unnecessary by the creation of a synthetic substitute in the early nineteenth century.

Egyptian Blue, Pompeii Blue/Blue Frit/Han Blue. Egyptian Blue is a glassy manufactured material consisting of copper, calcium, and silica. It is a made by fusing Ca, Cu, and SiO_2 using a sodium flux. The result corresponds to the mineral cuprorivaite (see Fourestier 1999) with the formula $CaCuSi_4O_{10}$. According to de Fourestier (1999), the mineral cuprorivaite ($CaCuSi_4O_{10}$) has also been called Egyptian Blue. Cuprorivaite is an azure-blue with a highly vitreous luster. It is best known from Mount Vesuvius in Italy and from the Sattelberg volcanic cone, Eifel district, Germany.

The earliest use of Egyptian Blue pigment dates to the third millennium BCE (Tite et al. 1984). It was used as a paint pigment and for the manufacture of small decorative objects such as beads, inlays, and talismans. It also was used as a pigment in ancient Mesopotamia and in Etruscan wall paintings. Vitruvius reports that the recipe was brought from Egypt. It was manufactured at Puzzuoli and was in common use at Pompeii and Herculaneum (Canti and Heathcote 2002). The manufacture of Egyptian Blue was similar to that of other ancient glasses. Egyptian Blue consists of relatively large, coarse particles. Unlike minerals in general, most paint pigments intensify in color as the pigment is ground to a finer consistency. This is because finer particles are more easily dispersed throughout the medium. Conversely, the more finely Egyptian Blue is ground, the less intense the color. It may be that the crude product always contains significant amounts of remnant quartz and glassy grains. The pigment may be improved by repeated sintering after washing (Giovanoli 1969).

Egyptian Blue was used in frescoes at Pompeii. This material was known to the Roman architectural writer Vitruvius, who wrote about its production from sand, natron, and metallic copper. There has been some confusion about the term Egyptian Blue that Onoratini et al. (1987) have attempted to clarify. These authors distinguish four separate products: (1) a sodium copper silicate "Hubert Blue", (2) a calcium copper silicate "true Egyptian Blue", (3) a ceramic containing "Hubert Blue", quartz, and tenorite, and (4) an "Antique Blue" ceramic which has "Egyptian Blue" as one component. This latter material corresponds with the *caerulea* of Vitruvius. Closely related to Egyptian Blue, with the substitution of barium for calcium, are the Chinese Han Blue ($BaCuSi_4O_{10}$) and Han Purple ($BaCuSi_2O_6$) (Berke 2007). Han purple (really a lavender color) was used on some of the Qin Dynasty terracotta warriors. Purple has often been called the color of royalty, partly because good quality purple pigment was rare.

Smalt. Smalt is the most recently developed pigment that is of any interest to the archaeomineralogist. Smalt is an artificial potash silicate colored with cobalt oxide. The modern European use of smalt began in the fifteenth century. However, smalt has been identified on Asian paintings predating European use (Roy 1993).

European smalt manufacture may represent the rediscovery of a forgotten technique. There is some speculation that smalt may have been known and used by the ancient Egyptians. Inconclusive evidence suggests that they could have used cobalt ores in antiquity as a colorant for glass objects (Riederer 1974). However, there is currently no evidence to suggest that the Egyptians ever used smalt as a paint pigment. Smalt was certainly employed as a glass colorant in China as early as the Tang Dynasty (Roy 1993).

Other Silicates. Analyses of Early and Middle Minoan white pigments from Crete revealed a complex situation where various substances had been used for paint on ceramics. Talc and calcium silicate have been identified as two of the mineral materials. In a recent study, Swann et al. (2000) have tentatively identified a white pigment from a site in eastern Crete as mixtures of calcium silicates and aluminosilicates, probably admixed with quartz.

9.11 Gold and Silver

Although its use in painting was never mentioned by Pliny or Vitruvius, gold leaf is known from at least a dozen examples of classical Roman walls (Ling 1991). Wealthy Roman ladies are said to have used gold dust as a cosmetic and as a hair powder or highlighting substance (Forbes III 1965). Gold leaf has been identified on an important Japanese tomb at Nara dated between the late seventh to the early eighth centuries (Yamasaki and Emoto 1979).

Silver sulfide was used in the Middle Ages to stain glass. The technique was first introduced in the early fourteenth century, and it contributed to the increasingly complicated designs of Europe's stained glass. The silver sulfide produced a yellow to orange color when applied to glass and fired. The precise effect depends on the amount of silver used and the firing temperature (Newton and Davison 1989).

Powdered silver has been identified as a pigment on ancient paintings at the Shosoin Repository in Japan. An unused sample of powdered silver from the eighth century CE is also stored at the Shosoin. Analysis revealed it to consist of over 94% silver, with traces of gold and copper (Yamasaki and Emoto 1979).

9.12 Tin Compounds

Cassiterite. Cassiterite, SnO_2, was used as an opacifier in ancient Egyptian glass in the 18th Dynasty and later (Lucas 1989). Around the ninth century, it was discovered that the addition of a small amount of cassiterite also acts as an opacifier in ceramic glazes (Flight 1989). This glaze served as an ideal undercoat to show off a second glaze of colorful designs. This technique was discovered by early Islamic ceramicists. Tin oxide glazes appeared in Italy about 1200 CE before spreading to other parts of Europe (Flight 1991).

Tin metal was used by medieval European artisans as tin leaf to gild sculpture, furniture, and art objects (Cennini 1960). The use of tin leaf was described by the Florentine monk Cennini in the fifteenth century.

9.13 Cobalt

The element cobalt (Co) is widely distributed in the earth's crust, but its abundance is only 0.001%. In archaeomineralogy the importance of cobalt is limited to its role as a pigment to impart a rich blue color to glass, glazes, and ceramics. It was used in the third millennium BCE in Egypt and Persia, in Roman Pompeii, and in the Tang Dynasty in China. Cobalt is the source of the dramatic blue color in Ming Dynasty porcelains. Prior to the isolation of the element cobalt in 1735, the blue color in glass often was attributed to bismuth, which occurred with the cobalt. Since antiquity cobalt has been a byproduct of the mining and smelting of copper ores. Smaltite, $(\mathrm{Co,Fe,Ni\ As_2})$ occurs as a significant ore in Saxony, which has long been a supplier of cobalt as a pigment, at least since the twelfth century CE.

The name cobalt comes from the German word "kobold", a term miners used for the ore. For some history of the use of cobalt as a pigment during the Italian Renaissance and earlier, see Zucchiatti et al. (2006). A cobalt-blue pigment used on painted pottery in the 18th Dynasty in Egypt (1400–1200 BCE) was determined to be from a CoAl-spinel recovered from cobaltiferous alums found in the Western Desert (Shortland et al. 2006). Alums are hydrated potassium-aluminum sulfates. Tite and Shortland (2003) suggest that the cobalt-rich alum colorant from the New Kingdom site of Amarna was pre-treated by precipitating cobalt hydroxide from a solution of the alum by the addition of natron. They also hypothesize that the cobalt-blue glass was produced by melting the cobalt-blue frit with additional plant ash and possibly quartz.

Chapter 10
Abrasives, Salt, Shells, and Miscellaneous Geologic Raw Materials

10.1 Introduction

This chapter contains reviews and discussions of geologic raw materials that did not fit conveniently into the systematics of the other chapters.

10.2 Abrasives

Since ancient times, many rocks and minerals have been used as abrasives, including emery, pumice, diatomite, feldspar, quartz minerals, and various metal oxides. Abrasives must be both hard and cohesive, i.e., not subject to easy fracturing. Throughout the ancient world, quartz (hardness of 7) was undoubtedly the most common abrasive. It was available nearly everywhere either as quartz sand or crushed quartz. By about 3500 BCE engravers were using quartz powder to engrave cylinder seals. It appears that emery powder came into use by the second millennium. One of the first major uses of abrasive grit was in the construction of the pyramids of Egypt where the surfaces of stone blocks were rubbed smooth for a remarkably good fit.

The creation of ground stone objects requires an abrasive material. Flaked axes with ground edges are found in Japan and northern Australia dated earlier than 10,000 years BP. By the ninth millennium BP, flaked axes appeared in northwestern Europe and southwestern Asia (Bordaz 1970). Quartz sandstones used as grinders also appeared at this time. Grindstone artifacts appeared in Egypt and Mesopotamia around 2000 BCE, in China around 1500 BCE, in Greece before 700 BCE, and in central Europe about 500 CE (Pinkstone 1974).

One useful abrasive is emery, which is a naturally occurring aggregate of corundum (Al_2O_3) and magnetite (Fe_3O_4), sometimes with spinel [$(Mg,Fe)Al_2O_4$] or sillimanite (Al_2SiO_5). Some emery contains plagioclase. The hardness and abrasive or cutting quality of emery depend on the amount of corundum present. Corundum has a hardness of 9 and is exceptionally cohesive and durable. Hence, emery deposits that are high in corundum make exceedingly good abrasives. The hardness of magnetite is 5.5–6.5; that of spinel is 7.5–8; and that of sillimanite is 6.5–7.5. The emery

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of most deposits is black and, whatever its composition, it is a heavy, tough rock with an average hardness of about 7.25. Emery is formed mainly by contact metamorphism and occurs in irregularly shaped pods in limestone, schist, or altered basic igneous rocks. The name comes from Cape Emeri in Greece. High-grade deposits occur on the island of Naxos, Greece, and in Aidin, Turkey. Emery from the island of Naxos was exploited in ancient Greece. Pliny called emery "naxium". In the Cycladic islands the use of emery may have begun in the Neolithic. Emery use in Crete has been dated to the Middle Bronze Age. The finely detailed sealstones of the ancient eastern Mediterranean and Near East required the concomitant exploitation of abrasive raw materials for finishing and polishing.

The vast quantities of finely polished hard nephrite jade artifacts (hardness 6.5) from the Chinese Neolithic may now be explained by the recent identification that corundum was worked during the Chinese Neolithic (4000–3500 BCE). These same corundum rocks later (circa 2500 BCE) may have been given a high polish by a diamond abrasive (Lu et al. 2005).

10.3 Salt (Halite)

The mineral halite (NaCl, common table salt) has been the source of salt for human nutritional needs from the beginning of human evolution (Fig. 10.1). It has also served as a preservative, a medium of exchange, and a significant source of tax revenue. Salt has been recovered from two major sources: (1) sedimentary deposits of rock salt, and (2) evaporation of seawater. Halite deposits form when arms of the sea are cut off from a water supply and the water evaporates. Seawater is about 3.0% NaCl. In coastal estuaries, evaporation can increase this percentage to about 8%. It should be noted that the simple evaporation of seawater to complete dryness

Fig. 10.1 Halite cleavage fragments

does not yield just halite but also other salts. The order of evaporation in natural saltpans is calcium carbonate (calcite), calcium sulfate (gypsum), sodium chloride (halite), and potassium magnesium chloride (carnallite). Halite is usually the most abundant. The composition of saltwater brine varies widely. Some would not be suitable for salt production. Pliny realized and described the different raw materials for salt production: rock salt beds from evaporite deposits, some brine waters, and seawater. Large-scale boiling of brine to recover salt dates back to the Iron Age in Europe. Also in the Iron Age salt was mined just south of Salzburg, Austria from 750 to 150 BCE. (Megaw et al. 2000).

Over most of the earth salt took little energy to exploit and was easily transported. It can be recovered from seawater by boiling or evaporating the water. Salt from Palmyra, in ancient Syria, was traded throughout the Persian Gulf. After the collapse of the Roman Empire, metal mining almost ceased, but salt mining continued because salt was vital in the human diet. The caravan route through the Libyan Desert in the time of Herodotus was located so that it passed through salt oases. Salt routes throughout the Near East, Europe, and Asia reflect the vital significance of this mineral to the social and economic needs of human populations. The salt mines of ancient India were the center of widespread trade. The salt of the port of Ostia, near Rome, supplied some of the Roman needs. Those of Caesar's soldiers who were "worth their salt" received part of the pay (their salarium) in the form of salt. The Romans also used salt medicinally in gum preparations for eye salves and for mouth and gum sores.

Salt in Egypt was most likely obtained from saline lakes near the Nile Delta. Pliny notes a lake near Memphis and sources at Pelusium (N.H. 31, 39; 74, 78). He also notes a particular type of salt found in the desert between Egypt and Arabia (Lucas 1989). Salt is also found as (1) an impurity in natron deposits of the Wadi Natrun, and (2) with gypsum at the Oasis of Ammon. During the Ptolemaic Period salt became a royal monopoly. The major locality for its manufacture gradually shifted from Pelusium to the area around Lake Mareotis, near the ancient metropolis of Alexandria. In addition to dietary uses, salt was employed as a drying agent and preservative (for example, in preserving fish). Salt was employed in metallurgy for refining gold and in the production of glazes. It also was used medicinally in the New Kingdom, as attested in the Ebers Medical Papyrus. Although natron was the principal mineral used in mummification, after the first century salt was interspersed among mummy wrappings to aid desiccation. It was used in tanning processes both in the Near East and in the classical world. Salt was marketed in lumps and bricks, and blocks of salt are included in religious donation lists.

Salt was also important in Mesopotamia where it was used in religious offerings, in medicines as an emetic, and in glass making and glazing. It was also used to catalyze the burning of fuels (such as cattle dung) in baking ovens (Singer et al. 1954). It was added to oil in lamps in both Mesopotamia and Egypt to brighten the flame and give it color (Herodotus 2, 180).

In prehistoric Europe the rock salt mines of the eastern Alps were a major source of this commodity. German place names with "hall" or "halle" and Anglo-Saxon "wich" frequently indicate a locality where salt production took place. The mines at

Salzburg, Hallstatt, and Hallein were worked on a scale far exceeding local needs. Miners dug as far as 350 m into the salt beds of the mountains. Important leather artifacts dating from the Iron Age, including a miner's bag with tools for salt mining and a bag for carrying salt, were found near Hallstatt, Austria. Remains of a Late Bronze Age/Early Iron Age oven for the production of salt was discovered at Eisleben, Germany (Marschall 1988).

Halite occurs in major beds in many Triassic sedimentary rocks in central Europe and England. During the Iron Age in southeastern England, salt-making from seawater was an important economic activity. From the latter half of the first millennium BCE, both large- and small-scale exploitation of coastal and inland salt resources took place in Wessex, Essex, Sussex, Hampshire, and Lincolnshire in Great Britain. Archaeomagnetic data (Borradaile et al. 1999), supported by ceramic evidence, indicate salt-making occurred in southeastern England in the last quarter of the first millennium BCE. During the Anglo-Saxon Period, charters were issued granting nobility and the clergy access to brine pits and rights to produce salt. At Droitwich, artifacts such as molds, briquetage, and clay and later lead-lined vats and utensils associated with salt manufacturing have been found. Salt manufacturing continued there into the sixteenth century (Woodiwiss 1992). Strabo notes sources of salt in Spain (3, 100.144).

Because salt is less dense than most rock, buried deposits of salt can literally rise upward through layers of solid rock, forming dome-like structures. There are only two salt domes in Europe, one in Romania and the other in Catalonia, Spain. Recent investigations indicate that the Spanish deposit was first exploited in the Middle Neolithic (4200–3600 BCE), making this source the earliest one mined in Europe (Weller 2002). In the Krakow region of Poland, the earliest salt-making sites date to the Middle Neolithic. Ditches, storage tanks, hearths, pits, and relevant ceramics have all been recovered in association with salt-making from brine springs. The brine was channeled through clay-lined ditches to prevent seepage into the sandy soil, then into storage tanks, and finally into ceramic vessels for heating and evaporation. The Krakow region also has salt mines that have been worked for more than 1000 years from a layer of salt nearly 400 m thick lying far beneath the surface. In Romania, many salt-water springs provided salt from the Neolithic through the Medieval Period.

In Mesoamerica, Yucatan was the greatest salt production area. Salt beds extended along the coasts (Fig. 10.2). Salt was collected at the end of the dry season. Underwater excavations off the coast of Belize have uncovered a site where the Maya produced salt from seawater more than 1000 years ago. The salt trade was important in the development of Classic Maya civilization. People in the tropics have high salt requirements because of sweating, but plants have a very low salt content, so inland agricultural societies needed a source of mineral salt. At the salinas in highland Chiapas, Mexico, salt was allowed to deposit around objects made of reed in order to manufacture salt artifacts (Andrews 1983). In Mesoamerica, salt was also recovered from Guatemalan wells. The Spanish exported salt from this area and used it for silver refining in the New World (Andrews 1980).

The indigenous peoples of the American Southwest had at least four salt mines: one near Camp Verde, Arizona; a second near St. Thomas on the Virgin River in

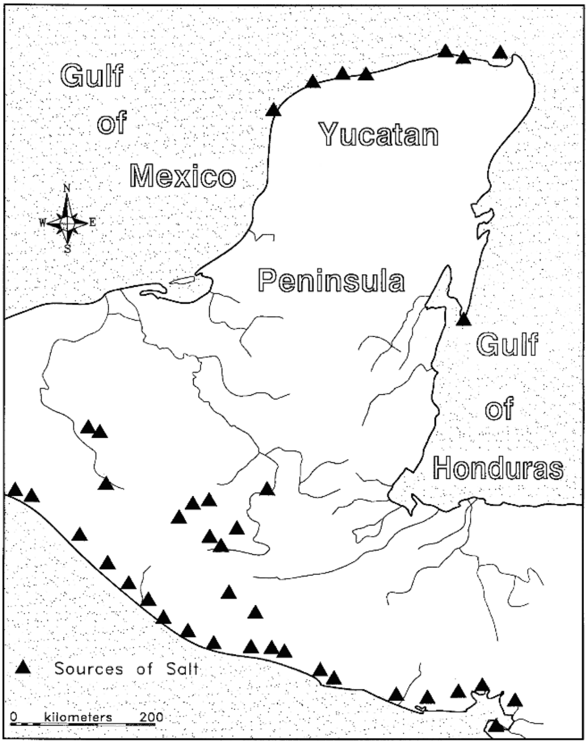

Fig. 10.2 Distribution of major Mayan salt sources. (After Andrews 1983)

Nevada; a third at the Zuni Salt Lake; and a fourth at a salt spring in the canyon of the Little Colorado River, which was used by the Hopi. The Arizona deposit occurs in the Tertiary Verde Formation, where ancient tunnels were driven into hillsides to locate the best salt strata in the formation. At St. Thomas, Nevada, the salt was recovered from caverns. Marine rock salt sourced to the Sevier Valley of central Utah, USA, was used as a trade item by native peoples who exported it to sites near Mesa Verde between 950 and 1200 CE (Baldwin 1976).

Salt deposits can form from the hot brines of hot springs. Since early in the first millennium, humans have utilized salt from brines and brine deposits emanating from the East African Rift system. Of special note are the deposits at Bunyoro on the eastern shore of what is now called Lake Albert. In West Africa, solar evaporation of salt may have been utilized on the shores of Lake Chad and at coastal sites. After camels became used as beasts of burden, inland resources such as the rock salt deposits of Mauritania, southern Algeria, and northern Mali were also exploited (Alexander 1995).

Salt in China has been considered an economic good and a state monopoly at least since the seventh century BCE (Chiang 1975). Easily accessible salt deposits are widespread in China, occurring in all but three provinces. Much of the salt was extracted from the sea, although there were many major inland production centers some based on salt lakes, others on brine pumped from deep wells, at least during

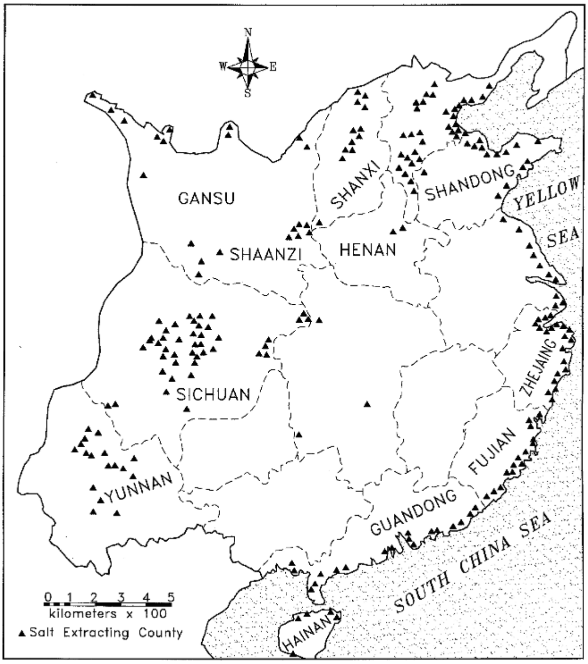

Fig. 10.3 Sources of salt in Ming Dynasty China

the Ming Dynasty (Fig. 10.3). In the quest for salt, the Chinese originated deep drilling, up to about 1500 m, by the first century BCE. During the Ching Period the salt supply was widely dispersed. Although four-fifths of the salt came from the coast, one-fifth came from salt lakes, brine wells, saline rock, gypsum mines, and salty earth. The spread of salt production in China had reached its maximum areal extent in the earlier Ming Period (1368–1644) (Chiang 1976).

In Japan, the environment for salt production is poor. Although surrounded by salt water, the islands of Japan lack coastal flats for evaporation fields and reliable sunshine without too much rain. As a result, at least for the last 1400 years, the Japanese have relied on a two-step process for concentration and evaporation. Seaweed soaked in seawater is dried and the salt that precipitates is rinsed off into more seawater, producing a more concentrated brine that is evaporated by heating in clay pots.

