Springer Earth System Sciences

Kate Horan

Falkland Islands (Islas Malvinas) in the Permo-Carboniferous

From Icehouse to Greenhouse





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Editorial Support to Author

Simon Crowhurst read Experimental Psychology at the University of Oxford and worked for more than 20 years with Nick Shackleton learning the principles of astronomical forcing of sediment sequences. He has many publications of which he is a co-author, and illustrated the Willis and McElwain book on the Evolution of Plants. He now works as the Senior Laboratory Technician at the University of Cambridge Earth Sciences department.

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Phil Stone is a Research Associate with the British Geological Survey in Edinburgh. Between 1998 and 2009 he acted as Geological Advisor to the Department of Mineral Resources, Falkland Islands Government, and was responsible for recovering from the Falkland Islands the borehole core that forms the basis of this study.

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Preface

The opportunity to study palæoclimate has been an exciting, challenging and rewarding experience. As a Natural Sciences undergraduate student at the University of Cambridge, I developed a strong interest in Earth Sciences, in particular climate change, sedimentology and geomorphology. During my master's degree, I was lucky enough to take these interests further in a three-month research project. It is the results of this project which provided the impetus for writing this book.

Developing an understanding of Earth's climatic history has become all the more intriguing and necessary in order to appreciate current climate change in the context of longer timescales. Transitions from icehouse to greenhouse worlds and vice versa are the largest of the climatic switches known to occur on Earth and they are accompanied by extreme palæoenvironmental changes. This book documents one such change, the Late Carboniferous to Permian deglaciation of southern Gondwana, by drawing upon evidence from a Gondwana fragment that became the Falkland Islands (Islas Malvinas) microplate following the break-up of the supercontinent.

The sedimentology of the Hells Kitchen Member of the Port Sussex Formation in East Falkland comprises deposits that document the switch from icehouse to greenhouse conditions. These Falkland Islands strata correlate with glacigenic units in South Africa and South America, all of which were deposited during the widespread, Late Carboniferous to Early Permian glaciation of Gondwana. Sedimentary logging, X-ray fluoresence (XRF) scanning and reflectance scanning were carried out on solid rock cores which host these sediments. The data collected was used to support a facies evaluation and an investigation into the nature of the climate change. In addition, it presented a unique opportunity to explore the application of Milankovitch orbital cycles to sedimentary sequences at this time.

This book is published as part of the series of Springer Earth System Sciences. It serves as a case study because the Falkland Islands cores pinpoint evidence from just one locality nested within the Gondwanan supercontinent at the time of the icehouse to greenhouse transition. The research complements other accounts of Falkland Islands geology, the climate and palæotectonic reconstructions of the Gondwanan supercontinent and long-term climate change. It is hoped that it will be a valuable resource to both scientists and students working across a range of disciplines within the Earth Sciences, but primarily its focus is geared towards those with research interests in the above areas.

Kate Horan

Acknowledgments

I am extremely grateful to my teachers, in particular Richard Tighe and Merrick Weems, who were responsible for sparking my initial interest in this subject area and inspiring me to go on to university to pursue my interests. Special thanks go to Simon Crowhurst for his strong support and enthusiasm throughout the project which, combined with his insightful contributions particularly into time series work, have been invaluable. The borehole cores on which this study was largely based were acquired between 2005 and 2007 by Falklands Gold and Mineral Ltd. Thanks go to Dr. Phil Stone for recovering these cores from the Falkland Islands and to the British Geological Survey for making them available for this study. Logistical support for shipping the borehole cores to the UK was provided by the British Antarctic Survey. Phil Stone also provided excellent scientific editorial guidance.

Additionally, I would like to thank Dr. Morag Hunter and Prof. David Hodell for their helpful discussions during the production of the project at Cambridge. Further thanks go out to James Rolfe who assisted with Total Organic Carbon measurements and to Dr. Claus-Dieter Hillenbrand, Vikki Peck and Claire Allen, from the British Antarctic Survey, who provided guidance on how to approach interpretations of glacial sediments. It has been a great pleasure to work with many different people all of whom have in some way provided me with some inspiration and made the project a lot of fun. Girton College, Cambridge, also kindly covered some of the project expenses.

Finally, I would like to thank my parents for their support during my studies.

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Abbreviations

LPIA	Late Palæozoic Ice Age	
TOC	Total Organic Carbon	
IRD	Ice Rafted Debris	

- ETP Synthetic Carboniferous orbital solution including eccentricity, tilt and precession
- L* Reflectance parameter: lightness
- a* Reflectance parameter: red/green ratio
- b* Reflectance parameter: blue/yellow ratio
- XRF X-ray fluorescence
- Fe10 For elements measured at more than one energy band by the Avaatech XRF core scanner, the number represents the voltage in kV; here iron measured on the 10 kV run
- pCO₂ Partial pressure of carbon dioxide
- $\delta^{13}C_{org}$ Isotope ratio of ${}^{13}C/{}^{12}C$ in organic matter
- $\delta^{13}C_a$ Isotope ratio of ${}^{13}C/{}^{12}C$ in atmospheric CO₂
- PCA Principal Component Analysis
- SPSS Statistical Package for the Social Sciences
- BGS British Geological Survey

Abstract

The Late Carboniferous to Early Permian 'icehouse to greenhouse' transition in the Falkland Islands was accompanied by cyclical waxing and waning of the Gondwanan, south polar ice sheet. The cyclical changes are manifested in the sedimentary deposits of the Fitzroy Tillite and Port Sussex formations. This study looks in detail at two sediment cores spanning these formations that were recovered from the Falkland Islands in 2008 following a mineral exploration programme. The lithologies and sedimentary fabrics appear to record a switch from deposition under a grounded ice sheet to glaciolacustrine or glaciomarine deposition punctuated by minor episodes of ice advance and retreat during a period of net ice sheet retreat. X-ray fluorescence and reflectance data have been used to quantify the change in terms of geochemical and geophysical properties respectively. Elements including zirconium, manganese, chromium, iron and titanium helped to constrain the cyclicity. Wavelet and spectral analyses, run to look for prominent periodicities in the data, were suggestive of orbitally forced oscillations within the transition. This permitted the development of a hypothetical time framework for the series spanning approximately 1.2 million years through age modelling. The integrated approach of this research, which combines sedimentological data with geochemistry, makes it a robust insight into this past climatic transition and may help to evaluate and inform predictions of future climate change.

Keywords Falkland Islands • Fitzroy Tillite Formation • Hells Kitchen Member • Permo-Carboniferous • Icehouse to greenhouse • Gondwana • Deglaciation

Chapter 1 Introduction

Abstract Investigating the dynamic behaviour of Earth's climate system remains a significant challenge. It is partly motivated by our limited knowledge of how the system will evolve in the future and the resilience of ice sheets to perturbations. Throughout geological history, the Earth has been subjected to extreme climatic transitions. These have taken place over various spatial and temporal scales ranging from localised decadal oscillations through to millennial- and multi-millennial-scale processes affecting the whole planet. The focus of this study lies within the latter kind, wherein the Earth flips between icehouse and greenhouse states. During the Permo-Carboniferous, when the Gondwanan supercontinent lay close to the South Pole, sedimentary deposits developed that documented one such transition. This chapter outlines the potential for study in material extracted from East Falkland during a mineral exploration programme in 2008. The geographical location of the Falkland Islands in the Permo-Carboniferous based upon Palæozoic reconstructions of Gondwana is discussed and the stratigraphic links between the Falklands deposits and other similar deposits from across the continent explored. Our understanding of how major climatic changes proceed, and the possible triggers behind them, could be significantly improved by studies of such deposits.

Keywords Permo-Carboniferous climate change • Icehouse to greenhouse • Gondwana • Falkland Islands • Ice sheets

1.1 Overview

The climatic conditions of the Late Palæozoic Earth oscillated between cold 'icehouse' states with persistent polar ice and warm 'greenhouse' states without polar ice (Fig. 1.1). With many questions about the long-term future of our climate,

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Fig. 1.1 Earth's long-term climate history modified from Scotese et al. (1999) to reflect the recent international chronostratigraphic chart (International Commission on Stratigraphy, August, 2012). *Numbers on the left hand side* of the figure refer to age in millions of years. Note that this figure does not account for the diachroneity of climate change across continents

it is increasingly important to improve understanding of how these major climatic changes proceed. The Late Carboniferous Ice Age provides the last complete record of a transition from icehouse to greenhouse conditions (Gastaldo et al. 1996) and forms the focus of this study.

Mineral exploration drilling in the Falkland Islands between 2005 and 2007 generated eight core sections located between Old House Rocks and Black Rock, East Falkland, that span the Permo-Carboniferous icehouse to greenhouse transition. Commercial interest in these cores declined in 2008 and permission was obtained from the exploration company, Falklands Gold and Minerals Ltd., for samples to be taken and returned to the UK for assimilation into the national core archive. This is maintained by the British Geological Survey (BGS) at their headquarters in Keyworth, Nottingham. The main objective of this book is to place sedimentological and geochemical data collected from these cores within a framework that explains the interactions between climate and glacier dynamics over

the segment of the Gondwanan continent from which the East Falkland Islands formed. The core sequences contain deposits belonging to the Fitzroy Tillite and Port Sussex formations. These are characterised by subglacial, massive diamictite passing upwards into glaciomarine/glaciolacustrine diamictites, mudstones and black shales; a record which provides an excellent opportunity to study ice sheet advance and retreat across the East Falklands margin.

The nature of the icehouse to greenhouse transition may be explored through addressing the following four questions.

- 1. Does the transition occur through gradual climatic drift to a warmer state or is it marked by oscillations, episodic or periodic, between the extremes before a tipping point is reached?
- 2. What are the links between the sedimentological and the physicochemical properties of the deposits?
- 3. Could the climate changes within the course of the transition have been orbitally forced? Improving our understanding of the climate system earlier in Earth's history may have relevance for our ability to gauge future climate change projections operating under similar climate dynamics.
- 4. How do the deposits in the Falkland Islands correlate with deposits in other localities that also span the transition? Synthesising the stratigraphic record from the Falkland Islands with records across Gondwana could help to constrain the waxing and waning of glacial intervals of the Late Palæozoic Ice Age (LPIA) and provide insights into the drivers of ice growth and deglaciation.

1.2 Geographical Context

Today, the Falkland Islands are an archipelago in the South Atlantic Ocean situated between 51° and 52° 30'S and 57° 30' and 61° 30'W. They comprise two main islands, East and West Falkland, and several hundred smaller islands (Fig. 1.2).

In contrast, current Late Carboniferous reconstructions of the Gondwana supercontinent place the Falkland Islands at high latitudes off the east coast of South Africa and in a rotated position close to Port Elizabeth. These reconstructions (e.g. Adie 1952; Marshall 1994) are based on the continuity of structural trends from the Gondwanan orogeny (Curtis and Hyam 1998), outcrop patterns, palæo-ice flow directions, palæomagnetic reconstructions (Mitchell et al. 1986) and palæocurrent data (Hyam et al. 1997) and are supported by the distribution of Early Devonian marine faunas of the Malvinokaffric Province (Bradshaw 1998). Comparison of Permian facies, ichnology and palæocurrents in the Falkland Islands and the Dwyka, Ecca and Beaufort (part) groups in South Africa also support this (Trewin et al. 2002). Nevertheless, despite the compelling evidence for microplate rotation arising from comparisons of onshore geology, it should be noted that there is a contrary view held mainly by those working with offshore data generated by the hydrocarbon exploration programmes currently active around the Falklands.



Fig. 1.2 Geographical location of the Falkland Islands with locations relevant to the LPIA in Gondwana labelled. *Inset* highlights study site. Images were taken and adapted from Google Earth

The offshore data provide no evidence in support of the rotational model. Indeed, they are more readily reconciled with a Gondwana break-up in which the Falklands remain a part of a fixed Falkland Plateau extending from the South American margin (e.g. Lawrence et al. 1999). This debate continues.

Gondwana migrated across the South Pole during the Late Palæozoic (Fig. 1.3), and as a result, glaciation began in western Gondwana (present-day South America) in the Famennian (Late Devonian) (Caputo et al. 2008) and ended in eastern Gondwana (eastern Australia) in the Capitanian (Middle Permian) (Fielding et al. 2008a). As a consequence, secular climate change associated with this latitudinal movement across zonal climatic belts was superimposed on the change from icehouse to greenhouse (Scotese et al. 1999).

Crowell and Frakes (1972), Crowell (1983) and Caputo and Crowell (1985) concluded that a centre of glaciation migrated across South America, South Africa and Antarctica from 350 to 240 Ma. Ice centres waxed and waned across the



Fig. 1.3 Palæomagnetic studies demonstrate that movements of the continents resulted in a relative drift in the position of the South Pole; figure adapted from Henry et al. (2012), and Crowell and Frakes (1972)

different sites during this time interval. Glaciation likely ensued when broad continental areas reached near-polar positions, and expanses of open water were sufficiently near to provide evaporative moisture. A reconstruction of ice cover in the Late Carboniferous is provided in Fig. 1.4 and illustrates the likely ice flow patterns.

In most localities from the Gondwanan landmasses, glacigenic deposits are relatively thin and consist of a variety of rock types and/or striated surfaces interpreted to indicate terrestrial or grounded marine ice sheets (Matsch and Ojakangas 1992). When Gondwana began to break up ~ 200 Ma (Stone et al. 2012), the glacial deposits became dispersed across the continents. Table 1.1 collates information from various sources on the thickness and age of the corresponding glacial deposits across the present-day continents, and Fig. 1.5 synthesises this information in time. Difficulties in correlating thicknesses arise because glacial strata are often eroded; only those dumped during glacial retreat are typically preserved. The correlation carried out in the time domain involved hypotheses about the relative timing of events documented in the sedimentary record. Some inconsistencies between sources (shown in Table 1.1) mean some boundaries are approximate, highlighting the need for improved chronology. Oman, Pakistan and Yemen were in the Northern Hemisphere at this time, which explains their deviation from the trend of glacial strata becoming progressively younger in successive stratigraphical columns from left to right across Fig. 1.5. Australia underwent early



Fig. 1.4 a Reconstruction of ice extent across Gondwana with supporting evidence from various authors utilised (e.g. Scotese et al. 1999). The Falkland Islands lay off the southeast coast of South Africa at this time. **b** Ice flow patterns in the Late Palæozoic; adapted from Stollhofen et al. (2008). Work by Visser (1987, 1997) and Grill (1997) showed that not all of these ice centres were active at the same time

glaciations and later Permian glaciations as a result of its position relative to the South Pole (Fielding et al. 2008b, c). Therefore, it is also difficult to correlate Australia with glaciations in Antarctica, Africa, the Falklands and South America.

1.3 Geological Context

The geology of the Falkland Islands has three main divisions: the Proterozoic Cape Meredith Complex, the Silurian to Devonian West Falkland Group and the Carboniferous to Permian Lafonia Group (Aldiss and Edwards 1999). These are illustrated in Fig. 1.6. The Lower Lafonia Group, of interest to this study, is composed of three stratigraphic units, the Bluff Cove, Fitzroy Tillite and Port Sussex Formations (Fig. 1.7).

1.4 Structural and Tectonic History

The Falkland Islands are just one segment of the Permo-Triassic Gondwanan Fold Belt which was displaced during the fragmentation of Gondwana and opening of the South Atlantic Ocean ~ 300 Ma. As the ocean opened, the Falkland Islands

