

INSIGHTS INTO THE BEHAVIOUR OF THE PLIOCENE EAST ANTARCTIC ICE SHEET FROM PROVENANCE STUDIES OF MARINE SEDIMENTS USING RADIOGENIC ISOTOPES

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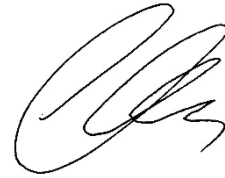
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Declaration of Originality

I declare that the contents of this thesis are completely my own, and that any work of others, published or otherwise, is fully and correctly acknowledged.

A handwritten signature in black ink, consisting of a large, stylized 'C' followed by a series of loops and a final flourish.

Carys P. Cook

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Abstract

Direct evidence for the response of Earth's largest continental ice mass, the East Antarctic ice sheet (EAIS), to climatic warmth is extremely limited. The primary aim of this thesis is to improve understanding of the behaviour of the EAIS during the warmer-than-present Pliocene Epoch (2.58 to 5.33 million years ago). To this end, I analysed the radiogenic neodymium and strontium isotopic provenance of fine-grained ($<63\mu\text{m}$) Pliocene detrital marine sediments deposited offshore of the East Antarctic continent, which can provide information on source bedrock characteristics, continental erosional patterns and marine sediment depositional processes. In addition, I also analysed argon isotopic ages of ice-rafted hornblende grains ($>150\mu\text{m}$), to infer sites of major iceberg production events through time.

Within this thesis, I present Pliocene marine sediment data from various cores drilled from the East Antarctic margin, thereby developing a detailed framework for linking provenance variability to ice sheet behaviour. My key findings have been collated into five distinct chapters, providing: i) the first evidence for significant retreat of the EAIS in the low-lying Wilkes Subglacial Basin in response to the earliest Pliocene climatic warmth; ii) insights into the benefits and pitfalls associated with utilising different tools in glaciomarine sediment provenance studies; iii) constraints on the behaviour of the EAIS and West Antarctic ice sheet during the warmth of Pleistocene super-interglacial, Marine Isotope Stage 31; iv) insights into the role of declining sea surface temperatures during the Pliocene on the flux and provenance of distally sourced ice-rafted detritus, along with evidence for potential ice sheet destabilisation events in the Aurora Subglacial Basin during Pliocene interglacials; and v) advances in understanding of the evolution of the EAIS during the Late Pliocene climatic transition, and its role in global Pliocene climate change. Hence, the findings presented within this thesis provide new and significant evidence for the behaviour of the EAIS during the Pliocene, and suggest it has in the past been more sensitive to climatic change than previously realised.

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CHAPTER 1

Introduction

1.1 Background and Rationale

Continental ice sheets today play an important role in Earth's climate system (e.g. Clark et al. 1999; Jansen et al. 2007), but their significance in a paleoclimatological context is less well constrained (e.g. Bond et al. 1993; Zachos et al. 2001; Miller et al. 2005). Improved understanding of ice sheet behaviour in the geological past is crucial for the ability of climate models to accurately predict their role in future climate change. In particular, the past evolution of Earth's largest continental ice mass, the East Antarctic ice sheet, is poorly understood.

Since its inception ~34 million years ago, fluctuations in the volume of the East Antarctic ice sheet (EAIS) have mainly been inferred indirectly via marine $\delta^{18}\text{O}$ isotope ratios (Shackleton et al. 1984; Zachos et al. 2001; Pekar and DeConto, 2006; Miller et al. 1991, 2005, 2012; Dwyer and Chandler, 2009) as a proxy for global ice volume, and paleoshoreline reconstructions (e.g. Dowsett and Cronin, 1990; Miller, 1996, 1998; Naish and Wilson, 2009). However, $\delta^{18}\text{O}$ isotope ratios are also dependent on bottom water temperatures (Labeyrie et al. 1987; Waelbroeck et al. 2002), and sea level estimates derived from distal paleoshorelines may be inaccurate if not corrected for more recent isostatic adjustment (Raymo et al. 2011). Therefore, in order to reconstruct ice sheet behaviour, particularly during warmer-than-present climate scenarios, direct evidence from proximal locations is required.

The Pliocene Epoch, ~2.58 to 5.33 million years ago, was the most recent geological period of prolonged climatic warmth, with atmospheric CO_2 levels reaching up to 450 ppm (Raymo et al. 1996; Tripathi et al. 2009; Pagani et al. 2010; Seki et al. 2010; Bartoli et al. 2011), and global temperatures estimated to have been up to 4°C warmer than today (Haywood and Valdes, 2004; Haywood et al. 2009; Pagani et al. 2010; Dowsett et al. 2012; Lunt et al. 2012; Fedorov et al. 2013). Due to the similarities between the climates of the Pliocene and today, and the wealth of paleoenvironmental data available for this 'geologically recent' time (e.g. Dowsett et al. 1992, 2012; Haywood et al. 2000; Naish et al. 2009; Salzmann et al. 2011; Fedorov et al. 2013; Brigham-Grette et al. 2013), the Pliocene has been recognised as an ideal analogue to study how Earth's future climate may respond to increased greenhouse gas concentrations (e.g. Haywood et al. 2009). In addition, the Late Pliocene saw a global cooling transition and growth of Antarctica's ice sheets (Ehrmann et al. 1992a; O'Brien et al. 2007; Naish et al. 2009; Passchier, 2011; McKay et al. 2012a; Miller et

al. 2012; Fedorov et al. 2013), hence this time represents an opportunity to study how the EAIS responded to and what role it played in major global climatic change.

A paucity of proximal Pliocene data from East Antarctica has led to much debate over the behaviour of the EAIS during this time. Discovery of the Pliocene Sirius Group marine diatoms high in the Transantarctic Mountains (Harwood, 1983; Webb et al. 1984) in the 1980's saw the establishment of the 'dynamicists' view of the Pliocene EAIS ice sheet – a view that the ice sheet advanced and retreated significantly during this time. This hypothesis developed because the original mechanism to explain the deposition of the Sirius Group was glacial transport from a marine setting within the low-lying Wilkes Subglacial Basin (Figure 1.1), a scenario that would require significant deglaciation of the EAIS and penetration of Southern Ocean waters into the basin (Webb et al. 1984; Mayewski and Goldthwait, 1985; Burckle and Potter, 1996). In addition to the Sirius Group, Pliocene sections of the Pagodroma Group and Sørsdal Formation in Prydz Bay, composed of marine sediments, imply that the ice sheet grounding line was potentially between 50 and 400 kilometres south of its current position (Quilty et al. 1999, 2000; Harwood et al. 2000; Hambrey and McKelvey, 2000; McKelvey et al. 2001; Whitehead and McKelvey, 2001; Fordyce et al. 2002; Whitehead et al. 2004) although there are uncertainties about the depositional ages of these sediments. Additional evidence for ice sheet retreat during the Pliocene comes from

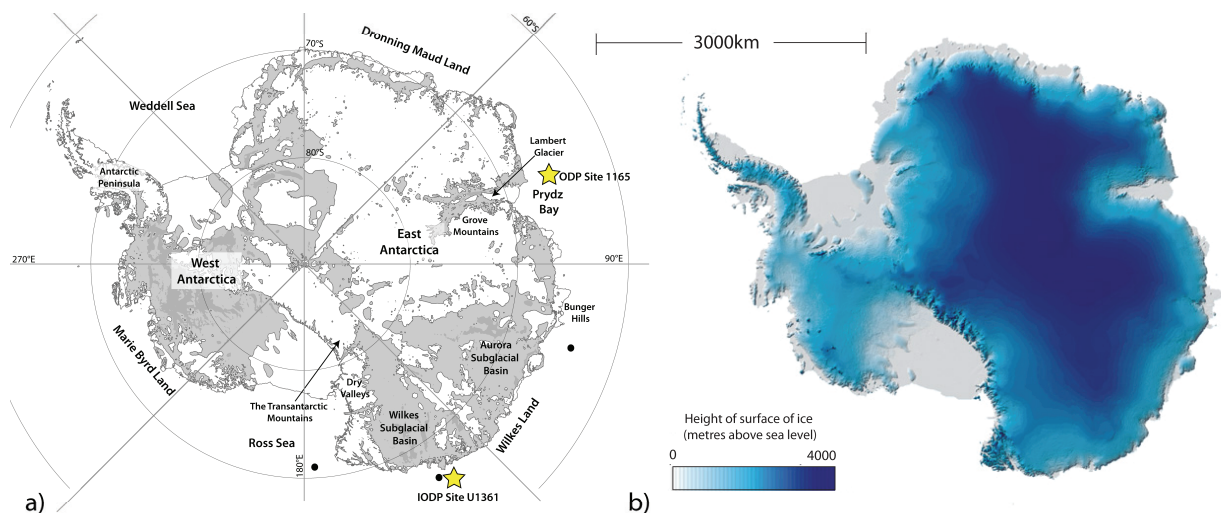


Figure 1.1. a) Map of Antarctica, showing subglacial topography with areas below sea level in grey (Fretwell et al. 2013), and the locations of major study sites within this thesis (stars) and minor supplementary study sites (black dots). b) Map illustrating the thickness of the current ice sheets covering Antarctica (Fretwell et al. 2013).

estimates of ice surface elevations, derived from cosmogenic nuclide exposure age dating, in the Grove Mountains (Liu et al. 2010) and the Bunger Hills (Holmlund and Näslund, 1994), which suggest that at times during the Pliocene, the EAIS was significantly deglaciated. Lastly, a scenario of ice sheet advance has also been interpreted from marine sediments around East Antarctica and in the Ross Sea, where Early Pliocene glacial unconformities have been inferred to represent expansion of ice onto continental shelves (Bart et al. 2001 and references therein; Naish et al. 2009; O'Brien et al. 2004).

However, a dynamic scenario for the behaviour of the EAIS has been challenged by 'stabilists' (e.g. Denton et al. 1993; Sugden et al. 1995), who argue that the ice sheet has remained unchanged since the middle Miocene (~14 Ma), when a large-scale permanent ice sheet became established on the continent (Kennett and Hodell, 1993; Flower and Kennett, 1994; Zachos et al. 2001). Much of the argument is built on geomorphological observations from particular areas of the Transantarctic Mountains, in the Dry Valleys, which are considered to have been unmodified by glacial activity since the Miocene (Denton et al. 1993; Sugden et al. 1995; Ackert and Kurz, 2004; Goff et al. 2002; Lewis et al. 2006). Additionally, the emplacement mechanism of the Sirius Group has since been disputed (Stroeven et al. 1996; Gersonde et al. 1997).

In summary, available geological data have revealed evidence for a range of behaviour of the EAIS during the Pliocene. This lack of agreement is further compounded by the results of ice sheet modelling, which have produced conflicting estimates for the degree of ice sheet retreat during the warmest times of the Pliocene (Hill et al. 2007; Pollard and DeConto, 2009; Dolan et al. 2011). Estimates of the total amount of global eustatic sea level rise produced by the Pliocene EAIS vary from minimal, at 3m (Pollard and DeConto, 2009), to 10m (Hill et al. 2007), up to a maximum of 16m (Dolan et al. 2011).

It is clear that the behaviour of the EAIS during the Pliocene was complex, and due to the poor spatial coverage and temporal uncertainties of available proximal records, many questions remain about how, when and where the ice sheet responded to elevated temperature and carbon dioxide levels in the Pliocene.

A novel way to improve our understanding on how different areas of the EAIS behaved during the Pliocene is to study the provenance of detrital glacial-marine sediments using radiogenic isotopes. The fingerprinting of glacially eroded continental material provides unprecedented insights into the geological characteristics of bedrock obscured by ice (e.g. Goodge et al. 2008; Veevers and Saeed, 2008, 2011; Thomson et al. 2013), and offers the potential to reconstruct the evolution of ice sheet behaviour through time (e.g.