10.4 Natron

Natron is a naturally occurring mixture of sodium carbonate ($NaCO_3$) and sodium bicarbonate ($NaHCO_3$). Strictly speaking, natron is $NaCO_3 \cdot 10H_2O$. The first use of the term "natron" appears to be in the glazing of quartz and steatite (Shortland et al. 2006b). The word (in Egyptian hieroglyphics "ntry") is most likely derived from the root "ntr", indicating its association with religious and funerary rituals. Its importance in Egyptian life is indicated by the fact that the Egyptians had at least eight words for this mineral (Harris 1961). Because the original name of the element sodium was natrium (chemical symbol Na), there are many names of mineral varieties with natron as a part of the name. This signifies only that they contain sodium.

Like salt, natron was produced under a royal monopoly during the Ptolemaic Period and was sold in block and granular form. Main sources for natron are mentioned by Strabo and Pliny (Strabo 17, 100.803; Pliny N.H. 31, 46.106ff) (See Fig. 10.4).

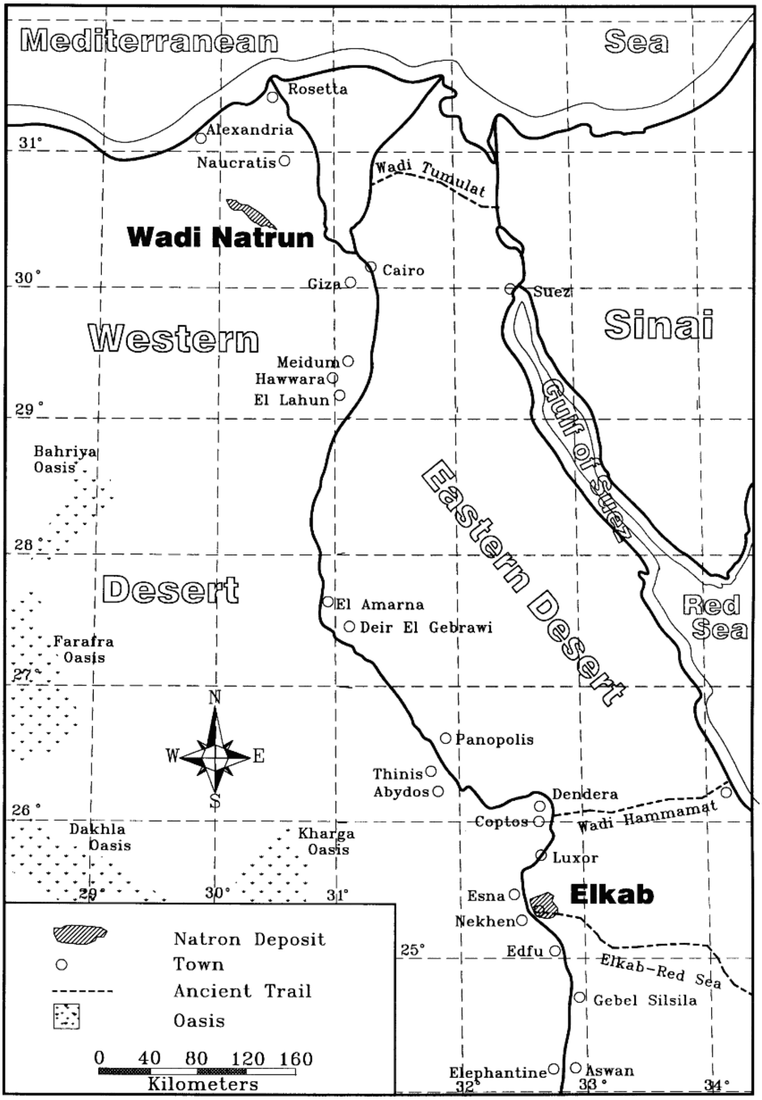

Fig. 10.4 Natron deposits in Egypt

It occurred most abundantly at Wadi Natrun (a depression in the Libyan Desert 60 km northwest of Cairo). Each Nile flood vastly increased the supply of water entering the wadi and its string of small lakes. During the dry season, evaporation resulted in deposition of natron at the bottom of the lakes and as an incrustation on the ground adjoining many of the lakes. It was also found near the port of Naucratis in the Nile Delta, and in a cluster of five localities near El-Kab in Upper Egypt. Pliny states that natron was also prepared artificially in ancient Egypt, in much the same manner as table salt, except that Nile water rather than seawater was used.

Natron was recovered from the Wadi Natrun in the Western Desert from early in the fourth millennium BCE. However, the dominant carbonate in these deposits frequently was trona, $Na_3H(CO_3)_2 \bullet 2H_2O$. Natron is first mentioned in the Pyramid Texts, which date to the Old Kingdom, as a substance with religious and magical properties. Natron was used for ritual purification either by itself or mixed with incense. It could also be chewed or used as a purifying mouth rinse. Other textual references cite its use in ceremonies connected with building construction. It was used for making glass, glaze, and faience, where it was combined with ground quartz and modeled or molded into small figurines or amulets. It also had medicinal uses, was employed as a bleaching agent for linen, and was used in cooking.

However, the Egyptians used natron principally for mummification. Leftover embalming materials, including natron, were buried in containers in the tomb of Tutankhamen. When analyzed, these substances were found to contain natron salts and carbonates as well as organic substances (such as myrrh, sandalwood, frankincense, and various herbs) (Singer et al. 1954).

10.5 Alum

Alum is a general term for hydrous alkali aluminum sulfates. Alum is found normally in a very pure state. In order to use alum as a **mordant** in dyeing and tawing, it has to be free of impurities. Thus, iron salts (which add color) must be removed from the alum. If ancients found it contaminated by iron sulfate, it was purified by recrystallization. Alum is historically important as the first substance deliberately prepared in what the modern chemist would regard as a substantially pure state (Singer et al. II 1954).

Ammonium alum and potash alum [$KAl(SO_4)_2 \cdot 12H_2O$] (or a mixture of the two) have been used since Greek and Roman times as a mordant to make vegetable dyes fast. In ancient Mesopotamia alum was used in tawing, dyeing, glass-making, washing, and in medicine. In Classical times it was used as a flux to solder copper (Levey 1958). Throughout antiquity and the Middle Ages, any astringent mineral substance that would act as a mordant was likely to be called alum (alumen).

Use of alum in the preparation of leather appears very early in the archaeological record. Analysis of the sheepskin lining of a Neolithic dagger sheath from Stade near Hamburg suggests that tawing may have been known in that area before the use of metals (Singer et al. II 1954). Tawed leather has been found from Predynastic times in Egypt. White and other colored leather sandals are seen in tomb paintings from the New Kingdom which may have been fabricated by using alum. Alum may also have been used in combination with honey as an astringent by the Egyptians to dress wounds (Lucas 1989). Herodotus relates that the Pharaoh Amasis offered 1000 talents for alum to be sent to Delphi (Harris 1961:197). The Ebers Papyrus prescribes its use as an eye salve. The use of alum for tumors is found in the Berlin Papyrus, and Pliny and Dioscorides note this particular use. Ancient workings have been found at the Dakhla and Kharga Oases west of the Nile valley. Greek papyri confirm that alum was used in the Hellenistic Period when it was extracted under a royal monopoly (Oxyrhynchus Papyri 17, 2116). Pliny and Dioscorides claim Egyptian alum is superior to that found elsewhere, and both state that there are several types. Pliny refers to its use as a mordant for dye and as an ingredient in medicines (N.H. 35, 52, 184). Alum was produced in large quantities in Roman Egypt. Surface pottery sherds at the Kharga Oasis indicate that this source continued to be exploited in Roman times.

There is evidence of tawed leather in Assyria, Babylonia, Phoenicia, and ancient India. There are deposits of alum in Mesopotamia near Kara Hissar on the Lycus River at Tuz Khurmatli, and Hamairan on the Persian Gulf. Alum was used by the Assyrians as a styptic (Campbell Thompson 1925), and its characteristic astringency is noted by Pliny. A Mesopotamian recipe for the use of oil and alum for making sandal leather has been translated by Thureau-Dangin (1920). It was also used in Mesopotamia in glass-making. Alumstone (alunite) was used to make seals. The alum derived from this mineral compound was roasted and boiled in water to be used in medical prescriptions. Late Assyrian texts mention that alum was imported from Egypt for use by dyers and leather workers.

In late Preclassical times, Cyprus seems to have produced plumed (plumous) alum, which may be the compound aluminum sulfate. This substance was imported to the near East. Alum deposits were also found in Palestine near the Dead Sea and in Peraea near the town of Machairus. Classical Greeks secured potash alum from the volcanic island of Melos.

The Romans had access to potash alum from volcanic regions such as the Lipari Islands and Sicily (Singer et al. II 1954). They also knew of the mineral alunogen (hydrated aluminum sulfate) and utilized a number of minerals with aluminum sulfate or compounds similar to alum. Caesar cites the use of tawed leather for sails (aluta) among the Veneti in Gaul (De Bello Gallico 3, 13).

Tawing with alum was practiced in eighth century Spain. Lucas (1989) mentions “extensive ancient workings of aluminum sulfate”, and quotes a fragmentary passage from Arab authors for more recent alum trading, associating the use of alum as a mordant in dyeing skins. By the thirteenth century, Arab writers discussed methods of preparing a pure alum from “the alum of Yemen” (native aluminum sulfate). The manufacture of tawed leather was also widespread in the Middle Ages, and alum continued to be the common mordant for dyeing fabrics, as evidenced by textual and pictorial representations (Singer et al. II 1954). In the thirteenth century, most alum came from the Greek islands and the Near East, especially the region around Izmir. Prior to the fifteenth century, alum was imported into Europe from a number of sources but mainly from the Byzantine Empire. After the Turks captured

Constantinople in 1453, alum became increasingly difficult to obtain. Shortly thereafter, vast deposits of alunite [$KAl_3(SO_4)_2(OH)_6$] were discovered at Tolfa, Italy, within the Papal States (Millard 1999). After the English Reformation this Papal control became a problem for the English cloth-dyeing industry. This led to an effort to establish an indigenous English alum source. Successful exploitation of the North Yorkshire alum shales began about 1600. The shale was calcined and then steeped in water to extract the soluble aluminum sulfate (Millard 1999).

10.6 Shells, Coral, Fossils, and Fossil Bone

Shell. The word "shell" originates from the Teutonic root *skal* (to peel off or separate), the Icelandic *skel* (a tile), and Middle English *schelle.* Shell ornaments are found throughout the world. Shell disk beads have been found in association with ancient Egyptian sites, which were used until the 22nd Dynasty (Lucas 1989). At Tell el Ubaid, an Early Dynastic Sumerian temple contains log columns inlaid with mother-of-pearl (Delougaz 1938). A fossil shell was sculpted into a female form during the Late Neolithic Period in southeastern Norway (Glørstad et al. 2004).

Shells have been exploited throughout history for food, dye, tools, ornaments, trade goods, talismans, money, and ritual objects. They have proven to be important indicators in both the natural geologic record and in the archaeological record. Shell is composed mainly of calcium carbonate with small amounts of calcium phosphate, magnesium carbonate, and silica.

Shells have been associated with ancient religious traditions and folklore throughout the world. For example, in Hindu mythology, the shell of conch (*Turbinella pyrum*) was carried as a trumpet by Krishna as a symbol of victory over an evil demon, Panchajana, who lived inside the shell. Shell-working at Harappa in the Indus Valley dates to the earliest levels, circa 3300 BCE (Kenoyer 1997). Triton carried a conch (probably *Charonia lampas*) trumpet in Greek mythology. Hawaiian legend tells of chief Kapuni, who had adventures while in pursuit of a sacred conch shell (*Charonia tritonis*). Cowries were associated with the goddess Venus in ancient Rome. Numerous Native American and African folktales and traditions are also associated with specific types of shells. These are only a few samples from a very long list. These traditions and myths sometimes elucidate possible ritual associations in archaeological contexts.

Shells are one of the oldest items to be made into jewelry. Beads, necklaces, and bracelets are found from the Palaeolithic Period in Europe, and necklaces of shells were found in Predynastic Egypt. Shell was also used to carve reliquaries, rosaries, and jewelry during the Middle Ages. Cameos were carved from shell in both France and Germany from the early sixteenth until well into the seventeenth century (McCrory 1988). In North America, shells were used as inlay in masks and were often deposited as funerary offerings.

Spondylus shells and jewelry made from them were used by cultures in the prehistoric American Southwest, West Mexico, Mesoamerica, and along the Pacific coast south to Peru. Trade in *Spondylus* shells covered very long distances, about 3800 km from Ecuador to west Mexico. The Hohokam of Arizona traveled from 200 to 600 km to obtain marine shells from the Pacific coast (Liu 2006). Shell ornaments were also favored throughout precontact North America, and evidence of their use extends into the continental interior, suggesting heavy trade. Shell was used for beads, personal ornaments, inlay, small carvings, and decorative surfaces. In precontact Mesoamerica, mother-of-pearl was used as beads and as an inlay in masks and stone sculptures. Several varieties of shell beads are represented from Chichen Itza, Mexico (Moholy-Nagy and Ladd 1992). Conch shell trumpets have a long history in Mesoamerica and other parts of the world. In precontact Mesoamerica, shell was cut, drilled, polished, and inlaid in the production of ornaments at least as early as the second millennium BCE. Over 190 species of seashell creatures and land mollusks have been found at Mayan sites. The shell most commonly used was *Spondylus*, but larger shells such as *Strombus*, *Busycon*, *Oliva*, and *Pinctada* were also used. The two valves of *Spondylus* were used as "caskets" for pieces of jade.

The shells of gastropods played a pivotal role in the industries and commerce of many ancient cultures. The production of "murex dyes", especially Tyrian purple (also called royal purple), is an example of the importance of ancient gastropod exploitation in the Mediterranean region (Fig. 10.5). Purple dye was introduced

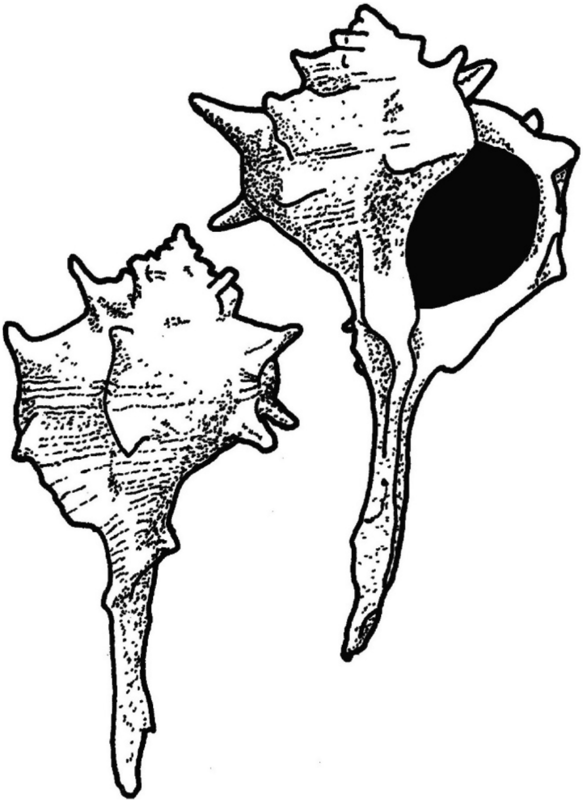

Fig. 10.5 The murex, *Bolinus brandaris*, formerly placed with the genus Thais

during the Bronze Age in Phoenicia. It was extracted from sea mollusks, the purpura shellfish murex.

The hypobrachial gland from three species of muricids (including *Stramonita haemastoma*, *Hexaplex trunculus*, and *Bolinus brandaris*) were used to manufacture dye. The term "murex" was formally to the latter two species, which have since been reclassified by scientists. Thus, the term "murex dyes" is a misnomer (Rosenberg 1992). The gland, which is located in the creature's mantle cavity, exudes a clear mucous fluid which, upon exposure to sunlight and the atmosphere, gradually turns to white, pale yellow, green, blue, and finally purple. Murex species are found all over the world, but most inhabit tropical waters. The most characteristic features of many of the murex species are the numerous spiny projections of their shells.

The production of murex dyes was notoriously wasteful. Large amounts of soft tissues were extracted either by crushing small shells or by removing the hypobrachial gland of larger specimens. According to some calculations, 12,000 individuals of *Bolinus brandaris* were required to produce 1.5 g of pure dye. The soft tissues were mixed with sea brine and simmered in covered vats for several days. Textiles were submerged into this mixture to impart color to the cloth. The end product is "chemical indigo or its brominated derivative dibromoindigo. Variation in the color of the dye results in methods of processing, and from differing proportions of these chemicals in extracts from each species. Indigo from mollusks is the same substance as indigo from plant sources" (Rosenberg 1992).

The manufacture of murex dye was known to the Cretans by 1600 BCE. Ancient Phoenician legend credits the invention of Tyrian purple to the mythological hero, Melkart. Somewhat later, the Phoenicians learned how to extract a purple dye from the murex gastropods. By about 1000 BCE, the production of murex dye became a thriving industry for the ports of Tyre and Sidon. This caused a significant depletion of the murex species along the Phoenician coast. Crushed murex shells have been found in Hellenistic Troy in the area where deposits of other dye- and pigment-producing materials were found. Tyrian purple was so highly prized by the Romans that they placed dye factories under state control and limited the use of purple to the ruling classes (Gerhard 1964).

Spanier (1986) has reported that some of the murex shells found in archaeological sites along the coasts of Israel had holes drilled in them. Biological study revealed that such holes were probably drilled by cannibalistic species, but only under artificial conditions. This would indicate that the ancient peoples may have maintained murex snails in captivity until they accumulated a sufficient quantity for their dyes.

Similar dye preparations were utilized in many other parts of the ancient world. In Ireland, *Nucella lapillus* was used to dye fabrics. The remains of this species' shells have been found in Irish middens dating to 1000 BCE. American gastropod species produce a range of colors including blues, purples, and reds. Purple shellfish dye has been found on 2000-year-old Peruvian fabrics (Rosenberg 1992). *Purpura patula pansa* was probably the shellfish species most often exploited for its dye in the Americas. Its habitat stretches from southern California to northern Ecuador. Unlike Mediterranean muricids, the dye can be obtained without killing this larger American cousin. Extraction is accomplished by simply irritating the creature until it ejects the fluid directly onto cotton yarn (Gerhard 1964). Although murex species were undoubtedly available in many eastern Mediterranean areas, the Phoenicians and later groups exploited the abundance in the coastal region south of Sparta, Greece.

A related dye was extracted from an insect. The Sumerians discovered the scarlet pigment, derived from the insect kermes. The Sanskrit word kermi means "worm;" in Arabic it is qirmiz (قرمز), and in Persian it is kerema. In modern English it has become "crimson". During medieval times, the Venetians made "Venetian Scarlet" from kermes (vermillium means "little worm"). The extract from kermes was also used as an astringent for wounds. An Arab doctor in the ninth century used it to stimulate the heart. Kermes lost its importance as a scarlet pigment when the Spanish discovered the Aztecs using an extract from the cochineal insect, which is indigenous to Central and South America.

Shell was often used as either currency or trade goods. One of the most widely prized shell currencies was the cowrie (Fig. 10.6), of which the most extensively circulated species was the *Cypraea moneta* or "money cowrie". Money cowrie is found throughout the Indo-Pacific; most of it originated in the Maldive Islands. The cowrie grows smaller (2 cm or less) in the Maldives than in other habitats, making it a convenient size for distribution. Cowries were less expensive to supply than minted coins and impossible to counterfeit (Rosenberg 1992). In addition, cowries had symbolic and ritual significance in many cultures, which must have contributed to their acceptance as a form of currency. Cowries were also used for human decoration in prehistoric Europe and North America.

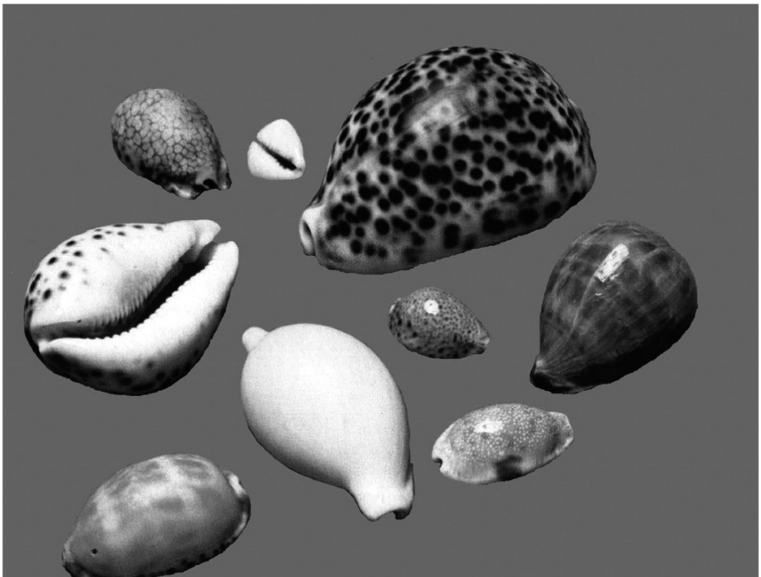

Fig. 10.6 A selection of cowries

Cowries are small gastropods with as many as two hundred different species. The word "cowrie" is from the Hindi and Urdu languages. Cowrie species vary in size from less than 1 cm to more than 4 cm. Most cowries used as money were about 1.5 cm long. Used both as money and strung as beads in a necklace, cowrie shells were quite durable. The earliest references to the use of cowrie shells come from China where they were in circulation as early as the second millennium BCE during the Shang Dynasty (Chang 1980). One Shang tomb in Shantung Province contained 3790 cowrie shells (Chang 1977).