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Tasmania	Wynard Formation	Ingls Fomation	Wysysad (Sramálon in Wysysad (Sramálon in were deposited in were deposited in southestern (Sordwana denni fenskus Carhoni (reas-Lur) Saramán (Henry et al., 2012).		The Wynger deviation of Thomania. A support of Thomania. A support provide the yarupest of provide the provide the yarupest of provide the support of the provident of the provident of the provident of the provident of the provident of the provident provident of the provident of the provident of the provident of the provident of the provident of the provident of the provident of the provident of the provident of the provident of the provident of the provident of the provident of the provident of the provident of the provident of	Henry et al., 2012
Western Australia	Lithostratigraphic nomenclature for Western Australia's glacial deposits varies considerably among basins and some busins have	more than one formation e.g. three in the Canning Basin.		Permian- Carboniferous sections deposited under glacial conditions >2000m.	The majority of glucial disposits are direct from phytohogical and metal disman metal disposits and metal disposit metal disposit checking and checking having checking having checking having disposit from the Kongurian (Lare Edity Permitual) (Lare Edit	Mory et al., 2008
Eastern Australia	Lithostratigraphic nomenclature for Eastern Australia's glacial deposits varies considerably among basins.		The late Palaozotic cape lasted for -67Ma. The earliest dentices for glacial conditions is dentified in duentified in Oueensland and New South Wales New South Wales (1,246) -2325, Ma Mississippian).	Very variable depending on basin.	The same of the LPM, in terms of the scale system, ice woltment and the properties of the hyperball state of the Perminan The glucial Perminan The scale state of the state plurid state state of the scale share of the state state of the state of the state state of the state state of the state state of the state of the state state of the state state of the state of the state of the state state of the state state of the state state of the state of the state state of the state of th	Fielding et al., 2008b
Pakistan	Tobra Formation		Carboniferous- Permian Permian correlated to the correlated to the South Oman biozone making it Late Permsylvanian in age.	The Carboniferous- Permian succession comprises ~610m of sedimentary rocks.	The Todan Formation in Formation in the educations observes present in cooperator procession cooperator procession with Arabia and Western Australia	Jan and Stephenson, 2011
Oman	Al Khlata	Gharif Formation	Al Khlau Formation is Moscovinn (Martin et Sakmarine (Martin et al. 2008) 15an, of glastial conditions in Oman have been inferred.	Al Khlatı Formation is up to ~800m.	Lower prices of the All Rilatin Formation Distribution and the analysis of the All betweenheaders of the All phytologyer of the and phytologyer of the All and All and a distribution of distribution of a distribution of distribution of a distribution and Stati Arabia and Stati Arabia and Arabia and Arabia Arabia and Arabia and Arabia Arabia and Arabia and Arabia and Arabia and Arabia and Arabia Arabia and Arabia and Arab	Martin et al., 2008
Yemen	Khulan Formation	Akbarah Formation	in building indextentioner in building indextentioner and the production of the second potential of the Alkenia Permution and the Alkenia Permution		diametric beneficient of the diametric beneficient. A sub- lease of the second on the the Endergy Arm Thie of Endergy and the the tea- ter of the teat of the teat of the over present density of the teat Martin et al. 2003) Martin et al. 2003) and second the teat of the Martin et al. 2003) and the teat of the teat of the mark of the teat of the teat of the teat of the teat of the teat of the teat of the teat of the teat of the teat of the teat of the teat of the teat of the teat of the teat of the teat of teat	Stephenson et al., 2011; Stephenson et al., 2012
Antarctica (Ellsworth Mountains)	Whiteout conglomerate	Polarsar Formation	is Pennet Carginomestare Neuro Carginal Carginal and Carginal in Antarctica may have existent for a may have existent for a may for a for an spectra to first. (253-258 Mb) to for may form the carginal for the maximum sector and Powerl, 1987. Powerl, 1987	Diamictites can be 1000m thick: In the Darwin Glacier Region, the Tillite is 148m thick and is unconformably overlain by 1370m of fluvial- delutic strata (Polarstar Formation).	inferral number origin inferral for deposits in Polarizati Formation in Polarizati Formation in Polarizati Formation in Polarizati Formation in solution in polarizati vision in PODM in the Without in nonlerar Without in the Polarizati in the Pallande Haroy entics in persols in some and the source discoversion source discoversion source discoversion source former discoversion complicate the picture.	Matsch and Ojakangas, 1992
Falkland Islands	Fitzroy Tillite Formation	Hells Kitchen Member is the transitional strata. Black Rock Member is post glacial.	-290 Ma 290 Ma	The Fitzroy Tillite is ~600-900m, the Hells Kitchen Member is ~7m and the Black and the Black -150-250m in East Falkland.	Rate archaosyathan Imaseone probles in the full correction control correction control Antaretica (Soun- Antaretica (Soun- Antaretica (Soun- Datasete (Dow- Datasete	Crowell and Frakes, 1972; Veevers and Powell, 1987
South Africa	Dwyka Tillie Formation	Prince Albert Shale is the transitional strata. Whitehil formation is post glacial. These formations form the Ecca Group.	Days Tilluc Enc Photoineau, Lare Wesphalman of Sephanian to the Early Permit Arritanian Lares galacipanic deposit is Arrinskain Kungunian Lares Lizub Yennun Pincse AbserVMachill Early Hennian and Early of Larup Hannian Early Charge The Early of Larup Han, bees deal photole Larup of Larup Han, bees deal photole and 286 0 ± 3.0 and 286 0 ± 3.0 Ma.	Glacial marine succession: 1000m	Galaspite dependence carry with the Kano basin throughout conditors (Arica. To evolution the characher paint costs and a <i>Charachers</i> (Dipper Cachendrens and proved Perturbation in Southers (Arica. and Charachers and Perturbations the second strategies and Perturbations the second strategies and Perturbations between Charachers and Perturbations intervents and the pass of the proving runner cost thesis in Equi-tor were regulated and the Devis and the Devis and the second strategies and proving and cost the second between the proving runner cost of the regulation and the Devis and the regulation and the Characher the regulation and the Characher the regulation in the Line Perturbation (and the second science (SHRMP) distor (Arica and Spacial Science) (SHRMP) distor (Arica distors (SHRMP) distor (Arica distors) (SHRMP) distors) (Visser, 1987; Isbell et al, 2008a; Trewin et al., 2002
Paraná Basin, Brazil	ltaræé Group	Palermation, Rio Bonito Formation	The littent Group strain are mought to be Permission to Early Permission (Modos)and to Early Permission (Stational) 17-23 my, Redsh- Skatamistor 17-23 my, Redsh- Avarape et al., 2005) Avarape et al., 2005 Avarape et al.	ltararé subgroup: up to 1500m. Glacial marine succession: 1100-1400m.	The slat Britansis galaxies in subschimde define the strand sector of the strand sharin suggests a temperature strand-saced regime for the galaxies. A least nume and sector beau recognised in the harme's addressing	Holz et al., 2008; Rocha- Campos et al., 2008; Stephenson, 2008
Argentina	c.g. Sauce Grande Formation, Sierre de la Ventana. ventana yada Verde Formation: Hoyada Verde, Tres Saltos and El Retamo subunits.	e.g. Piedra Azul Fromationa is the transitional strata, Bonete Formation is postglacial. e.g. Heyada Verde e.g. Heyada Verde Formation: Esquina Gris subunit.	Salos and Seder, Tess Salos and B Reaman submis are Lue submis are Lue Equina Griss, Early Permian (Salonarian).	The Sauce Grande Formation reaches a mix kness - 300m. In the study site of Heary et al. (2008) there were 175m of glacial deposits and 85m of post-glacial mudrocks.	Chiel,pote kana associated vin the proce-breaching more breaching ware deposited in the On Digense (yes) and the Paguen between and the Paguenta between and the Paguenta central Argentina.	Alessandretti et al., 2013; Amos and Gamundi, 1981; Henry et al., 2008
	Glacial strata	Transitional strata/ Postglacial strata	Jacob	Thickness	Comments	Key References

Missing information and inconsistencies reflect gaps in current understanding and a need, in particular, for improved chronology



(Fig. 1.5 Synthesis of existing stratigraphic records from Australia, Antarctica, South Africa and South America suggests that major climate events were diachronous across Gondwana. Dominantly, Carboniferous glaciation in South America was gradually succeeded by dominantly Permian glaciation in Antarctica and Australia

microplate was rotated clockwise by 120° and then translated 300 km south (Marshall 1994). Palæomagnetic poles from Jurassic dolerite dykes on West Falkland show significant rotation ($\sim 100^{\circ}$) occurred before the Cretaceous opening of the South Atlantic, which caused a further $\sim 55^{\circ}$ rotation (Rabinowitz and Brecque 1979). From the asymmetry of the aeromagnetic anomalies associated with individual dykes, Stone et al. (2009) suggested that rotation occurred between the intrusion of the Early Jurassic dykes at about 180–190 Ma and the emplacement of a second swarm of Early Cretaceous dykes that were intruded between about 121



Fig. 1.6 Geology of the Falkland Islands; modified from Stone and Aldiss (2001). *Inset* shows location of core sites: borehole DD029 [377975 4260500] and DD090 [374470 4261720]. A guide to lithologies is provided in the stratigraphic column (Fig. 1.7)



Fig. 1.7 Generalised stratigraphic column illustrating the three broad stratigraphic zones and the three lithologies found in these Late Carboniferous–Early Permian cores (the Fitzoy Tillite, the Hells Kitchen Member and the Black Rock Member)



Fig. 1.8 Summary of the deposits and structural deformation in the Falkland Islands ~180 Ma, modified from Trewin et al. (2002). Arrows indicate mean palæocurrent vectors. The Falklands microplate is rotated through almost 180° and placed off the east coast of South Africa in proximity to East Antarctica and the Ellsworth Mountains microplate. The Falkland Sound Fault marks a significant deformation edge to the Cape Fold Belt. Tectonism along the convergent margin of Gondwana resulted in the Karoo Basin of South Africa evolving into a foreland basin (during Dwyka Group accumulation) bounded by the southern (Cape fold belt) and northerm (Cargonian Highlands) uplands. In the Falkland Islands, the Fitzroy Tillite Formation is the equivalent of the Dwyka Group, while the upper part of the Lafonia Group equates to the Karoo foreland basin deposits

and 135 Ma (Richards et al. 2013). Geophysical models offshore find undisturbed Jurassic–Tertiary beds which support an Early Jurassic age for rotation (Hyam et al. 2000). This reconstruction is consistent with structural, geometric, seismic, palæocurrent and palæomagnetic constraints which also suggest the Falkland plateau arrived at its present geometry ~ 130 Ma. Based on the palæomagnetic data of Taylor and Shaw (1989), rotation must have taken place during or after the emplacement of the mafic dykes (190 Ma) and before or during the development of the sedimentary basins; this rules out rotation during the main phase of Gondwanan folding 278–230 Ma (Curtis and Hyam 1998). When the islands are restored to their prerotation position, palæo-ice flow directions from the tillites appear east to west, matching those in South Africa (Frakes and Crowell 1967) (Fig. 1.8). The final breakout and associated movements of these and other Gondwana fragments was rapid and correlated with a major magmatic pulse related to a mantle plume beneath Africa and Antarctica at 130 Ma (Curtis and Hyam 1998).

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Chapter 2 Materials and Methodology

Abstract Two borehole cores extracted between Old House Rocks and Black Rock, East Falkland, were studied using a combination of detailed sedimentary logging and geochemical analyses. The former involved grain and clast studies while the latter included X-ray fluorescence (XRF) and reflectance scanning using an Avaatech XRF core scanner. Logging data collected incorporated details on grain composition, size, shape, sorting, orientation, colour, sedimentary structures and fossils as well as a detailed account of variations in clast characteristics. A full scan of the original hand-drawn log is presented in the data postscript at the end of this book, and a digital version may be found online as a SPRINGER EXTRA. The high-resolution log was generated at a scale comparable to the X-ray fluorescence and reflectance data collected by the core scanner to encourage subsequent, more detailed climatic interpretations. The core scanner measured variations in element concentrations downcore and three reflectance parameters: lightness, red:green ratio and yellow:blue ratio. Total Organic Carbon (TOC) measurements on loose fragments throughout core DD090 were also taken. Cyclicity observed in the XRF and reflectance data was compared alongside Milankovitch orbital cycles through age modelling, thereby helping to constrain the time frame spanned by the deposits.

Keywords Sedimentary logging \cdot XRF \cdot Reflectance \cdot Clast content \cdot Total Organic Carbon \cdot Age modelling

2.1 Overview

Detailed sedimentary logging was combined with high-resolution X-ray fluorescence (XRF) and reflectance scanning of two borehole cores, DD029 and DD090, to allow precise stratigraphic correlations and detailed sedimentary and climatic reconstructions. The cores used in this study, DD090 and DD029, have incomplete recovery in the diamictite sections ($\sim 10-20$ %) but were selected because they captured the contact between the Fitzroy Tillite and the Hells Kitchen Member and because they appeared to have the most stratigraphically complete sequence through the Hells Kitchen Member, which is crucial to understanding the climatic transition. Table 2.1 summarises the sections of cores DD029 and DD090 that were available and used in this study.

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Core	Total core length	FT available	FT studied	HK available	HK studied	BRMa available	BRMa studied	BRMb available	BRMb studied (m)
	(m)	(m)	(m)	(m)	(m)	(m)	(m)	(m)	
DD029	227	222.8-181.3	181.3-190	181.3-176.4	181.3-176.4	176.4–170	176.4–170	0	0
DD090	395	395-392	395–392	392-383.5	392-383.5	383.5-375	383.5-375	153.8-161.8	155.8-156.7,
									157.9-158.7

Table 2.1 Measured thicknesses of the three main units in cores DD029 and DD090 and the parts involved in this study

Fizroy Tillite (*FT*), Hells Kitchen Member (*HK*) and Black Rock Member (*BRMa* and *BRMb*). Subdivision of core here is that of Stone (BGS report 2011)

Note Thicknesses indicated are not equivalent to stratigraphic thicknesses

2.2 Logging

A 2:1 stratigraphic log was produced by recording millimetre-scale changes in lithology along the length of both cores. Log depths were corrected for the drilling angle and the dip of the beds (Fig. 2.1). Scanned images of the original logs and a digital version are presented in the appendix.



Fig. 2.1 Technique for measuring bed thickness

Box 2.1 Conversion of Apparent Thickness (a) to True Stratigraphic Thickness (t)

The true thickness of a bed (*t*) is the perpendicular distance between adjacent bedding planes. However, because the beds were dipping and the drilling angle was oblique to bedding, the measured value '*a*' was multiplied by the cosine of the maximum angle the beds made with the horizontal (θ), measured on the curved surface, to find '*t*': *t* = *a* cos θ .

2.3 Reflectance Scanning

Reflectance scanning was carried out using the Avaatech core scanner in the sedimentary laboratory, University of Cambridge. Preparation of core samples included sanding the upper cut surfaces of the segments to remove the original ink labels and milling lines. Sanding by hand proved the most effective method since pieces were commonly fractured or brittle and had to be handled with care. Prior to scanning, the light in the scanner was allowed to warm up for around 30 min and a blind was drawn to avoid alteration to image brightness.



Fig. 2.2 CIE L*a*b* colour scale defined by the Commission international de l'Éclairage, HunterLab manual (2008); figure is modified from this manual. L* characterises lightness scaled from 0 (*black*) to 100 (*white*). The parameters a* and b* are chromaticity coordinates that define the colour: a* ranges from -60 (*green*) to +60 (*red*) and b* from -60 (*blue*) to +60 (*yellow*)

The cores were then illuminated by high-intensity light with a broad spectrum across all wavelengths to allow photographs and reflectance data to be collected. Scans were run at lens aperture '8+' against standard colour charts. This process is non-destructive and fairly rapid. Long reflectance measurement bands were then drawn on the images generated, over the same central section of the core where XRF data were also collected to ensure effective comparison later. Colour reflectance values were summarised using the L*, a* and b* parameters (Fig. 2.2). This ratio scheme was used because raw colour is dominated by brightness and so gives less independent information.

The reflectance scanning results have been assimilated onto a depth scale comparable to the log and clast data (Box 2.2) and are shown in the appendix.

Box 2.2: Generation of Depth Scale for Reflectance and XRF Data

Original depth labels on the segments were approximate and marked according to drilling depths rather than true stratigraphic thicknesses. They had been extrapolated from drillers' markings which amounted to a figure for the top and bottom of each core box (each box would hold about 5-6 m) and an insert, where present or legible, every 1-1.5 m marked with the depth figure. When producing a depth scale, the positioning of these labels was initially not corrected for using the dip of the beds because their positions were clearly vague and this adjustment would only have increased implied overlap. Some indication of the position of the labels within a segment was measured though and the depth correction to reach the segment top applied.

Complications also arose because the XRF and reflectance data were collected along the cut surface rather than perpendicular to bedding. Therefore, to make these data sets comparable with the log and clast data, depth control points were inserted into the XRF and reflectance scales for the two cores at the beginning and end of each segment and the depths in-between linearly interpolated. The full procedure is outlined in Appendix A.1.

2.4 XRF Scanning

A continuous record of elemental data was collected non-destructively at the split core surface using the Avaatech X-ray core scanner. Before running samples through the scanner, the X-ray tube was allowed a warm-up time of 30 s and four standards were run twice at the 10 kV energy band; the 10 kV band is the most sensitive measure to fluctuations in counts. The removal of the ink labels during sanding also prevented biases to the signal. The labels were found to cause considerable alteration to the chemistry on trial XRF runs. Non-continuous segments were positioned with sufficiently wide gaps such that the detector could skip between them and avoid damage to its Ultralene window. The level of the core segments was checked using a mini-spirit level, and they were secured where necessary using foam to prevent them being caught by the moving window.

The X-ray source progressively irradiated the cross-core and downcore directions causing fluorescent energy, characteristic of atoms of specific elements, to be emitted. The chemical composition of the sediment was measured as element intensities in total counts. Heavier elements require more energetic photons in order to fluoresce, so both cores were run on three different energy levels (10, 30 and 50 kV) to activate different sets of elements and provide reliable element intensities (Fig. 2.3). A computer registered the energy of every photon, allowing for the creation of a spectrum. A spectrum interpretation software package, WinAxilBatch, was then used to interpret spectra quantitatively by assigning distributions of photons (counts) at different wavelengths to elements. Each metre segment was run over 24 h collecting two replicates at an interval of 1:25, a step size of 2.5 mm, a downcore slit size of 2.5 mm and a slit size across core of 12 mm; a level of resolution comparable to the logs. The data were then normalised to aluminium (Box 2.3). Standards were run to check the consistency of results and machine behaviour. The complete XRF data sets from both cores are presented in the appendix on the same depth scale transformation as the reflectance data.

Box 2.3: Normalisation

In variable settings, such as lakes (the arguable depositional setting here; see Chap. 4), the strength of the XRF-scanning method lies in an analysis of the relative variations of the different elements compared to a major conservative element to obtain an environmentally relevant signal (Löwermark et al. 2011). Without such normalisation, biological or diagenetic processes can influence elemental counts and interpretations would be at risk of becoming a mirror of organic matter (or carbonate) variations (Löwermark et al. 2011). Even with an absolute calibration, changes in flux rate of particular elements and dilution effects are extremely difficult to separate. While normalisation does not compensate for the effects of sediment composition, it does help to compensate for some effects of surface irregularity (Weltje and Tjallingi 2008). Therefore, the relative signal strength was used as an indication of compositional change and interpreted in terms of climatological and sedimentological change. Normalisation also enables presentation of data from elements with very different XRF count rates. Log ratios accommodate the non-linearity of the relationship between relative intensities and concentrations. Table 2.2 evaluates possible elements which may be used for normalisation and the rationale behind the choice of aluminium.

Element	Comment on suitability
Fe or Mn	Unsuitable because of their redox sensitive nature
Na, K, Sr or	Easily dissolved and weathered out so unsuitable
wig	
Ti	Ti is an important component in many minerals, is abundant and not very active biologically. However, Ti is enriched in heavy minerals and in aeolian dust and is therefore used as a proxy for high current regimes or enhanced wind activity. Also, Ti content is highly influenced by the composition of the original protolith
Al	Normalisation to Al helps reduce problems associated with surface irregu- larities, which tend to decrease counts of most elements. Al is abundant and little affected by diagenetic and biological processes such as redox reactions. As it is a major structural component in the sand, silt and clay that enters basins, normalisation of the other elements against Al allows the changes in proportion of the individual elements in the lithogenic component of the sediment relative to each other over time to be indicated in terms of aeolian, terrestrial and biogenic inputs

Table	2.2	Reasoning	behind	the	choice	of	aluminium	for	normalisation	summarised	from
Löwer	mark	et al. (2011)								

2.5 Clast Data

Details on clast composition, size, frequency, sorting, roundness, sphericity and orientation were collected from core DD090 in order to better understand sediment source area and ice sheet flow patterns and processes. Frequency was recorded as a



Fig. 2.3 The range of elements that are activated for the different instrument settings (information from Xelerate Documentation, University of Delft, Bloemsma (2012)) are highlighted on the periodic table. Elements between 13 Al and 92 Ur could be detected and included in the deconvolution

percentage while sorting, sphericity, roundness and orientation were ranked on scales 0-2, 0-10, 0-10 and 0-10, respectively; where the higher number in each case corresponds to a higher degree of the variable in question. The comparator charts used are provided in Fig. 2.4. Plotted data from the clast analysis are presented in the appendix.