Goldstein and Hemming, 2003; Williams et al. 2010; Colville et al. 2011). This powerful approach has long been recognised as a way to reconstruct the history of Pleistocene continental ice sheets in the North Atlantic (e.g. Jantschik and Huon, 1992; Grousset et al. 1993; Bond and Lotti, 1995; Gwiazda et al. 1996a, 1996b; Hemming, 1998; 2000, 2003; Peck et al. 2007; Colville et al. 2011). For example, the geochemical provenance of ice-rafted detritus (IRD) carried in and deposited by vast armadas of icebergs during the Heinrich events of the Pleistocene North Atlantic (see review in Hemming, 2004), permitted for the reconstruction of iceberg discharges from different ice sheets.

Although geochemical provenance tracing has been comparatively underutilised in the Southern Ocean, more recent studies have identified distinct provenance regions in Holocene glacimarine sediments surrounding the Antarctic continent, which have been compositionally linked to distinct sources along the continental margins constrained by available outcrops (Farmer et al. 2006; Hemming et al. 2007; Roy et al. 2007; van de Flierdt et al. 2007; Pierce et al. 2011; Flowerdew et al. 2012a). Extensive surveying work of this type has been used to improve understanding of Antarctic sub-ice geology, variations in glacial erosional patterns, and locations of dynamic ice sheet behaviour in the past (e.g. Williams et al. 2010; Flowerdew et al. 2012b).

Detrital glacimarine provenance tools that have been shown to be particularly useful in proximal Antarctic sediments are Nd and Sr isotopes of fine-grained sediments (Farmer et al. 2006; Hemming et al. 2007; Roy et al. 2007; van de Flierdt et al. 2007; Pierce et al. 2011). The long-lived radioactive decay systems of rubidium-strontium and samarium-neodymium can be used to trace heterogeneous source rocks, as their parent and daughter elements are fractionated during melting of mantle material, meaning different areas of continental crust show different radiogenic isotopic compositions. Therefore, bedrock with different ages and lithologies can have characteristic Nd and Sr isotopic compositions. Importantly, in glaciomarine sediments, both isotope systems can provide an integrated signal of bedrock sources eroded by ice (e.g. Hemming et al. 1998; Goldstein and Hemming, 2003; Roy et al. 2007; Hemming et al. 2007; Colville et al. 2011). While detrital Nd isotopes are considered robust against alteration from sediment transport and depositional processes (e.g. reviewed in Goldstein and Hemming, 2003), Sr isotopes are prone to disturbance by weathering and grain-size selective sorting (Dasch, 1969; Eisenhauer et al. 1999; Blum and Erel, 2003) and due to their lower closure temperatures (e.g. Dodson, 1975) are more easily reset during metamorphic events (e.g. Faure and Powell, 1972). When combined however, Sr isotopes and

Nd isotopes in marine sediments can provide a suite of complimentary information on source rock characteristics, onland erosional histories, and marine depositional processes.

Another useful source of glacimarine sediment provenance information is derived from the $^{40}\text{Ar}/^{39}\text{Ar}$ ages of individual ice-rafted hornblende grains (Hemming et al. 1998, 2000, 2003; Hemming and Hajdas, 2003; Peck et al. 2007; Roy et al. 2007; Williams et al. 2010; Pierce et al. 2011). Radiogenic argon ages in mineral grains retain chronological information about the thermal evolution of their host source rocks (e.g. see Hodges, 2003 for review), and hence are an extremely useful tool in fingerprinting ice-rafted material derived from continental terranes with complex tectono-metamorphic histories, such as Antarctica (e.g. van de Flierdt et al. 2008; Roy et al. 2007; Williams et al. 2010; Pierce et al. 2011). Similar to the North Atlantic, this approach has revealed potential evidence for iceberg armadas released from the EAIS during the Pliocene (Williams et al. 2010), although this study was based on a limited data set.

To summarise, due to their established strengths as glacimarine provenance tools in the circum-Antarctic realm, I have used the Nd and Sr isotopic compositions of fine-grained sediments, and the $^{40}\text{Ar}/^{39}\text{Ar}$ ages of ice-rafted hornblende grains to reconstruct the behaviour

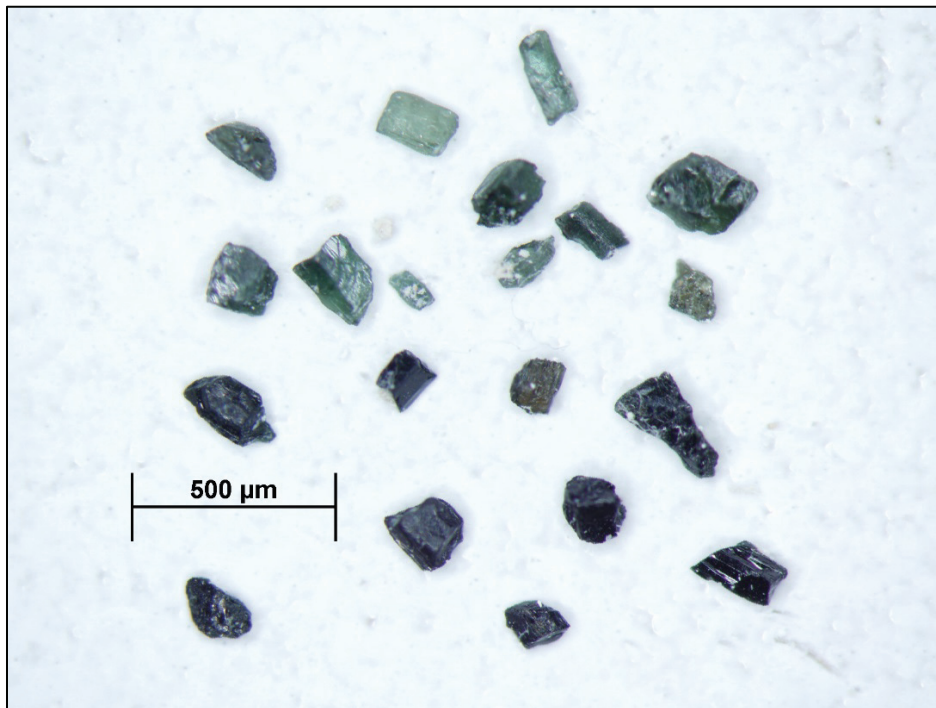


Figure 1.2. Photograph of ice-rafted hornblende grains from Pliocene Ocean Drilling Site 1165 sediments.

of the EAIS during the Pliocene for this thesis. However, a prerequisite for such a study is the careful selection of target study areas (i.e. sediment cores). Where are the most likely locations for very dynamic ice sheet behaviour during the Pliocene? Despite differences in boundary conditions, ice sheet models all agree that the most likely locations of Pliocene ice sheet retreat would be in areas of the continent that are in contact with the Southern Ocean, but that lie below sea level, such as in the Lambert Graben in Prydz Bay, and the Aurora and Wilkes Subglacial Basins located inland of the Wilkes Land and George V Land coasts, respectively (Hill et al. 2007; Pollard and DeConto, 2009; Dolan et al. 2011) (Figure 1.1). However, not all of these regions offer continuous and well-dated Pliocene marine sediment cores. For my thesis I therefore selected two primary drill sites – Ocean Drilling Site 1165 (64°22'77"S, 67°13'14"E), located offshore of Prydz Bay and down-current of the Aurora Subglacial Basin, and Integrated Ocean Drilling Program Site U1361 (64°24'5"S, 143°53'1"E) located offshore of the Wilkes Subglacial Basin.

1.1 Thesis Aim and Objectives

The overarching aim of this thesis is to improve understanding of the behaviour of the EAIS during the Pliocene Epoch. Within this framework, I attempt to fulfil the following objectives: i) improve constraints on the behaviour of the EAIS in the Wilkes Subglacial Basin during the Early Pliocene; ii) investigate the limitations associated with glaciomarine sediment provenance studies by comparing different provenance tools; iii) search for evidence for dynamic ice sheet behaviour during the warmth of Pleistocene super-interglacial Marine Isotope Stage 31; iv) improve constraints on the Pliocene behaviour of the EAIS in the Aurora Subglacial Basin and assess the effect of SST on distally sourced IRD records; and v) constrain the behaviour of the Pliocene EAIS in the Prydz Bay region and evaluate its role in global Pliocene climate change.

1.2 Thesis Outline

This thesis consists of five separate chapters that directly address the objectives set out above. Chapter 2 presents results of Nd and Sr isotope analyses of fine-grained Early Pliocene sediments drilled during the recent Integrated Ocean Drilling Program Expedition 318, offshore of the Wilkes Land margin. Provenance constraints, framed within a multi-proxy paleoenvironmental reconstruction, suggest that during prolonged intervals of warmer-

than-present regional temperatures, the margin of EAIS repeatedly retreated several hundreds of kilometres inland within the Wilkes Subglacial Basin, eroding bedrock that is currently covered by the ice sheet. This work was recently published in *Nature Geoscience* (doi:10.1038/ngeo1889), and provides the first direct proximal record of large-scale destabilisation of the EAIS in the Wilkes Subglacial Basin, during climatic conditions similar to those predicted for the near future. Chapter 2 is a modified version of the *Nature Geoscience* publication, with supplementary information including further discussion and methods presented in Appendix 2.

Following on from Chapter 2, Chapter 3 focuses on the same study area, the Wilkes Land margin, and integrates provenance results from three sites located offshore of the Wilkes Subglacial Basin and in the Ross Sea, to the east of Wilkes Land. The purpose of this chapter is to provide a unique perspective on the benefits and problems associated with utilising different glaciomarine sediment provenance tools when studying sediments deposited offshore of the glaciated Antarctic continent. In this chapter I present $^{40}\text{Ar}/^{39}\text{Ar}$ ages of ice-rafted hornblende grains and compare them to existing (Chapter 2) and new Nd and Sr isotopes on fine grained sediments from IODP Site U1361. The datasets are supplemented with two other more traditional provenance tools: clay mineralogy and visual petrographic characterisation of ice-rafted grains. Comparison of the provenance information provided by these four different tools reveals a significant disparity between the fine-grained provenance tools and hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages. This departure can be explained by mineralogical bias, whereby the lithologies of the main bedrock source supplying fine-grained sediments to IODP Site U1361 contain very few hornblendes. This observation highlights the importance of a multi-proxy approach when studying sediments derived from bedrock sources obscured by ice.

The third chapter to focus on sediments from Wilkes Land, Chapter 4, deviates slightly from the Pliocene focus of the thesis by presenting novel information on the provenance patterns of sediments deposited offshore of the Wilkes Subglacial Basin during the Pleistocene super-interglacial Marine Isotope Stage 31 (~1 million years ago). This interval has been the focus of numerous studies around Antarctica as it has been suggested that the West Antarctic ice sheet collapsed during the warmth of this interglacial. Sediments from IODP Site U1359 were analysed for Nd and Sr isotopes, and $^{40}\text{Ar}/^{39}\text{Ar}$ ages of ice-rafted hornblende grains, in order to search for evidence of increased supply of West Antarctic IRD in the context of Pliocene provenance studies presented in Chapters 2 and 3. I identify potential evidence for an increase in West Antarctic IRD, and suggest that the EAIS within

the Wilkes Subglacial basin was stable during this time, in contrast to available ice sheet modelling which suggest some limited retreat may have taken place.