Cowries were circulating in Africa by the tenth century. However, their use did not peak until the early 1500s, when the Portuguese imported cowries to West Africa to finance the slave trade. These cowrie shells were harvested in the lagoons of the Maldive Islands in the Indian Ocean but found their way to West Africa (Hogendorn and Johnson 1986). The Dutch and English began shipping cowries for the same purpose in the 1600s. Cowries could be used as ballast in ships and subsequently traded for a cargo of slaves (Rosenberg 1992). Cowries as money were circulated in parts of Africa until about 1900.

A number of indigenous peoples of North America had currency or barter systems that included the exchange of shells. For example, the Nootka of British Columbia collected *Antalis pretiosum* both as food and for its shells, which were traded with neighboring tribes to the south. The Yurok and Tolowa peoples of northern California used strings of tusk shells as money. The value of the string was based on the length of the string, and the number and size of the shells. The Pomo people of the central California coast used strings of beads made from the shell of the Pismo clam (*Tivela stultorum*) as currency. A higher value was placed on cylindrical beads made from the thickest part of the shell. On the northeastern seaboard, beaded belts made from the quahog (*Mercenaria mercenaria*) were used for ceremonial exchanges by native peoples. Purple beads were more highly valued than white since only a small part of the quahog shell is purple. These objects eventually became used as currency under Dutch and British colonialism (Rosenberg 1992). Thus, the Dutch were able to "purchase" the Island of Manhattan for a nominal amount of trade goods, which may have included shell beads.

Perhaps one of the best-documented exchange networks involving shells is the "kula" trade system of the New Guinean Trobriand Islands. A detailed ethnographic study of the kula was published by Malinowski (1922). The kula is a highly evolved ceremonial network principally involving the exchange of "arm-shells" made from the *Conus millepunctatus* and necklaces made from beads of red *spondylus* shell. According to Malinowski (1922) these goods always travel in one direction along the trade route. The tasks involved in the manufacture of exchange articles are differentiated by gender, and the finished articles are only exchanged by Trobriands of high social status.

Coral. Coral is a calcareous substance secreted as a skeleton by many kinds of marine polyps. Corals are composed of small fibers or granules of aragonite ($CaCO_3$) or calcite (also $CaCO_3$). Calcite corals are those that form in the deep sea. Modern reef-building corals are chiefly aragonite. Coral is found in various shades of red, white, pink, black, and rarely yellow. The name originates from Greek "korallion" (Latin "corallum"). Silicified coral is a smooth chert-like rock which, if heat-treated, makes good flaking tools. Agatized fossil coral is chalcedony that was used to make gems. White coral artifacts have been associated with ancient Egyptian contexts of the seventh to sixth century BCE. Precious red coral from the western Mediterranean was imported to Egypt during the Ptolemaic and Coptic Periods. Pipe coral also occurs on the shores of the Red Sea and was used in Predynastic times (Lucas 1989).

In the Mediterranean, coral occurs in a wide range of forms, which vary in association with different light levels, water currents, and competition for space. Red coral or precious coral (*Corallium rubrum*) is the best known, most valued, and most collected of the Mediterranean corals. Its often intense red color is durable, and the coral can be polished to a glassy shine. The earliest known use was in Mesopotamia about 3000 BCE (Cooke 1987). It also has been found in ancient Egyptian burials. A red coral was one of the gemstones sought by Pueblo Indians.

Potential sources of prehistoric coral in the central Mediterranean include coral reefs, death assemblages on beaches, and fossil deposits. Historically and recently recorded examples of coral reefs lie scattered along most of the central Mediterranean coasts, especially in areas where islands occur, although not apparently along the west coast of the Adriatic Sea (Skeates 1993).

A symbolic value appears to have been ascribed to coral during the Neolithic and Chalcolithic Periods. The distinctive red color of the coral seems to have been especially prized, for red pieces appear to have been selected almost exclusively. Red coral was not unique in this respect, for powdered red ochre was also regularly used at this time, in and around the Alpine region, to sprinkle over and around human remains in ritual deposits and as a pigment painted onto pebbles, pottery, and cave walls. Coral was transported over a distance of at least 300 km across the western part of the Alps (Skeates 1993).

To the Romans, the red color of coral led to its association with blood. Ovid recounts the tale that coral originated from the blood that flowed from the head of Medusa (Metamorphoses 4.741ff). The ancients were uncertain of its composition, and coral was variously described as a plant and a stone. Pliny was the first to describe it at length (N.H. 32.11.464; 37.59.665). It was carved into cameos and small statuettes. Medically, it was believed to have powers of fertility and was used to treat bleeding.

Coral was used by the Celts from the fifth to the third centuries BCE to decorate the hilts of weapons and as an inlay in vessels. Coral continued to be used during the Middle Ages as a medicine and for beads and amulets. It was fashioned into handles for knives and spoons, because it was widely believed that coral would indicate the presence of poison in food (Tescione 1965).

Fossils. Fossils have been used since the Upper Paleolithic in necklaces and pendants. In southwest Ireland fossils have been found as funereal adornments in a Neolithic site (3000–2500 BCE). Brachiopods, cephalopods, gastropods, bryozoans, and crinoids from a local limestone all were found in the tomb complex (Wyse and Connolly 2002). Diatomite is a friable, fine-grained, sedimentary rock resulting from the accumulation of the opaline skeletons of diatoms. These fossilized remains vary in size from 1 μm to 7 mm, but most are 10–200 μm. Diatomite was used by the Greeks as an abrasive.

Fossil Bone. Other geologic materials related to shells are bone fossils. The term "fossil" originally meant any curious or valuable item dug from the earth, including gems. Ancient peoples collected fossil bones and pondered their meaning. An excellent summary of human encounters from the Homeric Period to the late Roman Empire is provided by Mayor (2000). She begins with the legend of the griffin as the monster guardian of gold and continues through centuries of human discoveries of fossils, including the geoarchaeologic evidence.

The Greek philosophers of the last half of the first millennium BCE recognized that small fossil shells found far from the sea represented evidence of former oceans. Large vertebrate fossils, teeth, and tusks were well known in ancient Greece and Rome. Huge bones were displayed on the Greek island of Samos. In the Roman era, paleontological hoaxes originated as a response to the conflict between popular beliefs and scientific explanation. Tensions between science and ancient beliefs remain with us today.

Often the major human use of large and unfamiliar fossil bones was the creation of legends and mythical creatures. In antiquity, large bones of extinct mammals were often perceived to be from giant humans. Many of the large bones of the Mediterranean lands were those of extinct mastodons and early elephants. Giant skeletons were common in Egypt. At Wadi Natrun, desert winds laid bare complete skeletons of large Pliocene mammals. The size of the recognizable leg bones led people to believe that humans and animals in earlier times had been much larger and were continuing to decrease in size. In Egypt, ancient shrines were dedicated to the worship of large fossil bones.

Because zooarchaeology is a product of the mid-twentieth century, it is in its infancy. The first part of the twenty-first century should yield a much stronger picture of the role of fossil bone in antiquity. Mayor's (2000) book should inspire some of this.

The use of bone for tools goes back to the beginning of human activity. Bone tools were found in the cave deposits associated with "Peking Man" at Choukoutien, China. It is difficult to carve bone with a chert knife, so bone tools in early Paleolithic times were formed by breaking and chipping. Later, bone tools were shaped by splitting and then rubbing them with an abrasive rock.

10.7 Other Geologic Raw Materials

10.7.1 Mica

Mica is the name for a group of minerals familiar to almost everyone because of their sheet-like cleavage. Muscovite, the relatively colorless mica, can be split into sheets about 0.05 mm in thickness. Muscovite can withstand temperatures up to about 440°C, but above this temperature it begins to break down. The name mica is derived from the Latin word “micare”. The earliest use of mica was as a component of cave paintings dating back 40,000 years. Mica was known to the ancient Egyptians, the Greeks, Romans, Chinese, and the Aztecs. The great pyramid at Teotihuacán in Mexico contained locally mined mica in thick layers.

In the United States, the use of mica extends back at least 6000 years. Mica, galena, Lake Superior area copper, and sea shells were exchanged throughout the eastern United States in a complex network (Seeman 1979). The use of large sheets of mica for ceremonial purposes by indigenous peoples of the southeastern United States is well known. Ferguson (1974) describes the mica outcrops and ancient mining areas in western North Carolina and other areas in the southern Appalachian Mountains. Numerous prehistoric mines have been recorded.

10.7.2 Petroleum Products – Asphalt, Bitumen, and Pitch

Oil has been seeping out of the earth for hundreds of millions of years. Perhaps the first human record of this is found in Babylonian cuneiform tablets dating to about 2000 BCE. In the fifth century BCE, Herodotus reported that oil and asphalt oozed from the ground in Asia. At some point it was learned that absorbent materials soaked in pitch, resin, and especially naphtha, could be attached to spears or arrows to produce fire missiles. Later it was realized that better results could be achieved by combining naphtha with sulfur or quicklime. By adding saltpeter, the mixture was capable of spontaneous combustion. This became known as “Greek Fire”.

According to Pliny, Alexander the Great observed natural oil seeps burning in Bactria. Although there must have been some ancient trade in oil, no records confirm this until 632 CE. The geographer al-Maqdisi indicated that Georgia was an important exporter of naphtha and bitumen to Baghdad (Bilkadi 1995).

Useful, acid-resistant, organic materials are found in the form of mineral pitch. It is black to black/brown and can be found in various consistencies from a viscous liquid to a solid. Its principal uses are as an adhesive, mortar, or caulking agent. In some biblical writings it is referred to as “pitch” or “slime”. However, this may be a distinction for the type that was found floating on the surface of the Dead Sea or marshes (slime) – some ancient sources name the Dead Sea as Lake Asphaltes – or mineral pitch found in dry wadis (pitch).

Pitch and bitumen were highly prized in antiquity. Pitch was produced partly in the form of rock asphalt from the mountains and was known from the Sumerian Period through the Assyrian Period. Bitumen was widely available in the Near East in Iran, Iraq, and the Dead Sea region. It was exploited beginning as early as 40,000 years BP in the Mousterian at El Kown, Syria. The range of uses was very wide, from the early use as a hafting material to affix handles to flint tools, through its later use as a mortar and waterproofer, to medical uses as a disinfectant, insecticide, and a component in embalming mixtures (Connan 1999). The amount of bitumen in balms varied up to 30 weight percent. The largest quantity of bitumen in

Mesopotamia was reduced from the many seepages or wells near the ancient town of Hit located on the Is River, a tributary of the Euphrates, 150 km west of Baghdad. This location is mentioned as an important source by both Herodotus and Strabo (Strabo 16, 100, 743). Arab and European travelers testified to continuous production of bitumen in this area up to the present century (Singer et al. I 1954). Pitch could be obtained as a residue from distilling tar, wood tar, or petroleum, and it also occurs naturally as asphalt.

The word "asphalt" is derived from the Greek "asphaltos", meaning to make secure, in reference to its widespread role as a binder in antiquity. The Persian word for asphalt is "mumiya", likely related to its use in mummification. The Sumerians called it "esir". It is referred to several times in the Old Testament. In the Middle Ages Muslim physicians prescribed asphalt for skin ailments and wounds. In the Far East natural asphalt was boiled to remove the lighter fraction, leaving a material that became quite hard on cooling. Statuettes were cast from this material in Japan and possibly in China. Another ancient source for asphalt is India where Mortimer Wheeler found the substance used as a cement at Mohenjo-Daro. When excavating in Israel I routinely visited the excavations at Tel Arad where Dead Sea asphalt had been used as a binder on various utensils as early as Early Bronze Age I and II.

The world's largest known asphalt deposits are the Athabascan tar sands of Canada, which cover an area of 30,000 square miles (Singer et al. I 1954). The La Brea Tar Pits of California are another important source of this material. Asphalt was used as a mastic, and oil shale was used as a fuel at two prehistoric sites in what is now Jefferson County, Kentucky, USA (Collins 1981). Other New World sources include Pitch Lake on the island of Trinidad, where Columbus obtained asphalt to caulk his ships. This source is also mentioned by Sir Walter Raleigh. In the sixteenth century, French and English pirate ships were caulked with pitch found near Lake Maracaibo in Venezuela (Singer et al. I 1954).

Two major reviews of the use of bitumen in the ancient world, with analyses to fingerprint sources, have been presented by Connan and Deschesne (1991) and Connan (1999). Connan points out the use of asphalite as beads and dice at Susa in ancient Persia. Perhaps the earliest use of bitumen was at a Mousterian site near El Kown in Syria. The bitumen was from a source located about 50 km away (Connan 1999).

Bitumen was used in the form of an adhesive to attach mosaics and ornaments of carved wood and to affix parts of statues such as eyes of mother-of-pearl, ivory, or seashell. It was also used to secure precious gems in place. In some Sumerian statuary, the eye sockets were hollowed out and filled with capsules of bitumen to make the pupils. Bitumen was also used to paint the eyelashes. It was also applied as an adhesive backing to gold foil. Singer et al. (1954) note that more than 75 contracts from the Ur III Period mention its use as a mastic or mortar. In the Near East and in classical Greece, it was softened by heating and mixed with sand, fillers, and fibrous materials for use in floors and walls. It was also employed as a waterproofing agent on bricks of buildings, drains, sewers, embankments, and quay-walls. Roads were also surfaced with bitumen. The type used for floors, walls and thresholds was comprised of about 25% bitumen, while the type used as mortar for brickwork consisted of about 35% bitumen. By the Neo-Babylonian Period, nearly pure bitumen was used as a mortar. The use of asphalt to waterproof pillars in Mesopotamia was noted by Strabo (16.100, 739). Irrigation machinery was coated with this substance, and it was used to caulk ships in the ancient Near Eastern and Mediterranean civilizations. A lump of asphalt with basket impressions found at Ur suggests that the fluid material was hardened into cakes within baskets. The Persians used bitumen only to caulk ships (Singer et al. I 1954). Bitumen was a major component of the balms used by the Egyptians to prepare mummies. It was secured from the Dead Sea area (Connan 1999).

The use of "Greek Fire" is recorded during the Classical Greek Period by Procopius (ca. 490–507?–560 CE) who states: "The Persians were the inventors of this: having filled vessels with sulfur and that drug which the Medes call naphtha and the Greeks "oil of Media" and lighted them, then hurled them against the framework of battering rams, and soon set them ablaze, for this fire consumes the objects which it touches, unless they are instantly withdrawn" (Hist. Bellorum 8.9.35–38). During the later Byzantine Empire, the components used in Greek Fire changed slightly. Finely ground quicklime was mixed with a petroleum product and was then ignited by firepots. Sulfur was added to produce poisonous smoke. Julius Africanus (fl. 220–235 CE) provides a recipe for an incendiary that uses liquid bitumen or naphtha together with unburned sulfur.

Somewhere around the first century BCE, the Chinese began to use methane, a natural gas. They recovered the methane by drilling. The Chinese were the first to use petroleum and natural gas as fuel, perhaps as early as the fourth century BCE. Shen (1989) gives a detailed account of the exploitation of oil and gas in ancient China.

Perhaps the only use of coal as fuel in prehistoric North America was by the Hopi people about 1300 CE in Arizona when they discovered that the coal they found would burn. The coal was used to fire pottery to a more yellow color than had been achieved before. Using radiocarbon evidence, Selsor et al. (2000) have shown that Late Woodland Period inhabitants of western Pennsylvania, USA, (1415–1440 CE) extracted petroleum from the earth, perhaps for medicinal purposes.

10.7.3 Sulfur (S)

Sulfur was not shown to be an element until 1772. It is nonmetallic and occurs in nature as a free element or combined with other elements. Sulfur can be found as yellow crystals, masses, and crusts. It can be recovered as a native element from numerous deposits throughout the world. Native sulfur occurs as a product of volcanism, associated with hot springs, and in salt domes. Rich deposits of sulfur were mined in Campania (Sicily) and the Aeolian Islands, and during the Classical Period it was exported to Europe. Alexandrian chemists distilled or sublimed sulfur, but not on a large scale. The earliest use of sulfur was in cave paintings in southern Europe. In powder form, it is highly flammable and was used in matches as early as the Roman Period.

The medicinal uses of sulfur are recorded as early as 3000 BCE. According to the Ebers Papyrus, Egyptian physicians used an ointment of sulfur to treat granular eyelids. Another similar prescription was found on a clay tablet at Nineveh dating to ca. 600 BCE. Sulfur occurs in association with gypsum on the Red Sea Coast in Egypt, at Ras Jemsa, Bir Ranga, and Ras Benas (Harris 1961). Small fragments are found in limestone near Cairo, and there are sulfur springs near Helwan. It has been found in various connections in ancient Egypt. Mold-cast pieces dated to the Roman Period were discovered at Qau and Badari, and small pieces dated to Greco-Roman times were found at Tanis. Amulets in the form of rosettes, bullheads, and Bes heads molded of sulfur have been dated by Harris (1961) to the Late Egyptian Period.

In Preclassical Greece, sulfur was used in both secular and religious purification and fumigation. Homer also notes its "pest-averting" properties and describes Odysseus' use of sulfur to prevent disease in his palace after he killed Penelope's suitors. This factor was not lost on the Romans who used it as a lice preventative. They also used sulfur in various salves and liniments. Pliny (N.H. 35.174–77) notes the medical benefits of hot sulfur springs to treat rheumatic diseases. Ruins of ancient Roman baths have been found around sulfur springs on both sides of the Jordan River in ancient Judea. Nonmedical uses included preparation and cleaning of cloth, bleaching wool, and as an incendiary weapon by mixing it with bitumen, tar, resin, and other combustible materials. The method by which Romans refined sulfur is not known.

Crystalline sulfur was used as a cement or filler in "hollow" gold rings found in Roman burials (Eggert et al. 1999). This article reports that sulfur was the major filler in Roman objects, has been found in some Hellenistic pieces, and in gold objects through the Byzantine Period. It had gone out of use well before the twelfth century.

After Europeans learned of gunpowder from China in ca. 1200 CE, sulfur gained an added use since it comprises 10–15% of gunpowder. In the New World it was found in the crater of Popocatepetl and was used by Cortez to make gunpowder (Singer et al. II 1954). In the sixteenth century, crude sulfur was distilled; the vapor was collected in large earthen vessels where it condensed into liquid sulfur. This was then poured through a spout and solidified. Sulfur matches are referred to in the sixteenth century (Singer et al. II 1954).

10.7.4 Mercury (Hg)

Mercury was known to the ancient Chinese and Hindus and was found in an Egyptian tomb of about 1500 BCE. The Romans started to produce mercury in Spain about the first century CE. In the Roman Empire, mercury was a by-product of gold refining. Because of its chemical mobility, the extraction of mercury from ores is a relatively simple process. Mercury distills on roasting, so a furnace with facilities for condensation is required. Crushed gold ores were treated with mercury, and the resulting compound was separated from the gangue by pressing it through leather.

Mercury was distilled off as a final step. This process is mentioned in Pliny (N.H. 33, 32.99–100) and was a common practice in the Middle Ages (Singer et al. I 1954). Mercury was found in silver and lead mines and was used in the process of gilding copper and gold leaf. Mercury was also used in ancient pharmacopea. The physician Paracelsus (1493–1541) noted that syphilis could be treated successfully by ingestion of mercury compounds.

The discovery that liquid mercury metal was used in ancient Mayan ceremonies at Lamanai, Belize, led to a study of possible sources. Other Mayan sites had also produced evidence of the use of mercury (Pendergast 1982). There are a number of cinnabar (HgS) deposits in Mexico and a few of native mercury. Pendergast discussed the geography of the deposits and the likelihood that use of mercury by the Maya reflected a painstaking process that spanned a long period of time. Haury (1976) suggests that the Hohokam peoples of Arizona, USA, used cinnabar as a body paint, securing the material from deposits in southwest Arizona.

10.7.5 Saltpeter, Niter

Niter (KNO_3) or potassium nitrate, often called saltpeter, occurs as an efflorescence in caverns and on soils in arid regions. Extensive deposits are found in many of the world's arid regions including parts of Spain, Italy, Iran, India, Russia, Egypt, and the Arabian Peninsula. The name "niter" might derive from the ancient Egyptian city of Nitria which is located near niter deposits. In ancient times, niter also was extracted from the ashes of vegetable matter.

Although referred to in the Bible, biblical "niter" is actually natron, an entirely different substance (Wright and Chadbourne 1970). Classical and early translations frequently use the word niter for natron, which was used in glass making and mummification. For example, Tacitus discusses the use of niter in making glass by fusing niter with sand from Palestine and Syria, but this substance is not identified with potassium nitrate. After they had traveled in Egypt (ca. 1550), Peter Ballon and Prosper Alpinus introduced the word "niter" into Europe in order to distinguish soda and potash (natron) from saltpeter (niter). The word "natron" was introduced into mineralogy by Linnaeus in 1736 and applied to soda only (Singer et al. II 1954). Lucas (1989) notes that no evidence can be found that niter was either known or used in ancient Egypt.

Niter is an important element in the manufacture of explosives. The Chinese were the first to recognize and purify potassium nitrate, from which they developed gunpowder. The earliest record of its use as an explosive is found in a formula for the use of sulfur, saltpeter, charcoal, and pitch with other vegetable ingredients as recorded in the Wu Ching Tsung Yao, written in 1044 CE (Singer et al. II 1954). At present, the way in which the method of making gunpowder passed from China to Europe is unknown. However, it is possible that Arab travelers and merchants were the first to identify gunpowder in their travels to the Far East. Ibn al-Baitar of Malaga (d. 1248) mentions a substance called "Chinese snow" that may be gunpowder. Formulas that combine saltpeter, sulfur, and charcoal were available in Europe around the end of the thirteenth century CE. An explosive was known to Roger Bacon (1214(?)–1294). Almost at the same time, an Arabic source, Al-Hasan al Rammah (ca. 1280–1290), described how these explosive devices were made. Another contemporary account is found in the *Book of Fires for the Burning of Enemies* put together under the name of Marcus Graecus. This book includes many recipes and directions for purifying saltpeter and making gunpowder. Saltpeter was imported to Europe from India during the later Middle Ages and also extracted from European saltpeter deposits after 1300 CE. These deposits consisted of earth from old, dry sheep stalls and stables and from incrustations on old walls and cellars. Early saltpeter of European and Indian origin contained chemical impurities that caused it to become useless if exposed to a damp atmosphere.