Fig. 2.4 Comparator charts used for estimating clast \mathbf{a} size, \mathbf{b} abundance, \mathbf{c} shape (including *roundness and sphericity*) \mathbf{d} sorting. Figure compiles and modifies relevant diagrams from Tucker (2003)

2.6 Total Organic Carbon

Nine loose fragments from core DD090 were collected for Total Organic Carbon (TOC) measurements: one from the diamictite, five from the Hells Kitchen Member and three from the Black Rock Member. The samples were ground to a powder before being placed in an oven at 60 °C to remove any moisture. They were weighed after 4 and 8 h to ensure constant weight. Once their mass stopped declining, they were added to separate beakers containing ~ 15 ml 1 M HCl to remove inorganic carbon present as carbonate. TOC content was then determined by dry combustion. This procedure collected information on ¹³C isotopes also. The mass of the samples before and after drying and bathing in acid is shown in Table 6.1.

2.7 Development of an Age Model

The XRF and reflectance data were used to construct a relative age model, and the existing absolute dates from other localities across Gondwana informed judgements of when the transition took place in the Falklands. Spectral analyses and wavelet analyses were used to look for prominent periodicities in the depth domain and from these observations, a tentative relative age model was developed and further wavelet analyses undertaken (see Chap. 4). Although absolute timescales become increasingly imprecise with increasing age (Arthur and Garrison 1986), it was hoped that biostratigraphy in the form of micropalæontology might play a supporting role in constraining the time frame over which the icehouse to greenhouse transition took place. However, studies of similar Falkland Island material by Mike Stephenson of the British Geological Survey (personal communication) suggest a lack of suitable spores/fauna in the cores for absolute dating.

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Chapter 3 Analysis of Results

Abstract Understanding the environment of deposition in detail is crucial to appreciating the global context and significance of Permo-Carboniferous climate change. This chapter looks in detail at the nature of the Falkland Islands sedimentary deposits logged over the icehouse to greenhouse transition. A discussion of the underlying mechanisms driving the observed variations in sedimentology is presented. In outline, a massive diamictite deposited subglacially and with a variety of clast types, gives way to an interlaminated unit of diamictite and mudstone followed by a mudstone-dominated unit. The interlaminated zone forms the focus of this chapter since it is this stratigraphic section which tracks the icehouse to greenhouse transition. In the more stratigraphically complete core, DD090, four broad lithological zones are identified within this section. These are thought to represent two major episodes of advance and retreat of an ice sheet. This signal is overprinted by higher frequency oscillations depicted in millimetre-scale laminations and sedimentary structures. Dominantly subglacial deposition was replaced by a fluctuating ice-proximal to ice-distal environment before the onset of ice free open water conditions persisted. The sedimentary log is compared with the XRF and reflectance scans and correlations drawn where possible.

Keywords Diamictite • Mudstone • Dropstones • Ice • Aqueous deposition • Facies • Elemental variations

3.1 Sedimentology and Structure

3.1.1 Fitzroy Tillite Formation

Core DD029: corrected depths 190–183.1 m Core DD090: corrected depths 395.1–392.4 m

The Fitzroy Tillite is a glaciogenic diamictite widespread across the Gondwanan fragments. It records the glacial episode that the Falkland Islands region of the supercontinent experienced around 290 Ma (Stone et al. 2005). In both cores

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DD029 and DD090, the tillite is massive and unstratified with a relatively clast poor $(\sim 25 \%)$ silty matrix displaying no evidence of bioturbation or microfossils (Plate 3.1). The pale grey colour of the matrix reflects its low total organic carbon content of 0.18 % and the high proportion of quartz (see XRF plots of Si/Al log ratios in Sect. 6.3). The poorly sorted matrix of sand and mud supports angular to rounded clasts of a wide range of lithologies including, on average, 50 % mudstone intraclasts, 2.5 % chert, 12.5 % sandstone, 2.5 % calcite and 7.5 % granite (Plate 3.1d). The average diameter of the clasts is 4 mm, maximum 35 mm, and using visual estimates, average clast sphericity is 6.5 and average roundness is 3. The long axes of the clasts are randomly orientated, and their subangular nature suggests little transport prior to incorporation into ice. Gneiss and granite clasts may have been plucked or abraded from the Pre-Cambrian Cape Meredith Complex and guartzites, sandstones and mudstones from the West Falkland Group. Others, such as clay fragments, for example at 393.3 m (core DD090), are probably intraformationally derived. Rare limestone clasts with an Early Cambrian archaeocyath-trilobite fauna were most likely sourced from the Transantarctic Mountains. This indicates that the Late Carboniferous ice sheet flowed from the contemporary polar region to at least $\sim 60S$ before becoming waterlain (Stone and Thomson 2005; Stone et al. 2012).

Glaciotectonic structures are common in the tillite. Planar shearing is indicated by the shear lines running across beds and wrapped around clasts (Plate 3.1b), the dispersion tails of clay pinching out from clasts and the deformed soft sediment intraclasts. Whispy mudstone laminae and lenses in core DD029 often appear sheared, and well-defined clay rims surrounding some of the clasts probably formed by rotational processes in the deforming bed environment (Mckay et al. 2012). Fractures, brecciated bands, glossy surfaces, refracted cleavage, veins and slaty cleavage also reflect shearing and possibly ice sheet overriding and are found within the diamictite section.

Massive diamictites such as this may develop in subglacial, glaciomarine and/or open marine environments as a result of mass flow deposition (Anderson et al. 1980) or from homogenisation of glaciomarine sediment by iceberg scouring (Dowdeswell et al. 1994). Although waterlain till can form massive beds, any water movement causes reworking and sorting, so some stratification would be expected (Aldiss and Edwards 1999). The Fitzroy Tillite has no clear evidence for water sorting, suggesting there was limited subglacial meltwater and deposition occurred beneath grounded ice. Tentative minor intercalations of mudstone in core DD029 were later identified as joints lying subparallel to bedding, possibly similar to those described in outcrop by Aldiss and Edwards (1999). There is poor colour differentiation between them and the diamictite matrix. In addition, randomly orientated clasts, in particular bullet-shaped clasts (Plate 3.1c), are more indicative of lodgement till than waterlain deposits. Further, fissility of till, as found in core DD090, can indicate a subglacial origin (van der Meer et al. 2003) as do the shear structures in the top of beds (Plate 3.1b). The distal provenance of the clast compositions in the tillite might reflect large-scale grounded ice sheet expansion rather than local mass flows. Frakes and Crowell (1967) used evidence from palæocurrents, the orientation of linear sand bodies, the eastwards decrease in mean and maximum



Plate 3.1 Fitzroy Tillite (sketches are taken from original lithological log). **a** Representative section of Fitzroy Tillite with photograph (core DD090). Scale refers to depth in metres marked on core. A full lithological key to the digital log extract shown here is provided alongside the complete lithological log in Sect. 6.1. **b** Bed interpreted to have formed through shearing by the overriding glacier; there is no change in lithology across contacts. Later vertical shear lines perhaps associated with tectonic deformation (Gondwanan orogeny) were then refracted through this bed. **c** Bullet shaped clast characteristic of lodgement till deforms sedimentary fabric around sandstone clast. **d** Large granitoid clasts in the Fitzroy Tillite. Other clasts visible include quartz, calcite, limestone and chert as well as clay intraclasts and granules

clast size, clast fabrics, rare ripple marks and primary current lineations to deduce an overall west-to-east transport direction across the Falkland Islands in their current rotated position. This is consistent with ice flow in the Eastern Cape (Fig. 1.4).

3.1.2 Hells Kitchen Member (Port Sussex Formation)

Core DD029: corrected depths 183.1–173.6 m Core DD090: corrected depths 392.4–381.2 m

The massive diamictite is overlain by stratified muds and coarse beds belonging to the Hells Kitchen Member (Plate 3.2). This member is a transitional succession, comprising thinly interbedded diamictite, siltstone, claystone and rare wacke, that represents a temporary and fluctuating glacial regression. The interplay among depositional processes, including release of glacial debris from ice, gravity flows, iceberg calving and reworking by currents, makes the sedimentary facies complex. Depending on the thermal conditions of the ice and water, undermelting may also have been important, releasing debris close to the buoyancy line, or sea water may have frozen on resulting in sediment transport to the ice-shelf margin (Matsch and Ojakangas 1992). The following discussion focusses on the more stratigraphically complete core (DD090) which consists of four broad lithological zones in the Hells Kitchen Member.

 The first part of the transition in core DD090, depths 392.4–391.2 m, is dominated by silt and clay beds but pebble laminae are interspersed. The presence of stratification and sorting could indicate current activity in the depositional



Plate 3.2 Lithological changes at the Fitzroy Tillite to Hells Kitchen Transition. **a** Fitzroy Tillite to Hells Kitchen Member transition at \sim 392.4 m in core DD090. **b** Fitzroy Tillite to Hells Kitchen Member transition at \sim 183.1 m in core DD029

environment (Matsch and Ojakangas 1992). Finer material may reflect hemipelagic suspension settling of fines (Passchier et al. 2011) derived from winnowed waterlain diamictites and a shift away from subglacial conditions to an environment more distal to the grounding line. Linear, sorted clast layers (Plate 3.3a) suggest aqueous sedimentation (Michalchuk et al. 2009) and perhaps some transportation away from the grounding line. Alternatively, the clasts may be fall out from large icebergs (Fig. 3.1). Abundant dropstones reflect icebergs or a floating ice-shelf transporting larger clasts to the site. Pebble beds increase in thickness towards the top of this silty zone. Clasts are often erratics composed of reworked diamictite matrix.

2. Between depths 391.2–389.5 m in core DD090, a zone characterised by a higher frequency of coarse beds, there are a series of fining upwards sequences. An iceproximal environment can be a highly energetic zone depending on the stability of the ice margin. The fining up sequences may have formed by hyperconcentrated density flows or turbidity currents which are common in proximal proglacial environments where slopes are unstable (Powell and Dormack 2002). Alternatively, meltwater outflows at the retreating grounding line may be responsible. The gravelly and sandy laminae and occasional pods which follow have sharp upper and lower contacts, are millimetre to several centimetres thick and typically massive, and are interspersed with mudstone containing intraclasts and dropstones. Such coarse unstratified beds of diamictite may be interpreted as meltout through a narrow water column either directly from the basal debris layer of an ice shelf or from material transported in meltwater plumes (McKay et al. 2009). Their lack of internal structures and sharp contacts with dropstone bearing mudrocks and rhythmites is suggestive of deposits of rainout and debris flows (Henry et al. 2012).

Stratified diamictite beds have aligned clasts of similar size interspersed with wavy mud laminae (Plate 3.3a). Again, this could reflect meltout of basal debris associated with lift off and development of a floating ice shelf (McKay et al. 2012). The presence of intraclasts and the compositional similarities to the underlying massive diamictites might support this. However, this process would provide a wide variety of clast sizes, whereas clasts in the bedded diamictite are restricted to granules and small pebbles. Sediment gravity flows, suspension settling of clay and silt from underflows and overflows, subaqueous debris flows and turbidity currents common in ice-proximal settings (McKay et al. 2009) are thus expected to have played some role in sorting the material too. Lithification and variation in porosity and permeability may also have assisted in the formation of layering (Frakes and Crowell 1967).

Deformation in the diamictite beds is likely to be caused by a combination of glacial push, ice loading, compaction, debris flows and soft sediment deformation (Fig. 3.2). Deformation structures such as flames reflect water escape and loading by denser material, ice or dropstones into underlying water-saturated sediment (Plate 3.3 and 3.4). Some mudstone layers exhibit convolute bedding,



Plate 3.3 Styles of sedimentary deposition and soft sediment structures. **a** Stratified diamictite bed with wavy mud laminae and scattered dropstones are envisaged accumulating at the margin of a wasting glacier without significant alluvial or outwash reworking. Mud probably originated from suspension settling of hemipelagic material or from meltwater plumes during intervals when iceberg delivery was suppressed by the development of shorefast ice. Wavy individual layers 1 mm to 1 cm thick are deformed around clasts scattered within the sequence; they are examples of drape structures. **b** Flame structures either associated with loading by a diamictite layer which developed fissures on its upper surface by later dewatering, or alternatively this layer may comprise reworked clasts from the underlying till. **c** Example of large dropstone associated with sedimentary drape and tentative burrow structure.



Plate 3.3 d Examples of reworked silt and diamictite clasts, sometimes they have lensoid shapes probably due to compression prior to lithification. **e** Examples of sedimentary fabrics associated with clasts. *Left* Dropstone with sedimentary drape, shown with corresponding log section. *Top right* Sketch of diamictite rip-up clast. *Bottom right* Sketch of dropstone piercing stratification. **f** Rhythmic thinly laminated varve-like deposits consisting of distinct silt-clay couplets with sharp contacts. The coarse component is likely deposited from overflow and interflow plumes generated during the ablation season whilst the fine component records gradual settling of the finest material during winter when there is little or no incoming water to the lake/marine environment (Benn and Evans 2010). Perhaps the term varve should be used with some caution though as it cannot be demonstrated for certain that they represent seasonal depositional cycles

slumping and warped contacts and mix with underlying stratified diamictite; commonly, they have not retained an even thickness during compaction and cementation, reflecting their incompetency.

Clasts in this part of the Hells Kitchen Member are angular to rounded, poorly sorted and lithologically variable although overall they seem to have a more local provenance than those found in the massive diamictite, for example, there is a reduction in granite and an increase in siltstone. Till pellets may be products of ablation, while rip-up clasts were scraped or lifted off the tillite by basal ice. Large clasts that pierce stratification or appear to have deformed sediment on impact were probably ice-rafted debris (IRD). Evidence for floating ice discounts the possibility of a fluvial origin for these deposits. Similarly, clumps of small pebbles and granules in the stratified diamictite were probably frozen aggregates of coarse sediment, held together by interstitial ice that fell from icebergs (Gilbert 1990). The lack of fossils and bioturbation and dispersed clasts probably indicate limited sub-ice-shelf oceanic circulation with high sedimentation rates (McKay et al. 2009) and low light penetration close to the grounding line.

3. A second zone of interlaminated clay and silt in core DD090 occurs between depths 389.5–387.1 m and is broadly similar to the first. However, its base is marked by abundant dark grey to black well-rounded granules which may be volcanic lapilli (see XRF analysis) followed by a chert nodule (Plate 3.5d). Volcanic detritus has previously been found within the Fitzroy Tillite and was suggested to have been derived from a magmatic arc associated with subduction on the Pacific margin of Gondwana (Cole 1992). As the grounding line retreated upstream relative to the drill site, mudstones appear to have been deposited



Fig. 3.1 An example of how debris may be released from drifting and melting icebergs showing the effects of calving, fragmentation and overturn (redrawn from Drewry 1986). Material may be dropped as the ice melts, perhaps as frozen aggregates or be released from crevasse fills through overturn. Where possible the core DD090 deposits are linked to this analogy



Fig. 3.2 Schematic diagram of microstructures that can develop at the base of a debris flow diamictite (adapted from Phillips 2006: In Benn and Evans 2010)

beneath a floating ice sheet with less basal debris. Thick mudstones with sparse diamictites and sandstones also hint at an increased input of meltwater from nearby terrestrial sources during glacial minima and deposition by suspension settling from such plumes. Perhaps there were some sporadic debris flows: pelagic mud alternating with silt may be rhythmites originating from underflows or turbidity currents (Cole 1991). Around 388.7 m, thin coarse beds reappear. Coarse beds make up ~ 30 % of this zone and increase in thickness towards the top. It is possible that the spacing of these beds is a reflection of high-frequency orbital cycles such as precession (see Chap. 4).

4. Between depths 387.1–385.6 m in core DD090, coarse beds ~20 mm thick become abundant and some of them fine upwards. The sediments are composed of varying mixtures of terrigenous deposits in the form of IRD and hemipelagic components. The increase in pebbles could signify the final breakout of marginal ice (Michalchuk et al. 2009). Clay and silt pebbles dominate, and roundness values ~6 suggest some reworking took place. A clast count indicates cyclical changes in lithologies, average clast diameters, sphericity and roundness possibly reflecting waxing and waning of the glaciers and changes in clast provenance. Individual beds up to 4 cm thick grading from diamictite or wacke to mudstone may have been produced by bottom currents and represent interludes of more energetic water circulation accompanying the periodic retreat of the ice shelf in the generally quiet realm of aqueous sedimentation. Normally graded beds and rapid stratigraphic changes could also occur as a result of fluctuating discharge.



Plate 3.4 Deformation in the Hells Kitchen Member. **a** Small fault blocks may have formed from ice push or as material slid downslope. **b** Slumping and folding in stratified diamictite with associated loads and flames may be linked with ice-marginal deformation. Folding likely occurred due to frictional differences along the basal surface of the bed as it moved across the substrate. **c** Example of shear fabric wrapping around a clast. Since these deposits are not thought to be subglacial the shearing may be linked with later tectonic deformation such as the Gondwanan orogeny. **d** Second example of microfaulting with ~ 2 cm offset. It is from a zone of coarse beds (387.1–385.6 m) so the faulting maybe linked with the more energetic subaqueous conditions during increased glacier and iceberg cover



Plate 3.5 Diagenesis and volcanics. **a** Extensive calcite veining penetrates clay bed. Orange colouration in parts is probably due to iron staining. **b** Pale 'plume' probably caused by the introduction of silica-rich fluid in association with veining. **c** Chert nodule associated with microfaulting. **d** *Dark black* grains thought to be volcanic lapilli on account of their elemental composition (rich in heavy mineral elements and low in potassium). Up sequence there is a chert nodule; curved core surface indicated that it is not laterally continuous. **e** Pressure dissolution along silt-clay contact associated with stylolite. Some fine white calcite veins are also visible

In the youngest part of this zone, there are abundant black clasts less than 1 mm long. Their irregular shapes suggest they are deformed clay clasts rather than volcanogenic clasts. They are often elongated in the direction of shearing and may be interpreted as fragments of frozen sediment not fully lithified prior to deformation. Deformed lenses of clay and silt are also found. The mottled appearance of some of the silt may be due to bioturbation, dewatering or seismic activity disrupting the laminae. The frequency and thickness of pebbly beds decreases towards the top of the Hells Kitchen Member.

3.1.3 Black Rock Member (Port Sussex Formation)

Core DD090: corrected depths 381.2–374.8 m Core DD029: corrected depths 173.6–170 m

The transition from the Hells Kitchen Member into the post-glacial mudstone of the Black Rock Member is gradational. In this analysis, the Black Rock Member was distinguished from the Hells Kitchen Member by the absence of coarse laminae. The Black Rock Member is instead composed of black/dark grey, laminated, thinly bedded or massive mudstones over which dispersed ice-rafted clasts become scarcer, more scattered and smaller up sequence (Plate 3.6). Beds appeared dark and carbonaceous when seen on cut and polished surfaces, but TOC values of $\sim 3 \%$ suggest the dark coloration is due to dark minerals (perhaps containing iron or manganese) rather than organic material. Occasionally, beds are pyritic or cherty. Between depths 381.2–374.8 m in core DD090, there is high silt content. It is greenish with abundant clay lenses and laminae (Plate 3.6c). Core DD029 has comparable greenish silt with clay lenses beginning around 171 m. Bioturbation is rare.