Chapters 5 and 6 focus on another important East Antarctic study area, the Prydz Bay region. Chapter 5 presents a novel approach to interpret IRD provenance in the Southern Ocean, by integrating $^{40}\text{Ar}/^{39}\text{Ar}$ ages of ice-rafted hornblende grains from ODP Site 1165, located in Prydz Bay, with sensitivity tests of iceberg melting in an iceberg trajectory model. Provenance results reveal a significant increase in the amount of distally sourced IRD supplied from the Wilkes Land margin, located over 1500 km to the east, around 3.3 million years ago. Such a finding may be significant, as inland of the Wilkes Land margin lies the Aurora Subglacial Basin, and increased supply of icebergs from this region during the Pliocene has in the past been interpreted as evidence for deglaciation in this low-lying area. However, the increase in Wilkes Land IRD at ODP Site 1165 at ~ 3.3 Ma coincides with major growth of the EAIS and cooling regional climatic conditions. This pattern is in contrast to results presented in Chapter 2, which suggest that the EAIS was more unstable prior to this time, during the Early Pliocene, and hints that other processes, such as iceberg survivability and melting rates, may have effected IRD provenance patterns. Results suggest that the significant increase in Wilkes Land IRD in Prydz Bay at ~ 3.3 Ma can be largely explained by declining sea surface temperatures. However, further analysis of IRD provenance of sediments deposited over high temporal resolution during one Early Pliocene interval (~ 4.6 to ~ 4.75 Ma) and one Late Pliocene interval (~ 3 Ma) suggests that in addition to sea surface temperature change, orbitally-modulated fluctuations in IRD delivery took place, pointing to destabilisation of the EAIS during interglacial intervals.

Chapter 6 uses a relatively high resolution record of fine-grained sediment provenance offshore of the Lambert Glacier-Amery Ice Shelf system to reconstruct the response and role of the EAIS to changing global climatic conditions, from the warmth of the Early Pliocene and the transition to cooler global temperatures during the Late Pliocene into the Pleistocene. Results are based on Sr and Nd isotope analyses of fine-grained sediments at ODP Site 1165 and their provenance interpretation, and reveal that during the Early Pliocene, sediments were supplied primarily from terranes located on the flanks of the Lambert Graben, suggesting that the Lambert Glacier-Amery Ice Shelf system was likely retreated several hundreds of kilometres inland of its current position. After 3.42 Ma, sediment provenance is consistent with growth of the EAIS regionally, via an increase in the supply of material derived from the proximal continental shelf, hinting at the increased proximity of the ice sheet margin to the study site. Framing these long-term changes in the context of global

climate change reveals ice sheet growth in Prydz Bay was likely contemporaneous with growth of the West Antarctic ice sheet. Advance of the EAIS at this time may have played a role in increasing bottom water supply to the deep Atlantic, therefore helping to drive further global cooling in the Late Pliocene and Early Pleistocene.

CHAPTER 2

Dynamic behaviour of the East Antarctic Ice Sheet during Pliocene warmth

Modified from: Cook, C.P., van de Flierdt, T., Williams, T., Hemming, S.R., Iwai, M., Kobayashi, M., Jimenez-Espejo, F.J., Escutia, C., Gonzales, J.J., Khim, B.-K., McKay, R.M., Passchier, S., Tauxe, L., Sugisaki, S., Lopez Galindo, A., Patterson, M.O., Bohaty, S.M., Riesselman, C.R., Sangiorgi, F., Pierce, E.L., Brinkhuis, H., and IODP Expedition 318 Scientists, 2013, Dynamic Behaviour of the East Antarctic Ice Sheet during Pliocene Warmth. *Nature Geoscience*, 2013; doi:10.1038/ngeo1889; see Appendix 1.

Chapter Summary

Warm intervals within the Pliocene Epoch (2.58 to 5.33 million years ago) were characterised by global temperatures comparable to those predicted for the end of this century and atmospheric CO₂ concentrations similar to today. Estimates for global sea level highstands during these times imply possible retreat of the East Antarctic ice sheet, but ice-proximal evidence from the Antarctic margin is scarce. Here I present new data from Pliocene marine sediments recovered offshore of Adélie Land, East Antarctica, that reveal dynamic behaviour of the East Antarctic ice sheet in the vicinity of the low-lying Wilkes Subglacial Basin during times of past climatic warmth. Sedimentary sequences deposited between 5.3 and 3.3 million years ago indicate increases in Southern Ocean surface water productivity, associated with elevated circum-Antarctic temperatures. The geochemical provenance of detrital material deposited during these warm intervals suggests active erosion of continental bedrock from within the Wilkes Subglacial Basin, an area today buried beneath the ice sheet. I interpret this erosion to be associated with retreat of the ice sheet margin several hundreds of kilometres inland. This new data show that the East Antarctic ice sheet was sensitive to climatic warmth during the Pliocene.

2.1 Introduction

Recent satellite observations reveal that the Greenland and West Antarctic ice sheets are losing mass in response to climatic warming (Rignot et al. 2011). Basal melting of ice shelves by warmer ocean temperatures is proposed as one of the key mechanisms facilitating mass loss of the marine-based West Antarctic Ice Sheet (Pritchard et al. 2012). While thinning of ice shelves and acceleration of glaciers has been described for some areas of the East Antarctic margin (Pritchard et al. 2012), the mass balance of the predominantly land-based East Antarctic ice sheet is less clear (Shepherd et al. 2012). Its vulnerability to warmer-than-present temperatures may be particularly significant in low-lying regions, such as the Wilkes Subglacial Basin (Figure 2.1).

This hypothesis can be tested by studying intervals from geological records deposited under similar environmental conditions to those predicted for the near future. Warm intervals within the Pliocene Epoch are such analogues, with mean annual global temperatures between 2 and 4°C higher than today (Haywood et al. 2004; Fedorov et al. 2013) and atmospheric CO₂ concentrations between 250 and 450ppm, 25 to 60% higher than pre-industrial values (Pagani et al. 2010; Seki et al. 2010; Bartoli et al. 2011). Estimates for eustatic sea level highstands during these times, reconstructed from benthic foraminiferal oxygen isotopes (e.g. Miller et al. 2012) and paleoshoreline reconstructions (Naish and Wilson, 2009), are variable but indicate 22 ± 10 meters of sea level rise, although estimates derived from paleoshoreline reconstructions may need corrections for glacio-isostatic adjustments (Raymo et al. 2011). Complete melting of Greenland and West Antarctica's ice sheets could account for around 12 meters (Lythe et al. 2001) of eustatic sea level rise, indicating that most estimates for Pliocene sea level require a contribution from the East Antarctic ice sheet. While ice sheet modelling suggests that low-lying areas of the East Antarctic continent may be candidates for Pliocene ice sheet loss (Hill et al. 2007; Dolan et al. 2011), direct evidence from ice-proximal records on locations of ice margin retreat are limited (Whitehead et al. 2001; Whitehead and McKelvey, 2001; Williams et al. 2010).

2.2 Study Site: Integrated Ocean Drilling Program Site U1361

To improve our understanding of the response of the East Antarctica ice sheet to past warm climates, Integrated Ocean Drilling Program Site U1361 (64°24'5"S, 143°53'1"E; 3465m water depth) was drilled during Expedition 318 into a submarine levee bank, 310 kilometres offshore of the Adélie Land margin, East Antarctica (Figure 2.1). Approximately 75 meters of continuous Pliocene marine sediments, within the resolution of current biostratigraphic and magnetostratigraphic data (Tauxe et al. 2012), were recovered. Available physical property (Escutia et al. 2011), sedimentology (Escutia et al. 2011), and paleomagnetic and micropaleontology data (Tauxe et al. 2012) are here combined with new opal (%) data, bulk geochemistry data, and radiogenic isotope data from analyses of detrital sediments.

The Pliocene study section at IODP Site U1361 spans an interval between 3.3 and 5.3 million years ago and contains a sedimentary sequence alternating between eight diatom-rich silty clay layers, and eight diatom-poor clay layers with silt laminations (Figure 2.2). Diatom-

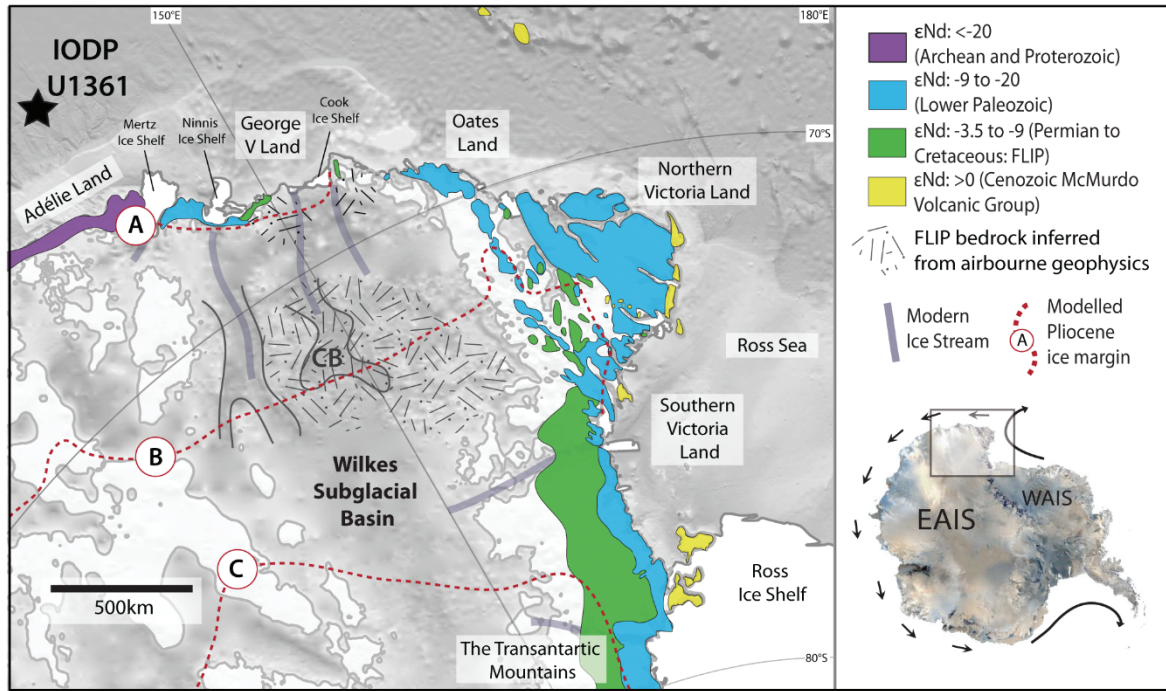


Figure 2.1. Regional map of study area, including geology of outcrops and inferred subglacial geology. Coloured shading represents the simplified geographical extent of four geological terranes differentiated according to their neodymium isotopic characteristics (expressed as ϵ_{Nd}) (see Supplementary Section 1 for detailed geological context). Areas above sea level are shown in pale grey with grey outlines, and ice shelves are shown in white (Fretwell et al. 2013). Outline of the Central Basin (CB) denotes its location within the Wilkes Subglacial Basin (Ferraccioli et al. 2009). Red lines denote the spatial extent of modelled maximum East Antarctic ice sheet retreat for the Pliocene: Line A - 3m (Pollard and DeConto, 2009), line B - 10m (Hill et al. 2007), line C - 16m (Dolan et al. 2011). The inset map illustrates the westward flowing Antarctic coastal current (arrows). EAIS: East Antarctic ice sheet; WAIS: West Antarctic Ice Sheet.

rich sediments have higher diatom valve and bulk-sediment biogenic opal concentrations, and distinctively lower signals in natural gamma radiation (Figure 2.2), indicating lower clay content. The diatom-rich units are also characterised by higher Ba/Al ratios (Figure 2.2), pointing to multiple extended periods of increased biological productivity related to less sea ice, and warmer spring and summer sea surface temperatures. This inference is supported by diatom and silicoflagellate assemblage and TEX_{86} paleothermometry data from marine and land-based records from the Antarctic Peninsula margin (Escutia et al. 2009), the Kerguelen Plateau (Bohaty and Harwood, 1998), Prydz Bay (Whitehead et al. 2001; Whitehead and McKelvey, 2001; Whitehead and Bohaty, 2003; Escutia et al. 2009), and the Ross Sea