Saltpeter is difficult to identify because it looks like many other simple salts. The Chinese were able to identify saltpeter by the third century CE using a potassium flame test – it burns with a violet or purple flame. The first use of saltpeter by the Chinese was to dissolve otherwise indissoluble ores, such as cinnabar. They also used it as a flux in metallurgical processes.

10.7.6 Epsomite ($MgSO_4 \cdot 7H_2O$, Epsom Salt)

Epsomite, also called Epsom salt, forms in a wide variety of surficial or near-surface geologic environments. It is readily soluble. Occurrences at Epsom, Surrey, England, and at Sedlitz and Saidschitz in Germany have long been known. The medicinal value of epsom salt was accidentally stumbled upon in 1618 at Epsom, south of London. A solution of epsom salt was found to be beneficial when taken internally or used externally.

A related mineral found in desert environments is mirabilite (Glauber's salt), $Na_2SO_4 \bullet 10H_2O$. Mirabilite has been used since antiquity as a purgative in traditional Chinese medicine. The Chinese call it "mang xiao" and consider it to be a treatment for constipation, sore throat, skin ulcers, and to help heal wounds. Johann Glauber (1604–1670) isolated the compound and called it "sal mirabilis" because of its medical properties, especially as a laxative.

Epsomite and mirabilite were mined in Salts Cave and Mammoth Cave, Kentucky, USA, beginning about 4000 BP. The miners likely sought these minerals as a cathartic. They also recovered gypsum for use as a pigment (Kennedy and Watson 1997). Prehistoric and historic indigenous peoples also mined epsomite in Wyandotte Cave in southern Indiana, USA (Cande 1993). Tankersley offers evidence to show that the mirabilite and epsomite were renewable deposits. Salts mined from cave walls were naturally replenished by the following season. Mirabilite grows relatively rapidly. In dry caves replenishment can take only a few months. Humidity can stunt or even prevent the regrowth of this mineral (Tankersley 1996).

10.7.7 Nitric Acid

The concept of acids as a class was not developed until the sixteenth century, although certain acids had been familiar from antiquity (Singer et al. II 1954). There is no Latin description of the preparation of nitric acid before the *Summa Perfectionis* of Geber, although such a description is given by the Arabic Jabir. Nitric acid is also mentioned in treatises falsely ascribed to Raymon Lull (1235(?)–1315), but written after 1330. It was made by distilling niter with sulfates of aluminum, copper, or iron, previously partly dehydrated. Acid was used in the separation of silver from gold (Singer et al. I 1954).

10.7.8 Tutty/Cadmea

Ancient authors correctly identified the natural zinc carbonate variety of calamine with the white zinc oxide that is frequently formed as a byproduct in copper smelting and condenses against the furnace roof during copper smelting. In the Classical Period, this substance was known as "cadmeia" or "cadmea" (Pliny N.H. 33.94; 34.2.4, 100, 101–106, 11, 117, 119, 128, 130, 169; Dioscorides 5, lxxiv–lxxv). Its natural (?) sources during Greco-Roman times were Italy, Germany, and Cyprus. It was also found as an efflorescence in Greco-Roman smelting furnaces. However, the zinc carbonate was considered an impure product and the purer condensate (zinc oxide) was favored. Tutty was used as a solder. It was also used medicinally to treat ulcers, cauterize wounds, and as a general cleansing or drying agent. Cadmea is identical to the later "tutiya" or "tuthy" of the Moslem writers and with present-day tutty.

10.7.9 Fuller's Earth

Fuller's Earth is a fine-grained, naturally occurring rock that possesses a high adsorptive capacity. It consists largely of hydrated aluminum silicates including the clay mineral montmorillonite. It forms as an in situ weathering product. Fuller's earth was used to remove impurities (such as dirt and fat) from cloth because of its fat-absorbing qualities (Singer et al. II 1954). Sometimes lye from natron or wood-ash was combined with it and used to clean clothes.

10.7.10 Stone Money

The use of large limestone disks as stone money by early Micronesians is worth mentioning. Large rocks (megaliths) were quarried on the island of Palau by Yapese

Islanders to serve as money. The size of these round stone disks in prehistoric times probably did not exceed 2 m in diameter and 30 cm in thickness. They must have weighed well over 2 tons. These money disks were used as gifts for marriage or payment of debts on Yap, but the quarry was on Palau because there was no limestone on Yap (Fitzpatrick 2001; Hazell and Fitzpatrick 2006). For the Yapese these sculptured disks could buy almost anything, including politicians (Fitzpatrick 2004). The value of a money disk was determined by the beauty of the stone, its shape and size, and the quality of the carving.

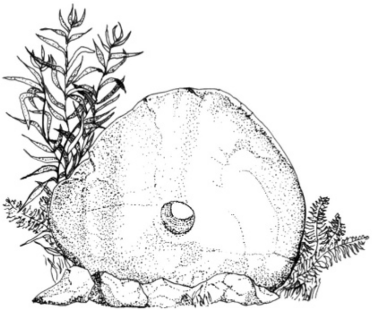

Fig. 10.7 Large limestone stone money disk

Chapter 11
Building, Monumental, and Statuary Materials

11.1 Introduction

Materials for construction are many and varied, as are their purposes and products. This chapter includes a survey of the major rocks and other earth materials used for the construction of buildings, monuments, and large statues. Not included is any discussion of the raw material needs for ancient roads, dams, or what is now called rip rap. Rock names applied to many building and monument stones are not related to mineralogy or petrology of the rock, e.g., serpentines called “green marble” and gabbro called “black granite”.

11.2 Building Stone

Humans have occupied rock shelters, caves, and grottoes since early prehistory. Early in their cultural evolution, humans turned to rocks for building shelters, first to improve a cave or rock shelter and later to construct dwellings. Before the advent of metal tools, people constructed buildings from loose rocks and boulders. Constructed stone structures began with the earliest settled communities. In the Near East, walls of stone are more than 7000 years old. For example, stone was incorporated into the walls found at Tell es-Sultan, near Jericho, dating from 6000 BCE (Prentice 1990). After the invention of metal tools, quarry techniques were developed for removing blocks of stone from geologic formations. In some instances, the quarry itself became the architecture, and the building was carved into the face of a cliff or rock outcrop. Naturally occurring caves and grottoes were also adapted and incorporated into man-made architecture. The Pueblo cliff dwellings at Mesa Verde in the southwestern USA are an example of this.

The nature of the building materials employed by any society depends on what is available. It was no accident that the great **tells** of the Middle East formed from the disintegration of mud-brick buildings. Neither hard rock outcrops nor trees were available as construction material for hundreds of kilometers around many Near Eastern habitation sites. At Çatal Höyük in Anatolia, walls and even built-in

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furniture were made of clay earth by 6800 BCE. Stone construction was a necessity in more northern regions, where timber was scarce and mud-brick walls would not survive. With the exception of timber, most building materials reflect the exploitation of stone resources. An interesting sideline on building stone was reported recently by Stone et al. (1998). In ancient Mesopotamia, building stone was rare indeed. The local craftsmen were able to manufacture a gray-black vesicular “rock” superficially resembling basalt by melting and slowly cooling local alluvial silts. Another interesting example of “artificial stone” can be seen from the Celtic vitrified forts of western Europe (Fredricksson et al. 1983). The Celts built fortifications of timber-laced, stone-filled walls. Some of these were burned, partly causing the vitrification. A wide variety of igneous, sedimentary, and metamorphic rocks were involved. The volume of the masses welded together by vitrification reached several cubic meters.

The people of ancient Egypt, Greece, and Rome were responsible for great advances in the use of quarried and dressed stone for building. By 5000 BCE, the Egyptians had learned to shape their comparatively soft Tertiary limestones into rectangular blocks. The great pyramids at Giza were constructed of limestone blocks weighing up to 16 tons that were quarried along the Nile River. Harrell (1992) has found that these ancient Egyptian limestone quarries in the Nile Valley occur in six geologic formations of Tertiary age. His investigations reveal at least 48 quarries easily recognized in the field, because the quarry walls show evidence of the careful extraction of rectangular blocks of stone. Harrell’s petrographic and chemical analyses indicate that the six geologic formations have distinct signatures.

Before 4000 BCE, the Egyptians had learned how to shape the harder granite and diorite. By the time of the 3rd Dynasty in Egypt there was a marked increase in the use of stone for buildings (Fig. 11.1). Limestone was the primary building material,

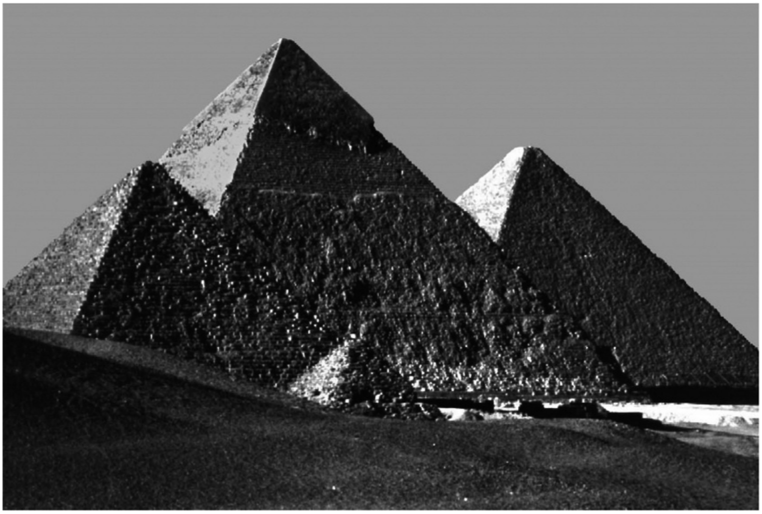

Fig. 11.1 Limestone pyramids, Giza, Egypt

but large blocks of granite were used in an unfinished pyramid located between Giza and Abusir and in the Step Pyramid of Djoser at Saqqara. By the 18th Dynasty, limestone had largely been replaced by more durable sandstone and granite. The great sandstone quarries along the Nile, about 60 km north of Aswan, bear inscriptions dating from the 18th Dynasty to Greek and Roman times.

The Egyptians removed surface layers of granite outcrops by burning papyrus on them and then drenching them with cold water. This procedure caused the granite to spall and disintegrate allowing easy removal of the partially altered surface layers. If no natural crack or joint could be exploited in quarrying the granite, a trench around the desired block was formed by pounding with balls of dolerite. Wooden wedges were inserted in cracks or trenches, driven tight when dry, then wetted to cause the rock to split in the desired direction. For an extensive coverage of stone masonry practices in Pharaonic Egypt, see Arnold (1991).

By the Late Bronze Age (latter half of the second millennium BCE), the Myceneans in Greece constructed **Cyclopean** walls by fitting angular blocks neatly together. The Greeks and the Romans developed the use of shaped (ashlar) blocks to a fine art.

Early observers realized that two types of rock were used in the construction of Stonehenge. Stonehenge is dominated by large "sarsens" which are quartzose rocks of local origin, also used at the great circle of Avebury. The other rocks, termed "blue stones," are doleritic igneous rocks. It was not until the early twentieth century that the exotic blue stones were traced, using petrologic and petrographic analyses, to the Preseli Mountains in Wales (Thomas 1923). More recent studies using X-ray fluorescence analysis have shown that the dolerites came from three sources in the eastern Preseli Hills and the rhyolitic rocks from four sources in the northern Preseli Hills (Thorpe et al. 1991). The altar stone of Stonehenge came from southwestern Wales. This variety of sources suggests that the monoliths may have been taken from a glacial deposit and not from an in situ quarry. In other words, the long transport of these large stones to the Salisbury Plain may have been accomplished by a glacier and not by humans.

Unfortunately, as with other uses of rocks and minerals, building stone is often misidentified by archaeologists. With rare exceptions, building materials are usually left at the site where they are exposed to deterioration, natural disasters, theft, and vandalism. If these materials do not survive, the notes taken by the archaeologist become the only surviving record of the site's architecture. The correct identification of building stone is crucial for in situ stabilization and conservation of the site.

The correct identification of building stone also has many implications for interpretation of a site's cultural, technological, and commercial history. Because the majority of ancient societies chose building materials that were readily available, the structural or aesthetic limitations of the material were secondary considerations to ease of procurement. The adaptations made by ancient builders to the limitations of these materials reflect technological advances and cultural bias. Conversely, the choice to use non-native materials imported from great distances provides information about trade, commerce, wealth, and political ties.

It is important to be aware of the frequency with which building stone was recycled in antiquity. This is especially true for rare and valuable decorative stone, but all types of masonry were recycled. Quarrying and dressing of stone was extremely labor intensive, and recycling structural materials was very economical. It is said that the city of Cairo was built using the facing stones of the great pyramids (Baines and Málek 1980). Systematic recycling of ancient Rome's pagan temples took place under Theodosius II with the edict of 435 (Napoleone 1997).

The most obvious evidence of recycled masonry is the presence of inscribed or carved masonry units that appear misplaced or out of context with the structure. More subtle clues can be discerned in the interconnections between the masonry units, inconsistencies in the placement of architectural details, and masonry walls containing a mixed variety of stone types and surface finishes. Full characterization and lithologic identification is essential to a complete understanding of the stone's archaeological context. Weathering patterns can also provide important information about the building stone. The **anisotropy** of sedimentary rocks is exhibited by the accentuation of the bedding planes as the stone weathers. In layered rock containing both quartz and calcite, the calcite weathers preferentially.

The varied geology of Liguria, Italy, has allowed a large number of rock types to be used in its architecture. These include a dark gray slate called "Ardesie"; a gray-pink limestone called "Pietra di Finale" (used since Roman times); a dark bluish-gray marly limestone called "Pietra di Promontorio"; a very durable sandstone of many colors; a serpentine breccia cemented by calcite veins; and a dark limestone "Portoro" used since the first century CE (Cimmino et al. 2004).

Rock-cut architecture. Rock-cut architecture first appeared in Persia around 1000 BCE. Rock-cut architecture is the practice of creating structures such as temples (India), tombs (Petra, Jordan), or dwellings (Cappadocia, Turkey) by carving the rock formation in situ. Rock-cut architecture goes back at least to the Temple of Ramases at Abu Simbel dating to about 1280 BCE. (Fig. 11.2). The Etruscans created rock-cut tombs; the Nabataeans at Petra carved massive temples and tombs in sandstone cliffs from 100 BCE to 150 CE. Buddhist monks in India carved multi-story monastic spaces beginning in the third to second centuries BCE. In Cappadocia, extensive rock-cut houses and churches were built prior to the fifth century CE. Rock-cut architecture in India is more abundant and more varied than in any other place in the world. The earliest cave temples were carved in the western Deccan around 100 BCE. Also in the Deccan Plateau is the Kailash Temple (eighth century CE), which was carved in the basalts of the Deccan Trap.

The structural qualities of stone are of great importance to the durability and utilization of building stone. These include qualities such as **compressive strength**, tensile strength, resistance to **shear**, and plasticity. The ability for structures to span openings and achieve vertical heights is limited by these structural qualities of the building masonry. For example, a limestone slab supported at either end may sag and bow over time without cracking. Gypsum is also known to be particularly weak in this regard. Igneous rocks may have less tensile strength than certain types of

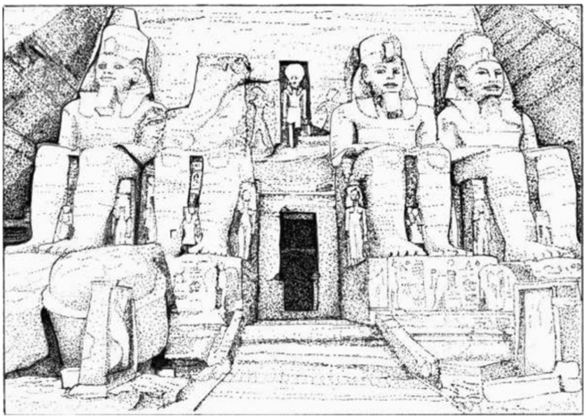

Fig. 11.2 The great rock-cut temple of Abu Simbel of Rameses II, south of Aswan on the west bank of the Nile, carved out of sandstone rock cliffs about 1280 BCE

limestones and marbles, but they have relatively high compressive strength. The often severe directional weaknesses in metamorphic rocks frequently preclude their use in large-scale structures. Following are summaries of the physical and chemical characteristics of the major building stones. Readers may want to review these rock types in Chap. 3.

11.2.1 Granite/Diorite

A typical granite is composed of 65% feldspar, 25% quartz, and 10% hornblende. The hardness of feldspar and hornblende ranges from 5.0 to 6.5, and the hardness of quartz is 7.0. Thus, granite is a hard rock. Most granites possess structural features that are important in the quarrying of **dimension stone** and material for monuments or statuary. One of the most important features is parting. Fortunately, one direction of parting is nearly vertical, and the other direction is nearly horizontal in outcrop. The ancient Egyptians took advantage of this in quarrying their huge granite obelisks (Fig. 11.3). Granites normally provide high strength in all directions. The major drawback of granites is their tendency to spall off in thin layers.

High-quality granites that were widely used for building stone occur throughout most of the British Isles, in northwestern France, in much of Scandinavia, in Italy, and in Russia. Iron Age peoples in England used granite blocks picked up from moors. Perhaps the most famous architectural granitic rock is the syenite outcropping between Aswan and the first cataract of the Nile River. This rock has been exploited since the First Dynasty for tombs, temples, and sarcophagi. It was exported to other parts of the Mediterranean for obelisks and statues. Other well-known granites are the gray granite from Aswan that was used for buildings in Egypt and exported, and the red granite porphyry quarried near the first cataract of the Nile that was used for sphinxes and statues in Egypt. The Romans shipped this stone to Italy and other provincial cities throughout the Roman Empire.

Fig. 11.3 Unfinished pink granite obelisk, Aswan, Egypt

Fairly abundant, often mechanically tough and free of cracks, aesthetically pleasing, and capable of taking a high polish, these igneous rocks were widely used in construction of large monuments. They were also used as early as Predynastic times in Egypt for bowls and vases, and for statues, obelisks, and stelae.

The Pharaonic Egyptians carved single large obelisks from Aswan granite and used diorite for carving large statues. The granite quarry at Aswan was worked since 4000 BCE and was used for the famous obelisks known as “Cleopatra’s Needles”. Diorite has been used in Egypt since Neolithic times when it was used for axes, palettes, and mace heads. Granite and diorite vary considerably in composition, texture, color, and durability.

Unfortunately, nonspecialists have identified many igneous rocks from archaeological contexts erroneously, and these errors have been compounded and perpetuated by archaeological tradition. Once in the literature, wrong names are hard to correct. Diorite is a good example. Some true diorites were quarried in Egypt for statues and bowls, but many Egyptian monumental and statuary rocks that were granite or monzonite have been misnamed “diorite”.

Harrell and Brown (1993) have clarified some of the misunderstandings surrounding the misuse of the word “diorite”. Their work on Chephren’s Quarry in the Nubian Desert of Egypt identifies the rock as a gneiss. This stone was called “mentet” by the ancient Egyptians and was a major rock used since the 4th Dynasty.

The Great Wall of China, which I have visited throughout much of its 6000 km length from Gansu Province on the west to the Bohai Sea on the east, was constructed from many varieties of local materials. Near Beijing a section was built using granite block at the base and bricks above. In most sections it is rubble-filled. Many sections, including the section near Beijing and the section where the wall reaches the sea, have been nearly completely rebuilt. The early Qin and Han Dynasty walls used some stone but also employed soil, clay, sand, wood, and tile.

11.2.2 Porphyry

Many rocks called “porphyry” in the archaeomineralogic literature are granite porphyries. To geologists, *porphyry* is a textural term (large crystals in a finer matrix) that can modify many rock names. The Green Porphyry of Greece and the Red Porphyry of Egypt have been widely used as ornamental stones since at least the early days of the Roman Empire. The stone from the Marathonisi Quarries, Laconia, Greece, the “Marmor Lacedaemonium Viride” of Pliny (*N.H.* 36.55) was later known as *Porfido Serpentino* or *Verde Antique/Antico.* Mineralogically, this latter term refers to an andesite porphyry containing crystals of feldspar. In the second century CE, Pausanias observed that the stone was quarried near the village of Krokeae, in western Laconia, Greece, and that it was used to decorate swimming-baths and fountains (*Description of Greece* 3.21.4). Porphyry was extensively used throughout the Roman Empire and can be found in Roman villas in Great Britain and in Ireland (Ashurst and Dimes 1998).

“The [red porphyry] was first quarried from Lykabettus, north of the hill Gebel Dukhan in the Eastern Desert of Egypt apparently by the Romans and not by the Egyptians. This is the only known locality where this rock occurs. Columns nearly 40 ft (12 m) high were sent from Rome for use in St. Sophia, Constantinople” (Ashurst and Dimes 1998, p. 54). The Romans used porphyry for inlaid panels at the Pantheon (Werner 1998). The quarries at Gebel Dakhan ceased operation after the Arab conquest of Egypt in the seventh century CE. After this date, the use of Egyptian porphyry became very rare, even in Egypt. However, exploitation of the stockpile of Egyptian porphyry in Rome continued into the medieval era (Deér 1959). Thus, the porphyry found in medieval structures was most likely salvaged from earlier classical structures.