To characterise fully these post-glacial deposits, two sections were also taken from further up sequence in core DD090; corrected depths 158.88–157.67 m and 156.75–155.71 m. Here, the Black Rock Member consists of clay and authigenic pyrite sometimes in bands (Fig. 3.3). Some white acicular grains may be glendonites, calcite pseudomorphs after ikaite.

The low clast content in the Black Rock Member suggests deposition by suspension settling and occasional iceberg rainout in a quiet, distal proglacial setting with little dissolved oxygen and soft-sediment deformation. The increase in clay probably reveals a deepening water body and a decrease in energy. The greenishblack organic-rich laminated sediments, if bentonitic, may reflect the onset of open water conditions. Silt laminations in clay likely reflect increased meltwater outflow. The presence of localised currents is indicated by the small channel structure in core DD090, and these may have been generated by wind shear, upwellings, ice melting or sediment gravity flows.



Plate 3.6 Sedimentary features of the Black Rock Member. **a** Fragmentary organic layer with load structures or borings and a small concentration of pyrite indicating an anoxic microenvironment. **b** Green silt (bentonitic?) with abundant clay lenses. **c** Mudstone bed with cusp-shaped flame structures formed due to deposition of coarse sandstone up sequence. **d** Dropstone deforming pale (opal?) band which has a possible flame structure





3.2 Reflectance Data

Colour reflectance served as a proxy for lithological variability through the cores. In the diamictite, the moderately high L* (lightness) values, ~ 55 , reflect the mediumgrey colour of the silty quartz-rich matrix. Coarse beds are typically pale because they are rich in silica, while hemipelagic deposits are usually dark and 'red'. L* and a* (red/green) therefore provide fairly reliable indicators of whether sediment was deposited during ice advance or retreat and were used in wavelet analyses (see Chap. 4). Cyclicity in reflectance parameters parallels the lithologies logged. Extreme excursions in lightness were caused by calcite veins (Plate 3.5a). In the outlier sections of the Black Rock Member, the b* (yellow/blue) and L* decline, while the a* rises because this clay is geologically very dark and red. The sharp downward deflection at 377 m in core DD090 is due to the concentration of light coloured pyrite.

3.3 XRF Data

The variations in elemental ratios show trends through time related to sedimentary processes. This means they contain clues about environmental shifts and climatic changes comparable with the physical properties of the sediment logged. In the tillite, elemental ratios are fairly stable reflecting the fairly homogenous matrix composition. A few peaks in certain elements can however be tied with clast mineralogy or veins, for example, the peak in all elements around 393 m in core DD090 and the corresponding granite clast. Based on the sedimentological analysis,

the Fitzroy Tillite to Hells Kitchen Member transition seems to reflect retreat of an ice shelf and the establishment of aqueous deposition distal to an oscillating ice margin. The first major shift in the elemental concentrations in the XRF record occurs at this boundary (Fig. 3.4). There is an increase in the amplitude of the signal in all records and log ratios of the elements silicon, manganese, chromium and zirconium, and iron decrease; zirconium by a factor ~ 3 .

The XRF profiles pick out subtle changes in source area and help to identify glacier advance and retreat. The elements zirconium, titanium and chromium are associated with heavy minerals (zircon, rutile/ilmenite, spinel, respectively), and their variation may reflect changes in sediment provenance. There is a positive correlation between the terrigenous elements, silicon, iron, manganese, chromium and zirconium, and the physical properties documented by the L* and b* parameters. There are, however, some deviations from the broad elemental correlations. For example, at 391.4 m, there is a rise in zirconium (with potassium), while some element ratios fall. Perhaps this reflects the high granite clast content of the coarse beds here which are rich in potassium feldspar and detrital zircon grains from weathered granitic sources.

The $\ln(Si/Al)$ ratio (where ln is the natural logarithm) was used as a proxy for sand:mud ratio because sand (SiO_2) is rich in silica, while clays are typically richer in aluminium. This approximation appeared reasonable since trends in $\ln(Si/Al)$ closely matched grain size trends documented in the logs. In addition, potassium is found mostly in clay minerals such as illite (McKay et al. 2012) so may be used to



Fig. 3.4 Elemental ratios at the transition to Hells Kitchen Member. Transition occurs within the outlined zone. Depth scales are in metres



estimate clay content. Ln(K/Al) is lowest in the diamictite beds where potassiumpoor clasts and abundant quartz are found, and higher in the muddy intervals. Ln(K/ Al) is generally inversely correlated with the heavy mineral elements and correlates positively with the a* parameter. Two sharp peaks in all elements but potassium around 389.4 m in core DD090 correspond to the beds with dark black granules which are thus more likely to be volcanic lapilli than clay (Fig. 3.5).

Ln(Ti/Al) is often used as a measure of provenance or energy change (e.g. Spofforth et al. 2008). Overall, this ratio shows a decrease to more negative values from the diamictite to the mudstone, reflecting the gradual decrease in energy up sequence. An elevated ln(Ti/Al) ratio, for example at 391.5 m (DD090), could be interpreted as arising from a decrease in aeolian dust input, since the absolute counts in titanium and iron show a temporary decrease indicating a drop in the input of these elements. Minerals such as quartz and those rich in aluminium remain in the sediment, while more mobile minerals are rapidly weathered and transported away. The increase in Ln(Ti/Al) could therefore be interpreted to be a consequence of periods of increased precipitation causing increased chemical weathering, enhanced flushing of organic matter into the water and possibly also higher water levels which causes dysoxic conditions at the sediment surface and hence enhanced organic matter preservation (Löwermark et al. 2011).

There are two places where there is a clear negative correlation between iron and silicon in core DD090 (\sim 382.6 and 383.3 m), and both coincide with the presence of pyrite. Thus, the iron here has an authigenic rather than a terrestrial origin, supported also by the peak in manganese, a redox element, in these beds.



Fig. 3.6 Elemental ratios across the Hells Kitchen Member to Black Rock Member transition. The transition begins at \sim 383 m in DD090 and 174.3 m in core DD029. Refer to key provided in Fig. 3.4

Manganese correlates almost precisely with iron in both cores except for around 387.7, 387.5 and 392.2 m. The difference at 387.7 m can be explained by diagenetic veining, and around 387.5 m, there is a zone of dewatering which may be linked with oxygenation of the bottom waters and hence an increase in the production of manganese oxides. Similarly, in core DD090, 392.2 m marks the start of the Hells Kitchen Member, and this transition to subaqueous rather than subglacial conditions may be linked with a rise in oxygen and hence a more pronounced peak in manganese oxide formation than iron compounds.

The gradational lithological shift between the Hells Kitchen Member and the Black Rock Member is captured well by the XRF data of core DD090 (Fig. 3.6). Throughout the cores, there is a gradual upwards increase in the potassium content from 1 to 1.3 on the natural log scale, reflecting the increasing proportion of clay. This is supported by the grain size measurements. Sharp peaks in iron are typically related to concentrations of pyrite. Potassium is inversely correlated with iron because the proportion of clay declines in the layers where authigenic pyrite precipitates. Pyrite was probably formed in situ, as elevated ln(Fe/Al) ratios are indicative of scavenging of iron from the water column. Presence of pyrite also indicates a relatively constant replenishment of iron and sulphur to the water. Reducing conditions at the base of the water column and within the sediments can lead to alteration of much of the iron and manganese oxyhydroxides within the sediments via redox cycling (Dean 1993).

3.4 Total Organic Carbon

As far as it was possible to determine, TOC values reached a maximum of 0.34 % in the Hells Kitchen Member. This probably reflects the cold sub-ice-shelf conditions which are unfavourable to life. Changes in $\delta^{13}C_{org}$ (isotope ratio of $^{13}C/^{12}C$ in organic matter) in marine and lacustrine settings often relate to changes in productivity and/or changes in water and continental organic matter burial that drive or act together with changes in pCO_2 and $\delta^{13}C_a$ (isotope ratio of $^{13}C/^{12}C$ in atmospheric CO_2) (Birgenheier et al. 2010). The general positive shift in $\delta^{13}C_{org}$ could suggest a drop in pCO₂ and/or an increase in $\delta^{13}C_a$ and warming. The negative $\delta^{13}C$ values in the green, possibly bentonitic, silt at \sim 382.2 m might indicate de-oxygenation of the sediments since an injection of ash can increase local productivity (Frogner et al. 2001). Increased proximity to openwater zones of primary productivity would have caused the increase in TOC. Previous analysis of the organic carbon and kerogen in the Black Rock Member found TOC contents up to 40 % (mean 15.5 %) that were dominated by amorphous organic matter (Marshall 1994). The lower values found in the Black Rock Member in core DD090, ~ 3 %, suggest either lower organic productivity, more aerobic conditions or a dominance of terrigenous input.

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Chapter 4 Discussion

Abstract The depositional framework outlined for the Falkland Islands deposits in the previous chapter is investigated in the context of the Gondwanan supercontinent. The focus in this chapter switches from trying to recognise the immediate physical processes responsible for the sedimentological variations, to seeking an explanation for the underlying mechanisms responsible for initiating the dynamic environmental setting. The sedimentology, combined with a review of the existing literature, points most convincingly towards the idea that Gondwana was host to a large subglacial lake. Milankovitch orbital forcing is explored as an explanation for the cyclical nature of the deposits. Firstly, the XRF and reflectance data were subjected in the depth domain to spectral analysis through which prominent periodicities (in depth) could be identified. Then, by considering the data alongside a synthetic Carboniferous orbital solution, an age model and a time constraint for deposition were developed. Orbital cycles appear to be expressed in this stratigraphic record at 100 and 400 kyr periodicities, implying the transition took approximately 1.2 myr. Within the course of the transition, glaciological processes (including the build-up of an unstable ice sheet regime following the intense and prolonged icehouse state) may also have assisted in driving the oscillations. Taking into consideration the phases of glaciation documented across other landmasses that were also once part of Gondwana, together with the expected diachroneity of climate change across the continent, the transition in the Falkland Islands is constrained to the Sakmarian Stage of the Early Permian. Possible causes of deglaciation are also briefly explored in this chapter.

Keywords Lacustrine • Orbital forcing • Age modelling • 400 kyr • Sakmarian • Principal Component Analysis • Wavelet analysis

4.1 Understanding the Environments of Deposition: Facies Evaluation

4.1.1 Overview

The sedimentological and geochemical results support the idea of dynamic and fluctuating glacial and non-glacial conditions in a high latitude, ice-proximal environment within the overall Permo-Carboniferous icehouse to greenhouse transition. The facies interpretation for the sedimentary sequences and structures observed is summarised in Table 4.1.

Two cycles of glacial advance and retreat are recorded clearly by coarse bed frequency and thickness in core DD090. The scarcity of erosional contacts reflects the fact that the deposits preferentially record glacial retreat. Core DD029 shows a less clear environmental signal with coarse beds distributed throughout the transition; the early silt dominated zone found in core DD090 is less well distinguished in core DD029. A possible explanation for this trend is that the more easterly location of core site DD029 remained under grounded ice for longer. However, wavelet and spectral analyses suggest there are the same number of orbital cycles documented in the both cores and principal component analysis (PCA) suggests that climate is the main cause of variance in the sediments rather than sedimentological processes such as turbidites (see Sect. 4.4). Further, core DD029 has similar sedimentary features to several different parts of core DD090; for example, turbiditic sequences near the start and a zone rich in deformed clay clasts further up sequence. The volcanic lapilli in core DD090 are not found in core DD029 probably because the later core is less complete but possibly because of a local shielding effect from the dust. Overall, it seems most likely that the differences between the cores arise from the less complete nature of core DD029.

In summary, the sedimentology of both cores reveals the evolution of a palæoenvironment in which a subglacial diamictite interpreted to have formed by in situ wasting of debris-laden ice became overlain by a marine/lacustrine ice-shelf succession comprising deposits originating from subaqueous mudflow deposits, mobilised till and outwash material. The climate transition is interpreted to have taken place though climatic oscillations rather than occurring gradually. A fluctuating grounding line or periodic anchoring and detachment of a large ice shelf on a submarine topographic high are envisaged, similar to the interpretation of Matsch and Ojakangas (1992) for the Meyer Hills deposits, Antarctica.

4.1.2 Core Comparison: Autocorrelation Test

A 21-point least squares smoothing was applied to the a* reflectance parameter data sets linearly resampled at 0.0001 Ma and an autocorrelation was run (Fig. 4.1). A 21 points smoothing was used because this is the widest smoothing permitted in a

able 4.1 Sedir acies	nentological interpretati	on summary Sedimentology	Denositional environment, characteristic	Glacial revime and
sociation	THURDER S	ocumentor of	sedimentary processes	grounding line proximity
llite srmation	Glaciogenic diamictite	Poorly sorted terrigenous clastic sedimentary rock with a wide range of grain sizes, polymict composition	Meltout and shearing of continental subgla- cial lodgement till	Subglacial, non-aqueous environment
ells titchen ort Sussex ormation	Interbedded mud- rock and conglom- erate-dimictite Rhythmites Mudrocks with outsized dispersed clasts	Alternating well-sorted laminae and beds of fine and coarse- grained lithologies with isolated dispersed gravel and some soft sediment deformation Rhythmically interstratified clay- stones and siltstones with dis- persed gravel, dropstones, deformed bedding and microfaults Laminated mudstone with drop- stones and soft-sediment defor- mation such as loading	Seasonal or other periodic influx of mixed sediment from ice melt into a lake or marine environment or suspension fallout from cyclic meltwater pulses. Hydroplastic defor- mation occurs through slumping and dewa- tering. Some of the coarse material may be destabilized glacigenic debris that accumu- lated proglacially on a basin ramp and moved downslope by mass flow processes Influx of sediment into the lake or shallow sea environment under strongly seasonal (varved) or other periodic discharge, gravel indicates ice-rafted debris Water-saturated sediments and the remobili- sation of sediment suggest rapid deposition such as meltwater plumes (Henry et al. 2012). The fine sand and were likely deposited by meltwater plumes and waning turbidity currents in a sea or lake floor setting with coarse debris dropped or dumped from	Fluctuating ice-proximal to ice-distal environment as floating ice-shelf expands and retreats
		_		(continued)

Facies	Lithologies	Sedimentology	Depositional environment, characteristic	Glacial regime and
association			sedimentary processes	grounding line proximity
			floating ice (ice-rafted debris). Sand aggre- gates may record fall of frozen sand masses	
			through the water column	
	Coarse ash tuff	Granules in mudstone, no grain	Subaqueous pyroclastic fallout from distal	
		size grading	source	
Black Rock	Anoxic black	Lamination, dropstone-free, rare	Suspension settling, rare signs of	Glacial retreat and devel-
Member,	mudstones	borings	bioturbation	opment of sediment
Port Sussex				starved open water
Formation				conditions
This sedimentolo	wical analysis character	ises and intermets changes in denositi	onal processes and environments documented in	the loce over the icehouse to

This sedimentological analysis characterises and interprets changes in depositional processes and environments documented in the logs over the icehouse to greenhouse transition. Relevant references are cited in the text as appropriate to the discussion of this summary

Table 4.1 (continued)



Fig. 4.1 Measure of the correlation between the two cores based on the a* reflectance parameter

single step on the analyseries programme used. The purpose of this exercise was to find how closely the sediments of the two cores were correlated and if there was an offset in time that would improve the stratigraphic correlations. Smoothing the data sets improved the correlation between them by a factor of two (see preliminary autocorrelation in the appendix) but it is still low (coefficient ~0.24). The positive peak at ~40 kyr could suggest that a 40 kyr offset of one of the cores would improve the correlation the most. However, it is likely that the autocorrelation was affected by finer-scale sedimentary changes (e.g. on the obliquity and precession scales) and the age modelling thus far does not attempt to match cycles at these scales (see Sect. 4.4.3). Finer-scale age modelling would improve the correlation between the two sites, although increasing the risk of artificial enhancement of the match.

4.2 Lacustrine Versus Marine Environment

The depositional environment in East Falkland during the Permo-Carboniferous has previously been suggested to have been marine. Frakes and Crowell (1967) claimed that the presence of poorly sorted turbidites, the lack of laminated layers and the great thicknesses of associated diamictite supported this interpretation. Stone et al.

(2005) also suggested a terrestrial to glaciomarine facies transition occurred across the Falklands microplate based on fieldwork studies of the Fitzroy Tillite. Interstadial phases in the Dwyka Group have also been characterised as brackish–marine conditions according to the stratigraphic distribution and abundance of marine fossils, ichnofauna and geochemical salinity proxies (Bangert et al. 2000; Scheffler et al. 2003).

However, on the basis of these Falkland Island cores, there is no clear evidence that the deposits are marine. Instead, the finely laminated varve-like layers lend themselves better to an interpretation involving a lacustrine environment. Further, there is no hummocky or swaley cross-stratification which might be expected in a wave-dominated environment and there is no palaeontological evidence for marine conditions; the borings and tentative burrows noted do not verify either environment. In support of a lacustrine hypothesis, Simões et al. (2012) described nonmarine bivalves and identified leaf fossils belonging to Glossopteris sp. cf. G. communis, in the Middle Permian strata of the Falkland Islands. It therefore seems logical to infer that the preceding strata found in the cores were also deposited on land. Further support for the lacustrine hypothesis comes from Trewin et al. (2002) who noted trace fossils in the Brenton Loch Formation belonging to Late Palæozoic typically freshwater lacustrine ichnofacies. These compared well with Late Carboniferous forms from lake deposits in Argentina (Buatois and Mangano 1993, 1995; Acenolaza and Buatois 1993). Simões et al. (2012) also note that morphologically similar bivalves are found in Permian freshwater deposits of Tanzania, South Africa and the Ohio Range Antarctica, all of which formed part of the same Gondwanan sedimentary province. In addition, Botyrococcus spp., a fresh to brackish water algae, was found to occur in the Kuhlan Formation in Yemen (Stephenson and Kader Al-Mashaikie 2011). The absence of marine macrofauna in Yemen, coupled with the presence of palynological assemblages dominated by continental spores and fauna, therefore favours a glaciolacustrine rather than a marine depositional setting here also (Osterloff et al. 2004). In South Africa, Visser (1987) found no marine forms in the Eastern Cape Province. In situ Glossopteris foliage found in Permian strata of the Ellsworth Mountains, West Antarctica (Taylor and Taylor 1992), would also support a lacustrine environment with the terrestrial lithologies immediately overlying the transitional strata.