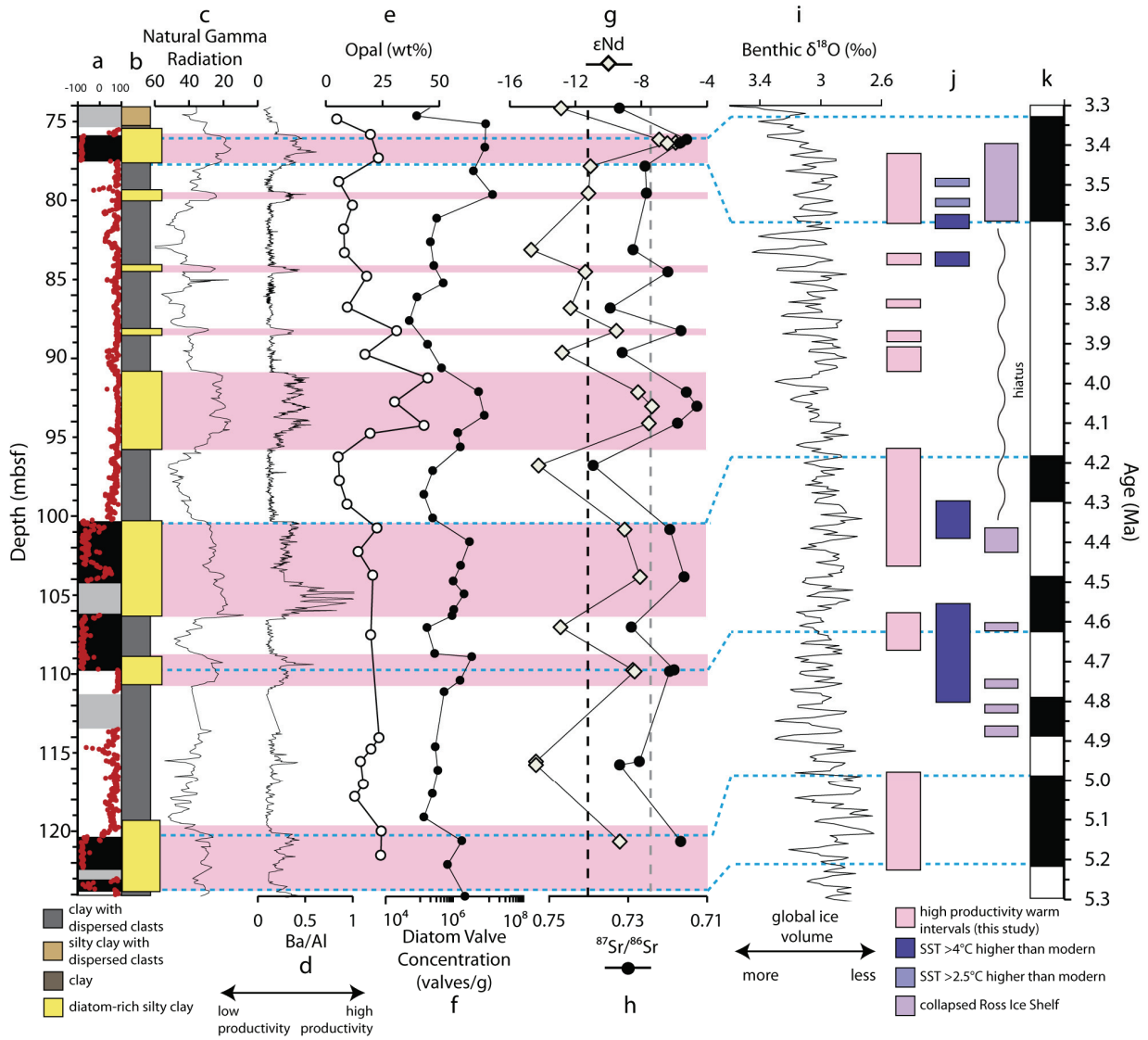


Figure 2.2. Pliocene records from IODP Site U1361 in comparison to other circum-Antarctic and global records. From left to right: (a) Paleomagnetic chron boundaries based on inclination measurements (red data points) (Tauxe et al. 2012); grey shading indicates intervals with no data; (b) lithostratigraphy (Escutia et al. 2011) (c-h) Expedition 318 shipboard record of natural gamma radiation, and new records of Ba/Al, opal wt.%, diatom valve concentrations, and Nd and Sr isotopic compositions; pink shading: high productivity intervals based on natural gamma radiation; vertical black stippled lines: Holocene Nd and Sr isotopic compositions (core-tops); (i) global benthic oxygen isotope stack (LR04) (Lisiecki and Raymo, 2005); (j) circum-Antarctic indicators for warm temperatures; pink: Pliocene high-productivity intervals at IODP Site U1361; dark blue: diatom and silicoflagellate assemblages from the Kerguelen Plateau (Bohaty and Harwood, 1998) and Prydz Bay (Escutia et al. 2009); light blue: silicoflagellate assemblages from Prydz Bay (Whitehead and Bohaty, 2003); lilac: diatomite deposits from ANDRILL cores in the Ross Sea (Naish et al. 2009); (k): paleomagnetic timescale (Gradstein et al. 2012).

(McKay et al. 2012a). These reconstructions identify elevated mean annual Pliocene sea surface temperatures (Bohaty and Harwood, 1998; Whitehead et al. 2001; Whitehead and Bohaty, 2003; Escutia et al. 2009), spring and summer sea surface temperatures between 2 to 6°C above modern levels (Escutia et al. 2009; McKay et al. 2012a), and prolonged warm intervals spanning up to 200,000 years in duration, superimposed on a baseline of warmer-than-present temperatures.

2.3 Results

In order to constrain the effects of prolonged warming on the dynamics of the East Antarctic ice sheet, I produced a Pliocene record of continental erosion patterns based on detrital marine sediment provenance (<63µm grain-size fraction) from IODP Site U1361. I used the radiogenic isotope compositions of neodymium ($^{143}\text{Nd}/^{144}\text{Nd}$, expressed as ϵ_{Nd} , which describes the deviation of measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratios from the Chondritic Uniform Reservoir in parts per 10,000) and strontium ($^{87}\text{Sr}/^{86}\text{Sr}$), both of which vary in continental rocks based on the age and lithology of geological terranes. In IODP Site U1361 sediments, both ratios show significant variations throughout the studied Pliocene interval, with ϵ_{Nd} values ranging from -5.9 to -14.7, and Sr isotopic compositions from 0.712 to 0.738 (Figure 2.2). Notably, both ratios co-vary in a distinct pattern that parallels lithological units, physical properties and bulk sediment geochemistry (Figure 2.2), with a more radiogenic Nd isotopic composition and a less radiogenic Sr isotopic composition characteristic of sediments deposited during periods of Pliocene warmth (ϵ_{Nd} : -5.9 to -9.5; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.712 to 0.719) (Figs. 2.2 and 2.3).

2.4 Discussion

2.4.1 Provenance of fine-grained sediments at IODP Site U1361

East Antarctic continental geological terranes in the vicinity of IODP Site U1361 encompass a diverse range of lithologies and ages (see Figure 2.1 for locations): (i) **Archean to Proterozoic** basement along the adjacent *Adélie Land* coast, (ii) **Lower Paleozoic** bedrock in the vicinity of the nearby *Ninnis and Mertz Glacier's*, along the *Oates Land coast*, in *Northern and Southern Victoria Land*, and in the *Transantarctic Mountains*, (iii) **Jurassic to**

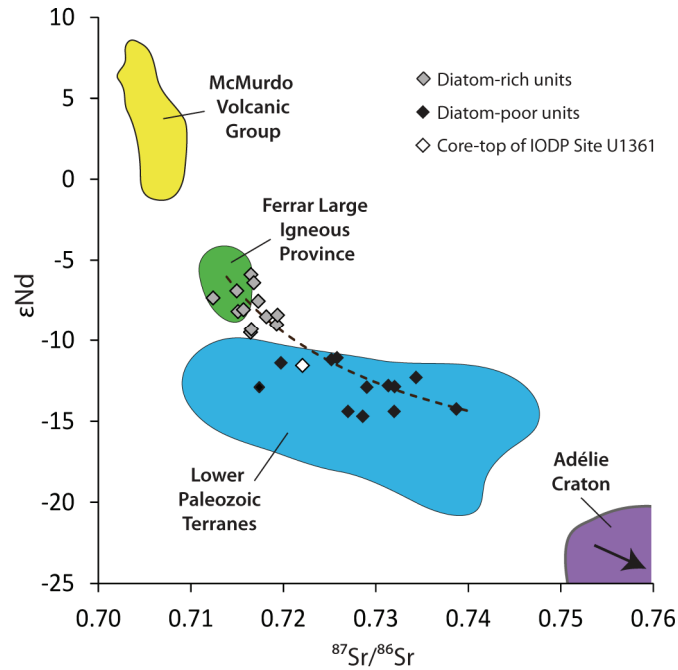


Figure 2.3. Neodymium and strontium isotopic composition of Pliocene detrital sediments from IODP Site U1361 and East Antarctic geological terranes proximal to the study area. Fields for the isotopic composition of various terranes are based on literature values (see Appendix 2). Data corresponding to the Adélie Land Craton primarily plot outside of the neodymium and strontium isotopic space shown (ϵ_{Nd} : -20 to -28; $^{87}Sr/^{86}Sr$: 0.750 to 0.780).

Cretaceous volcanic rocks (the **Ferrar Large Igneous Province** [FLIP] and associated sedimentary rocks of the **Beacon Supergroup**) along the *George V Land* coast, in Northern and Southern Victoria Land, and in the Transantarctic Mountains, and (iv) **Cenozoic** volcanics of the **McMurdo Volcanic Group**. Each of these terranes can be characterised in Nd-Sr isotope space (Figure 2.3).

The provenance signatures of the two Pliocene sedimentary types at IODP Site U1361 (i.e. diatom-rich and diatom-poor) can be best explained by a mixture of FLIP bedrock (ϵ_{Nd} : -3.5 to -6.9; $^{87}Sr/^{86}Sr$: 0.709 to 0.719), and Lower Paleozoic bedrock (ϵ_{Nd} : -11.2 to -19.8; $^{87}Sr/^{86}Sr$: 0.714 to 0.753; Fig. 2.1) (Figure 2.3; see Appendix 2 for further details on local geology and potential end-members). Diatom-poor sediments have a provenance signature that matches Lower Paleozoic bedrock, most likely sourced from granitic bedrock exposures in the hinterland of the nearby Ninnis Glacier (Figure 2.1). In contrast, the provenance fingerprint of sediments deposited during warm Pliocene intervals (i.e. diatom-rich units) reveal that they are predominantly composed of FLIP material. This FLIP provenance

fingerprint is not found in Holocene deposits at IODP Site U1361 or in sediments in its vicinity, and appears to be unique to diatom-rich Pliocene marine sediments over the past 5.3 million years (Figure 2.1 and Appendix 2).

2.4.2 *The Wilkes Subglacial Basin as a source for FLIP material*

I suggest that the most likely source of eroded FLIP material is the Wilkes Subglacial Basin, which requires Pliocene retreat of the East Antarctic ice sheet. Aeromagnetic data collected over the Wilkes Subglacial Basin between $\sim 70^{\circ}\text{S}$ and 74°S (Ferraccioli et al. 2009) reveal anomalies that resemble exposed FLIP bedrock in Southern Victoria Land, indicating the presence of abundant intrusive sills, as well as two large several kilometre deep graben-like sub-basins (Figure 2.1). Recent subglacial topographic data compilations (Fretwell et al. 2013) furthermore demonstrate that these sub-basins are directly connected to the Southern Ocean below sea level, and aerogeophysical data suggests that the Central Basin contains unconsolidated sediments inferred to be FLIP in origin (Ferraccioli et al. 2009) (Figure 2.1).