11.2.3 Basalt/Andesite/Dolerite

Basalt is composed of plagioclase feldspar and ferromagnesian minerals, particularly augite. It is fine-grained and often extremely tough. Basalt has been widely used for tools, querns and, in Egypt and Central America, for statues. For a more detailed explanation of the compositional and textural relationship between basalt, andesite, and dolerite, see Chap. 3.

The earliest stone vessels in Egypt were Neolithic vases made of basalt. Basalt is widely distributed in Egypt and was used as early as Old Kingdom times as a paving material in the necropolis stretching from Giza to Saqqara. The source of the basalt was the Fayum, where one can still observe the ancient quarry. During Pharaonic times, basalt was used in statues and sarcophagi. When found in commercial deposits, basalt is sometimes called trap or trap rock.

Volcanic tuff can be of andesitic or basaltic composition. It is fine-grained and easy to work. Tuff was used by the ancient Etruscans and Romans as both a pozzolanic compound to manufacture cements and as building blocks (Ashurst and Dimes 1998). The ancient Byzantine city of Cappadocia was carved into the surrounding andesitic tuff.

Basalt rocks have also been used for architecture (Fig. 11.4) and megalithic works of art. Thirty-four monasteries and temples were carved into a basaltic cliff at Ellora, India (600–1000 CE). The world's largest Buddha statue (eighth century CE) is carved into the basalt peak of Mount Lingyun at Leshan, China. The famous Buddhist temple of Borobudur (ninth century ACE) in Southeast Asia is constructed of andesite (Shadmon 1996). In the large buildings they constructed, the Incas used big blocks of andesite from quarries in the southern sierra of Ecuador and also from quarries near their capital in Peru. Some of these andesite blocks apparently were transported up to 1600 km from their source (Ogburn 2004).The Romans used dolerite to build part of Hadrian's Wall. Large blocks of dolerite were incorporated into an Iron Age camp at Titterstone Clee, England (Ashurst and Dimes 1998). Dolerite was also used for carvings in the New World; for example, a miniature bat from the coast of Ecuador (Bushnell 1965). Basalt was used widely in the Valley of Mexico for monumental stone throughout Precolumbian times.

The most widely used stone in the historical architecture of Naples, Italy, called "Piperno", was secured primarily from underground quarries. Piperno is a volcanic rock with feldspar and pyroxene as the major constituents. It was used as far back as the eighth century BCE and became the stone of choice for the monuments of Naples (Calcatera et al. 2007).

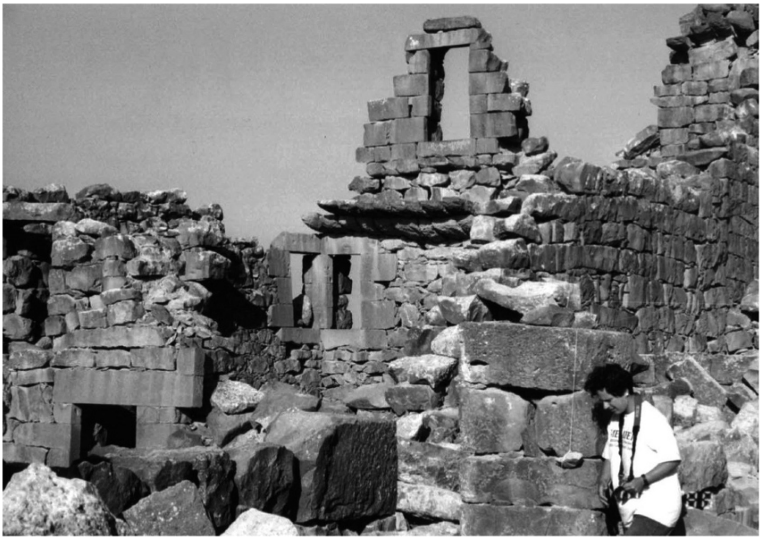

Fig. 11.4 Umm el-Jimal, Jordan, is constructed almost entirely of local basalt

"Basaltina" is a unique Italian light gray basalt with specks of volcanic ash that has been used as an elegant building stone for more than 1000 years. Basaltina has a dense and uniform structure and is frost resistant. It has been a common building stone in Umbria, Italy.

11.2.4 Limestone/Sandstone

The first use of the term "limestone" was in the literal sense: a stone from which lime could be extracted. In modern geologic usage, the term limestone includes sedimentary rocks composed of 50% or more calcium carbonate. Most limestones exploited throughout history contained more than 90% carbonate. Limestones form in several ways. They may be detrital, chemical precipitates, or biogenic (often made up largely of shells). The outer facing of the great pyramids of Egypt is limestone. The great Gothic cathedral at Chartres, France (begun in 1194 CE), is constructed of limestone. Limestone was used by the Inca to construct Sacsahuaman (ca. 1500 CE), a fortification built of megalithic polygonal blocks (Von Hagen 1961). Another example of a well-known site that was constructed of limestone is ancient Troy near the Aegean Sea in northwest Turkey. I worked at Troy on and off for many years. (Rapp and Gifford 1982) The massive walls and structures were built from the abundant local bedrock limestone. (Fig. 11.5)

Tufa is another rock that is composed principally of calcium carbonate. It forms when calcium carbonate is precipitated out of water near hot springs or along shorelines. Large deposits of tufa are found in Italy, and these deposits

Fig. 11.5 The author inspecting the walls of ancient Troy built out of the local bedrock limestone (Rapp 1982)

were exploited by ancient Romans. Because of its porosity, the stone is lightweight and is a good insulator. Tufa was used in some medieval cathedrals to fill the spaces between the **voussoirs** of vaulted ceilings (Ashurst and Dimes 1998). Called "Lapis Tiburtinus" by the Romans, *travertine* is a compact form of tufa. It was used by Romans to construct the Colosseum. Travertine was employed in the construction of monuments in Umbria, Italy, from the Etruscan Period to the Renaissance (Petrelli et al. 2004). A light brownish travertine was one of ancient Egypt's most popular ornamental materials. Prolonged exposure to sunlight bleaches this rock to nearly white because ultraviolet light destroys color centers in the calcite that were generated by natural radioactivity in the mineral (Harrell et al. 2007).

Onyx-marble stone is actually fine-grained calcite (Ashurst and Dimes 1998). It is generally not used as dimensional stone, but for decorative veneers and objects. Pure dolomite rock, composed of the mineral dolomite $CaMg(CaCO_3)_2$, is rare. However, the mineral dolomite frequently occurs in limestones.

Dolomites do not weather well in heavily polluted atmosphere (Ashurst and Dimes 1998).

An interesting Devonian limestone with a deep black color has been used in inner and outer architectural elements in historic buildings in Kracow, Poland. The black color is caused by an admixture of bitumens and/or the alteration of pyrite. The rock releases an odor of petroleum if struck with a hammer. The properties of this rock – density, compressive strength, and durability under atmospheric factors – have made it a favorite building stone.

Sandstone is a sedimentary rock formed of interlocking grains. When poorly cemented, sandstone lacks the inherent durability of igneous rocks such as granite. Sandstones that are well cemented by silica, calcite, or iron oxide make durable building stone. In the past, sandstone used for dimensional stone was quarried in much the same fashion as other building stone. In addition, stonecutters took advantage of joints, bedding surfaces, and type of cementation. Many sandstones exhibit layers called "bedding planes". The orientation of the bedding planes in a wall is particularly important since they are potential planes of weakness. Thus, laying the bedding planes vertically may encourage **exfoliation** of the stone. Even when bedding planes are laid horizontally, differential weathering tends to occur along these layers, resulting in recessed bands. Pueblo sites of North America, like Mesa Verde, incorporated sandstone into the natural sandstone cliffs and grottoes.

The ancient city of Petra is located in Jordan's Wadi Musa, a canyon eaten into sandstone by centuries of wind and water erosion. The site is entered through a narrow passage known as the "syk". Evidence of occupation at Petra includes rock shelters dating from the upper Paleolithic (10,000 BCE). However, the most famous and elaborate buildings were carved directly into the rock by Nabatean stonemasons in the first century CE (Fig. 11.6).

In Britain, Durham Cathedral, begun about 1093 CE, was constructed of the local Low Main Sandstone, a fine-grained sandstone with angular quartz grains making up 70–85% of the rock. Other mineral constituents include feldspar, muscovite, and

Fig. 11.6 El Khazneh, Petra, Jordan, first century CE

a small percentage of clay minerals. Carbonate minerals are mostly absent, making this rock more durable under weathering conditions. Interior floors and columns were made of marble (Dunham 1992).

11.2.5 Marble

Marble is a metamorphic rock consisting of recrystallized calcite (and/or dolomite). Some marbles contain a significant percentage of dolomite. The hardness of calcite is 3.0, and the hardness of dolomite is 3.5–4.0. Marble's softness allows it to be quarried easily and cut or carved into columns or statuary with relative ease. The durability of marble surfaces depends to some extent on texture and composition of the stone, but more especially on atmospheric conditions. The compressive strength of marble is sufficient to support many times the weight of structures in which it was commonly used. Marble can be found in thick deposits of wide areal extent that are relatively free of cracks and easy to quarry. It takes a high polish. The chief drawback of marble is its high susceptibility to disintegration under the action of acid rain. Marble is not a hard rock and tends to wear rapidly if used on floors and steps.

Marbles occur in a wide range of colors. Pure marble (calcite) is a brilliant white. Disseminated graphite in the marble changes the color to gray or blackish-gray. Green tints result from the presence of chlorite. Pink and red marbles owe their color to finely dispersed hematite or manganese carbonate. Yellowish or cream-colored marbles contain limonite. These colors may be evenly distributed or they may occur in bands.

There has often been some confusion in archaeology in the identification of marble versus what is now called lithographic limestone. Marble has a granular texture with grains that are large enough to see with the naked eye, whereas lithographic limestone is an extremely fine-grained and durable limestone that has a conchoidal or subconchoidal fracture. The most famous example of lithographic limestone is the Solenhofen limestone of Germany.

Marble is plentiful in western Anatolia, Italy, Greece, and elsewhere in the Mediterranean area, so it was widely used in that region. The principal marble production in Italy for the last 2000 years has been the quarries at Carrara. During the Roman Empire, this marble was exported all over the ancient world. These quarries are in the Apuan Alps, about 50 km northeast of Pisa.

In the Greek and Roman Periods, both Greece and western Turkey provided major building and statuary marble. Greek sources included the Cycladic islands of Paros and Naxos, the northern Aegean island of Thasos, two quarry areas in Athens (Mount Pendelikon and Mount Hymettus) and Doliana, near Sparta. In western Turkey, the principal sites included Proconnesus, Ephesus, and Afyon. However, many smaller or secondary sources were exploited throughout the Aegean area. In the early 1990s, the author visited a new marble quarry near ancient Troy. There was no indication of ancient quarrying; however, such evidence could have been obliterated by modern quarrying in the area.

The Parthenon in Athens, Greece, is without doubt the most famous marble structure in the world. The Parthenon, completed in 438 BCE, is constructed of local marble (Richter 1980; Fig. 11.7). Pliny took great interest in describing the various decorative marbles available in ancient Rome (*N.H.* 36 passim). Marble was the preferred stone for statuary and monuments in the classical world. In Egypt, it was also used for vases.

A dolomitic marble from the Monte Pisano quarries was the stone most often used during the Middle Ages in the construction of religious buildings in the Tuscan cities of Pisa and Lucca. The Monte Pisano Marble is sometimes called "Calcare Ceroide" (waxy limestone) in the geologic literature. This rock outcrops over an area of 7 km^2. Exploitation goes back to the Etruscans, but it was the Romans, probably in the first century BCE, that began intensive quarrying. Lithologically there are two distinct types of Monte Pisano Marble: a high dolomitic type and a low dolomitic type (Franzini and Lezzerini 2003).

The internationally famous Taj Mahal at Agra, India, was made of white marble and other precious stones in the mid-seventeenth century CE. The rocks came from all over India and nearby countries. The white marble came from Rajastan, India; the jasper from Punjab; the jade from China; the turquoise from Tibet; the lapis lazuli from Afghanistan; the sapphire from Sri Lanka; and the carnelian from Arabia.

Fig. 11.7 Acropolis, Athens, Greece: structures built from local marble and limestone

11.2.6 Slate/Schist/Quartzite

Slate is a microcrystalline metamorphic rock characterized by a highly developed rock cleavage. The common colors of slate are black, gray, purplish, and greenish. Composed of quartz and stable sheet silicates (such as muscovite mica), slate has a high durability. Prehistoric tombs built of slate in the French Alps are still in good condition after 2500 years. Slate is commonly used for roofing and paving tiles.

Schist is a metamorphic rock composed largely of quartz and muscovite, with a pronounced foliation. It was used as building stone in ancient Greece. Large blocks of schist were incorporated into the acropolis of the ancient city of Karthaia on Keos Island (Kolati and Mendoti, in Waelkens et al. 1992). On Knossos, the "use of irregular slabs of blue-green schist as the underlying material of painted stucco is itself a marked characteristic of Minoan houses belonging to the transitional era that marks the end of the Middle and the beginning of the late Minoan Age" (Evans 1964, Vol. II, Part II). Most schists fracture too easily along the planes of schistosity (foliations) to be used in buildings or monuments.

In southwest India, during the eleventh to mid-fourteenth centuries CE, the temples and sculptures were built from local talc or chlorite schists (Newman 1988). With these two soft minerals as major components of the rock, shaping was

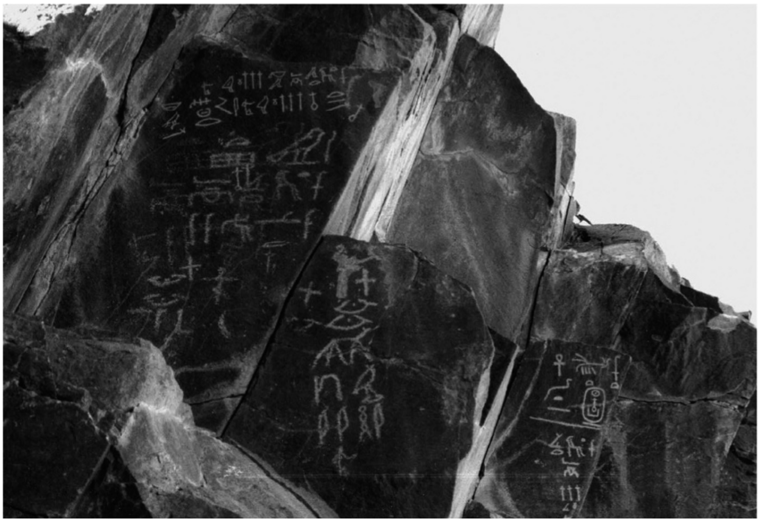

Fig. 11.8 6th Dynasty Pharaonic inscriptions on quartzite, Bir Mueilha, Egyptian Eastern Desert

relatively easy. The author has visited dozens of stone monuments and sculptures in the northwestern half of India. A wide variety of igneous, metamorphic, and sedimentary rocks were carved in situ or quarried for the stone. Newman (1992) has investigated and characterized many of these rocks throughout India. Newman found mainly carbonaceous schist, mica schist, steatite, and sandstone.

Despite its hardness and great cohesion, quartzite was used in ancient Egypt for sculptures and architecture. Egypt has several quartzite deposits including one near Cairo, and the other just north of Aswan. These two were the sources for many of the quartzite monuments (Stross et al. 1988).

Rocks exposed to weathering over long periods of time develop a weathering rind of alteration products. An interesting example of how some ancient scribes took advantage of this can be seen in Fig. 11.8. By scribing through the dark weathering rind on the quartzites and related metamorphic rocks of the Egyptian Eastern Desert to the lighter quartzite underneath, the scribes were able to have the inscribed hieroglyphics stand out in sharp contrast.

11.2.7 Gypsum

Gypsum is both a mineral, $CaSO_4 \cdot 2H_2O$, and a rock composed chiefly of the mineral gypsum. Gypsum rock was generally not used for dimensional masonry. An exception to this is the Palace of Minos at Knossos, where gypsum blocks and slabs were used as units (Evans 1964, Vol. II, Part II). Gypsum was more commonly used as decorative veneers and objects, especially the fine-grained form of gypsum known as alabaster. Gypsum is found in nodules in sedimentary rocks, and may be present in dimensional stone as inclusions. Gypsum is often found as chinking between blocks or in rubble fill of cavity walls. However, large nodules when plentiful were sometimes used in construction of desert cobble walls (Ashurst and Dimes 1998, p. 87).

11.3 Cements and Mortars

11.3.1 Lime

Since at least the third millennium BCE, lime has been used as one of the most basic components of mortar (Dix 1982). Lime can be procured by burning limestone, marble, shell, coral, or bones (Mazzullo and Teal 1994). Limestone is the most common source, and both calcitic and dolomitic limestones can be used.

Lime is simple and cheap to prepare. Limestone is heated in a kiln to over 900°C; the CO_2 is driven off and CaO remains. The resulting product (calcium oxide) is traditionally referred to as "quicklime" or "unslaked lime". This **slakes** with water and, when mixed with sand, makes mortar or plaster; 100 kg of pure limestone yield 56 kg of lime.

The minimum effective temperature for burning limestone is 880°C, but, in order to achieve this temperature throughout the limestone, the overall surface temperature must be about 1000°C. Conversely, excessively high temperatures are also undesirable. "Excessive temperature produces 'hard burned' lime of high shrinkage, high density, and low chemical reactivity. In contrast, lower burning temperatures result in 'soft burned' lime of low shrinkage, low density, high porosity, and high chemical reactivity" (Adams et al. 1992).

After burning, lime is further processed by "slaking", which refers to a hydration process. The resulting calcium hydroxide is traditionally referred to as "slaked" lime. There are four basic methods for slaking lime (McKee 1973). These include:

1. "Sprinkling" or "drowning" in which the correct amount of water is sprinkled over the quicklime.
2. "Immersion" in which the quicklime is placed in a basket and submerged into water. The basket is drawn up after a time. The slaking is completed by exposure to moisture in the air.
3. "Exposure" in which quicklime is exposed to the air in a shelter. It absorbs moisture from the air, but may also absorb any unreacted calcium carbonate, thus resulting in an inferior product.
4. The "lime paste" method in which the lime is mixed with water in pits. The slaked lime is aged in the pits or clay jars for weeks, sometimes even months or years. This method produces the most satisfactory product.

Due to the caustic nature of the lime and the potential for violent chemical reaction, slaking can be a dangerous task. If not done carefully, the heat of the reaction can raise the water temperature to the boiling point and cause serious burns to people. The amount of time required to slake lime properly depends on the composition of the quicklime and how it is processed. “The hydration of ‘hard-burned’ lime may take years at atmospheric pressure. Other factors can also retard the hydration of lime to produce $Ca(OH)_2$. Impurities can coat the oxide with a slag, resulting in low water adsorption. Excessive water will mute the heat of the reaction” (Adams et al. 1992).

As the slaked lime mixture ages, it becomes gelatinous. The workability and plasticity of the mixture continues to improve over time, as long as it is protected from the air. Lime also increases in volume according to the type and amount of impurities present. For example, “fat” lime (lime that contains a large amount of clay) absorbs approximately half the amount of water as a lime that does not contain large amounts of clay (McKee 1973).

An adequate temperature for burning lime can be easily attained in an open wood-burning fire if a bellows is used. Limestone and fuel can also be placed in a shallow pit, lit, and covered with earth (Dix 1982). However, higher and more controlled temperatures can be achieved with a kiln. A crude kiln can be formed by constructing alternating layers of lime and fuel, and covering them over with a clay skin ventilated through stoke holes (Ashurst and Dimes 1998). In the Middle East, evidence for basic lime-burning technology can be found on archaeological sites dating from the Neolithic Period.

Archaeological evidence of lime plasters “can be traced back to the Epi-Paleolithic Geometric Kebaran (ca. 12,000 BCE) and its use in architecture to the Natufian (10,300–8,500 BCE)” (Kingery et al. 1988). The utilization of lime plasters in the Near East became widespread during the Pre-Pottery Neolithic after sedentarism and the domestication of plants and animals, but before the development of pottery and metal smelting.

Prehistoric cultures also used lime as an adhesive and for the manufacture of vessels, beads, and sculptures. The various uses of lime expanded during the Greco-Roman Period, and ancient classical authors wrote of lime’s many uses in agriculture, medicine, and manufacturing (Dix 1982).

The production of lime was a major industry during antiquity in nearly every region. As a result, it was widely commented on in ancient texts, and we are well informed regarding ancient lime manufacture. The first step in lime processing entailed the burning of limestone in a kiln. Marcus Porcius Cato (Cato the Elder) instructs his readers on the burning process as follows:

> Build the lime-kiln ten feet across, twenty feet from top to bottom, sloping the sides in to a width of three feet at the top. If you burn with only one door, make a pit inside large enough to hold the ashes, so that it will not be necessary to clear them out. Be careful in the construction of the kiln; see that the grate covers the entire bottom of the kiln. If you burn with two doors there will be no need of a pit; when it becomes necessary to take out the ashes, clear through one door while the fire is in the other. Be careful to keep the fire burning constantly, and do not let it die down at night or at any other time. Charge the kiln, let the throat run straight down. When you have dug deep enough, make a bed for the kiln so as to give it the greatest possible depth and the least exposure to the wind. If you lack a spot for building a kiln of sufficient depth, run up the top with brick, or face the top on the

> outside with field stone set in mortar. When it is fired, if the flame comes out at any point but the circular top, stop the orifice with mortar. Keep the wind, especially the south wind, from reaching the door. The calcination of the stones at the top will show that the whole has calcinated; also, the calcinated stones at the bottom will settle, and the flame will be less smoky when it comes out (On Agriculture, xxxviii).