Figure 4.2 summarises how a lacustrine environment might have developed and led to the formation of the deposits observed. The location of the lake in the Late Palæozoic tectonic configuration is marked tentatively in Fig. 4.3. In the reconstruction of Veevers et al. (1994) a shallow sea lay to the west of South Africa and an arm of the sea extended east into the Karoo about as far as Ecca Pass area, an embayment formed during glacio-eustatic transgression; this might explain the marine–brackish fossils in the Dwyka Group.





Stage 2: The glacier shrinks and lifts off the bedrock causing a subglacial lake to develop. Glacio-isostacy may have played some role in lake formation. Deposition under the floating ice-sheet forms well-bedded intercalations with, for example, submarine mudflow depositing bedded diamictites and ice-rafted debris releasing dropstones. Basal melt and water circulation are also important.



Stage 3: The glacial front continues to thin and retreat; primary sources of sediment input are gravity flows, meltwater outflows, IRD and hemi-pelagic deposition. Eventually, the ice cover is so reduced that clast-poor hemipelagic deposits dominate.

Fig. 4.2 Deposition of core sequence in a subglacial lacustrine environment. An analogue for this facies interpretation might be Lake Agassiz, which developed during the Wisconsin Glacial in North America. Diagrams are not to scale

Another potentially important aspect of the Fitzroy Tillite cores is the evidence therein for soft-sediment deformation. This can be indicative of a supraglacial lake environment due to the continuous meltout of underlying ice and ice walls (Benn



Fig. 4.3 Large subglacial lake envisaged is shown here bounded to the south by the Cape Orogenic Belt. Outline of continents after Crowell and Frakes (1972)

and Evans 2010). However, this second hypothesis (Fig. 4.4) can be rejected on the basis of abundant dropstones in the Hells Kitchen Member. A third hypothesis is a marine environment (Fig. 4.5).

4.3 Phases of Glacial Activity

Many reconstructions of the LPIA (e.g. Veevers and Powell 1987) invoke a single long-lived ice sheet, $\sim 150 \times 10^6$ km³ (Fig. 1.5). More recent research into the direct, ice proximal record of glaciation (e.g. Isbell et al. 2003) instead suggests it was less spatially extensive and occurred in shorter discrete intervals (during the Mississipian, Pennsylvanian and Early Permian). Although most reviews of the LPIA suggest it collapsed during the Late Early Permian, the eastern Australian record shows persistence of glacial conditions for a further 20 myr (Birgenheier et al. 2010). Figure 4.6 summarises how understanding of the LPIA developed. Figure 4.7 explores the evidence across the various fragments of Gondwana that supports the most recent account, which is detailed in box 4 of Fig. 4.6. Hypothesis 2



Equivalent Stage 2 on figure 4.2: During glacier wastage, large volumes of meltwater become dammed between the ice margin and local topography. This results in the development of supraglacial lakes into which stratified sediments and mass flow diamictites can accumulate (Eyles et al. 1987; Schomacker and Kjær 2008).



Equivalent stage 3 on figure 4.2: Sedimentary sequences and structures observed in a supraglacial lake comprise thick units of inter-stratified sorted sediments and diamictite. The dominant grain size varies with distance from the sediment influx point so upward-fining sequences from stratified diamictite to rhythmites reflect increasingly distal sedimentation as ice recedes from the basin. Ablation of the ice results in various degrees of disturbance of the sediment pile either post or syndepositionally.

Fig. 4.4 Alternative lake interpretation for stages 2 and 3. The thick lake infill shows the lake plain was probably stable, so glacier melting was probably slow (adapted from Benn and Evans 2010)

4.4 Understanding the Cause of the Facies Changes

4.4.1 Overview

The evolving configuration of continents about the South Pole has been suggested to be the first order cause of the LPIA (e.g. Blakey 2008). However, although the South Pole lay over Gondwana from the Late Proterozoic until the Early Triassic, Gondwana did not have extensive glacial events throughout the Palæozoic so other factors must have been at play. Veevers and Powell (1987) argued that uplift in South America and Australia and the closing of the Palæo-Tethys-Rheic Ocean were important. Eyles (1993) suggested atmospheric CO₂, temperatures of the global continents, long-term Milankovitch controls, volcanism and tectonic supercycles might have been significant too. The general circulation model of Horton et al. (2012) suggests atmospheric pCO_2 concentration exerted the primary control on



Hypothesis 3

Equivalent stage 2/3 on figure 4.2

Fig. 4.5 Deposition in an ice-proximal marine environment under a floating ice sheet, equivalent to stages 2–3 in Fig. 4.3. This interpretation fits with that of Frakes and Crowell (1967) for East Falkland. The basin requires a moderately steep gradient to accommodate the Hells Kitchen Member sequence; in Sect. 4.4.3, this is calculated to span ~ 1.2 Ma. Perhaps strong discharges of freshwater from melting of the ice masses in this coastal setting could explain freshwater fauna found by other researchers e.g. Trewin et al. (2002)

high-latitude Late Palæozoic continental ice sheets. The model indicates that within 840 ppm < $pCO_2 < 420$ ppm, high-latitude glaciers waxed and waned (by up to 33 m in sea-level equivalent) in response to orbital insolation fluctuations. However, it does not consider continental landmass distributions. When eccentricity is high, precessionally driven changes are amplified and seasonal variability is increased but when eccentricity is low, precessional changes are damped, seasonal variability remains relatively constant and high-latitude continental ice sheet stability is promoted. Significant ice sheet volume increases occurred during anomalously cold Southern Hemisphere summer orbits (high eccentricity, low obliquity and Southern Hemisphere summer solstice at aphelian) whereas ice sheet volume decreases coincided with anomalously warm Southern Hemisphere summer orbits (high eccentricity, low obliquity and southern hemisphere summer orbits (high eccentricity, low obliquity and southern hemisphere summer orbits (high eccentricity, low obliquity and southern hemisphere summer orbits (high eccentricity, low obliquity and southern hemisphere summer orbits (high eccentricity, low obliquity and southern hemisphere summer orbits (high eccentricity, low obliquity and southern hemisphere summer orbits (high eccentricity) is su

4.4.2 A Role for Orbital Forcing? Milankovitch Theory and its Application in the Carboniferous

To understand the climatic history of the Earth, it is important to understand accurately its orbital evolution. Milankovitch cycles with current periodicities ~ 23 kyr (precession), ~ 41 kyr (obliquity), ~ 100 (eccentricity) and ~ 400 kyr (eccentricity) are the orbital parameters that modulate ice age climate (Hays et al. 1976; Schwarzacher 1993; Ruddiman 2003). Eccentricity modulates the amplitude of the precessional cyclicity and leads to summer temperature maxima and minima

1. Crowell (1978) and Frakes (1979) - In: Fielding et al. 2008a

Three phases of late Palæozoic glacial activity within the context of a single overall glacial epoch:

1. A late Carboniferous period of mainly localized, alpine glaciation involving mainly valley glaciers in mountainous terrains bordering sedimentary basins.

2. An early Permian phase in which continental ice-sheets covered large areas of Gondwana.

3. Gradual decay and eventual disappearance of the ice-sheets over the remainder of the Permian period.



2. Veevers and Powell (1987) and Frakes and Francis (1988)

- Initial glaciation in the Early Carboniferous.

- A more widespread, long-lived and climatically severe glaciation in the Pennsylvannian that extended into the Early Permian, after which ice centres collapsed through the late Early Permian.

- The LPIA reached a peak in the Pennsylvannian when cold based, continental-scale ice-sheets extended across large parts of Gondwana.

- Initiation of this climatic phase of the LPIA was facilitated by the formation of orogenic highlands which promoted the nucleation of large ice centres that then expanded via climatic feedback effects.

The increase in areal distribution and stratigraphic thickness of glacial facies in the Permian was due to decay of
glaciers which produced extensive ice marginal deposits. However, other workers have viewed the greater
abundance and lateral extent of Permian deposits as evidence of peak glacial activity at this time (e.g. Frakes and
Francis 1988).

- The idea of a Pennsylvannian peak to the LPIA considered attractive because it coincided with the development of cyclical stratigraphic successions in Europe and North America (cyclothems) inferred to have formed under large scale eustatic fluctuations in sea level caused by major changes in polar ice volume.



4. Fielding et al. (2008a)

Throughout Gondwana, shorter periods of glaciation, ~1-8 myr, separated by intervals that experienced very little if any glaciation are now recognized in several regions. Correlation of biozones (Stephenson et al. 2012) does however confirm the widespread nature of glacial sediments of a narrow biostratigraphic late Pennsylvanian age in basins across part of the north Gondwana margin. However, geochemical proxies including increased δ^{18} O and δ^{13} C from brachiopod shells and carbon burial (Grossman et al. 2008) indicate maximum expansion of Gondwanan ice-sheets during the Asselian and early Sakmarian, coinciding with major interpreted decreases in pCO₂ levels and surface temperature (Montanez et al. 2007).

Fig. 4.6 Flow diagram summarising how understanding on the LPIA developed based on information supplied in Fielding et al. (2008a), Veevers and Powell (1987), Frakes and Francis (1988), Isbell et al. (2003), Grossman et al. 2008, Stephenson et al. (2012) and Montanez et al. (2007)

in the high latitudes. Uncertainties in the orbital calculations mean that the precise orbital solution for the Earth may be limited to 35-50 Ma (Laskar 1999). The 400 and 100 kyr eccentricity periods are the product of interplanetary gravitational forces so have probably remained stable through at least the last 600 myr (Walker and Zahnle 1986). By contrast, the 41-kyr obliquity and 23-kyr precession cycles depend partly on the precession of the equinoxes. Approximation of orbital palæoperiods indicates that obliquity period was ~35 kyr in the Carboniferous (Levrard and Laskar 2003).

Energy balance models have indicated that supercontinents are very sensitive to Milankovitch fluctuations (Crowley et al. 1993) and Milankovitch cyclicity has previously been identified in Permo-Carboniferous sediments. Periodic variations in

Earth's orbit and consequent variations in the amount and pattern of solar insolation received at the surface influence climate and sedimentary deposits. For example, 5–10 m thick Carboniferous cyclothems have been related to orbitally driven glacioeustatic changes associated with waxing and waning of Gondwanan ice sheets in the Southern Hemisphere at eccentricity frequencies 100 and 400 kyr (Heckel 1986; Wright 1992). Permo-Carboniferous rhythmites from the Paraná Basin, southeastern Brazil (Franco et al. 2012) and several formations in eastern Australia, such as the Lower Permian Pebbly Beach Formation also have strong indications of Milankovitch components.

This section explores the possibility that the cyclical processes encoded in the sediments of East Falkland may be understood in terms of Milankovitch cyclicity. This seems plausible because the log, clast, XRF and reflectance records from the Hells Kitchen Member show some cyclicity on the scale of metres. If Milankovitch forcing is able to provide a physical framework for explaining the output signal of the climate system at this time, this will also help constrain the duration of the record and clarify the geophysical and climatological mechanisms involved. The results of this investigation are presented below.



Fig. 4.7 Summary of the series of short glaciation events, $\sim 1-8$ myr in duration, in the LPIA, adapted from Fielding et al. (2008a). Fielding et al. present evidence for eight discrete glacial intervals in the Permo-Carboniferous based on Eastern Australian strata (Grossman et al. 2008). Stratigraphic records suggest that the LPIA began with short-lived localised glacial events in South America during the Late Tournasian and the Visean. These events were followed at the start of the Serpukhovian by ice expansion into other areas of Gondwana. At the start of the Bashkirian, ice expanded further across South America and Australia and at the start of the Moscovian, into southern Africa. This accounts for the diachroneity of glacial episodes. A large expansion of ice occurred at the Pennsylvanian–Permian boundary and glaciation became bipolar (Fielding et al. 2008a). However, the exact timing of waxing and waning of ice centres during each glacial episode will have been influenced by basin dynamics, topographic barriers, glaciation styles and other local factors. Abbreviations used in this figure: Penn Pennsylvanian, Ser. Serpukhovian, Bas. Bashkirian, Mos. Moscovian, Kas. Kasimovian, Gzhelian, Asse. Asselian, Sakm. Sakmarian, Artin. Artinskian, Kung. Kungurian, Road. Roadian, Word. Wordian, Cap. Capitanian and Wuch. Wuchiapingian, Chan. Changhsingian. I The yellow band denotes the region within which the cores of this study lie. There were no further glaciations in the Falklands as shown by the very fine clay that continues above the Hells Kitchen Member, noted on sample collection at BGS. The limestone clasts from Antarctica also suggest that the record in these cores coincided with the occurrence of ice in Antarctica although the clasts could have come from recycling of earlier glacial deposits. 2 Lower Permian Dwyka Group of South Africa has been divided into four upward deglaciation sequences, each up to 350 m thick and of 5–7 myr duration and each capped by glaciolacustrine or glaciomarine deposits. The longer duration of the Dwyka cycles compared to the Pleistocene (~1.8 myr) could suggest a tectono-eustatic cause, or they may represent composite records of multiple glacial cycles. 3 There may be as many as four deglaciation sequences in the Falkland Islands but more evidence is required to validate this. Sedimentary dykes filled with diamictite in West Falkland are one of the oldest records of Gondwanan glaciation (Hyam et al. 1997). Two dykes dated using palynomorphs were found to be of Late Visean to Sakmarian age, which is older than the Fitzroy Tillite (Permian). The assemblage is also different and older than the Dwyka in South Africa but the similar and internally consistent nature of the dyke spore assemblages suggests they were not reworked from strata eroded before the main onset of glacial sedimentation. Comparable microfloras are described from the Carboniferous of Australia. 4 Three glacial episodes are identified in the Upper Devonian and Mississippian strata in South America. The earliest evidence for glaciation is a short-lived event at the end of the Famennian (Upper Devonian) in Brazil, Peru and Bolivia (Caputo et al. 2008). The second episode is of late middle to early late Tournaisian age and the third of Visean age. Western Gondwana underwent a steady drift from mid-latitudes (~50S) in the Early Carboniferous to lower latitudes (<40S) by Late Carboniferous time, and glacial deposition had ended in Bolivia by the early Pennsylvanian (Morrowan). 5 In Brazil, late Palæozoic glacial deposits are preserved in the Parana Basin showing multiple glacial intervals over the period from the base of the Serpukhovian to the top of the Gzhelian, an interval of ~ 27 myr. Holz et al. (2008) define three major glacial cycles. 6 The occurrence of multiple diamictites within the Antarctic succession led to the suggestion that four to six major glacial-interglacial cycles occurred during the Lower Permian, with possibly as many as 13 minor advances and retreats of the ice front across the Transantarctic Mountains. In Antarctica, late Palæozoic glaciogenic strata occur throughout the Transantarctic, Ellsworth and Pensacola Mountains and in the Shackleton and Heimefrontfjelles (Isbell et al. 2008b). The glacial record in the Transantarctic Mountains of Antarctica is restricted to the Lower Permian; the base of the Asselian to lower Sakmarian (Isbell et al. 2003). A correlation of fossil spores and pollen with Australian palynomorph zones suggests that the Antarctic glacigenic strata are restricted to the Lower Permian. 7 In Eastern Australia, eight discrete glacial intervals, 1-8 myr in duration, have been recognised (Fielding et al. 2008b) spanning c. 327–260 Ma (Asselian through Capitanian time). The timing and duration is consistent with interpreted minima in atmospheric pCO₂ and surface temperature inferred from mineralogical proxies (Montanez et al. 2007), with turnovers in palæobotanical assemblages from Euramerica (e.g. Gastaldo et al. 1996), and to an extent with interpreted sea-level trends (Rygel et al. 2008). 8 Multiphase glaciation in Western Australia from the Gzhelian to the mid-Sakmarian and a shorter discrete glaciation straddling the Artinskian-Kungurian boundary. All Palæozoic basins in Western Australia contain extensive Permo-Carboniferous deposits

4.4.3 Development of an Age Model

Data on an overlapping depth scale were used in preliminary spectral analyses to look for any prominent periodicities in depth (see Appendix A.2). On the basis of peaks plausibly corresponding to eccentricity periods (Fig. 4.9), it seemed reasonable to place age control points at least at the beginning and end of the sequences. To do this, the a* reflectance data were plotted alongside a synthetic 'Carboniferous ETP', representing the patterns of orbital variation that could be encountered in an orbital geometry with a more rapid ~ 35 kyr obliquity cycle (Fig. 4.8). The actual orbital variations for the Carboniferous cannot be calculated because of uncertainties in the orbital solution before about 50 Ma. However, the synthetic 'Carboniferous ETP' is intended to provide an impression of how the combination of cyclicities in the Carboniferous might appear in a climate record that, like the Late Pleistocene. might have a strong 100 kyr component, but in this case with a higher frequency obliquity component. Aspects such as details of the amplitude modulation of the 100 kyr component are likely to be incorrect. If appropriate, this transformation transfers the records from the depth domain to the time domain enabling the rate of the climatic transition to be hypothesised. Interpreting the large-scale cycles as 400 kyr cycles means that the implied accumulation rates fall between 5.6 and 13.5 m/Ma. This appears a reasonable estimate (Algeo and Wilkinson 1998) given that these old sediments must have undergone a considerable degree of compaction since the Carboniferous-Permian time (e.g. Arthur and Garrison 1986).

Two additional control points were inserted into the core DD029 record using Analyseries software in the places where maxima in the a* data coincided with a minima in insolation, to attempt to correct for some of the depth distortion. Stretching and squeezing of the record were considered justified because sedimentation rates would not have been linear throughout the cores. They would have



Fig. 4.8 Synthetic Carboniferous orbital solution including eccentricity, obliquity and precession *(ETP)*. The obliquity (only) was shortened to a 35 kyr central periodicity, then resampled at 1 kyr intervals, and the Southern Hemisphere precession cycle was used (the precession cycle is out of phase between the two hemispheres). ETP (eccentricity, tilt and precession) cycles were chosen to create the forcing signal because the effect of the eccentricity cycle, the main cycle of interest, is under represented in insolation forcing

Fig. 4.9 Alignment of a* reflectance data and PC1 and PC2 against the synthetic 'Carboniferous ETP' to show how the age model was developed. The *x*-axis represents time in millions of years



	Depth range (m)	Accumulation rate (m/Ma)
Core DD029	173.00–175.59	9.4
	175.59–179.75	5.6
	179.75–183.56	9.5
Core DD090	374.85-395.1	13.5

Table 4.2 Table showing the accumulation rates implied by the age model in the two cores based on the insertion of two age control points in core DD090 and four in core DD029

varied depending on the original debris content of the icebergs as well as on the size, melting rates and flux of the icebergs. Higher rates of accumulation are generally associated with proximity to the grounding line (Matsch and Ojakangas 1992). The accumulation rates used are given in Table 4.2.