I propose that enhanced erosion of FLIP material in the Central Basin was achieved by multiple retreats of the ice margin. Ice sheet modelling and modern observations suggest that sub-surface melting at the ice edge in response to warm ocean temperatures drives retreat in areas where grounding lines lie below sea level (Pritchard et al. 2012), such as the mouth of the Wilkes Subglacial Basin (Fretwell et al. 2013) (see Appendix 2). Warm Pliocene ocean waters would have facilitated retreat into the Central Basin, contemporaneous with ice shelf collapse and ice margin retreat in other circum-Antarctic locations, such as in the Prydz Bay area (Whitehead et al. 2001; Whitehead and McKelvey, 2001) and the Ross Sea (Naish et al. 2009).

2.4.3 *Evidence for Pliocene retreat of the EAIS*

Zones of maximum glacial erosion are typically associated with the margins of an ice sheet (Alley et al. 1997; Jamieson et al. 2010), suggesting that the retreated Pliocene ice margin was situated on FLIP bedrock within the Central Basin. Existing ice sheet models imply that between $\sim 3\text{m}$ (line A, Figure 2.1; Pollard and DeConto, 2009) and $\sim 16\text{m}$ (line C, Figure 2.1; Dolan et al. 2011) of Pliocene glacio-eustatic sea level rise could be derived from retreat of the East Antarctic ice sheet. While the smallest estimate (3m) is unlikely to accurately represent the response of the ice margin to the warmest range of Pliocene climate

conditions (Pollard and Deconto, 2009) larger estimates (10 to 16m; Hill et al. 2007; Dolan et al. 2011) are influenced by initial ice sheet configurations used within climate modelling frameworks. This new data, as well as maximum modelled erosion for the northern part of the Wilkes Subglacial Basin (Jamieson et al. 2010) are in agreement with retreat of the ice margin several hundred kilometres inland. Such retreat could have contributed between 3 and 10m of global sea level rise from the East Antarctic ice sheet, providing a new and crucial target for future ice sheet modelling.

2.5 Concluding Remarks

In summary, irrespective of the extent of ice retreat, data present here document a dynamic response of the East Antarctic ice sheet to varying Pliocene climatic conditions, revealing that low-lying areas of Antarctica's ice sheets are vulnerable to change under warmer than modern conditions, with important implications for the future behaviour and sensitivity of the East Antarctic ice sheet.

CHAPTER 3

An evaluation of marine sediment
provenance tools in Pliocene detrital
sediments from the East Antarctic
margin: radiogenic isotopes and clay
minerals in fine-grained fractions versus
hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages from
ice-rafted detritus

Chapter Summary

Constraining the geochemical provenance of glaciomarine sediments can provide information about continental terranes covered by ice, and help unravel ice sheet dynamics through time. Here I present a detailed provenance investigation of Pliocene marine sediments from IODP Site U1361 (64°24'5"S, 143°53'1"E), located offshore of the Wilkes Subglacial Basin, East Antarctica, based on: i) Nd and Sr isotopes of fine-grained detrital sediments (<63µm); ii) clay mineralogy; iii) hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages of ice-rafted detritus (IRD) (>150µm) supported by visual petrographic characterisation of ice rafted mineral grains and clasts (>150µm).

The provenance fingerprint of fine-grained detrital sediments from IODP Site U1361 reveals supply is dominated by material sourced from proximal continental sources located upslope and to the east of the study site, along the Wilkes Land margin and Northern Victoria Land, including from terranes within the Wilkes Subglacial Basin. Comparison of the provenance of hornblende grains and petrographic characterisation of ice-rafted fractions with the provenance of fine-grained sediments reveals only a limited overlap of source areas (e.g. the proximal coast). However, IRD provenance also shows increased supply of material from the Ross Sea and Marie Byrd Land, West Antarctica. Results therefore imply a decoupling of the fine-grained and coarse-grained Pliocene sediment provenance signatures at IODP Site U1361.

Particularly striking is the observation that fine-grained sediment provenance (based on Sr and Nd isotopes) parallels sedimentological changes, and points to the retreat of the East Antarctic ice sheet into the nearby Wilkes Subglacial Basin during intervals of enhanced climatic warmth. However, IRD provenance based on hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages shows an absence of hornblende grains with $^{40}\text{Ar}/^{39}\text{Ar}$ age ranges typical for lithologies within the Wilkes Subglacial Basin, and shows no change in supply of IRD from East Antarctic sources during times of inferred ice sheet retreat.

This mismatch can be explained by a lithological bias in the main chosen IRD provenance tool (i.e. hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages). The major bedrock source supplying detrital material to IODP Site U1361 during ice sheet retreat is the Ferrar Large Igneous Province (basalts and dolerites, emplaced at ~178 Ma). This lithology is however characterised by only trace abundances of hornblende grains. Hence, even large amounts of erosion of Ferrar Large Igneous Province bedrock would not produce a significant hornblende fingerprint in the IRD assemblage of IODP Site U1361.

I conclude that selection of appropriate provenance tools, especially when using single mineral provenance techniques, requires a priori knowledge of source rock lithology, which is often difficult to obtain in glaciated terranes. Nonetheless, integration of multiple single grain thermochronological tools with bulk radiogenic isotope fingerprints in fine-grained sediments provides complementary provenance information, allowing for the evaluation of source rock types, their geological age and different sedimentary processes, therefore offering a more robust picture of ice sheet variability and erosion through time.

3.1 Introduction

The ‘provenance’ of a detrital marine sediment assemblage describes its derivation from erosion of its continental source rocks to its subsequent burial at the ocean floor. Of particular interest in ocean/ice sheet paleoclimatic studies is the provenance of glaciomarine sediments, as the compositional fingerprinting of glacially eroded continental detritus offers valuable insights into the geological diversity and erosional history of bedrock obscured by ice (e.g. Goodge et al. 2008; van de Flierdt et al. 2008; Thomson et al. 2013), and provides opportunities to reconstruct the evolution of ice sheet behaviour through time (Hemming, 2004; Williams et al. 2010; Colville et al. 2011). For example, the geochemical provenance of ice-rafted detritus (IRD) deposited by vast armadas of icebergs during the Heinrich events of the Pleistocene glacial North Atlantic revealed specific ice stream sources for this detritus (Jantschik and Huon, 1992; Grousset et al. 1993; Huon and Jantschik, 1993; Bond and Lotti, 1995; Gwiazda et al. 1996a, 1996b; Hemming et al. 1998; Hemming, 2004), permitting for the reconstruction of iceberg discharges from various circum-North Atlantic ice sheets. Similarly, Holocene glaciomarine sediments surrounding the Antarctic continent can be compositionally linked to distinct continental margin source regions as constrained by outcrops (Farmer et al. 2006; Hemming et al. 2007; Roy et al. 2007; van de Flierdt et al. 2007; Pierce et al. 2011; Flowerdew et al. 2012a). Extensive surveying work of this type can be coupled with results from airborne geophysical surveys (e.g. Studinger et al. 2004) and tectonic reconstructions of conjugate margins (e.g. Li et al. 2008) to gain important insight into sub-ice geology, variations in glacial erosional patterns, and locations of dynamic ice sheet behaviour in the past (e.g. Williams et al. 2010; Flowerdew et al. 2012b).

Tools utilised to determine the provenance of detrital marine sediments include: i) petrographic analyses of mineral grains and clasts (e.g. Bond et al. 1992; Elverhoi et al. 1995; Andrews et al. 1995; Licht et al. 2005; Talarico et al. 2012; Thierens et al. 2012); ii) magnetic

analyses of bulk sediments and mineral grains (Brachfeld and Banerjee, 2000; Brachfeld et al. 2002; Peters et al. 2008); iii) major and trace elemental geochemistry (e.g. Passchier and Krissek, 2008); iv) clay mineralogy (e.g. Ehrmann et al. 1992b; Hillenbrand et al. 2009, 2010); v) radiogenic isotope geochemistry (e.g. Dasch, 1969; Jantschik and Huon, 1992; Nakai et al. 1993; Bareille et al. 1994; Revel et al. 1996; Grousett et al. 1988, 1998; Hemming et al. 2007; Roy et al. 2007; VanLaningham and Mark, 2011; Colville et al. 2011); and vi) thermochronological ages of individual mineral grains (Gwiazda et al. 1996a, 1996b; Hemming, 2004, 2008; van de Flierdt et al. 2008; Cox et al. 2010; Veevers and Saeed, 2011).

In this chapter I focus on five specific provenance tracers, applied to marine sediments from IODP Site U1361, East Antarctica (Figure 3.1): (i), fine-grained (<63µm) detrital Sr isotopes, (ii) fine-grained (<63µm) detrital Nd isotopes (iii), ice-rafted (>150µm) hornblende grain $^{40}\text{Ar}/^{39}\text{Ar}$ ages, iv) petrographic characterisation of ice-rafted mineral grains (>150µm) and clasts (>2mm), and (v) clay mineralogy (<2µm).

The $^{40}\text{Ar}/^{39}\text{Ar}$ ages of individual hornblende grains retain chronological information about the thermal evolution of their host rocks (Hodges, 2003), and hence are an extremely useful tool in fingerprinting ice-rafted material sourced from continental terranes with complex tectono-metamorphic histories, such as Antarctica (e.g. Roy et al. 2007; van de Flierdt et al. 2008; Williams et al. 2010; Pierce et al. 2011). In addition, the long-lived radioactive decay systems of rubidium-strontium and samarium-neodymium can be used to trace heterogeneous source rocks, as their parent and daughter elements are fractionated during melting of mantle material, creating reservoirs with different radiogenic isotopic compositions in continental crust (i.e. high Rb/Sr ratios and low Sm/Nd ratios) and mantle material (i.e. low Rb/Sr ratios and low Sm/Nd ratios). Hence, bedrocks with different ages and lithologies can have characteristic Nd and Sr isotopic compositions. Additionally, Rb and Sr are significantly geochemically different, relative to the differences between Sm and Nd. Thus the Sr isotope composition of sediment sources tends to show much more variability than the Nd isotope system. Together however, both isotope systems can provide an integrated signal of bedrock sources eroded by ice (e.g. Hemming et al. 1998; Roy et al. 2007; Hemming et al. 2007; Colville et al. 2011). While detrital Nd isotopes are considered robust against alteration from sediment transport and depositional processes (e.g. reviewed in Goldstein and Hemming, 2003), Sr isotopes are additionally prone to disturbance by weathering and grain-size selective sorting (Dasch, 1969; Eisenhauer et al. 1999; Blum and Erel, 2003). In addition to the above provenance tools, the clay mineral composition of fine-grained marine sediments has traditionally been the most commonly utilised provenance tool

for the circum-Antarctic realm (Ehrmann and Mackensen, 1992; Ehrmann et al. 1992a, 1992b; Petschick et al. 1996; Diekmann and Kuhn, 1999; Hillenbrand et al. 2010), and is a product of both the continental bedrock sources of detrital material, and the intensity of chemical weathering subjected to source bedrock (Biscaye, 1965; Robert and Kennett, 1994). This latter characteristic has been an advantage for documenting glacial initiation in Antarctica (Ehrmann and Mackensen, 1992; Robert and Kennett, 1997), due to the large-scale change to more physical weathering relative to chemical weathering with glaciation.

Alongside detrital U-Pb zircon age studies (e.g. Jacobs et al. 1998; Fitzsimmons, 2000a; Goodge et al. 2010; Veevers and Saeed, 2011), and investigations into the Pb isotopic composition of individual feldspar grains (Flowerdew et al. 2012a, 2012b), the tools I study here are commonly utilised in circum-Antarctic marine sediments (e.g. Farmer et al. 2006; Hemming et al. 2007; Roy et al. 2007; Pierce et al. 2011). This study can therefore provide the basis for a discussion on the suitability of different provenance tools in glaciomarine sediments, and highlight the strength of using multiple provenance tools to avoid lithological bias when studying detrital sediments derived from ice-covered continents.