Cato's description refers to a "periodic" or "flare" kiln that did not burn continuously. The lime did not come into contact with the fuel during the firing (utilizing radiant heat), which resulted in a clean product free of ash. The quality of the final product was also influenced by the presence or absence of impurities in the limestone. Vitruvius, Pliny, and Cato all discussed the merits of silex, a hard, compact limestone. Pliny also discussed the manufacture of hydraulic limes achieved by burning millstones. Palladius included travertine, various gray and red limestones, marble, and "spongia" as suitable materials for lime manufacture (Dix 1982, p. 334).

Pliny recommended using slaked lime that had been aged for at least 3 years. Lime that had not been slaked long enough would ultimately crack on the walls and produce an inferior result. According to Pliny, the slaked lime should be lumpy. It is tested by its adhesion to a trowel and "should cling like glue" (*N.H.* 36. 175–177).

Lime is the basic binder in most mortars. However, lime was not always available, so mud was also a commonly used binder. Some societies discovered that the mud mortar was easier to work with and stronger if they mixed it with burned lime. This required much smaller amounts of lime. Thus, combining mud and lime was an alternate solution if there were no kilns for burning lime in large quantities, or if limestone was only available through trade. Certain types of soils also contain naturally occurring calcium carbonate, so analyses of these ancient materials must distinguish unaltered mud mortars from those that have been modified with additives such as lime, straw, ash, blood, or other locally available organic material. Sascab is a powdery white to reddish yellow carbonate sand found in Yucatan, south Mexico, Belize, and Guatemala. It was used as a plaster by the early Maya when the production of lime was insufficient.

11.3.2 Gypsum

Historically, gypsum has been used in the manufacture of both mortar and plaster. Gypsum occurs in association with limestone, halite, calcite, and anhydrite. Most gypsum is formed as the result of evaporation of seawater that has a large amount of calcium sulfate in solution. The gypsum occurs as long parallel needles, fine-grained alabaster or selenite (clear) sheets.

Gypsum minerals heated between 130 and 160°C form the hemi-hydrate. If it is over-heated, anhydrite will be formed. When the hemi-hydrate is mixed with water it reforms crystalline gypsum in the plaster of Paris reaction. Gypsum may be used by itself or it may be mixed with lime putty. During prehistoric use, gypsum was sometimes preferred over limestone as a plaster especially in areas with limited fuel for burning because it required lower firing temperatures.

Gypsum can also be added to mortars and cements. A gypsum mortar ideally has 25–30% gypsum. Gypsum itself often contains clay impurities that contribute to the chemical properties of the resulting mortar (Almagro 1995). Gypsum mortars develop an interlocking crystal structure in the presence of water (Adams et al. 1992). Gypsum used in this manner controls shrinkage and slows setting time in mortars and cements (Lechtman 1986). The slower the setting time, the stronger the mortar or cement will be. Gypsum-lime mortars have been shown to be superior in strength to lime mortars, especially in tension.

11.3.3 Aggregates

Aggregate is a mass of rock or mineral particles used for mixing with a cementing material to form mortar or plaster. Aggregates can include bits of crushed pottery or terracotta (grout), crushed stone, or even debris from old buildings (Lechtman 1986). However, the most common aggregate used in cements and mortars is quartz sand. Vitruvius divided sand into three categories: sea sand, river sand, and pit sand. He recommended the use of the latter, because the other two categories can contain harmful impurities. This is particularly true of sea sand containing salt, which can recrystallize in the mortar or concrete causing accelerated deterioration.

Ideally, a binder is mixed with the aggregate in a proportion that will fill all the voids present in the volume of the aggregate. The ratio of voids will increase according to the aggregate's coarseness and uniformity of size. Relatively coarse particles of varying sizes are preferable for filling in voids and producing a strong mortar (Ashurst and Dimes 1998).

Aggregates used as filler have an important influence on the final physical properties of mortars and cements. In addition to potential reactivity, aggregates also influence porosity and strength. The qualities that the aggregates impart to mortars and cements are based on mineralogical composition and the size and shape of the aggregate particles, as well as preparation of the material before it is added to the mortar or cement mixture.

Aggregates can be either reactive (i.e., pozzolanic) or nonreactive (see Sect. 11.3.4). The level of reactivity depends on the amount of amorphous silica and alumina in the aggregate as well as the size of the particles. Smaller particles increase the surface area with which the lime can react chemically. Thus, a cement with small particles of a reactive aggregate is stronger in compressive strength than a mixture of the same composition with larger particles. The use of well-sorted small volcanic aggregates insures maximum reactivity.

Vitruvius recommended washing aggregates before using them in cements. This turns out to be very important. Unwashed volcanic sands contain large amounts of nonreactive earth materials. The Romans added the volcanic sand based on proportional measurements. The use of unwashed sand could thus result in the inclusion of a smaller amount of reactive material, resulting in an inferior grade of cement (Lechtman 1986).

11.3.4 Hydraulic Reactions

There are two methods by which limes and mortars "set" or harden. (1) Nonhydraulic limes and mortars set by evaporation of water vapor. For example, a slurry of nonhydraulic lime, quartzite sand and water hardens as the water evaporates. (2) Conversely, some mortars, some limes (those which contain more than 10% silicates) and all cements set by nonevaporative chemical reactions that do not require atmospheric evaporation. These are hydraulic reactions in which water is one of the constituents of the chemical reaction.

Cements and hydraulic mortars are classified as ceramics. The hardness of ceramics is a result of partially covalent bonding. Ceramics can be usefully divided into three groups: naturally occurring ceramics, ceramics produced by chemical reaction, and ceramics produced by heat treatment (Cotterill 1985). Cements and hydraulic mortars are ceramics produced primarily by chemical (i.e., hydraulic) reaction, and thus fall into the second group.

Thorough mixing of a cement or hydraulic mortar is important to the final product. Simply turning over the mixture is inadequate. In ancient times, the mixture was traditionally chopped, beaten, and rammed with wooden paddles. The result was improved workability and performance of the mixture. "The value of the impact is to increase the overall lime-aggregate contact and to remove the surplus water by compaction of the mass" (Ashurst and Dimes 1998).

Cements develop in two stages. During the initial setting reaction, the cement achieves only a small percentage of its ultimate strength. During the subsequent curing stage, the cement mixture experiences slower hydration and eventual conversion to a hydrated calcium silicate glass. In modern Portland cements this process can take years (Lechtman 1986). In fact, the slower the cement cures, the stronger the final product. This is one reason cement can achieve a higher strength under water. The absence of evaporation encourages maximum water absorption into the chemical reaction. However, there are many factors that can affect strength, and there are currently no data available regarding the curing time of Roman cements.

Lime-based compounds formed by chemical reaction are said to be *hydraulic* or *pozzolanic*, and the materials that drive these reactions are called *pozzolana.* The term has been used since ancient times and derives from the name of the town Pozzuoli in southern Italy. The ancient Greeks and Romans were familiar with this technology, although they did not understand the chemical reaction. The ancients knew that not all soils and rocks produced a hydraulic reaction with slaked lime. Thus, they had to depend on trial and error when attempting to make cement. The Romans discovered that by adding certain volcanic materials to lime, a very hard cement was produced, which would harden even under water.

In order to understand hydraulic lime reactions, it is important to understand the nature of silica. Silica plays the central role in chemical reactions that produce cements. Reactive silicas have weak ionic bonds that can be broken easily. This enables the silica to react chemically in the cement mixture. Conversely, nonreactive silica, such as quartz, has very strong ionic bonds.

Reactive silicas tend to become "colloidal" when exposed to highly alkaline substances such as lime. Colloidal silica refers to stable dispersions or **sols** of discrete particles of amorphous silica. Ideally, reactive silica has a high specific surface area that enables it to be absorbed into the chemical reaction. Put another way, the aluminosilicates that comprise pozzolanic sands are chemically reactive, in part because the grains of sand preserve the highly porous internal structure and large surface area that results upon solidification of the molten, gassy magma generated during volcanic eruption (Lechtman 1986).

11.3.5 Natural Pozzolana

There are a variety of materials that will produce hydraulic reactions of varying intensity. Pozzolana can be divided into two groups: natural and artificial. Natural pozzolana includes diatomaceous earth, pumice, volcanic tuffs, and some shales. Natural pozzolana can be further subdivided based on how it formed. In one group of natural pozzolanas, the main component is glass produced by fusion. This group includes volcanic ashes and tuffs, pumice, scoria, and obsidian. The second group of natural pozzolanas includes those derived by the weathering of rocks. The ingredients common to all natural pozzolana are reactive silica and alumina.

The proportion of silica has a significant impact on the strength of the resulting cement. For example, pumice and tuff have a high reactivity since they are high in silica. Basalts and other mafic volcanic rocks will not react as well, because they are too low in silica. Rocks that resulted from explosive volcanism are generally higher in silica than those that resulted from lava flows.

In pozzolanic materials derived from rock weathering, the "silica constituent contains opal, either from precipitation of silica from solution or from the remains of organisms. Examples of these are diatomaceous earth, chert, opaline silica, lava containing substantial amounts of glassy component, and clay which has been naturally **calcined** by heat from a flowing lava" (Hill et al. 1992). Again, not all varieties of these materials will make good pozzolana; it depends on their specific constituents. Most natural pozzolanas owe their activity to one or a combination of five substances: (1) volcanic glass, (2) opal, (3) clay minerals, (4) zeolites, and (5) hydrated oxides of aluminum (Price 1975).

Certain types of limestone can also be pozzolanic by themselves. These limestones are used to manufacture "pozzolanic" or "natural" cements. Lea (1956) gives the following definition: "Natural cements are materials formed by calcinating (heating) a naturally occurring mixture of calcareous and argillaceous (clay) substances at a temperature below that at which sintering (in a fusible powder, just below the melting point, particles do not melt but are fused together) takes place." Natural cements obtain all of their physio-chemical properties from the limestone without the aid of other pozzolanic additives (Insley 1955:197).

The production of lime cement appears to go back about 9000 years at Galilee in Israel where a mortar floor was discovered (Bentur 2002). The floor consisted of several layers of calcium carbonate that resulted from the natural alteration of slaked lime. The Egyptians began using gypsum and lime mortars about 5000 BP. The Romans improved on lime mortar by adding volcanic ash to make a pozzolana cement. Following the fall of Rome the technology of cement manufacture was lost until the Middle Ages.

11.3.6 Artificial "Pozzolana"

Artificial pozzolanas are materials that produce a hydraulic reaction similar to the reaction produced by natural pozzolana. Artificial pozzolana can be organic or inorganic material. Examples of inorganic materials include calcined clays and shales, furnace slag, fly ash, and brick powder. Organic artificial pozzolanas include ashes from rice husks and coffee hulls. The use of rice husk ash is particularly well documented. After burning, the remaining material is predominantly reactive silica. Mixing these fine-grained pozzolanic materials with wet lime develops a gel-like structure that expands as it sets, making it a tight, essentially permanent bonding agent.

Pottery and brick dust are the most popular artificial pozzolanas. Their main constituent is calcined clay. Clays are products of mechanical and chemical weathering of igneous rocks. Microscopically, clays are flat plate-like crystalline particles less than 2 μm in size. Clays can be considered active or inactive depending on how much water they are capable of absorbing. Thus, the amount of alternate swelling, shrinkage, warping, and cracking will depend on the type of clay. Clay mineral particles will stack in layers and adhere to each other much the way two layers of wet plastic sheets sometimes do. When fired, the clay becomes vitrified or glassy.

If fired at a high enough temperature, calcined clay may make an excellent pozzolana. High-fired brick and pottery dust makes a much better pozzolana than low-fired brick and pottery dust (Lea 1973). Research has shown that the size and distribution of the clay particles in the matrix of the cement can also have an impact on its strength.

Fired clay in itself possesses "little or no cementitious value, but that in finely divided form and in the presence of moisture will chemically react with alkali or alkaline earth hydroxides" (Adams et al. 1992). In other words, in order to be absorbed into the chemical reaction, the clay product (usually crushed brick or pottery) must be crushed into a fine powder. "These reactions take place at ordinary temperatures to form compounds possessing cementitious properties" (Adams et al. 1992). The nature of the pozzolanic reaction can be described as follows:

"The so-called pozzolanic character of crushed brick mortar is attributed to the adhesion reactions of physicochemical character occurring at the ceramic-matrix interface; their nature depends both on the type of ceramic and the calcium hydrate content of the mortar. The observed reactions could probably be attributed to calcium silicate formations at the interface along the brick fragment, acting as the silicate source and membrane and the lime, which makes the interfacial surface alkaline and causes the chemical reaction. The penetration of lime into the ceramic and the consequent reaction transform the microstructure of the ceramic by transforming pore radii into smaller pores, decreasing the total porosity and augmenting the apparent density. The reduction of the pore radii confirms the cementitious character of the mortar matrix, imparting high strength to the mortar" (Moropoulou 1995a).

The reaction between the brick dust particles and the lime has also been described as a "boundary reaction." Microscopically, the rims of these events are manifested at the ceramic-matrix interface "in the form of veins along the matrix, as if they fill the vacancies and discontinuities of its structure" (Moropoulou 1995b, p. 762).

11.3.7 Modern Portland Cement

It is important to point out the differences between the ancient cements and modern Portland cements. These differences begin with the materials and the manufacturing techniques.

As previously mentioned, the reactivity of the pozzolana can be altered by exposing the material to high temperatures before mixing it with the lime. This is the key to the manufacture of modern Portland cement. Clay containing iron oxide and calcium carbonate is fired to approximately 1400°C in a rotary kiln. The silica begins to soften and fuse, resulting in the formation of "clinker". This material is mixed with gypsum and ground to form Portland cement powder. Portland cement is extremely hard and has a high compressive strength. The chemical reaction that produces modern Portland cement results in interlocking crystals. The structures produced by pozzolanic cements are more difficult to analyze, since the product is very fine-grained and not easily observed under a microscope.

Like its predecessors, the main catalyst for the chemical reaction in Portland cement is colloidal silica. However, it is imperative to control the **pH** of the mixture carefully in this modern material. In highly alkaline Portland cements, the silica can become gelled by the lime (Ilers 1979). Gelling occurs when the silica particles of the sol become linked together in branched chains. These chains fill the whole volume of the sol so that there is no increase in the concentration of silica in any macroscopic region in the medium. Instead, the overall medium becomes viscous and then is solidified by a coherent network of particles that, by capillary action, retains the liquid (Ilers 1979). In a Portland cement, the result of this process will be swelling and cracking of the material.

11.4 Masonry

Masonry units can be laid dry or with mortar. For example, the Inca laid enormous polygonal masonry blocks without any mortar. In some types of construction, mortar does not play a role in the building's structural strength. For example, in ancient

Egyptian architecture, gypsum was used as a lubricant for sliding megalithic blocks into place rather than to hold them together. In other forms of construction, mortar plays a significant role in consolidation of the masonry construction. In Roman architecture, some types of walls were merely stone veneers that depended on cement to hold the masonry together. Mortars can play a significant role in reducing moisture infiltration, thus impeding freeze-thaw damage.

11.5 Mud Brick, Terracotta, and Other Earthen Architectural Materials

Earth mixed with water and various additives has been used as a building material for more than 10,000 years and is still in use. More than one-third of the world's population is still living in adobe and similar structures (Sumanov 1990). Earthen building materials were traditionally utilized by a wide variety of peoples in a vast array of geologic contexts and geographical locations including Africa, Asia, Europe, North America, and South America. Earthen architecture was used not only for humble residences, but also for monumental works by many of the ancient world's great civilizations. The ancient city of Nineveh had major mud-brick structures. Unfortunately, little remains of Nineveh except a pile of amorphous earthen material.

Earthen architectural materials are used primarily in climates with relatively low annual rainfall. The earthen material must be continually repaired as it disaggregates. Ancient remains tend to be those that have been either continuously occupied, and thus maintained, or have been somehow protected from the rain. Despite the increasing popularity of modern construction materials, the tradition of earthen construction has continued. As a result, archaeologists and architectural historians have been able to make many inferences regarding ancient mud-brick technology based on recent constructions. Famous examples of monumental earthen architecture include the great mosque at Djenne in Mali (ca. 1907) and the mud-brick cities of the Arabian Peninsula, whose multi-level apartment buildings have been continuously repaired for centuries (Leslie 1991).

Most, although not all, earthen construction materials are processed mixtures containing components from various sources. Ancient builders learned through trial and error that the addition of certain additives could affect plasticity, durability, and shrinkage of the material. Calcium carbonate is still a widely used binder. Its chief advantage is that it controls shrinkage in montmorillonite clays. Other traditional additives such as egg albumen and blood reportedly improve moisture resistance and may also have symbolic importance in some cultures. Straw controls shrinkage, acts as a binder, and makes the earth mixture lighter by introducing tiny air spaces.

There are many varieties of earthen masonry, with as many local names for the materials. However, earthen masonry products can be generally divided into the following categories: mounded earth, rammed earth, unbaked clay or mud, and sun-dried mud brick.

Mounded Earth. Earth materials have been used with minimal processing by many societies, most notably on the North American continent. Cahokia in Illinois, Grand Mound in Minnesota, and Poverty Point in Louisiana are probably the most famous examples of monumental architecture built by the excavation, transportation, and mounding of large quantities of earth. The mounds incorporated burials and served as platforms for roofed houses or temples (Nabokov and Easton 1989). On a smaller scale, earthen pit houses were popular with a number of indigenous groups. For example, the Maidu and Miwok people of California excavated circular pits in the earth and covered them with a roof of wood rafters and grass mats. The excavated earth was spread over the top of the roof (Nabokov and Easton 1989). These structures were easy to build, practical, and thermally efficient. Beyond the excavation and movement of the soil, no further processing was required.

Rammed Earth. Called "pise", or "terre pise" in some regions, other traditional names for rammed earth compacted by pounding include "humra" (used for floors in the Levant area of the Middle East), "tub" and "tabya" (Arabian Peninsula) (Michon 1990:100), and "tappa" (Sri Lanka) (Nandadeva 1990). Pise was also used in some parts of western Europe, including the Rhone Valley of France (Dethier 1985). Sand should comprise 50–75% of the earth mixture in order to prevent excessive shrinkage. "The size range of the sand and coarse particles has no effect. In rammed earth walls only a relatively small amount of clay is desirable and over 30% clay results in rapid erosion" (Rapp and Aschenbrenner 1978). Recently, my colleagues and I have used buried rammed earth (called *hang-tu* in China) city walls (Fig. 11.9) and building platforms as a guide to ascertain when core drilling has located first and second millennium BCE major sites. Shang and Zhou Dynasties used *hang-tu* extensively for durable structures.

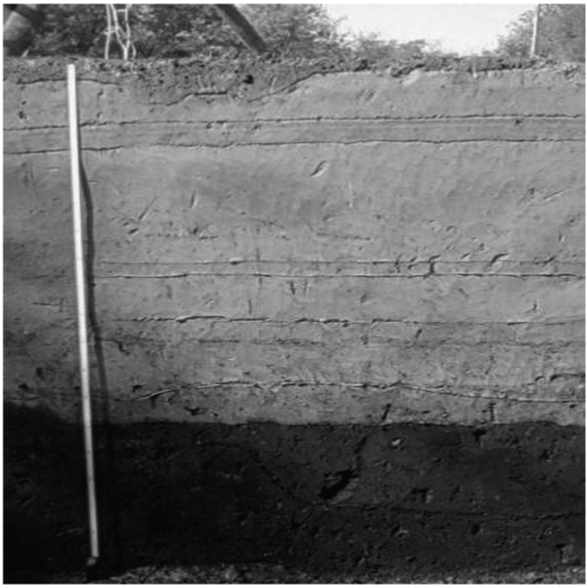

Fig. 11.9 Top of buried wall of rammed earth (hang-tu in Chinese), Shang Dynasty, China

Unbaked Clay or Mud. This category includes “clay lump,” “chalk mud”, “wichert”, “clay daubins”, and “cob” of England. These terms refer to various clayey soils mixed with sand, straw and sometimes chalk. Unbaked clay materials were utilized in a variety of related construction methods throughout England in all historical periods. Clay lump is compacted into wood molds, and the resulting masonry units are permitted to air dry. Cob walls are formed in place by the simple process of pitching on a soft but cohesive mixture of the materials mentioned, in layers, the wall surface being pared down with a flat-backed spade to form a fair face as the work proceeds (Ashurst and Ashurst 1988).

The unbaked clay category also includes mud “plasters” and mortars that may be applied over other types of earthen masonry or onto other types of substrates as a protective and decorative surface finish. Mud plasters can be used as the leveling or “brown” coat under a finished layer of lime plaster. Unlike lime plasters, mud plaster does not require burning, thus saving on both fuel and labor.

The use of mud over fiber probably has prehistoric origins. A number of scholars have speculated that the ancient dwellings of the Fertile Crescent and Nile Valley were constructed of reeds to which layers of wet alluvial mud were applied. “Wattle and daub” is a good example of the traditional use of mud plaster in a two-part system. The “daub” is a thick layer of mud composed of sand, clay, straw and dung, applied onto the wood or fiber frame called “wattle” (Kholucy 1990). This method was known and used by the Romans as an inexpensive construction technique. Vitruvius was critical of wattle and daub, urging his readers against its use.