This exercise attempted to understand the short duration cyclicity that operated over the transition (refer to Fig. 1.1) with reasonable success. If the 400 kyr Milankovitch cycles were correctly identified, this astronomical tuning should be a fairly robust means of age-depth determination since there are no major erosional hiatuses in these cores; although there may be non-depositional episodes. However, it is still important to be cautious since factors independent of orbital modulation that affect cycle thickness and sedimentation rate could be important (Algeo and Wilkinson 1998). The Milankovitch-cycle paced changes in climate suggested do not account for all the sedimentological variability. Some variability arises from autocyclic depositional processes, periods of non-deposition, the changing morphology of the ice sheet/shelf and underlying tectonic processes such as mountain building during the Gondwanan orogenic phase. Stochastic deposits such as turbidites are the most likely cause of error here. The varves which capture the interannual climate variability could help constrain the age model further if it can be proven that they are seasonal lacustrine deposits rather than tidal cycles (see Chap. 5). Perhaps complexities inherent to orbital parameters such as the harmonics of Milankovitch cycles or differences related to regional climate were important also.

4.4.4 Principal Component Analyses

PCA is a simple, non-parametric method for reducing complex high-dimensional data sets to more manageable, lower dimensional linearly uncorrelated forms without losing too much information. The technique can help filter out noise and reveal underlying simplified structures in terms of the main causes of variance. A PCA was run using 'SPSS' software. Silver and tin were excluded from the multi-element XRF data sets prior to this analysis because they are present in the detector. Elements, such as iron, that were measured at more than one energy band were only considered once to avoid weighting the analysis. Further details on the PCA method are outlined in Box 4.1. The output correlation matrixes and factor tables with loadings are shown in Appendix A.3.



Fig. 4.10 Core DD029 PCA results

The results are presented in Figs. 4.10 and 4.11 together with annotations showing the elements loading positively or negatively on the components. PC1 seems to be responding to grain size since elements such as Rb and K, common to clays, peak in the fine-grained zones. Positive excursions correlate with most of the


Fig. 4.11 Core DD090 PCA results

other elements found in higher abundance in the coarse beds. However, there are also sharp peaks associated with veins. PC2 seems to be related to redox processes with elements Fe, Mn and Ti loading negatively against Ba and Sr. PC3 shows positive loadings on Sr and Ca. These elements are linked since Sr may substitute for Ca in dolomitisation, and so this principal component may characterise carbonate; it also shows sharp excursions at veins. PC4 and PC5 account for little of the variance and had noisy traces. They may be related to noise introduced through sanding during sample preparation or biases from clast compositions.

Box 4.1: Principal Component Analysis in More Detail

The projection of the original data vectors may be summarised into fewer directions and principal components, which span the subspace. The principal components are derived by finding the projections which maximise the variance. The first principal component is the direction in feature space along which projections have the largest variance and each succeeding component has the highest variance possible under the constraint that it is orthogonal to (i.e. uncorrelated with) the preceding components (Shlens 2009). Therefore, the second principal component is the direction orthogonal to the first component with most variance. Selecting orthogonal directions for principal components is the best solution to predict the original data. PCA assumes linearity which restricts the set of potential basis vectors.

The principal components of the XRF elemental data are the eigenvectors of the covariance matrix of the data. The eigenvalues (provided in the appendix) are proportional to the portion of the 'variance' (the sum of the squared distances of the points from their multi-dimensional mean) that is correlated with each eigenvector. Component scores are the transformed variable values corresponding to a particular data point, and loadings are the weight by which each standardised original variable should be multiplied to get the component score. Sometimes the components do measure real variables but sometimes they just reflect patterns of covariance which have many difference causes. The measurement of the variance along each principal component provides an opportunity to compare the relative importance of each dimension. The covariation matrix measures the degree of the linear relationship between two variables. A large positive value indicates positively correlated data, and a large negative value denotes negatively correlated data. An explanation was attempted for the first three principal components, any interpretation of other factors becomes increasingly speculative.

4.4.5 Wavelet Analyses

Palæoclimate signals vary in both amplitude and frequency over long periods of time. Wavelet analysis attempts to solve these problems by decomposing the data into time/frequency space simultaneously; thus, it can be applied to geological records that are proxies of palæoclimatic variations (Liu and Chao 1998). It provides information on the amplitude of any periodic signals within the series and how this amplitude varies with time (Box 4.2). Wavelet analyses were run using

Fig. 4.12 Wavelet analyses on the a* parameter, PC1 and PC2 for core DD029. In each case, **a** is the timeseries, **b** is the wavelet power spectrum, using the Morlet wavelet. The x-axis is the wavelet location in time. The y-axis is the wavelet period in kyr and **c** is the spectral analysis showing the power of frequencies in the core



online software developed by Torrence and Compo initially on the a* and L* reflectance data (see Appendix A.2). Subsequently, on improved depth scales, they were applied to the PC1 and PC2 and a* data over depths 380.035-390.398 m ('0.384–1.1514 Ma') and 173-183.2 m ('0.1–1.14 Ma') for cores DD090 and DD029 respectively. The diamictite was inappropriate to use because it was a

Fig. 4.13 Wavelet analyses on the a* parameter, PC1 and PC2 for core DD090. *Note* over the time interval used, there could not be more than two full 600 kyr cycles so the strong power at 600 kyr must be an edge effect. Edge effects degrade the reliability of the signal at the edge of the plot



sudden dump of material and was incomplete. Some of the Black Rock Member was also excluded due to its incomplete nature. The purpose here was to see how much of the observed climate variability could be accounted for by considering the period and amplitude modulations of the orbital forcing parameters. The results are shown in Figs. 4.12 and 4.13.

Box 4.2: Wavelet Analysis

Wavelet analysis works by using a variety of window sizes to build a picture of the changes in variance versus both time and window width. Frequency localisation is good at low frequencies, and time resolution is good at high frequencies. A wave packet of finite duration and with specific frequency can be used as the window function for the analysis of variance; this wavelet has the advantage of incorporating a wave of a certain period, as well as being finite in extent. The Morlet wave used here is a sine wave multiplied by a Gaussian envelope. By sliding this wavelet along the timeseries, it was possible to construct a new timeseries of the projection amplitude versus time. The scale of the wavelet was varied by changing its width; the size scaled up or down with the size of the window though its shape remained constant. The problem with this technique is that the box shape of the window introduces edge effects. The plots show the power (absolute value squared) of the wavelet transform. The (absolute value)² gives information on the relative power in terms of periodicity at a certain time. The wavelet analysis also plots a power spectrum to describe the data in the frequency domain similar to the spectral analyses used in the preliminary investigation (Appendix A.2).

The results indicate that PC1 and PC2 have strong power in bands where 100 and 400 kyr periodicities would lie. Hence, the geochemical variation is compatible with an interpretation of climatic changes induced by Milankovitch forcing. The identification of cyclicity in these old records does not appear to have been hindered by diagenesis, such as compaction and cementation, which alter the original chemical and stratigraphic relationships across cycles. Further, although there is poor constraint on the absolute timescale for this sequence and limited determination of orbital variations older than 50 Ma adds further ambiguity, the results still provide a tenable timeframe over which this large climatic transition may have taken place (1.2 Ma). The age models are themselves deliberately simple and while they may be the best currently supported by the internal evidence of the cyclicities in the cores, this does not rule out the possibility of improvement or even major revision. For example, the section around '500-900 kyr' in core DD090 may be too compressed since the band of strong 100 and 400 kyr power deviates around this region. Perhaps the core DD029 record had the most striking power bands because it already had two extra control points in this central region.

In summary, this section emphasises the likely importance of external orbital forcing in controlling the phase, amplitude and frequency of the climate signal over

the course of the transition. The combined effect of the duration and intensity of insolation variations arising from orbital eccentricity in particular appears to be a key component. However, orbital forcing probably operated in conjunction with glaciological processes to drive the climate system. For example, the build-up of unstable ice sheet regimes, following an intense and prolonged glacial state, may have played a dynamic and pivotal role and led to self-sustained oscillations. Carbon cycle changes tied to abrupt millennial climate perturbations could have served secondary amplifying roles. Since both external and internal factors operate simultaneously, it becomes difficult to tease apart which are critical for driving the climate system, which serve as feedbacks and those which play little role. Some factors may also have had varying importance through time. The superposition of stochastic processes on the system increases the potential complexity and scope of the problem.

4.5 Demise of the Ice

Widespread collapse of ice sheets occurred in the Early Permian (mid-Sakmarian) with the onset of rising atmospheric CO_2 levels (López-Gamundí and Buatois 2010), though glaciation continued intermittently in Australia and Siberia throughout the Late Early and Middle Permian (Fig. 4.14) (Montanez et al. 2007). The transition to a relatively ice-free world, which was sustained until the Late Pleistocene, probably occurred once a CO_2 threshold had been reached and



Fig. 4.14 pCO₂ history across the icehouse to greenhouse transition, adapted from Montanez et al. (2007). Stable isotope compositions of soil-formed minerals, fossil-plant matter and shallow water brachiopods were used to estimate pCO₂. The *red box* outlines the time over which the \sim 1.2 Ma deglaciation sequence in the Falklands accumulated. P2 and P3 refer to the Permian Australian glaciations 2 and 3

greenhouse stability precluded the reestablishment of glacial conditions. However, the diachroneity of glaciation across Gondwana means the demise of glaciation could not have been solely caused by global pCO₂. It is possible that the drift of the continents was the final trigger out of the icehouse state (Frank et al. 2008). Further, the glacier waxing and waning cycles observed in these cores took place when pCO₂ was high so another mechanism, probably orbital forcing, was at play throughout the transition. The upper part of deglaciation sequence 4 in the Karoo Basin coincides with the oldest event associated with the Cape orogeny (dated at 292 ± 5 Ma). Therefore, orogenesis may have triggered shelf subsidence and a rapid final collapse of the ice sheets in this part of Gondwana (Isbell et al. 2008a).

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Chapter 5 Conclusions Summarised and Research Opportunities Reviewed

Abstract The borehole core sections illustrating the Late Carboniferous to Early Permian glaciogenic succession in the Falkland Islands provide an insight into palæoenvironmental changes experienced in the Southern Hemisphere during an 'icehouse to greenhouse' transition. The critical data were acquired by detailed analyses of two core sections recovered from East Falkland that spanned the lithological transition zone. Within Gondwana, the Falkland Islands occupied relatively high latitudes at the time and the cores preserve glacial diamictite deposits from the Fitzroy Tillite Formation passing up into black mudstones from the Port Sussex Formation. The borehole cores provided a unique opportunity to investigate the relationship between ancient lacustrine depositional dynamics and climatic variations. The study used a combination of detailed sedimentary logging and high-resolution XRF and reflectance scans. It provides the first high-resolution data set from this part of the Gondwana supercontinent for the Carboniferous–Permian climatic transition. The XRF and reflectance scans enabled the identification of subtle changes in both sediment provenance and the prevailing environmental conditions.

Keywords Absolute dating · Accumulation rates · Climate transition

5.1 The Principal Conclusions

The geological material available for the study reported here afforded a rare opportunity to evaluate climate change relatively early in the Earth's Phanerozoic history, so providing a valuable complement to the many climatic studies that have concentrated on Quaternary changes. For this reason, data were collected at a very high resolution to generate results that ensured a comprehensive analysis. It is hoped that this research will improve understanding of the ancient geological record of climate change, while lending some insights into how major icehouse to greenhouse climatic transitions on Earth take place. The study illustrates how links

between sedimentology and glacier processes may be tied to climate conditions and demonstrates the way in which Milankovitch orbital solutions may provide an explanation of the punctuated nature of such transitions. The Falkland Islands results may help to validate other projected Milankovitch estimates and calculations of the planet's orbital configuration and climatic responses in the distant past.

The following principal conclusions are stressed:

- 1. The depositional sequence preserves evidence of dynamic climate change with cyclic advance and retreat of a water-based ice sheet. There is broad shift in the style of sedimentation from terrigenous subglacial diamictite through interlaminated coarse and fine deposits to hemipelagic muds.
- 2. There is no clear evidence that the deposits are marine, and a lacustrine setting is preferred on the basis of palynology (e.g. Osterloff et al. 2004), a lack of marine fauna, presence of freshwater fauna such as bivalves in the Brenton Loch Formation (Simões et al. 2012), in situ Permian plant macrofossils (e.g. Taylor and Taylor 1992) and varve deposits (although it is appreciated that varves can sometimes form in marine settings).
- 3. Wavelet analyses of reflectance data and the first two principal components from XRF data reveal strongest power in zones where 100-kyr and 400-kyr Milankovitch periodicities might be expected to lie suggesting that changes in the eccentricity of Earth's orbit paced the accumulation and ablation of the ice sheets.
- 4. A tentative attempt at age modelling suggests that the transition spans ~ 1.2 Ma. This is the interval over which glaciers appear to have waxed and waned in response to Milankovitch forcing. It is possible, however, that some cycles were destroyed by the erosive power of an advancing glacier and that this timeframe is an underestimate; this is thought to be unlikely as no unconformities were noted.
- 5. Sedimentological analysis suggests that the glacial cycles were part of an overall period of retreat, with the second wave of coarse beds appearing to be more distal in character than the first with, for example, deformed clay clasts.
- 6. Superimposed on these short cycles was a movement of the Falklands out of the high southern latitudes. It is hypothesised that this drift provided the climatic tipping point to permanent non-glacial conditions. Additionally, although changing patterns of thermohaline circulation and volcanic activity (for which there is evidence at this time in these cores) may also have had a role to play in the transition out of the icehouse world, the available data were insufficient to allow the consideration of those factors as a part of this study.
- 7. The borehole sections can be placed in the broader, regional context of coeval glacial records from other parts of Gondwana. Comparison and correlation of the Falkland Islands deposits with those elsewhere suggest that in the Falklands area, the transition took place during the Sakmarian stage of the Early Permian.

5.2 Potential Research Opportunities

The borehole cores that formed the basis of the work reported here are held by the British Geological Survey in the UK's National Geoscience Data Centre at Keyworth, Nottingham. The cores are therefore still available for further study, as are several additional core runs through the Falkland Islands glacigenic succession that were not utilised in this study. An inventory of the extant material is provided by Stone (2011) in a British Geological Survey Report that is available as a free download at www.nora.nerc.ac.uk/14415/.

The main opportunities for future research may lie within the following areas, all of which are acknowledged limitations of the reported study.

- 1. The lack of absolute dates on the cores and the approximations of the age modelling mean that uncertainties in the timing of events remain. Ideally, further constraints on core chronology are required, particularly for ages assigned to the base and top of the sequence; such data would help validate the relative age modelling. However, in general, the Pennsylvanian to Cisuralian, non-marine and cold marine sediments of the Gondwana continent have proved difficult to correlate both within the continent and with the standard stages. There is a lack of key zonal fossils, which are largely marine (Stephenson et al. 2012), while palynological correlation is made difficult by disparate stratigraphic and taxonomic methods and different standards of documentation across Gondwana (Stephenson 2008). It may be possible to date the volcanic lapilli in the Hells Kitchen Member if they are accompanied by volcanogenic zircons amenable to the U–Pb method.
- 2. The current age model is largely dependent upon the assumption of uniform accumulation rates throughout the sequence and consequently is subject to a depth distortion. Improvement to the age model may be possible by looking in more detail at sediment patterns such as the possible varves if it can be proven that they represent seasonal cycles. Also, turbidity currents in glacial lakes may last only a few minutes, but deposit several centimetres of sediment, whereas quiet-water settling of clays may only deposit a few millimetres or less over many months (Benn and Evans 2010), and an ideal age model would take this into account. A more thorough analysis of feedbacks in the system, such as albedo changes, would also be required to achieve a more robust understanding of the sedimentation changes.
- 3. Wavelet analyses could be run on the third and fourth principal components, and spectral analyses could be used to investigate the data further in the depth domain.
- 4. Further elemental analyses could be used. For example, barium or bromine only considered briefly could be investigated more thoroughly in an attempt to better characterise the organic content of the sediment. It might also be useful to look for any correlation between iron and phosphorus. A correlation between iron and phosphorus points to the formation of iron phosphates as a possible control on the amount of phosphorus available for primary producers making

phosphorus a limiting nutrient. Negative correlations between iron and organic carbon could be preceded by a breakdown in the correlation between iron and phosphorus rather than an in-phase relationship between the elements.

5. A more in-depth isotopic analysis using ¹⁸O as well as ¹³C on many samples through the cores may yield better insights into ice volume, organic productivity and whether a lacustrine or marine setting is most likely. However, this would be a destructive process and ¹⁸O is almost certainly affected by diagenesis. In addition, since there were no clearly identifiable bioclasts, the oxygen and carbon isotope measurements would have to be carried out on bulk sediment, which is difficult to interpret.

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Chapter 6 Data Postscript

Abstract The complete scan of the hand-drawn logs for cores DD029 and DD090 are presented in this chapter. Plots of reflectance data, and XRF data for the elements silicon, potassium, chromium, titanium, manganese, iron and zirconium are also shown for both cores. The XRF logs incorporate annotations tying the element fluctuations observed to sedimentological variations. Results from the clast analysis showing clast frequency, sorting, roundness, sphericity, size and composition are presented for core DD090, as is the raw data on total organic carbon. Details regarding the measurements made to generate the depth scales are provided alongside images of the polished cores. Please refer to the appendix for a summary of the preliminary age modelling work and the outputs generated from the principal component analysis.

Keywords Log • XRF scans • Reflectance scans • Clast composition • Total organic carbon • Preliminary spectral analyses • Principal Component Analysis output

Electronic Supplementary Material The online version of this Chapter (DOI 10.1007/978-3-319-08708-5_6) contains supplementary material, which is available to authorized users.

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6.1 Logging Data: Digital Version and Original Scans












































































































6.2 Reflectance Scanning Data



Reflectance Data Overview



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6.3 XRF Data



XRF Data overview



Core DD029 XRF Data





Core DD090 XRF Data



6.4 Clast Data



Core DD090 All data is plotted with a 50 point running mean

40

Maximum clast size

Average clast size

50 per. Mov. Avg. (Maximum clast size)

50 per. Mov. Avg. (Average clast size)





6 Data Postscript





6.5 Total Organic Carbon Data

Tables 6.1 and 6.2.