3.2 Geological Overview

Detailed knowledge of the local and regional geology of the Antarctic continent in the vicinity of the regional study area is vital to my provenance investigation, as this region has a complex geological history spanning several billion years. Here I briefly summarise known spatial occurrences of major bedrock terrains along with their lithologies (Figure 3.1), thermochronological ages (Figure 3.2), and Nd and Sr isotopic compositions (Figs. 3.3 and 3.4, respectively). I focus on the area from Wilkes Land (~135°E) in the west, to Marie Byrd Land (~120°W) in the east. Supplementary provenance information is derived from fine-grained sediments and mineral grains in proximal Holocene marine sediments.

Bedrock in the heavily glaciated *Wilkes Land margin* (100-135°E), located to the west of IODP Site U1361, is poorly exposed (Figure 3.1). Sparse outcrops consist of **Proterozoic** charnockites and metasediments (Möller et al. 2002), which yield U-Pb zircon and monazite ages between 1140 to 1340 Ma (Post et al. 1996, 2000; Fitzsimmons, 2000a; Möller et al. 2002). Holocene marine sediments offshore of the Wilkes Land margin are characterised by $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende ages between 1100 and 1300 Ma (Roy et al. 2007; Pierce et al. 2011),

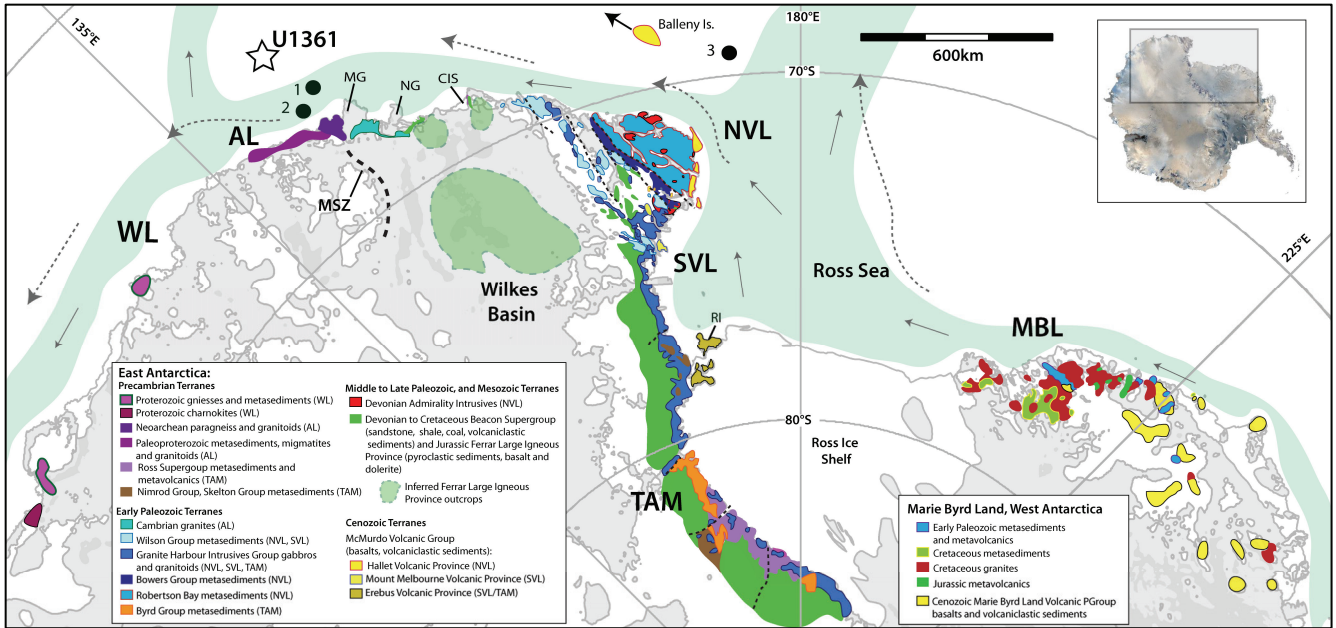


Figure 3.1. Geological map of the study area, illustrating the diverse range of ages and lithologies of exposed terranes (modified from Bushnell and Craddock, 1970). Also shown is the continental subglacial topography (BEDMAP 2; Fretwell et al. 2013) with continental regions below sea level to -2000m in light grey, and regions below -2000m in darker grey. Dashed lines refer to major structural features (Flottmann et al. 1993; Ferraccioli et al. 2009). Offshore, the star indicates the location of IODP Site U1361; sites 1, 2 and 3 (offshore black dots) refer to IODP Site U1358, IODP Site U1360 and DSDP Site 274 respectively. Blue shading offshore represents the approximate transport region of modern icebergs (Antarctic Iceberg Tracking Database (1978–2012); available at <http://www.scp.byu.edu/data/iceberg/database1.html>) with direction of movement shown with small grey arrows. Larger dashed arrows indicate the approximate location of major flows of Antarctic Bottom Water (from Orsi et al. 1999). Inferred subglacial extent of the Ferrar Large Igneous Province is from Ferraccioli et al. (2009). AL: Adélie Land, NVL: Northern Victoria Land, SVL: Southern Victoria Land, TAM: Transantarctic Mountains, MBL: Marie Byrd Land, NG: Ninnis Glacier, MG: Mertz Glacier, MSZ: Mertz Shear Zone; CIS: Cook Ice Shelf; RI: Ross Island.

matching onshore ages. These same sediments yield ϵ_{Nd} values of -12.3 to -14.9 (Roy et al. 2007; Pierce et al. 2011; [ϵ_{Nd} describes the deviation of a measured $^{143}\text{Nd}/^{144}\text{Nd}$ ratio from the Chondritic Uniform Reservoir in parts per 10,000; Jacobsen and Wasserburg, 1980]).

The boundary between Proterozoic terranes in Wilkes Land and the Archean and Neoproterozoic **Adélie Craton** to the east is unexposed. However provenance variability in nearby Holocene marine sediments suggests the most westerly extent of the Adélie Craton can be inferred to be located near to 135°E. The Adélie Craton is composed of Archean

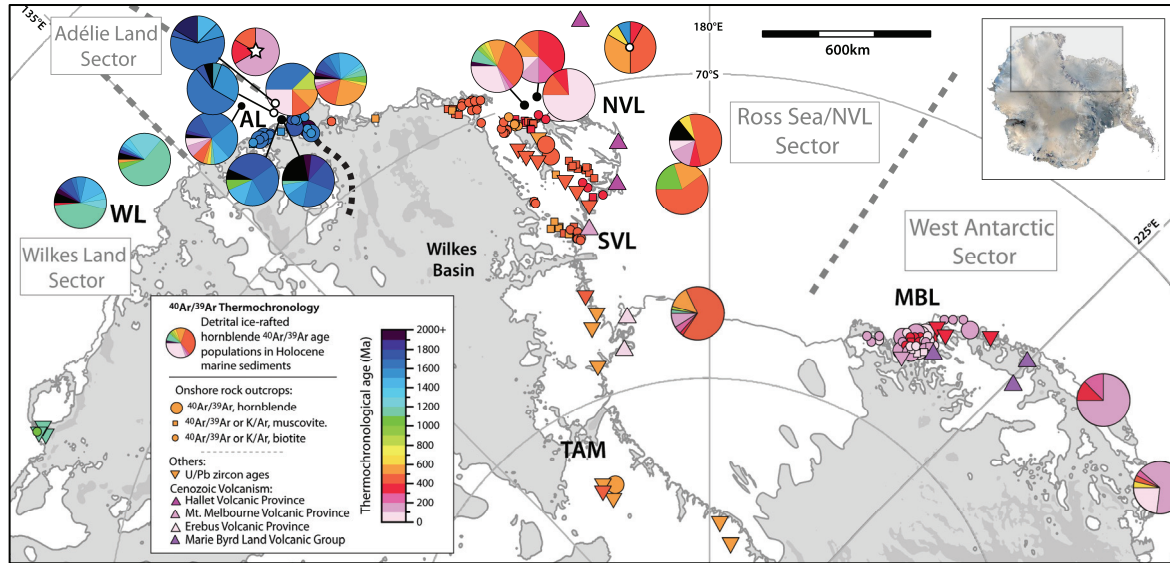


Figure 3.2. Thermochronological map of study area, illustrating the good agreement between detrital hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age populations in Holocene marine sediments (Brachfeld et al. 2007; Roy et al. 2007; Pierce et al. 2011; this study), and onshore ages (Klee et al. 1990; Dallmeyer and Wright, 1992; Goodge and Dallmeyer, 1992; Richard et al. 1994; Luyendyk et al. 1996; Post et al. 1996, 2000; Pankhurst et al. 1998; Peucat et al. 1999; Schussler et al. 1999; Storey et al. 1999; Möller et al. 2002; Fitzsimons, 2003; Wysoczanski and Allibone, 2004; Siddoway et al. 2005; Adams, 2006; Di Vincenzo et al. 2007; Duclaux et al. 2008; Menot et al. 2005; Di Vincenzo et al. 2007; Goodge, 2007; Phillips et al. 2007; Copper et al. 2007). Thermochronological ages correspond to colours shown in the scale bar and delineate four distinct provenance sectors: a Wilkes Land sector to the west of 135°E , an Adélie Land sector ($135\text{--}142^\circ\text{E}$), a Northern Victoria Land and Ross Sea sector ($\sim 142^\circ\text{E}$ to $\sim 195^\circ\text{E}$), and a West Antarctic sector (east of 195°E). Also shown are the locations of numerous Cenozoic volcanic centres, shown as triangles (see the following for their eruptive histories: Müller et al. 1991; Di Vincenzo et al. 1997, 2010; Armienti and Baroni, 1999; Rossetti et al. 2000; Acton et al. 2008; Dibble et al. 2008; Kelly et al. 2008; Mortimer et al. 2008; Smellie et al. 2011; Giordano et al. 2012). See Figure 3.1 for abbreviations.

paragneisses and granitoids with U-Pb zircon ages of 2420 to 2500 Ma (Goodge and Fanning, 2010), metasedimentary rocks with U-Pb zircon ages of 1700 Ma (Oliver and Fanning, 1997; 1997; Peucat et al. 1999), and isolated Paleoproterozoic migmatites and granitoids with U-Pb zircon and hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 1600 and 1740 Ma (Duclaux et al. 2008; Goodge and Fanning, 2010). Detrital zircons and hornblendes in marine sediments offshore of the Adélie Craton have similar age ranges (Roy et al. 2007; Goodge and Fanning, 2010; Pierce et al. 2011). Bedrock in Adélie Land is characterised by ϵ_{Nd} values between -20.0 and -29.1, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of between 0.750 and 0.780 (Borg and Depaolo, 1994; Peucat et al.