> As for “wattle and daub” I could wish that it had never been invented. The more it saves in time and gains in space, the greater and the more general is the disaster that it may cause; for it is made to catch fire, like torches. It seems better, therefore, to spend on walls of burnt brick, and be at expense, than to save with “wattle and daub,” and be in danger. And, in the stucco covering, too, it makes cracks from the inside by the arrangement of its studs and girts. For these swell with moisture as they are daubed, and then contract as they dry, and, by their shrinking, cause the solid stucco to split (De Architectura II.viii.20, pp. 57–58).

Considering Vitruvius’s comments, it is not surprising that it is difficult to find archaeological evidence for this type of construction. Wattle and daub is usually inferred from pieces of fired “mud” containing the impressions of organic materials.

Sun-Dried Mud Brick. Adobe is unfired earthen architectural material common in the desert southwest of the USA. Adobe is applied as courses rather than shaped into brick. It usually is called pisé outside of the Americas. The raw materials for adobe wall construction between 1275 and 1450 CE at a pueblo near Albuquerque, New Mexico, were local clay-rich soils composed primarily of Na-Ca montmorillonite, bentonite, and goethite. During different phases of construction the source of the raw material changed. Some soil types were preferred and some local soil types were unsuitable (Balsam et al. 2007).

Adobe mud brick is generally composed of mud, sand, straw, and various additions. “Mud” is a geologic term meaning a mixture of silt- and clay-sized particles. The word “clay” is also commonly used to describe mixtures of silt- and clay-sized particles. In addition to mud or clay, the mixture may include various mineralogical and organic impurities. Sand in the mixture helps control shrinkage. Sharp coarse sand is better than fine-grained or rounded types (Boudreau 1971). Straw acts as a binder, controls shrinkage and prevents cracking. Straw does not give added strength to adobes but serves to make the brick dry and shrink as one unit. Without it, more than one center of contraction develops and major cracks appear (Boudreau 1971). Lime and other materials can be added to the mixture to further control shrinking and cracking.

Adobe bricks must have a high percentage of clay. Too much clay causes the brick to develop cracks as it dries; too little clay leaves the brick weak and crumbly. The Roman architect Vitruvius specified the type of clay suitable for mud-brick manufacture:

> They should not be made of sandy or pebbly clay, or of fine gravel, because when made of these kinds they are in the first place heavy; and, secondly, when washed by the rain as they stand in walls, they go to pieces and break up, and straw does not hold together on account of the roughness of the material. They should be made of white and chalky or of red clay, or even coarse grained gravelly clay. These materials are smooth and therefore durable; they are not heavy to work with, and are readily laid (De Architectura II.iii, pp. 42–43).

It should be noted that different clay minerals have different bonding properties and that the lime content as well as the organic content affect the physical properties of the finished product. Sand/silt/clay ratios cannot tell the full story.

In the Western Hemisphere, sun-dried mud brick is often referred to as “adobe.” This term is Spanish, but it is derived from the Arabic “al-toubeh” (الطوبة “the brick”). The Arabs borrowed the word from Coptic (τωωϐε), the Afro-Semitic language of ancient Egypt. The Egyptians also used adobe extensively for the construction of walls and fortifications (Clarke and Engelbach 1990).

The etymology of the name “adobe” hints at the antiquity of mud brick technology. Evidence for mud brick construction has been associated with Neolithic villages in Mesopotamia dating from about 7000 BCE (Steen 1971). Steen also notes that mud brick has also been found in the remains of Neolithic villages in Anatolia and Crete dating from about 5000 BCE. Mud brick has been used in Egypt for at least 6000 years (Lucas 1989). Mud brick was used for the construction of the pyramids at El-Lahun, Hawara, and Dashur.

Although an Old World term for adobe was transferred to the New World, mud brick was actually known in the Americas long before the arrival of the Spanish explorers. Prehistoric Native Americans in New Mexico and Arizona lived in apartment-style dwellings called pueblos, which were above-ground structures originally constructed of sticks and mud or adobe. Later pueblos were more often made of masonry and/or adobe. Classic Mimbres pueblos were made of cobbles held together by adobe. Later pueblos in southwestern New Mexico were constructed almost entirely of adobe. In South America, adobe was used in the Chicama Valley of Peru as early as 3000 BCE (Steen 1972).

Fired Brick. The change from impure clay to fired brick is analogous to high temperature thermal metamorphism. To be suitable for brick making, fine-grained, clay-rich sediments must have the following properties: they can be molded into the desired shape, they can be fired without excessive shrinkage, and they have the necessary mineralogy to transform to a fired material with sufficient compressive strength and durability. Brick clays include quartz as a major constituent. Most brick clays include illite and kaolinite and may include smectitie, feldspar, and chlorite. In firing, the first process involves driving off any absorbed water; then comes (1) the dehydration of clay minerals, (2) loss of the carbon dioxide and hydrocarbons, (3) the transition of alpha-quartz to beta-quartz, (4) various solid state mineral transformations, and (5) partial melting at grain boundaries with the formation of new minerals, including mullite. I have witnessed brick making in the lower Yellow River area of China where the raw materials are silt-rich and clay-poor, resulting in a poor grade of brick. Modern brick is 60–75% clay and up to 10% sand. The first fired bricks were made by the Babylonians about 4000 BCE.

Mosaic. Mosaic is the art of decorating a surface with designs of closely set small pieces, called *tesserae*, of colored stone, ceramic, or opaque glass called *smalti.* Smalti is made from silica, lime, soda, potash, alumina, lead oxide, boric acid, and colored with cobalt, copper, chrome, nickel, iron, silver, and manganese oxides. The earliest mosaics were in buildings in Sumer. The Romans perfected the craft and imported marble, lapis lazuli, malachite, turquoise, jasper, and especially travertine from Tivoli for floors and wall art. Pliny (NH 36) discussed the mosaic technique.

11.6 Weathering and Decomposition

Weathering is the breakdown of rocks and minerals at or near the earth's surface into products that are more in equilibrium with the conditions found in this environment. Chemical weathering involves the alteration of the mineral constituents of the rock. Physical weathering is the breakdown of minerals by entirely mechanical methods that lead to the rupture of the rock.

A number of different processes can result in chemical weathering. The most common chemical weathering processes are hydrolysis, oxidation, reduction, hydration, carbonation, and solution. Hydrolysis is the weathering reaction that occurs at the surface of minerals reacting with water; it results in the decomposition of the rock by forming new minerals. Oxidation is the reaction that occurs between minerals and oxygen. The net result of this reaction is the removal of one or more electrons from a mineral, which causes it to become increasingly unstable. Reduction is simply the reverse of oxidation. Hydration involves the rigid attachment of H^+ and OH^- ions to a reacted compound. Carbonation is the reaction of carbonate and bicarbonate ions with minerals.

The processes that may cause physical weathering and mechanical rupture are abrasion, crystallization, thermal insolation, wetting and drying, and pressure release. Crystallization can cause the necessary stresses needed for the mechanical rupturing of rocks. There are primarily two types of crystal growth that occur; they are ice and salt. Upon freezing, the volumetric change of water from liquid to solid is 9%. The crystallization of salt exhibits volumetric changes from 1% to 5%.

The deterioration of stone monuments is largely the result of: (1) chemical dissolution, (2) mechanical disintegration caused by freezing of water in pores and cracks, (3) abrasion due to wind-driven particles, (4) exfoliation due to rapid heating and cooling, (5) disintegration resulting from the activities of organisms, (6) the formation of crystals on the surface, and (7) damage resulting from ill-advised efforts at conservation or restoration.

When buried, an artifact enters a new environment in which it must find a new stable state. When excavated, the artifact is again exposed to a different set of physical, chemical, and biological conditions. Rapid transformation to a new stable state often destroys the artifact in the process. The extent of alteration caused by burial or excavation depends on the structure and composition of the material and the severity of the contrast between the old and new environments. The oxidizing potential, acidity (pH), moisture, and soluble salt content of each environment all affect the stability of the artifact.

All materials have a stable state for the environment in which they exist. A significant change in this environment may result in a transformation to a new stable state. Water, ice, and steam are each a stable state of H_2O in different temperature and pressure environments. Minerals formed at high temperatures under anhydrous conditions weather rapidly under moist conditions at the earth's surface.

Chemical breakdown of feldspars provides a good example of the weathering process. Feldspars make up nearly 60% of the earth's crust. As feldspars weather, potassium, calcium, and sodium are lost, leaving newly formed clay minerals behind. Because of its high solubility, most of the sodium finds its way into the oceans. Most of the potassium remains in the soil. Some potassium becomes part of new minerals such as illite, and some becomes part of growing plants. Calcium has an intermediate fate, with some ending up in the oceans and some remaining in groundwater systems where it is precipitated out as carbonate and sulfate minerals. Calcium is the most common cation in fresh water, and the precipitation of calcium carbonate crusts on sherds is common.

The presence of chlorides, sulfates, and nitrates of calcium, magnesium, and sodium in masonry is deleterious because these salts, by repeated solution, crystallization, and hydration, generate sufficient pressure to fragment and spall the masonry. Although these salts are seen commonly as efflorescence on buildings in all climatic conditions, they are far more deleterious in arid regions, where the lack of precipitation results in accumulation of these salts. In wetter climates they are washed away by rain. In arid regions, condensation on stone surfaces during the night, followed by evaporation at sunrise, leaves behind a small but significant amount of the harmful salts, which crystallize as the evaporation proceeds.

In damp conditions, underfired or low-fired earthenware will gradually rehydrate to clay, which leads to crumbling. This is especially true where the fabric of the earthenware is coarse and porous. Crumbling is exacerbated in acidic conditions by loss of calcite or other carbonate components. High-fired ceramics are reasonably stable in most burial conditions. Even well-fired ceramics may become softened under alkaline conditions by dissolution of any vitreous phase. Deposits of both soluble and insoluble salts readily form on buried ceramics. Porous pottery is prone to staining, particularly by iron oxides. Iron oxide encrustations may form if there is a localized high pH caused by calcium carbonate within the pottery.

Soluble salts such as chlorides, sulfates, and carbonates are ubiquitous in ground water and are absorbed by any porous object below the water table. Upon excavation, moisture begins to evaporate, and dissolved salts will crystallize. The wall paintings of the tomb of Nefertari in the Valley of the Queens at the Theban necropolis in Egypt present a classic example of this geoarchaeological conservation problem. The tomb was hewn to a depth of about 12 m in poor quality, fractured clayey limestone. Layers of plaster were placed on the tomb walls. The exquisite tomb paintings were then placed on the plaster. Salts, especially gypsum and halite, have crystallized behind the plaster layer, pushing it outward. These dissolved salts were carried by ground and surface water that seeped in during heavy rains. A significant part of the conservation program must be control of microdrainages to the tomb (Getty Conservation Institute 1987). Alhambra is a famous monumental Islamic site in Granada City, Spain. It was constructed beginning in 1238 CE of red brick and a sandy limestone. Although the climate is semi-arid, deterioration has proceeded by salt weathering processes initiated by wet deposition of air pollutants. The salt weathering has had a great impact on both the red brick and the limestone (Kamh 2007). Late Baroque monuments in the ancient city center of Catania, Sicily, were built using local basalts and limestones. The limestone has suffered chemical weathering from airborne SO_2 pollution with the formation of calcium sulfate (Punturo et al. 2006). A good overview of the role of salts in the deterioration of porous materials has recently been provided by Charola (2000).

Smith et al. (2005) provide information on similarities and differences between natural rock weathering and urban stone decay. In a related paper Meierding (2005) presents quantitative data on many aspects of urban versus rural stone decay. Although a little dated, the best overall summary of stone decay is Winkler (1975). Paradise (2005) summarizes a series of studies conducted from 1990 to 2003 that scrutinized the lithologic weathering on the sandstones at Petra, Jordan. Surface recession rates for the sandstone in the Roman Theater ranged from an amazing 15–70 mm per thousand years on horizontal surfaces to 10–20 mm per thousand years on vertical surfaces. Studies of surface recession rates measured on more than 8000 marble tombstones in North America show that air pollution (largely SO_2) is responsible for the deterioration of carbonate building stone and statuary. Granular disintegration is induced by the growth of gypsum crystals between the calcite grains. New marble tombstones tend to be very smooth with a pearly luster, but after ten to twenty years they lose their luster and become grainy.

In Venice, Italy, building stone is subject to the severe salt water environment of the local marine lagoon (exacerbated by modern air pollution). Only one stone, called Istrian stone, has successfully resisted deterioration. Istrian stone is a very compact microcrystalline limestone with few natural planes where dissolution can proceed. Exposure to atmospheric sulfuric acid causes the formation of white gypsum powder on its surface, but its low porosity and impermeability protect it from rapid deterioration. The famous marble from Carrara has been especially beleaguered by the corrosive environment. Carrara marble has been used throughout the eastern Mediterranean since ancient times. Differential thermal expansion and contraction of the megascopic calcite crystals oriented in multiple directions in the marble cause microcracks along the edges of the crystals allowing penetration by pollutants.

To understand the archaeomineralogy of stone structures, it is necessary to comprehend the complete history of the rocks even before they were removed by quarrying. Unloading of confining pressure as a rock formation migrates toward the earth's surface due to erosion, along with a secondary unloading during quarrying, lead to jointing and microfracturing of the rock. These phenomena affect the later durability of the rock. After shaping and construction, the rock undergoes the effects of natural weathering as well as various treatments and mistreatments by human agents. There are many ways that earth scientists examine structural stone including visual inspection, microscopy, x-ray diffraction, chemical analysis, and the determination of physical and mechanical properties.

All materials expand and contract with temperature changes. Simple expansion and contraction is not harmful. Mechanical disintegration is caused by dissimilar expansions or contractions where two different materials are combined. For example, lime mortar has a coefficient of linear thermal expansion that is approximately 50% greater than that for bricks. In making ceramics, it is necessary that any additives, such as temper, have a coefficient of expansion similar to that of the clay matrix. Many sedimentary rocks used in buildings and monuments contain clays that cause differential swelling when wetted.

Fire has damaged a large percentage of ancient buildings. Sippel et al. (2007) tested limestones, sandstones, granites, tuffs, gneisses, marbles, and gypsum to determine the effects of fire. Every rock has its own thermal expansion and thermal shock characteristics. Some rocks incur damage from phase changes in constituent minerals. Others suffer dehydroxylation reactions, and some are subject to cracking (e.g., feldspars in granites). The response of building stones to fire is controlled both by mineral composition and by fabric.

The amount of water vapor that is absorbed by a rock depends on both the relative humidity of the air and the porosity of the rock. Frost damage in building stone is common where temperature variations around the freezing point cause cycles of freezing and thawing. The influence of frost action on dry stone is limited, but it can be substantial on wet stone, because, when water freezes, it expands by about 10%. When freezing occurs in a confined or limited space, the resulting pressures are enormous. Therefore, building stone with high porosity is more vulnerable than compact stone.

Most damage occurs during the process of drying out, not during absorption, as mineral salts recrystallize and cause structural damage and discoloration. A related process that occurs during drying is the crystallization of soluble salts. As salts crystallize, they can cause cracking similar to frost action. Salts also form crusts on the exterior of the stone. The most common salts occurring on walls are $CaSO_4 \cdot 2H_2O$ (gypsum) and Na_2SO_4 (sodium sulfate) in various hydration states. Calcium sulfate ($CaSO_4$) dry deposits are difficult to remove. The damage caused by sulfates is the result of different hydration states. As moisture conditions change, one hydration state converts to another. Transformation to more hydrated states leads to increased pressure on the walls of the pores in the stone.

Clastic sedimentary rocks are composed of the reworked products of weathering, so it is important to know whether these rocks are the end products or intermediate, immature, products of weathering. This is important because further weathering of immature rocks is deleterious in building and monumental stone.

The durability of igneous and metamorphic rocks under atmospheric weathering depends on their mineral constituents. Minerals that formed under high-temperature, anhydrous conditions are generally not stable under atmospheric conditions. The most unstable minerals are olivine, pyroxene, and calcic plagioclase. Hornblende, biotite, and the other feldspars are only of modest stability, as are the sedimentary carbonates. Quartz, muscovite mica, and the clay minerals are stable under normal atmospheric conditions.

The Goldich Stability Series, shown in the chart below, describes the order in which silicate minerals weather and gives an indication of the ease with which igneous rock minerals break down Goldich (1938).

Olivine
Calcic plagioclase
Augite
Calcic-alkalic plagioclase
Hornblende
Alkali-calcic plagioclase
Alkalic plagioclase
Biotite
Potassium feldspar
Muscovite
Quartz

Minerals at the bottom of the chart are most stable under the atmospheric conditions at the earth's surface. Mafic igneous rocks (gabbro, basalt) are composed of the mineral constituents near the top of the chart; as a result they break down when exposed to the atmosphere. Felsic igneous rocks (granite) are composed of the more stable minerals near the bottom of the chart, and these rocks break down more slowly. In the United States the National Institute of Standards and Technology has constructed a stone test wall to study the performance of stone subjected to weathering. It contains 2352 individual samples of stone, of which 2032 are domestic stone from 47 states. There are 320 stones from 16 foreign countries. More than 30 rock types are represented. Common rock types used in building, such as marble, sandstone, limestone, and granite, are represented by many varieties.

The deterioration of sandstone building materials is directly affected by their chemical composition; those which contain carbonate as the natural cementing agent are very susceptible to attack by acid rain. The loss of just a small amount of the carbonate deprives the sand grains of their cementation. As with other rock types, moisture is also a major destructive agent. Coarse-grained and porous sandstones usually withstand freezing and frost action better than fine-grained ones because water escapes more readily. However, some porous sandstones are also poorly cemented and therefore friable. Figure 11.10 illustrates the extensive damage caused by wind-blown sand and silt on poorly cemented sandstone building blocks.

The Republican and Early Imperial monuments in Rome were constructed (largely) of tuffs quarried from local pyroclastic deposits. Over the centuries,

Fig. 11.10 Weathering of sandstone blocks

Roman builders developed a good knowledge of the diverse properties of these deposits concerning their durability. Early construction utilized weakly durable, soft or vitric, tuffs. As time progressed, Roman builders quarried specific tuffs for specific structural elements. Lighter weight material was selected for upper stories supported by robust material in pillars reinforced with travertine. Since tuffs, in general, are not durable building stones, the Romans preserved them with protective stucco, travertine, and marble coatings (Jackson et al. 2005).

The historical buildings in Upper Egypt were built largely of local sandstone. The Horus temple at Edfu was completely constructed of local sandstone. The Abu Simbel temples were cut in the Nubian sandstone quarry in South Aswan. These sandstones are composed mainly of quartz grains cemented by ferruginous, siliceous, carbonaceous, and clay cements. Diurnal and seasonal changes in temperature and relative humidity are the principal threats to monuments constructed of these rocks. The temperature and humidity variations cause the growth of halite and gypsum crystals that result in cracking and structural failure.

A dramatic case of change in environment is seen in the removal of the large obelisks from Egypt. Sculpted in the middle of the second millennium BCE, these monuments stood in Egypt for 3000 years with little surficial damage. Over a century ago, three were exported, one to Paris about 1840, one to London about 1870, and one to New York about 1890. In the more humid and polluted atmospheres of these cities, the three obelisks have suffered major deterioration. Sulfur and nitrogen acids in the atmosphere have done most of the damage. The recent increase of vehicle emissions in Cairo does not augur well for the preservation of those surviving in Egypt.

An important part of our culture is chiseled in stone, and these stones are slowly weathering away. Even ancient Greek and Roman writers were aware of this phenomenon. Based on the rate the limestone has weathered in the great pyramids of Egypt, now nearly 5000 years old, they could last another 100,000 years. This is due largely to the low rainfall. However, the recent dramatic increase in the acidity of the rain could reduce this time to substantially less than 10,000 years. Their companion structure, the Sphinx, is not so "lucky". In recent years the Sphinx has deteriorated rapidly. The Sphinx is carved from the natural limestone of the Giza Plateau. The lowest stratum of the Sphinx is composed of member I, which is hard rock of a reef limestone (Figs. 11.11 and 11.12). This rock has not weathered appreciably.

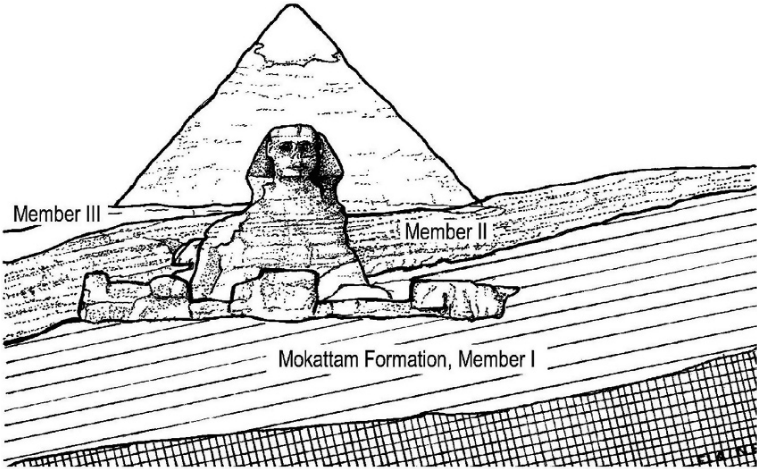

Fig. 11.11 The Sphinx was carved in situ from bedrock

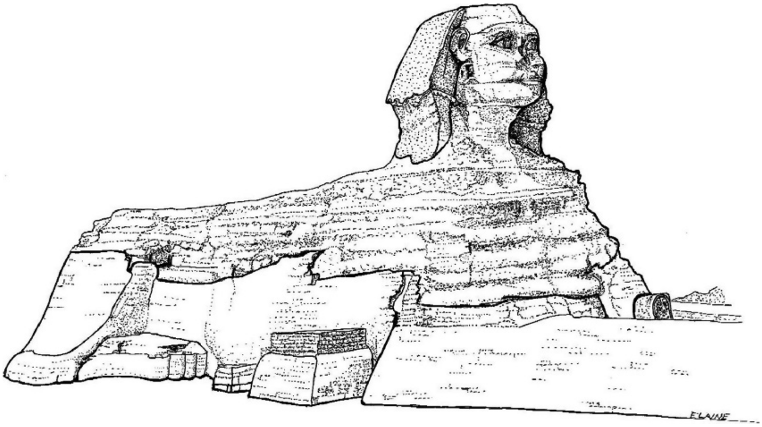

Fig. 11.12 The Mokattam Formation, members I and II, the lowest rock layers from which the Sphinx was carved, require regular conservation because they are soft and constantly crumble

However, most of the body of the Sphinx is carved from much softer layers of member II, lying above the reef limestone. This layer displays the most deterioration. The head is carved from member III, a much more durable rock. Without intensive conservation, the Sphinx could crumble in less than 100 years.