Sample: segment label	Lithology	Mass prior to drying/g (includes sample bag)	Mass after drying/g for 4 h (includes sample bag)	Mass after drying for 8 h/g (includes sample bag)	Mass before add- ing to HCl/ g (excludes sample bag)	Mass after adding to HCl/g (excludes sample bag)
395	Diamictite	1.743	1.738	1.738	1.185	1.037
391.7	Coarse bed	2.435	2.430	2.430	1.879	1.674
391.4	Clay	9.425	9.410	9.408	8.864	8.473
391	Diamictite and clay	1.277	1.272	1.271	0.726	0.633
387.3	Clay	2.768	2.760	2.759	2.210	1.959
385.5	Silt and silt clasts	2.424	2.418	2.419	1.870	1.697
382.2	Green silt	0.988	0.983	0.984	0.441	0.410
382.0	Interlaminated silt and clay	3.785	3.772	3.772	3.231	2.953
155.9	Fine clay	8.039	8.018	8.018	7.468	7.333

 Table 6.1 Preparation details for total organic carbon procedure

Table 6.2 Total inorganic and organic carbon content and $\delta^{13}C/^{12}C$ for samples

Sample: segment label	Total inorganic carbon content (%)	Total organic carbon content (%)	δ^{13} C/ ¹² C
395	12.5	0.18	-23.82
391.7	10.9	0.20	-23.65
391.4	4.4	0.12	-23.48
391	12.8	0.15	-23.08
387.3	11.4	0.34	-23.59
385.5	9.3	0.15	-23.38
382.2	7.0	0.10	-25.54
382.0	8.6	0.07	-23.83
155.9	1.8	3.00	-20.93

Appendix

A.1 Generation of Depth Scale

- 1. Measure offset to the top of each segment from the labels marked approximately on segments.
- 2. Calculate the position of the base of the segments: = segment label + (segment top offset to top). Make sure to divide the difference in brackets which is in millimetres by 1,000 to convert to metres.
- 3. Calculate the position of the beds (= position of base bed height).
- 4. For segments that are continuous, there should be no overlap or spacing implied by the labelling. However, because the labels were approximate this is not the case. The offset to top should therefore be recorded for the youngest segment in a sequence. The offset for the segment above it (which should but will not be continuous) is then calculated: = offset for youngest segment + (position of this segment top – position of segment below's base). Again, make sure to multiply the part in brackets by 1,000 to put it in mm.
- 5. Calculate the position of segment top: = segment label offset to top recorded in youngest segment.
- 6. There should now be no overlap within groups of segments that join together. However, sometimes gaps which are clearly present appear to overlap due again to errors in the original labelling. Adjust the 'offset to top' measurement by as little as possible to make the numbers work (continuous sequence). Make sure the position of segment top is a formula (e.g., in excel) when doing this adjustment so the adjustments propagate through groups of segments.

Further stages for plotting clast data

- 1. Copy all data including the y-axis into a second spreadsheet and duplicate it using the sort function in excel.
- 2. Copy the position of the segment base, position of beds and y-axis variable (e.g., clast frequency) into a third spreadsheet. Where there are gaps, insert a row so that there are three empty rows in any gap. Then move the segment base numbers to the position of beds column. There should now be only one row in any gap.

K. Horan, *Falkland Islands (Islas Malvinas) in the Permo-Carboniferous*, Springer Earth System Sciences, DOI 10.1007/978-3-319-08708-5

3. Shift the y-axis variable data up one row and insert a '0' at the top and bottom of each segment/segment group so that the line plotted returns to the axis before a gap.

Further stage for plotting XRF/reflectance data

1. The extent of overlap is greater in the XRF and reflectance data than in the clast/ log data because the measurements were not taken perpendicular to bedding. Although the log/clast data and the XRF/reflectance data can be linked through the photographs, it is difficult to compare them directly. To improve the correlation between them, depth control points were inserted into the depth scales for reflectance and XRF data at the beginning and end of every segment in both cores, and the depths between calculated by linear interpolation. Care must be taken when more gaps are present in the XRF/reflectance data than in the log. Using linear interpolation has the disadvantage that the XRF data was not always measured from the start to the end of each segment where broken edges necessitated starting and stopping the detector within a segment. In such cases, the XRF/reflectance data is stretched slightly over the segment interval defined by the log/clast scale depths.

The following core images show the measurements used to improve the depth scale for cores DD029 and DD090, respectively.



555-490=65

330-110=220

22



Appendix













Appendix









Appendix







A.2 Preliminary Spectral Analyses and Age Modelling

Prior to the depth scale adjustment, the XRF and reflectance data were used in preliminary spectral analyses, wavelet analyses and age modelling and an autocorrelation was run between the cores. Although the outcome was suggestive of cyclical forcing, this was tentative due partly to the overlaps on the depth scale and could not be used alone to draw reliable conclusions. In these preliminary tests, the a* reflectance parameter showed the best-defined power peaks and these had frequency ratios suggestive of Milankovitch astronomical forcing of the depositional process. Use of this parameter was, therefore, pursued further (see Chap. 4).

Spectral analysis identifies periodicities (where present) and calculates their temporal ratio. It was used first in this study to look for Milankovitch cyclicity over the Hells Kitchen Member where cyclical changes in sedimentation were observed during logging. Spectral analyses were run using Analyseries software on data from both cores independently and compared. Both data sets suggested the possibility of strong power at frequencies corresponding to eccentricity and obliquity. Precession, if present in the cores, may have been lost in the background noise at the high frequency end of the spectrum. Some results are presented in Figs. A.1, A.2 and A.3.

The prominent periodicities identified in the spectral analysis were used to develop a relative age model (Fig. A.4). Based on the presence of high power at frequencies plausibly representing Milankovitch cycles, a time frame ~ 1.3 Ma was placed on the length of the Hells Kitchen Member. This initial age model appears to have 400 kyr cyclicity which would have been used to refine the age model if the data was non-overlapping. Such adjustments would be valid since the assumption that sedimentation rates were constant throughout the Hells Kitchen Member is poor.



Fig. A.1 Spectral analysis in the depth domain on the a* parameter of core DD090 when the data still had overlaps. The *vertical lines* represent the recurrence ratio of cycles if the eccentricity were to be fixed in the position shown. The calculated periods correspond approximately to those of the anticipated orbital parameters



Fig. A.2 Spectral analysis on the a* parameter of core DD029 in the depth domain when the data still had overlaps. The *vertical lines* represent the recurrence ratio of cycles if the eccentricity were to be fixed in the position shown. Note, however, the absence of power at the 'precessional' depth periodicity. A sedimentation rate of 0.9 m/100 kyr (9 m/Ma) is implied



Fig. A.3 An example of a spectral analysis on the elemental data Ln(Fe/Al), for core DD029, which showed one of the most promising set of peaks

Sudden inputs of meltwater or turbidites for example introduce rates higher than the average when tuning to eccentricity periods. Such abrupt changes would usually be swamped by longer term changes, such as river runoff or productivity, but repeated turbidites or meltwater events might have an effect on the long-term rates.



Fig. A.4 Preliminary age modelling showing some clustering of cycle periods around Milankovitch Periods represented by the ETP (eccentricity, obliquity and precession forcing). Power units are reflectance ratios. The eccentricity units are normalised eccentricity

There is some suggestion of similarity between the wavelet spectra of the orbital variations and palæoclimatic cycles even in these preliminary experiments (Fig. A.5). A preliminary autocorrelation was carried out with the hope of finding an adjustment in time on a simple age model which would be required for the cores to have the closest correspondence (Fig. A.6). This autocorrelation suggested that there is very low correlation between the two cores over the Hells Kitchen Member with a correlation coefficient maximum of ~0.08. However, it is possible that a higher correlation between the cores has been obscured by the high frequency nature of the data since the spectral and wavelet analyses showed prominent periodicities that could reflect Milankovitch forcing in both. The datasets therefore benefitted from smoothing before the autocorrelation was run (see Sect. 4.1.2).



Fig. A.5 Wavelet analysis showing the prominent periodicities in the depth domain through the cores



Fig. A.6 Preliminary autocorrelation between cores calculated using the a* reflectance data when the cores had an overlapping depth scale

A.3 Principal Component Analysis Output

Core DD029 (Tables A.1 and A.2). Core DD090 (Tables A.3 and A.4).

Total variance ex	kplained				
Component	Initial eig	genvalues		Extraction squared l	n sums of oadings
	Total	% of Variance	Cumulative %	Total	% of Variance
1	9.253	48.700	48.700	9.253	48.700
2	2.457	12.931	61.632	2.457	12.931
3	1.327	6.982	68.614	1.327	6.982
4	1.043	5.490	74.104	1.043	5.490
5	0.784	4.124	78.228	0.784	4.124
6	0.685	3.603	81.832		
7	0.591	3.112	84.944		
8	0.451	2.372	87.316		
9	0.415	2.183	89.498		
10	0.402	2.118	91.617		
11	0.341	1.795	93.411		
12	0.312	1.645	95.056		
13	0.270	1.423	96.479		
14	0.186	0.977	97.456		
15	0.159	0.836	98.292		
16	0.133	0.699	98.992		
17	0.098	0.514	99.506		
18	0.066	0.348	99.853		
19	0.028	0.147	100.00		

Table A.1 Results from a Principal Component Analysis on core DD029 XRF data

Component matrix

	Component				
	1	2	3	4	5
Si/A log ratio	0.782	0.292	-0.070	-0.205	0.197
S/Al log ratio	0.466	0.429	0.405	0.289	-0.293
Cl/Al log ratio	0.865	0.216	-0.006	-0.178	0.064
K/Al log ratio	-0.816	0.326	0.182	0.125	-0.19
Ca/Al log ratio	0.756	0.151	-0.480	0.156	0.007

(continued)

Ti/Al log ratio	0.736	-0.56	-0.007	0.163	0.095
Cr/Al log ratio	0.868	0.252	0.114	-0.113	0.001
Mn/Al log ratio	0.847	-0.229	-0.255	0.096	-0.085
Fe/Al log ratio	0.663	-0.663	0.101	0.029	0.035
Cu/Al log ratio	0.502	0.239	0.282	0.553	0.359
Zn/Al log ratio	0.626	-0.287	0.238	0.387	0.238
Br/Al log ratio	0.784	0.041	0.216	-0.224	-0.112
Rb/Al log ratio	-0.931	0.274	-0.039	0.093	0.045
Sr/Al log ratio	0.173	0.544	-0.681	0.266	-0.44
Zr/Al log ratio	0.770	0.115	-0.227	-0.35	-0.004
Pb/Al log ratio	0.603	0.174	0.194	0.147	-0.597
Ni/Al log ratio	0.739	0.373	0.101	-0.198	0.006
Br/Al log ratio	0.495	0.194	0.180	-0.384	0.216
Ba/Al log ratio	-0.292	0.811	0.162	-0.042	0.181

Table A.1 (continued)

Extraction Method: Principal Component Analysis^a ^a 5 components extracted

Aŗ	pendix																														167
	Ba/Al log ratio	0.022	0.143	-0.062	-0.547	-0.160	-0.388	0.002	-0.452	-0.637	0.056	-0.313	-0.161	0.484	0.234	-0.189	-0.086	0.103	0.008	1.000	0.062	0.000	0.000	0.000	0.000	0.000	0.454	0.000	0.000	0.000	nued)
	Br/Al log ratio	0.413	0.264	0.448	-0.311	0.316	0.280	0.479	0.332	0.212	0.224	0.219	0.433	-0.412	0.056	0.349	0.265	0.419	1.000	0.008	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	(conti
	Ni/Al log ratio	0.687	0.434	0.711	-0.455	0.526	0.424	0.778	0.508	0.261	0.375	0.320	0.621	-0.611	0.191	0.579	0.477	1.000	0.419	0.103	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	Pb/Al log ratio	0.392	0.483	0.486	-0.356	0.415	0.394	0.554	0.458	0.283	0.303	0.323	0.490	-0.512	0.120	0.432	1.000	0.477	0.265	-0.086	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	Zr/Al log ratio	0.666	0.338	0.658	-0.677	0.621	0.519	0.617	0.623	0.350	0.342	0.394	0.527	-0.663	0.275	1.000	0.432	0.579	0.349	-0.189	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	Sr/Al log ratio	0.246	0.155	0.201	-0.057	0.515	0.045	0.174	0.192	-0.272	0.126	-0.072	0.009	0.025	1.000	0.275	0.120	0.191	0.056	0.234	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	
	Rb/Al log ratio	-0.640	-0.327	-0.767	0.870	-0.618	-0.701	-0.772	-0.832	-0.808	-0.360	-0.605	-0.752	1.000	0.025	-0.663	-0.512	-0.611	-0.412	0.484	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	Br/Al log ratio	0.578	0.404	0.700	-0.581	0.477	0.493	0.741	0.592	0.496	0.328	0.420	1.000	-0.752	0.009	0.527	0.490	0.621	0.433	-0.161	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	Zn/Al log ratio	0.367	0.281	0.426	-0.501	0.371	0.539	0.445	0.532	0.624	0.460	1.000	0.420	-0.605	-0.072	0.394	0.323	0.320	0.219	-0.313	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
	Cu/Al log ratio	0.393	0.449	0.404	-0.253	0.372	0.366	0.448	0.313	0.208	1.000	0.460	0.328	-0.360	0.126	0.342	0.303	0.375	0.224	0.056	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	
	Fe/Al log ratio	0.303	0.064	0.420	-0.704	0.357	0.686	0.432	0.713	1.000	0.208	0.624	0.496	-0.808	-0.272	0.350	0.283	0.261	0.212	-0.637	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000	
	Mn/Al log ratio	0.507	0.252	0.634	-0.735	0.807	0.648	0.660	1.000	0.713	0.323	0.532	0.592	-0.832	0.192	0.623	0.458	0.508	0.332	-0.452	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000	0.000	
	Cr/Al log ratio	0.729	0.476	0.815	-0.554	0.638	0.585	1.000	0.660	0.432	0.448	0.445	0.741	-0.772	0.174	0.617	0.554	0.778	0.479	0.002	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000	0.000	0.000	
	Ti/Al log ratio	0.465	0.220	0.535	-0.589	0.524	1.000	0.585	0.648	0.686	0.366	0.539	0.493	-0.701	0.045	0.519	0.394	0.424	0.280	-0.338	0.000	0.000	0.000	0.000	0.000	Ι	0.000	0.000	0.000	0.000	
	Ca/Al log ratio	0.582	0.244	0.653	-0.569	1.000	0.524	0.638	0.807	0.357	0.372	0.371	0.477	-0.618	0.515	0.621	0.415	0.526	0.316	-0.160	0.000	0.000	0.000	0.000	Ι	0.000	0.000	0.000	0.000	0.000	
67	K/Al log ratio	-0.668	-0.201	-0.674	1.000	-0.569	-0.589	-0.554	-0.735	-0.704	-0.253	-0.501	-0.581	0.870	-0.057	-0.677	-0.356	-0.455	-0.311	0.547	0.000	0.000	0.000	1	0.000	0.000	0.000	0.000	0.000	0.000	
	CI/AI log ratio	0.828	0.431	1.000	-0.674	0.653	0.535	0.815	0.634	0.420	0.404	0.426	0.700	-0.767	0.201	0.658	0.486	0.711	0.448	-0.062	0.000	0.000	I	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
IOI COI	S/Al log ratio	0.367	1.000	0.431	-0.201	0.244	0.220	0.476	0.252	0.064	0.449	0.281	0.404	-0.327	0.155	0.338	0.483	0.434	0.264	0.143	0.000	I	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
maunx	Si/Al log ratio	1.000	0.367	0.828	-0.688	0.582	0.465	0.729	0.507	0.303	0.393	0.367	0.578	-0.640	0.246	0.666	0.392	0.687	0.413	0.022	I	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
Correlation	029 Correlation	Si/Al log ratio	S/Al log ratio	CI/Al log ratio	K/Al log ratio	Ca/Al log ratio	Ti/Al log ratio	Cr/Al log ratio	Mn/Al log ratio	Fe/Al log ratio	Cu/Al log ratio	Zn/Al log ratio	Br/Al log ratio	Rb/Al log ratio	Sr/Al log ratio	Zr/Al log ratio	Pb/Al log ratio	Ni/Al log ratio	Br/Al log ratio	Ba/Al log ratio	Si/Al log ratio	S/Al log ratio	CI/Al log ratio	K/Al log ratio	Ca/Al log ratio	Ti/Al log ratio	Cr/Al log ratio	Mn/Al log ratio	Fe/Al log ratio	Cu/Al log ratio	
I able A.2	BGS Core DD(Matrix	Correlation																			Sig. (1-tailed)										

Table A.2 Correlation matrix for core DD029

Table A.2	(continued)																			
BGS Core DD0.	29 Correlation	Si/Al	S/AI	CI/AI	K/AI	Ca/Al	Ti/Al	Cr/Al	Mn/Al	Fe/Al	Cu/Al	Zn/Al	Br/Al	Rb/Al	Sr/Al	Zr/AI	Pb/Al	Ni/Al	Br/Al	3a/Al
Matrix		log	og																	
		ratio	atio																	
	Zn/Al log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Br/Al log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000	0.279	0.000	0.000	0.000	0.000	0.000
	Rb/Al log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.041	0.000	0.000	0.000	0.000	0.000
	Sr/Al log ratio	0.000	0.000	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.000	0.000	0.279	0.041	I	0.000	0.000	0.000	0.000	0.000
	Zr/Al log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000	0.000	0.000	0.000
	Pb/Al log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000	0.000	0.000
	Ni/Al log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000	0.000
	Br/Al log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.303
	Ba/Al log ratio	0.062	0.000	0.000	0.000	0.000	0.000	0.454	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.303	I