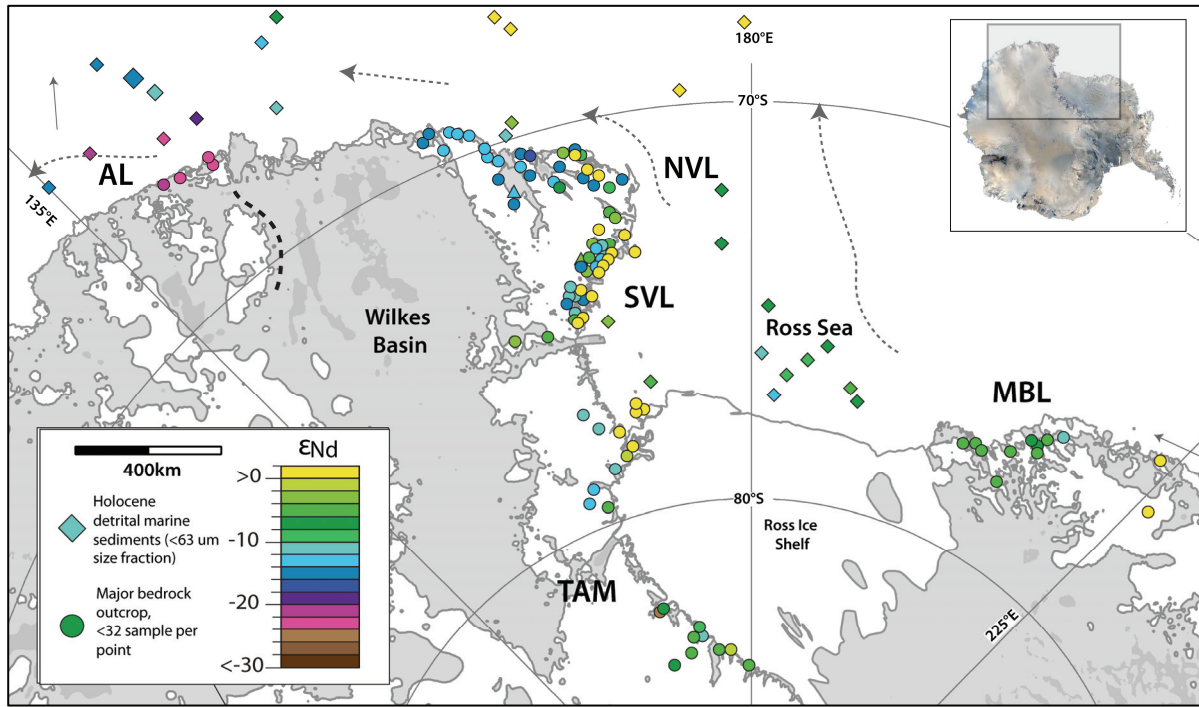


Figure 3.3. Map of study area, with published Nd isotopic compositions of bedrock (circles) and detrital marine core-top sediments (<63μm fraction; diamonds) superimposed. Colours of neodymium isotopic compositions correlate to ϵ_{Nd} values indicated on the scale bar. Each data point represents between 1 and 32 individual reported values (see Section 2 for East Antarctic terranes, West Antarctic terranes: Futa et al. 1983; Hart et al. 1995; 1997; Wysoczanski et al. 1995; Panter et al. 1997; 2000; Pankhurst et al. 1998; Storey et al. 1999; Korhonen et al. 2010; Le Masurier et al. 2011). Marine data are taken from Farmer et al. (2006), Roy et al. (2007), Pierce et al. (2011) and Chapter 2.

1999). Proximal detrital marine sediments have slightly more radiogenic Nd and less radiogenic Sr isotopic compositions (ϵ_{Nd} : -17.0 to -24.0; $^{87}Sr/^{86}Sr$: 0.730 to 0.744) (Hemming et al. 2007; Roy et al. 2007; Pierce et al. 2011; Chapter 2).

A major structural feature, the **Mertz Shear Zone (MSZ)** marks the eastern boundary that separates the Adélie Craton from Paleozoic and younger terranes to the east (Talarico and Kleinschmidt, 2003; Ferraccioli et al. 2009). Most recent activity has been dated at 1500 to 1550 Ma ($^{40}Ar/^{39}Ar$ hornblende ages; Di Vincenzo et al. 2007). Detrital hornblende and biotite grains in modern marine sediments proximal to the MSZ have very similar $^{40}Ar/^{39}Ar$ ages (Pierce et al. 2011).

To the east of the MSZ, in the vicinity of the *Ninnis Glacier*, granitoids are exposed that have U-Pb zircon ages, and biotite and muscovite $^{40}Ar/^{39}Ar$ ages of ~500 Ma (Adams, 2006; Di Vincenzo et al. 2007; Goodge, 2007; Goodge and Fanning, 2010). Zircon grains

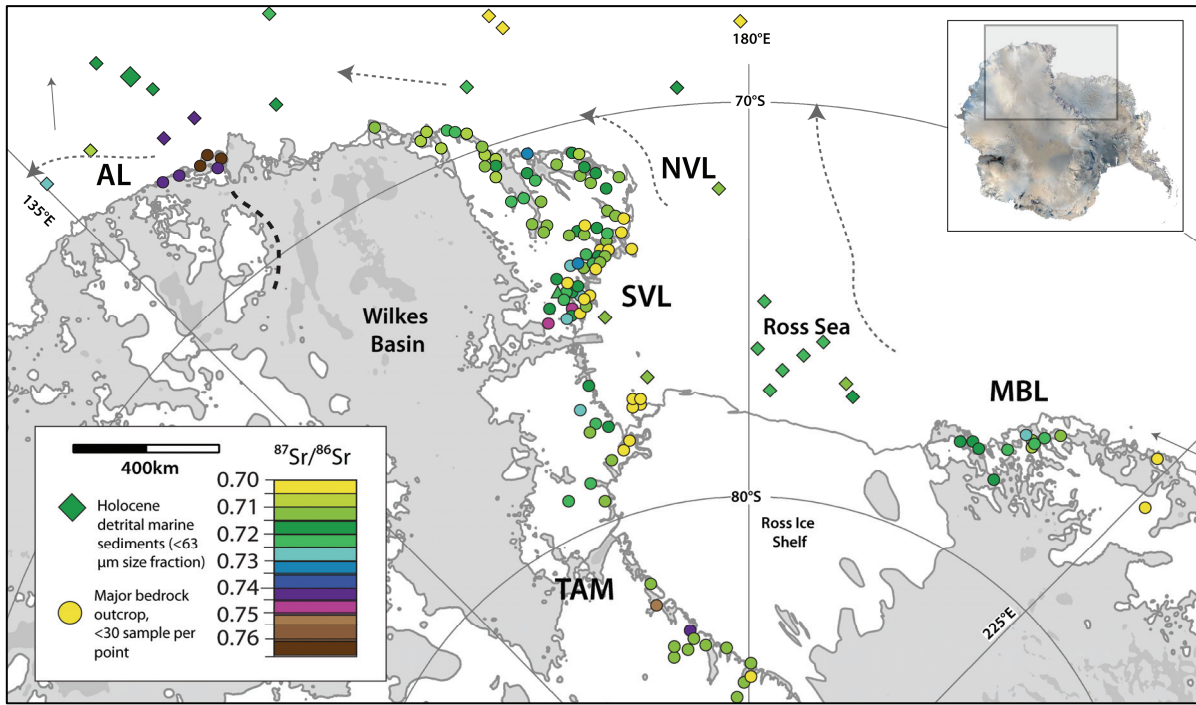


Figure 3.4. Map of study area with published Sr isotopic compositions of bedrock (circles) and detrital marine core-top sediments (<63µm fraction; diamonds) superimposed. Colours of strontium isotopic compositions of individual points correlate to the scale bar. Each data point represents up to 30 individual reported values. See Section 2 (Geological Overview) for East Antarctic terranes; see Figure 3.3 caption for references for West Antarctic terranes. Marine data are taken from Farmer et al. (2006), Hemming et al. (2007), and Chapter 2.

from detrital shelf sediments between the Mertz Glacier and Ninnis Glacier (see Figure 3.1 for locations) have U-Pb ages of between 500 and 600 Ma (Goodge and Fanning, 2010). Hornblende and biotite grains in shelf sediments are dominated by slightly younger $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 450 and 550 Ma (Pierce et al. 2011). While no Nd and Sr isotopic data exists for these granitoids, proximal Holocene shelf and offshore sediments (Goodge and Fanning, 2010; Pierce et al. 2011), are composed of detrital material with ϵ_{Nd} signatures between -11.0 and -14.5.

Lithologies of the **Beacon Supergroup** and the **Ferrar Large Igneous Province** are exposed to the east of the Ninnis Glacier (~147°E) (Goodge and Fanning, 2010) and to the east of the *Cook Ice Shelf* (~152°E) (Bushnell and Craddock, 1970; Hornig, 1993). The sedimentary strata of the Beacon Supergroup are found throughout Northern Victoria Land, Southern Victoria Land and the Transantarctic Mountains (e.g. Barrett, 1981). The Beacon Supergroup is composed of a 2.7 to 3.5km thick undeformed sequence of Devonian to Cretaceous fluvial, glacial, and shallow marine sediments (Barrett et al. 1987) dominated by

diamicts, sandstone, quartzose sandstones, shale and coal (Elliot and Fleming, 2008). No Nd and Sr isotopic data are available for the Beacon Supergroup, but detrital zircons are dominated by U-Pb ages of 430 to 620 Ma (Goodge and Fanning, 2010), suggesting a genetic link to regionally abundant Neoproterozoic and Early Paleozoic terranes (see below).

The intrusive and extrusive rocks of the Jurassic Ferrar Large Igneous Province occur within and above the Beacon Supergroup, and are composed of mafic dolerite, flood basalts, tuffs and pyroclastics (Elliot and Flemming, 2008). The Ferrar Large Igneous Province was emplaced at ~178 Ma (Foland et al. 1993; Hiemann et al. 1994; Encarnacion et al. 1996; Duncan et al. 1997; Minor and Mukasa, 1997), and is characterised by ϵ_{Nd} values between -3.5 and -6.9, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.709 to 0.719 (Faure, 1972, 1974, 1982; Thompson et al. 1983; Mensing et al. 1984; Siders and Elliot, 1985; Brotzu, 1988; Fleming et al. 1992, 1995; Elliot et al. 1995; Mensing and Faure, 1996; Molzahn et al. 1996; Wilhelm and Worner, 1996; Antonini et al. 1999; Elliot et al. 1999; Demarchi et al. 2001).

In the most westerly region of *Northern Victoria Land*, outcrops of the **Wilson Terrane** and its associated felsic **Granite Harbour Intrusives** are exposed (Borg et al. 1987; Goodge et al. 2002; Rocchi et al. 2004). These terranes are composed of metagreywackes, slates, schists, psammites, gneisses and granites (Turner et al. 1993; Schussler et al. 1999; Henjes-Kunst and Schussler, 2003). Wilson Terrane metasediments are characterised by whole-rock K-Ar ages of 460 to 500 Ma (Schussler et al. 1999; Adams, 2006) and U-Pb zircon ages of 490 Ma (Schussler et al. 1999), with whole-rock ϵ_{Nd} values ranging from -11.0 to -19.0, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.714 to 0.750 (Armienti et al. 1990; Talarico et al. 1995; Rocchi et al. 1998; Schussler et al. 1999; Cox et al. 2000; Henjes-Kunst and Schussler, 2003). Granite Harbour Intrusives are characterised by ϵ_{Nd} values of -9 to -17, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.712 and 0.744 (Borg et al. 1987; Armienti et al. 1990; Borg and Depaolo, 1994; Dallai et al. 2003). Hornblendes from Holocene marine sediments offshore Northern Victoria Land yield $^{40}\text{Ar}/^{39}\text{Ar}$ ages of 400 to 550 Ma (Pierce et al. 2011).