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Glossary

Alloying The process of chemically combining two or more metals.

Amphibole A group of dark-colored aluminum silicate minerals containing magnesium, iron, and calcium or sodium. Amphiboles are significant constituents of silicic igneous rocks as well as some metamorphic rocks. The most common amphibole is hornblende.

Anisotropy The condition of having different properties in different directions.

Anorthosite An essentially monomineralic intrusive igneous rock composed of calcic plagioclase.

Aphanitic An igneous rock texture in which the grains are too small to distinguish with the unaided eye.

Argillite A compact sedimentary rock, derived either from mudstone or shale, that is well-indurated and non-fissile.

Bauxitic Containing much bauxite – a product of tropical weathering that is rich in hydrous aluminum oxides and aluminum hydroxides.

Bloomery The first forge (for hammering) in iron working after the smelting process.

Botryoidal Having the form of a bunch of grapes.

Brine A geological term for hot saline fluids in restricted basins that contain Ca, Na, K, and Cl.

Calcareous Pertaining to a rock that contains a significant percentage but less than 50% calcium carbonate.

Calcined Heated to the temperature of chemical dissociation, e.g., heating limestone to form $CaO + CO_2$.

Campanian The middle Upper Cretaceous

Cast Iron An alloy of primarily iron and carbon.

Cation A positively charged ion such as Fe^{2+} or Al^{3+}.

Celadon Chinese stonewares with a opaque green-gray glaze, first made in the Sung Dynasty [969–1279 CE].

Celt A prehistoric axe-like tool.

Chlorite A mica-like sheet silicate that derives its name from its green color. It is a common accessory mineral in low-grade metamorphic rocks.

Clastic Pertaining to a rock or sediment composed of particles derived from preexisting rocks and transported some distance from their origin.

Coccolith A general term for various microscopic calcareous skeletal remains of fossils found in chalk.

Colloidal This term refers to a state of suspension of very small particles in a liquid. The particles are in a size range smaller than clays and tend not to sediment out from the liquid.

Compressive strength The maximum stress that pushes a material together from opposite sides that can be applied to a material before rupture occurs.

Cretaceous The final system in the Mesozoic Era. It follows the Jurassic and precedes the Tertiary period.

Cupellation Used in the recovery of silver from lead minerals, it involves smelting the lead mineral in a shallow crucible to oxidize the lead to litharge. Any other base metals dissolve in the litharge while silver (and any gold) remains in the metallic state.

Cyclopean Formed with, or containing, large undressed stone (as in a wall).

Detrital Pertaining to detritus, particles (such as sand, silt, or clay) or fragments of preexisting rocks formed by erosion or weathering.

Diagenetic Pertaining to those physical, chemical, and biological processes undergone by a sediment after its initial deposition and during lithification.

Dimensional stone Building stone that is quarried and prepared in regularly shaped blocks.

Dimorph Having two distinct forms.

Dolomitic Containing a significant amount of the mineral dolomite $CaMg(CO_3)_2$.

Eolian Pertaining to the wind, especially wind-formed deposits such as sand dunes.

Epidosites Metamorphic rocks composed of epidote, quartz, and generally chlorite.

Exfoliation The process by which concentric layers or shells of rock are spalled or stripped from the surface of a rock mass.

Facies The characteristics of a rock that differentiate it from adjacent rock units, and usually reflecting its origin.

Ferric Iron in its +3 ionic state.

Ferrous Iron in its +2 ionic state.

Fissility The property of splitting easily into thin layers along planar parallel surfaces.

Flux A substance used in smelting to refine metals by combining with impurities to form a molten mixture that can be removed readily.

Gangue The valueless rock in an ore body. It is separated from the valuable ore minerals during processing.

Gastropod A class of mollusks with bodies contained in a helically coiled shell.

Glauconite A green mica-type mineral often found in extensive green sand deposits.

Gossan An iron-rich product overlying a sulfide deposit, formed by the oxidation of the sulfides and the leaching out of the sulfur and most other metals.

Grog Potsherds crushed to a small particle size and added to a clay as temper in pottery manufacture.

Heavy minerals Minerals in clastic sedimentary rocks with a specific gravity greater than 2.85, e.g. magnetite, zircon, garnet, and tourmaline.

Hornblende The most common amphibole.

Hornfels A fine-grained rock with equidimensional grains of no preferred orientation, typically formed by contact metamorphism.

Hue A shade or tint of color resulting from wavelength or dominant spectral color.

Intonaco Term used in fresco technique for the final, wet coat of plaster to which pigments are applied.

Intrusive Pertaining to the intrusion of a magma into a preexisting rock body. The name refers both to the process and the solidified magma.

Isotope One of a species of a chemical element that is differentiated from other isotopes of the same element by the number of neutrons in the nucleus.

Jointing The presence of planar fractures or parting in rock, often occurring in parallel sets.

Karst A topography found on limestones, characterized by sinkholes, caves, and subsurface drainage.

Kohl Finely powdered antimony or lead sulfide used in eastern societies as a cosmetic to darken features such as eyelids, and eyebrows.

Lag deposits The residual accumulation of coarse material at the earth's surface after the fine material has been blown away by wind.

Lake A pigment consisting of organic coloring matter with an inorganic base or carrier.

Lateritic Pertaining to a highly weathered red soil, rich in the oxides of iron and aluminum.

Levigate/levigation To rub or grind into a fine powder.

Lithology The description of rocks in hand specimens and in the field, on the basis of their mineralogy, grain size, color, etc.

Lode A mineral deposit in a host (consolidated) rock, as opposed to a placer deposit.

Luminescence The emission of light not caused by incandescence and occurring at a temperature below that of incandescence.

Mafic Used to describe an igneous rock composed of dark-colored silicate minerals high in iron and magnesium.

Magma A naturally occurring molten rock material emanating from within the earth. Magmas form igneous rocks when crystallized.

Marl A term applied to earthy deposits composed of a mixture of clay and calcium carbonate, especially in lake deposits.

Mastaba From the arabic word “bench,” this term describes an ancient Egyptian tomb with a rectangular base, sloping sides, and a flat roof.

Matte An unfinished metallic product of the smelting of copper-iron sulfides; matt will contain both copper and iron.

Metasomatized Having been subjected to nearly simultaneous dissolution of mineral constituents and replacement by other minerals of different chemical composition.

Molassic A thick sedimentary sequence of soft sandstones, shales, and marls formed in a partly marine, partly continental environment.

Mordant Serving to fix colors in dyeing. A reagent such as tannic acid, used to fix coloring matter in textiles, leather or other materials.

Neogene The later part of the Tertiary, consisting of the Miocene and Pliocene.

Netsuke A small Japanese toggle, used to fasten a purse or other article to a kimono.

Nicols In a polarizing microscope, the polarizing prisms are called Nicols, after their inventor.

Nummulitic Adjective modifying limestones that contain abundant foraminifer fossils of the nummulite variety.

Oolite A sedimentary rock, usually a limestone, made up primarily of ooliths: also one of the ovoid particles of an oolite.

Opacifier A chemical added to a glaze but which does not completely melt into the glaze. This produces a whiteness in the glaze.

Ophiolite An assemblage of both mafic and ultramafic intrusive and extrusive rocks, believed to represent oceanic crust.

Orthoquartzite A clastic sedimentary rock composed primarily of quartz sand that has a silica cement, making it well-indurated and cohesive.

Orthostats Stone slabs set vertically rather than horizontally in a building.

Oxidized For an element: to be increased in valence, to lose electrons. For a mineral deposit: to have elements oxidized by combination with oxygen.

Parting The breaking of a mineral along planes of weakness separate from cleavage planes.

Paste Clay material used as the essential ingredient in pottery manufacture.

Pedogenesis Soil development.

Pedology The study of soil morphology, genesis, and classification. Sometimes used as a synonym for soil science.

Petrography The study of rocks by means of microscopic examination of thin sections using a polarizing microscope.

pH A measure of the alkalinity or acidity of a solution, numerically equal to 7 for neutral solutions; alkalinity is indicated by numbers above 7, acidity by numbers below 7.

Playas Dry, flat areas at the lowest part of an undrained desert basin.

Porcellanite A dense siliceous rock having the texture, luster, and conchoidal fracture of unglazed porcelain. The term has been applied to a wide variety from impure chert to baked clay to silicified tuff.

Provenance Pertaining to the geologic/geographic source of a raw material.

Pseudomorphous The outward crystal form of a mineral that is a relic feature of a preexisting mineral, altered to the new mineral.

Pyrophyllite A white or gray sheet silicate resembling talc.

Pyroxenes A group of dark-colored silicate minerals having the general formula $AB(SiO_3)_2$ where A = Ca, Na, or Mg, and B = Mg or Fe. They are common constituents in mafic igneous rocks.

Pyroxenite An ultramafic intrusive igneous rock composed chiefly of pyroxene with accessory hornblende, biotite, or olivine.

Pyxis/pyxides From ancient Greek and Roman times – a cylindrical container having a lid with a knob in the center; used for toilet articles.

Radiolarian Pertaining to material composed of siliceous skeletal material from marine radiolaria fossils.

Reducing atmosphere An atmosphere where oxygen is absent and elements can be reduced by gaining electrons, usually by the concomitant conversion of $CO{\cdot}CO_2$.

Refractory Said of a material that is exceptionally resistant to heat; having a high temperature of softening or melting.

Schistose A metamorphic rock texture displaying foliation due to the parallel alignment of platy minerals such as mica.

Shear (resistance to) Resistance of a material to deformation resulting from stresses that cause parts of the material to move relative to each other.

Shield A large area of very old, exposed, tectonically stable, rocks surrounded by younger sedimentary rocks.

Sintering A solid-state process by which bonds develop at high temperatures between grains of solid material brought into contact.

Slag A furnace product resulting from the fusion of waste material (principally iron and silica) after the separation of the metal phase.

Slake To treat lime with water to give hydrated lime.

Sluice A conduit for carrying off surplus water, often at high velocity. It can be used to concentrate heavy minerals such as gold or cassiterite.

Smalt A smelted product using a pigment and colorant; composed of cobalt, aluminum, and potassium silicates.

Smelting A pyrotechnology for separating a metal from the rest of an ore, normally by inducing a liquid metal phase and a liquid slag phase.

Sol Denotes a homogeneous suspension of colloidal matter in a fluid or a completely mobile mud (more fluid than a gel).

Supratidal The shore area just above the high-tide level.

Tawing To convert skin into white leather by mineral tanning as with alum and salt.

Tell A mound site formed by successive human occupations over a considerable period of time.

Telluric iron Metallic iron that has formed naturally in the earth rather than produced from smelting.

Tempera A general term applied to a type of paint in which the pigment is suspended in an albuminous, gelatinous, or colloidal medium. Egg, gum, and glue were all used to manufacture tempera in antiquity.

Tensile strength The maximum stress that tends to pull a material apart that can be applied to a material before rupture starts.

Tephra A term used for all pyroclastic material ejected during an explosive volcanic eruption.

Terrigenous Pertaining to the land or the continents (as distinct from marine).

Tufa A chemically deposited calcium carbonate rock formed by evaporation as a thin, porous incrustation.

Tuff Consolidated or cemented volcanic ash.

Ultrabasic The same meaning as ultramafic.

Ultramafic An adjective describing an igneous rock composed chiefly of mafic minerals such as olivine and augite (a common pyroxene).

Vesicular An igneous rock texture characterized by abundant vesicles (voids) formed as the result of the expansion of gases during the fluid stage of a lava.

Voussioir Any of the pieces, in the shape of a truncated wedge, which form an arch or vault.

Zeolites A large group, often white or colorless, of hydrous aluminosilicates commonly found in cavities in basalts.

Appendix A
Pigments Used in Antiquity

Pigment	Origin of the name	Alternate names	Chemical formula	Color	Source	Hardness	Uses
Antimony Yellow	Latin *antimonium*	Naples Yellow	$Pb_3(SbO_4)_2$	Yellow	Artificial		Paint pigment; colorant in glass and ceramic glazes
Azurite	Persian *lazhward* meaning “blue”	Ultramarine	$2CuCO_3{\cdot}Cu(OH)_2$	Blue	Natural	3.5–4	Paint pigment best in tempera paints
Bole	Greek *bolos* meaning “a lump of clay”	White bole; china clay; pipe clay; kaolin; red bole; Armenian bole		Various shades of white and red	Natural		Colorant for ceramic glazes; ground for gilding
Celadonite	French *celadon* meaning “sea green”, alluding to its color	Terre verte; green earth	$K(Mg,Fe^{+2})(Fe^{3+}{}_1Al)Si_4O_{10}(OH)_2$	Yellow-green to pale greenish-gray	Natural	2	Paint pigment; colorant in ceramic glazes
Chalk	Anglo-Saxon *cealc* meaning “chalk” or “lime”; from Latin *calx* or calcis meaning “limestone” or “chalk”	Whiting; lime white	$CaCO_3$	White	Natural		Paint pigment best in tempera; adulterant; base for lake colors
Chrysocolla	Greek chrysos and kolla meaning “gold glue”		$CuSiO_3{\cdot}H_2O$	Bluish			Paint pigment
Cinnabar	Arabic *zinjafr* or Persian *zinjifrah* meaning “dragon’s blood”	Vermilion	HgS	Red	Natural or artificial	2–2.5	Paint pigment; cosmetic pigment

Appendix A (continued)

Pigment	Origin of the name	Alternate names	Chemical formula	Color	Source	Hardness	Uses
Cobalt			Co	Blue	Element		Colorant in glass and ceramic glazes
Copper oxide				Green, turquoise blue, metallic orangy-red	Natural or artificial		Colorant in glass and ceramic glazes
Diatomaceous earth	Greek *dia* meaning "through" and *tome*, "a cutting"	Infusorial earth/ diatomite/celite	Hydrous silica	Light colored	Natural		Bleaching agent for oils and waxes; base for lake colors
Egyptian Blue	Modern name	Pompeian Blue; blue frit	$CaCuSi_4O_{10}$	Blue	Artificial		Paint pigment
Galena	Latin *galena*, referring to its use as a lead ore		PbS	Lead gray	Natural	2.5	Cosmetic pigment, especially for eye-liner
Glauconite	Greek *glaukos* meaning "bluish-green"	Terre verte; green earth	$(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$	Yellow-green to pale greenish-gray	Natural	2	Paint pigment; colorant in ceramic glazes
Goethite	Named after Johann Wolfgang von Goethe (1749–1832), German poet and scientist	Limonite; ochre	FeO(OH)	Yellow to brown	Natural	5–5.5	Paint pigment; colorant in glazes, glass and ceramics

Appendix A (continued)

Pigment	Origin of the name	Alternate names	Chemical formula	Color	Source	Hardness	Uses
Gold leaf			Au		Natural		Paint pigment and for gilding; colorant in glass when combined with salts and annealed; when powdered used in cosmetics
Graphite	Greek *graphein* meaning “to write”	Carbon black; plumbago	C	Black	Natural	1–2	Rarely used as pigment; used in drawing
Gypsum	Greek *gypsos* meaning “plaster”	Terra alba; selinite; alabaster	$CaSO_4 2H_2O$	White	Natural	2	Inert paint filler; component of some ochre compounds; base for lake colors; preparation of gesso grounds
Hematite	Greek *haimatitis* meaning “blood red”	Ochre; Venetian red	Fe_2O_3	Red	Natural; or by roasting goethite	5–6	Paint pigment; burnisher for gold leaf; colorant in glazes, glass and ceramics
Kaolin	Chinese *kao-ling* meaning “high ridge”	China clay; pipe clay; white bole	$Al_2SiO_5(OH)_4$	White	Natural		Colorant and main compound in glazes and ceramics; used in preparing painter’s grounds

Appendix A (continued)

Pigment	Origin of the name	Alternate names	Chemical formula	Color	Source	Hardness	Uses
Lapis lazuli	*Lapis*, Latin for "stone" and Persian *lazhward* meaning "blue"	Lazurite	$(Na,Ca)_8(Al,Si)_{12}O_{24}[(SO_4),Cl_2(OH)_2]$	Blue	Natural		Paint pigment
Limonite	Greek *leimon* meaning "meadow"	Goethite; ochre	$FeO(OH)$	Yellow to brown	Natural		Paint pigment; colorant in glazes, glass and ceramics
Litharge	Greek *lithargyros* meaning "rock silver"	Massicot	PbO	Yellow	Natural or artificial; processed by roasting lead white	2	Paint pigment; colorant for ceramic glazes
Malachite	Greek *moloche* meaning "mallow" alluding to green color	Mountain green	$Cu_2(CO_3)(OH)_2$	Green	Natural	3.5–4	Paint pigment; cosmetic pigment, especially eye-liner
Manganese dioxide				Shades of pink, purple, brown and black in glass and ceramic glazes			Paint pigment; colorant in glass and ceramic glazes; pigment in cosmetics
Massicot	French, from Spanish *mazacote*, from Arabic origin	Litharge	PbO	Yellow	Artificial, by roasting lead white		Paint pigment; colorant for ceramic glazes
Minium	Term originally applied to cinnabar. From Latin, derived from Iberian word	Red lead/orange mineral	$Pb^{2+}{}_2Pb^{4+}O_4$	Red	Artificial	2.5	Paint pigment; cosmetic pigment

Appendix A (continued)

Pigment	Origin of the name	Alternate names	Chemical formula	Color	Source	Hardness	Uses
Muscovite	Derived from *Muscovy* (Russian province) where it was used in windows	White mica	$KAl_2(Si_3Al)O_{10}(OH,F)_2$		Natural	2.5 parallel to (001); 4.0 4.0 perpend. to (001)	Paint pigment; lubricating agent in paints
Naple's Yellow	Modern name	Antimony yellow	$Pb_3(SbO)_2$	Yellow	Artificial		Paint pigment; colorant in glass and ceramic glazes
Ochre	Greek *ochros* meaning "pale yellow"	Sienna; umber; goethite; limonite; hematite; Indian red	Various iron oxide compounds	Yellow and red to brown	Natural		Paint pigment; burnisher for gold leaf; colorant in glazes, glass and ceramics; cosmetic pigment
Orpiment	Latin *auripigmentum* meaning "golden paint"	King's yellow	As_2S_3	Yellow	Natural or artificial	1.5–2	Paint pigment; cosmetic pigment
Realgar	Arabic *rahj al-ghar* meaning "powder of the mine"	Sandarack	AsS	Red	Natural or artificial	1.5–2	Paint pigment; cosmetic pigment
Red bole	Greek *bolos* meaning "a lump of clay"	Armenia bole	Ferrigiinous aluminum silicate	Red	Natural		Paint pigment; colorant in ceramics and glazes
Sienna	From city of Sienna in Tuscany, Italy	Burnt sienna; raw sienna; goethite	$Fe_2O_3H_2O$ plus alumina and silica	Yellow	Natural		Paint pigment
Silver leaf			Ag		Natural		Paint pigment and for gilding

Appendix A (continued)

Pigment	Origin of the name	Alternate names	Chemical formula	Color	Source	Hardness	Uses
Smalt	Old High German *smalzjan* meaning "to smelt"		CoO plus SiO_2 plus K_2O and alumina	Blue	Artificial		Paint pigment; colorant in glass and ceramic glazes
Stibnite	Latin *stibium*, old name for antimony		Sb_2S_3	Pale to dark gray	Natural	2	Cosmetic pigment, especially eye liner
Talc	Arabic *talq* meaning "pure"	Soapstone/steatite	$Mg_3Si_4O_{10}(OH)_2$	Pale green, greenish, to grayish-white	Natural	1	Inert filler in paints; base for lake colors
Terre verte	French meaning "green earth"	Celadonite/glauconite/green earth	$K(Mg,Fe^{2+})(Fe^{3+},Al)Si_4O_{10}(OH)_2$ or $(K,Na)(Fe^{3+}Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$	Yellow-green to pale greenish gray	Natural	1	Paint pigment; colorant in glass and ceramic glazes
Ultramarine	This term usually refers to the artificial version of the pigment, but can also refer to natural mineral. From Latin *azurrum ultramarium* meaning "beyond blue"	Azurite	$Cu_3(CO_3)_2(OH)_2$	Blue	Natural or artificial		Paint pigment
Umber	Latin *umbra* meaning "shade" or Italian *Umbria* after province	Burnt umber/raw umber	Earth pigment with ferrous iron oxide plus manganese dioxide	Brown	Natural or processed		Paint pigment
White Lead	*Lead* from Old English meaning "metal"	Flake white/Cremnitz white	$PbCO_3Pb(OH)_2$	White	Artificial		Paint pigment best in oil; colorant in ceramic glazes

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