(continued)
A.2
able

CI/AI log ratio

K/AI log ratio

Ca/AI log ratio

Ti/AI log ratio

Cr/AI log ratio

Mn/AI log ratio

Fe/AI log ratio

Cu/AI log ratio

Zn/AI log ratio

0.936

-0.693

0.782

0.244

0.917

0.683

0.147

0.737

0.575

Total variance e	xplaine	d								
Component	Initial	l eige	nvalues				Ex squ	traction lared loa	sums o adings	f
	Total		% of Var	iance	Cum	ulative	То	tal	% of 1	Variance
1	9.595		50.501		50.	501	9.5	i95	50.501	L
2	2.556		13.454		63.	955	2.5	56	13.454	ł
3	1.388		7.306		71.	260	1.3	88	7.306	5
4	0.943		4.962		76.	223	0.9	943	4.962	2
5	0.818		4.307		80.	530	0.8	318	4.307	/
6	0.741		3.897		84.	427				
7	0.563		2.961		87.	388]			
8	0.439		2.309		89.	697]			
9	0.374		1.969		91.	666]			
10	0.295		1.555		93.	221	1			
11	0.282		1.484		94.	705]			
12	0.213		1.119		95.	824]			
13	0.198		1.041		96.	865]			
14	0.153		0.807		97.	671]			
15	0.137		0.722		98.	394				
16	0.104		0.550		98.	944				
17	0.084		0.444		99.	387				
18	0.065		0.345		99.	732]			
19	0.051		0.268		100.	000]			
Component mat	rix ^a									
		Con	nponent							
		1		2		3		4		5
Si/AI log ratio		0.8	352	-0.155		-0.037		-0.207		0.012
S/AI log ratio		0.7	773	-0.249		-0.097		0.083		-0.166

-0.154

0.005

0.081

0.714

0.018

0.523

0.900

-0.154

0.384

-0.022

0.151

0.516

0.054

-0.013

0.416

-0.098

-0.159

-0.248

-0.104

0.461

-0.019

0.437

-0.008

-0.057

-0.073

0.325

0.314

Table A.3 Results from a Principal Component Analysis on core DD090 XRF data

(continued)

0.111

0.410

-0.090

0.155

0.267

-0.008

0.108

-0.284

-0.339
Br/AI log ratio	0.889	-0.028	-0.127	-0.099	0.183
Rb/AI log ratio	-0.879	-0.190	0.190	0.254	0.011
Sr/AI log ratio	0.416	-0.151	0.834	0.059	-0.185
Zr/AI log ratio	0.569	-0.074	-0.231	0.210	-0.192
Pb/AI log ratio	0.748	0.045	-0.095	0.177	0.014
Ni/AI log ratio	0.895	-0.139	-0.034	0.020	0.233
Br/AI log ratio	0.714	-0.095	-0.045	-0.030	0.347
Ba/AI log ratio	0.336	-0.762	-0.047	0.331	0.143

Table A.3 (continued)

Extraction Method: Principal Component Analysis^a ^a 5 components extracted

		40 - 0.724 0.	ratio	ratio ratic	o ratio	log ratio
577 11000 0.660 -0.563 0.506 -0.011 0.668 0.381 -0.071 0.667 880 0.690 1000 -0632 0.711 0.099 0.891 0.545 0.014 0.647 673 0.501 1000 -0532 0.711 0.052 0.113 0.501 673 0.711 -0.502 1000 0.257 0.476 0.552 0.113 673 0.511 0.050 0.257 1.000 0.556 0.131 0.501 674 0.381 0.545 -0.418 0.783 0.476 0.552 0.131 0.502 6041 0.047 0.511 0.513 0.476 0.552 0.131 0.502 0.035 4041 0.417 0.511 0.513 0.545 0.143 0.575 0.339 0.575 4052 0.541 0.474 0.552 0.131 0.562 0.563 0.575 740 0.511 0.55	0.582 0.403 0.7		326 0.456	0.572 0.7	797 0.596	0.332
880 0.690 1.000 -0.632 0.711 0.090 0.891 0.545 0.041 0.647 679 -0.532 1.000 -0.502 1.000 -0.522 -0.418 -0.070 -0.477 633 0.506 0.711 -0.502 1.000 0.252 0.618 0.783 0.113 0.501 773 0.668 0.891 -0.522 0.668 0.783 0.113 0.502 1.000 0.552 0.113 0.502 468 0.381 0.545 -0.418 0.783 0.476 0.552 0.131 0.502 403 0.402 0.414 0.501 0.113 0.552 0.181 0.502 0.539 0.539 0.539 0.539 0.552 0.539 0.552 0.539 0.552 0.539 0.552 0.539 0.552 0.553 0.553 0.553 0.553 0.553 0.553 0.553 0.553 0.553 0.553 0.553 0.553 0.551 <t< td=""><td>0.662 0.402 0.6</td><td>71 -0.615 0.</td><td>315 0.419</td><td>0.683 0.6</td><td>669 0.513</td><td>0.428</td></t<>	0.662 0.402 0.6	71 -0.615 0.	315 0.419	0.683 0.6	669 0.513	0.428
679 -0.532 -0.632 1.000 -0.502 1.000 -0.502 1.000 -0.512 0.011 0.001 0.013 0.0113 0.0113 0.0113 0.013 0.0113 0.000 0.252 0.0476 0.532 0.113 0.001 773 0.686 0.891 -0.522 0.668 0.783 0.113 0.502 0.133 0.502 0.133 0.502 0.133 0.502 0.039 0.000 0.522 0.131 0.502 0.133 0.502 0.133 0.502 0.039 0.000 0.523 0.133 0.502 0.039 0.000 0.502 0.039 0.000 0.052 0.039 0.000	0.647 0.423 0.8	57 -0.828 0.	360 0.535	0.648 0.8	881 0.672	0.413
633 0.506 0.711 -0.502 1.000 0.265 0.668 0.783 0.113 0.501 773 0.668 0.891 -0.022 0.668 0.257 0.476 0.552 0.113 468 0.381 0.545 -0.418 0.783 0.476 0.562 0.181 0.607 468 0.381 0.545 -0.418 0.783 0.476 0.562 1.000 0.562 0.103 582 0.668 0.571 0.613 0.572 0.181 0.607 0.562 0.039 0.575 403 0.471 0.501 0.113 0.567 0.535 0.039 0.575 403 0.471 0.501 0.113 0.567 0.535 0.635 0.545 0.566 403 0.471 0.873 0.541 0.783 0.673 0.673 0.666 0.576 0.535 0.566 0.575 0.566 0.575 0.567 0.566 0.576 0.576	-0.477 -0.397 -0.5	86 0.737 -0.	211 -0.408	-0.441 -0.5	523 -0.416	-0.059
0.01 0.00 0.262 1.00 0.57 0.476 0.532 0.11 7.73 0.688 0.81 -0.722 0.668 0.257 1.000 0.562 0.111 0.607 4.68 0.311 0.543 -0.418 0.733 0.476 0.562 0.562 0.537 4.61 0.071 0.501 0.572 0.613 0.572 0.632 0.539 0.039 4.74 0.071 0.501 0.113 0.572 0.133 0.602 0.039 0.739 4.01 0.014 0.737 0.531 0.732 0.732 0.732 0.731 0.672 0.732 0.632 0.732 0.632 0.732 0.632 0.732 0.632 0.732 0.632 0.732 0.632 0.732 0.632 0.732 0.632 0.732 0.632 0.732 0.632 0.732 0.632 0.732 0.632 <td>0.501 0.382 0.6</td> <td>12 -0.632 0.</td> <td>596 0.361</td> <td>0.487 0.4</td> <td>536 0.498</td> <td>0.228</td>	0.501 0.382 0.6	12 -0.632 0.	596 0.361	0.487 0.4	536 0.498	0.228
773 0.668 0.831 -0.722 0.6668 0.237 1.000 0.562 0.181 0.660 468 0.381 0.545 -0.11 0.783 0.416 0.562 1.000 0.562 0.363 0.363 3.82 0.647 -0.71 0.014 -0.701 0.113 0.567 0.039 1.000 0.035 3.82 0.662 0.647 0.317 0.501 0.13 0.567 0.039 0.039 0.039 0.039 3.71 0.612 0.531 0.532 0.347 0.536 0.545 0.039 0.567 3.71 0.611 0.871 0.327 0.536 0.511 0.631 0.563 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 <	0.113 0.395 -0.1	64 -0.229 0.	0.209	0.242 0.i	172 0.123	-0.306
468 0.381 0.545 -0.418 0.733 0.476 0.626 1.000 0.562 0.363 0.14 -0.071 0.014 -0.070 0.113 0.552 0.181 0.562 1.000 0.039 382 0.662 0.647 -0.477 0.501 0.13 0.667 0.339 0.039 1.000 403 0.402 0.477 0.501 0.316 0.474 0.398 0.575 403 0.671 0.877 -0.397 0.582 0.147 0.594 0.737 405 0.671 0.877 -0.229 0.812 0.546 0.143 0.607 326 0.315 0.737 -0.229 0.816 0.737 0.637 0.567 0.536 326 0.315 0.326 0.211 0.669 0.031 0.326 0.471 0.637 0.567 327 0.612 0.229 0.231 0.236 0.241 0.244 0.032 0.427 326 0.316 0.321 0.672 0.231 0.671 0.671 0.671 327 0.681 0.723 0.612 0.741 0.737 0.672 328 0.412 0.723 0.612 0.741 0.751 0.751 328 0.412 0.723 0.612 0.741 0.751 0.761 328 0.612 0.723 0.723 0.712 0.724 0.724 329 0.612 0.723 <	0.607 0.454 0.8	62 -0.810 0.	325 0.441	0.687 0.5	887 0.678	0.323
014 -0.071 0.014 -0.070 0.113 0.552 0.181 0.562 1.000 -0.039 .582 0.662 0.647 -0.477 0.501 0.113 0.607 0.359 -0.039 1.000 .403 0.601 0.581 -0.137 0.501 0.133 0.603 0.536 .403 0.671 0.887 -0.397 0.586 0.612 0.164 0.847 0.398 0.575 .714 0.671 0.875 -0.239 0.737 -0.537 0.632 0.546 0.143 0.602 .724 0.611 0.861 0.711 0.867 0.731 0.612 0.741 0.737 0.531 .737 0.561 0.737 -0.239 0.731 0.723 0.531 0.531 0.531 0.531 0.531 0.531 0.531 0.531 0.531 0.531 0.531 0.531 0.531 0.531 0.531 0.531 0.531 0.531 0.531 <t< td=""><td>0.359 0.474 0.5</td><td>46 -0.630 0.</td><td>518 0.244</td><td>0.471 0.5</td><td>517 0.414</td><td>-0.134</td></t<>	0.359 0.474 0.5	46 -0.630 0.	518 0.244	0.471 0.5	517 0.414	-0.134
582 0.664 0.477 0.501 0.113 0.607 0.359 0.003 1.000 403 0.402 0.423 -0.397 0.382 0.397 0.474 0.398 0.575 740 0.671 0.875 -0.386 0.612 0.164 0.842 0.474 0.398 0.575 730 0.671 0.875 -0.586 0.612 0.164 0.862 0.546 -0.143 0.602 336 0.315 0.837 -0.537 -0.537 0.631 0.603 0.631 0.635 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.536 0.547 0.563 0.536 0.537 0.563 0.536 0.536 0.537 0.563 0.536 0.536 0.547 0.561 0.563 0.536 0.547 0.561 0.563 0.547 0.561 0.563 0.547 0.561	-0.039 0.398 0.1	43 -0.327 -0.	173 -0.035	0.157 0.0	0.047	-0.571
403 0.402 0.433 0.383 0.382 0.382 0.434 0.474 0.398 0.573 740 0.671 0.857 -0.586 0.612 0.164 0.842 0.474 0.398 0.575 734 0.671 0.857 -0.586 0.612 0.163 0.826 0.633 0.603 0.613 0.603 0.614 0.603 0.613 0.613 0.613	1.000 0.575 0.6	02 -0.563 0.	251 0.452	0.561 0.0	526 0.479	0.393
740 0671 0.837 -0.636 0612 0.164 0.862 0.546 -0.143 0.603 724 -0.615 -0.828 0.737 -0.632 -0.229 -0.837 -0.633 -0.327 -0.535 326 0.315 0.366 -0.211 0.6696 0.031 0.325 0.518 -0.173 0.5051 456 0.419 0.535 -0.408 0.361 0.209 0.441 0.244 0.035 0.452 572 0.683 0.441 0.487 0.242 0.637 0.471 0.157 0.561 573 0.649 0.723 0.643 0.172 0.877 0.414 0.439 596 0.513 0.646 0.172 0.877 0.414 0.637 0.531 596 0.513 0.656 0.172 0.878 0.414 0.439 0.541 597 0.513 0.616 0.498 0.172 0.878 0.414 0.541 0.561	0.575 1.000 0.4	50 -0.539 0.	0.319	0.441 0.4	402 0.324	0.003
724 -0.615 -0.828 0.737 -0.632 -0.229 -0.830 -0.337 -0.535 .36 0.315 0.360 -0.211 0.666 0.031 0.325 0.318 0.173 0.531 .46 0.419 0.535 -0.408 0.361 0.209 0.441 0.347 0.035 0.435 .57 0.663 0.361 0.209 0.441 0.341 0.435 0.435 .57 0.663 0.411 0.487 0.241 0.035 0.435 .57 0.663 0.723 0.636 0.172 0.877 0.147 0.561 .57 0.613 0.636 0.172 0.877 0.414 0.637 0.439 .59 0.513 0.616 0.172 0.871 0.171 0.647 0.439 .59 0.513 0.616 0.030 0.000 0.000 0.000 0.000 0.000 .59 0.513 0.512 0.123	0.602 0.450 1.0	00 -0.839 0.	241 0.465	0.634 0.8	825 0.647	0.318
.326 0.31 0.360 -0.211 0.666 0.031 0.325 0.518 -0.173 0.251 .456 0.419 0.535 -0.408 0.361 0.209 0.441 0.244 0.035 0.452 .777 0.683 0.648 -0.441 0.487 0.242 0.657 0.471 0.157 0.561 .777 0.669 0.811 -0.432 0.636 0.172 0.887 0.517 0.014 0.563 .591 0.616 0.818 -0.2416 0.488 0.123 0.614 0.607 0.414 0.647 .591 0.512 0.616 0.172 0.878 0.414 0.647 0.547 .592 0.513 0.616 0.200 0.000 0	-0.563 -0.539 -0.8	39 1.000 -0.	166 -0.509	-0.606 -0.2	749 -0.592	-0.079
456 0.419 0.535 -0.408 0.361 0.204 0.431 0.244 0.035 0.435 572 0.683 0.648 -0.441 0.487 0.242 0.687 0.471 0.157 0.561 797 0.669 0.811 -0.432 0.636 0.172 0.887 0.517 0.014 0.563 596 0.513 0.616 0.438 0.123 0.636 0.172 0.887 0.517 0.014 0.563 596 0.513 0.616 0.438 0.123 0.678 0.414 0.647 0.437 597 0.512 0.513 0.528 -0.306 0.323 -0.134 0.571 0.393 597 0.413 0.000 <td>0.251 0.062 0.2</td> <td>41 -0.166 1.</td> <td>000 0.134</td> <td>0.257 0.2</td> <td>326 0.238</td> <td>0.253</td>	0.251 0.062 0.2	41 -0.166 1.	000 0.134	0.257 0.2	326 0.238	0.253
572 0.648 0.644 0.441 0.487 0.242 0.687 0.471 0.157 0.561 797 0.669 0.81 -0.523 0.636 0.172 0.887 0.517 0.014 0.638 596 0.513 0.672 -0.416 0.498 0.123 0.678 0.414 0.047 0.647 332 0.413 0.672 -0.416 0.498 0.123 0.678 0.414 0.047 0.479 332 0.413 0.050 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000	0.452 0.319 0.4	65 -0.509 0.	134 1.000	0.388 0.4	484 0.368	0.222
797 0.669 0.881 -0.523 0.636 0.172 0.887 0.517 0.014 0.628 596 0.513 0.672 -0.416 0.498 0.123 0.678 0.414 0.047 0.479 332 0.428 0.413 -0.059 0.228 -0.306 0.323 -0.134 0.677 0.397 - 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.00 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000	0.561 0.441 0.6	34 -0.606 0.	257 0.388	1.000 0.6	660 0.467	0.208
356 0.513 0.672 -0.416 0.498 0.123 0.678 0.414 0.047 0.479 .332 0.428 0.413 -0.059 0.228 -0.306 0.323 -0.134 0.671 0.393 - 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.00 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.00 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.00 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.00 0.000 </td <td>0.628 0.402 0.8</td> <td>25 -0.749 0.</td> <td>326 0.484</td> <td>0.660 1.0</td> <td>0.658 0.658</td> <td>0.420</td>	0.628 0.402 0.8	25 -0.749 0.	326 0.484	0.660 1.0	0.658 0.658	0.420
.332 0.428 0.413 -0.059 0.228 -0.306 0.323 -0.134 -0.571 0.393 - 0.000 0.00	0.479 0.324 0.6	47 -0.592 0.	238 0.368	0.467 0.6	558 1.000	0.306
- 0.000 0.0	0.393 0.003 0.3	18 -0.079 0.	253 0.222	0.208 0.4	420 0.308	1.000
.000 0.000 0.189 0.000 0.0	0.000 0.000 0.0	00 0.000 0.	000 0.000	0.000 0.0	000.0 000	0.000
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Table A.4 Correlation matrix for core DD090

Table A.4 (co.	ntinued)																			
BGS Core DD090 Correlation Matrix		Si/Al log	S/AI log	CI/AI log	K/Al log	Ca/Al log	Ti/Al log	Cr/Al log	Mn/Al log	Fe/Al log	Cu/Al log	Zn/Al log	Br/Al log	Rb/Al log	Sr/Al log	Zr/Al log	Pb/Al log	Ni/Al log	Br/Al log	Ba/Al log
		ratio	ratio	ratio	ratio	ratio	ratio	ratio	ratio	ratio	ratio	ratio	ratio	ratio	ratio	ratio	ratio	ratio	ratio	ratio
Fe/A	l log ratio	0.128	0.000	0.140	0.000	0.000	0.000	0.000	0.000	I	0.001	0.000	0.000	0.000	0.000	0.002	0.000	0.139	0.000	0.000
Cu/A	I log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	I	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Zn/A	l log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.417
Br/A	l log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Rb/A	I log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000	0.000	0.000	0.000	0.000	0.000
Sr/A	log ratio	0.000	0.000	0.000	0.000	0.000	0.007	0.000	0.000	0.000	0.000	0.000	0.000	0.000	Ι	0.000	0.000	0.000	0.000	0.000
Zr/A	log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	0.000	0.000	0.000	0.000	0.000	I	0.000	0.000	0.000	0.000
Pb/A	l log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000	0.000	0.000
Ni/A	l log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.139	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000	0.000
Br/A	l log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	I	0.000
Ba/A	l log ratio	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.417	0.000	0.000	0.000	0.000	0.000	0.000	0.000	ı

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