Metamorphosed siltstones and greywackes of the allochthonous Middle Cambrian to Ordovician **Bowers Terrane** is found east of the Wilson Terrane (Weaver et al. 1984; Borg et al. 1987; Rocchi et al. 2004). These metasedimentary rocks are typically characterised by whole-rock K-Ar ages of 320 and 450 Ma (Adams, 2006), and ϵ_{Nd} and $^{87}\text{Sr}/^{86}\text{Sr}$ signatures of -12.8 to -21.8 and 0.716 to 0.722, respectively (Di Vincenzo et al. 1997; Henjes-Kunst and Schussler, 2003). The **Robertson Bay Terrane** comprises the most easterly area of Northern Victoria Land, and is composed of homogenous, low-grade, Ross Orogeny-related metamorphosed turbiditic greywackes and mudstones (Henjes-Kunst and Schussler, 2003;

Rossetti et al. 2006). While no $^{40}\text{Ar}/^{39}\text{Ar}$ ages are available, whole-rock K-Ar ages are between 470 and 490 Ma (Adams, 2006) reflecting well Ross Orogeny signatures, and ϵ_{Nd} values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of -12.3 to -15.6 and 0.713 to 0.717, respectively (Henjes-Kunst and Schussler, 2003). The Robertson Bay Terrane was intruded by the Middle to Late Devonian granite association of the **Admiralty Intrusive** series (Borg et al. 1987; Bracciali et al. 2009). Granites of the Admiralty Intrusives exhibit ϵ_{Nd} signatures of -3.0 to -8.2 (Borg et al. 1987). Surface sediments offshore of Northern Victoria Land are dominated by $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende and biotite age populations of 450 to 500 Ma, and 350 to 500 Ma, respectively (Pierce et al. 2011), again reflecting on-land bedrock thermochronological ages associated with the regional metamorphism of the Ross Orogeny (Goodge, 2007).

Coastal regions of *Southern Victoria Land* and the northern *Transantarctic Mountains* are dominated by metasediments of the Wilson Terrane and Granite Harbour intrusives, composed primarily of granites and granodiorites (e.g. Rocchi et al. 1998; Zattin et al. 2010). Exposed bedrock further inland of Southern Victoria Land and the northern Transantarctic Mountains is primarily composed of the Beacon Supergroup and Ferrar Large Igneous Province (Elliot and Fleming, 2008). Limited exposures of Precambrian metasediments and metavolcanics of the Ross Supergroup, and Nimrod and Skelton Groups (e.g. Cooper et al. 2011) also comprise areas of the Transantarctic Mountains.

The Cenozoic **McMurdo Volcanic Group** (Kyle and Cole, 1974; LeMasurier and Thomson, 1990; Tessensohn, 1991) forms an important geological feature in the Ross Sea region. The McMurdo Volcanic Group is comprised of the **Hallett Volcanic Province** (Kyle et al. 1990; Smellie et al. 2011) located along the Ross Sea margin of Northern Victoria Land, the **Mount Melbourne Volcanic Province** in Southern Victoria Land (Kyle, 1990; Giordano et al. 2012), and the **Erebus Volcanic Province** in the vicinity of Ross Island (Kyle and Cole, 1974; Kyle et al. 1992). Also considered part of the McMurdo Volcanic Group are the volcanic edifices of the **Balleny Islands** (Johnson et al. 1982), located ~300km north of Northern Victoria Land and ~900km to the east of IODP Site U1361. Exposures of McMurdo Volcanic Group bedrock are characterised by ϵ_{Nd} values between +8.4 and -0.1 and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.703 to 0.713 (Goldich et al. 1975; Shen-Su, 1976; Kyle and Seward, 1984; Gamble, 1985; Hart, 1988; Worner, 1989; LeMasurier and Thomson, 1990; Ben Othman et al. 1990; Armienti et al. 1991; Green Trevor, 1992; Caldwell and Kyle, 1994; Rocholl et al. 1995; Müller et al. 1991; Rocchi et al. 2002; Armienti et al. 2003; Hornig, 2003; Cooper et al. 2007; Kelly et al. 2008; Sims et al. 2008; Nardini et al. 2009; Oppenheimer et al. 2011; Perinelli et al. 2011).

West Antarctic terranes in **Marie Byrd Land** are comprised of Paleozoic metasedimentary rocks and metavolcanic rocks, with hornblende and biotite $^{40}\text{Ar}/^{39}\text{Ar}$, and U-Pb zircon ages between 340 and 375 Ma (Richard et al. 1994; Luyendyk et al. 1996; Pankhurst et al. 1998). Regionally widespread Cretaceous metasedimentary rocks and granitoid plutons are also present, with U-Pb zircon, K-Ar biotite and hornblende, and $^{40}\text{Ar}/^{39}\text{Ar}$ biotite and muscovite ages between 95 and 125 Ma (Richard et al. 1994; Luyendyk et al. 1996; Pankhurst et al. 1998; Storey et al. 1999; Wysoczanski and Allibone, 2004). These ages agree well with $^{40}\text{Ar}/^{39}\text{Ar}$ ages of hornblendes deposited as IRD grains offshore of the Marie Byrd Land margin (97 to 125 Ma; Roy et al. 2007). Onshore whole-rock ϵ_{Nd} and $^{87}\text{Sr}/^{86}\text{Sr}$ signatures of these terranes range from -4.6 to -12.4, and 0.711 to 0.740, respectively (Pankhurst et al. 1998; Korhonen et al. 2010). Cenozoic volcanic terranes of the Marie Byrd Land Volcanic Province are also regionally prevalent, and are characterised by ϵ_{Nd} values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from -1.4 to +7.6, and 0.702 to 0.709, respectively (Futa et al. 1983; Hart et al. 1995, 1997; Wysoczanski et al. 1995; Panter et al. 1997, 2000; Storey et al. 1999; LeMasurier et al. 2011).

3.3 Study Sites and Materials

Integrated Ocean Drilling Program (IODP) Site U1361 (64°24'5"S, 143°53'1"E) (Figure 3.1) constitutes the main study site for this investigation, and was drilled in 3466m water depth, approximately 315km offshore of the Wilkes Land margin, during IODP Expedition 318 (Escutia et al. 2011). A total of ~388m of sediment were recovered, and dated by palaeomagnetic inclination data and biostratigraphy (diatom and radiolarian datums) (Escutia et al. 2011; Tauxe et al. 2012) (Figure 3.5). Today, detrital sediments are supplied to IODP Site U1361 by ice sheet-driven turbidity currents, transporting shelf sediments downslope in submarine channels orientated perpendicular to the coast (Buseti et al. 2003; Donda et al. 2003; Escutia et al. 2000, 2003). In addition to turbidity deposition, ice-rafting supplies material to the area (Pierce et al. 2011), and bottom contour currents may additionally influence sedimentation (Donda et al. 2003; Escutia et al. 2003). In this chapter I focus on Pliocene sediments from an 80m interval between 45 and 125 mbsf (Figure 3.5). Within this interval, five lithostratigraphic units occur (Figure 3.5), representing variable depositional and environmental conditions during the Pliocene. Facies 1 (clays), facies 2 (clays with dispersed clasts) and facies 3 (silty clays with dispersed clasts) are dominated by

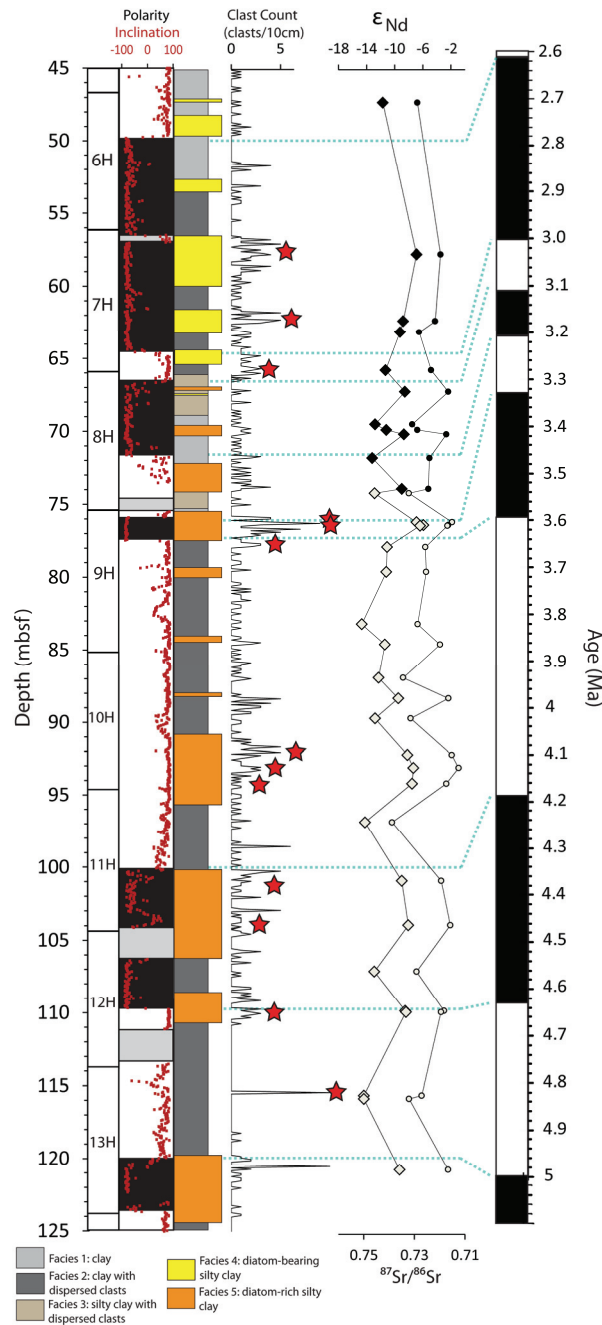


Figure 3.5. Downcore summary of Pliocene sediments recovered from IODP Site U1361. From left to right: i) depth in meters below sea floor; ii) core intervals; iii) paleomagnetic chron boundaries (Tauxe et al. 2012) with inclination data shown in red, and grey shading indicating areas with no data; lithostratigraphy (modified after Escutia et al. 2011); iv) visual clast counts (Escutia et al. 2011) >2mm in diameter, red stars indicate the depths of samples analysed for ice-rafted hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age populations; v) detrital neodymium isotopic compositions (ϵ_{Nd} : diamonds) and detrital strontium isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr}$: circles) for Pliocene marine sediments from IODP Site U1361, filled symbols represent new data from this study, and open symbols are results taken from Chapter 2 (uncertainties are smaller than data points); vi) paleomagnetic chron boundaries from (Gradstein et al. 2012).

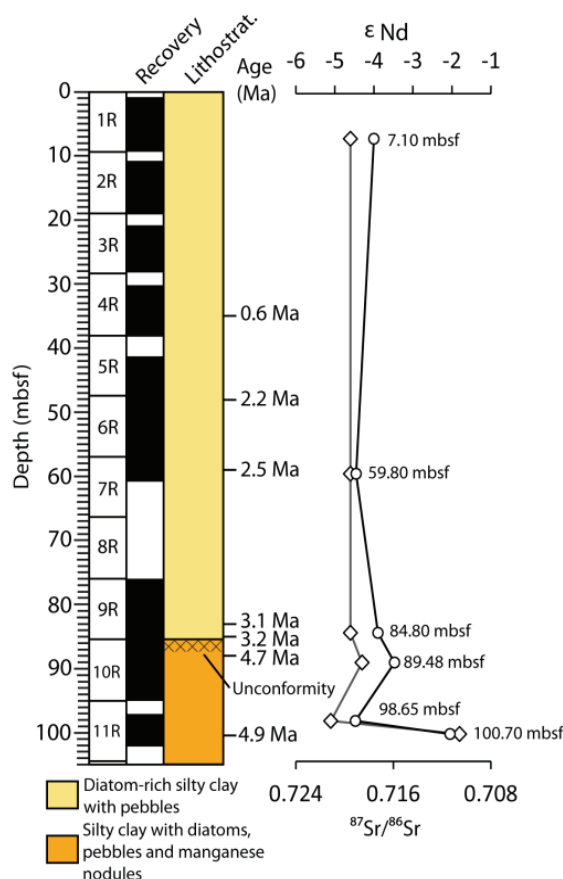


Figure 3.6. Downcore section of Quaternary and Pliocene sediments recovered from DSDP Site 274. From left to right: i) depth in meters below sea floor; ii) core intervals; iii) recovery, with white indicating areas with no recovery (Hayes et al. 1975); iv) lithostratigraphy (Hayes et al. 1975); v) approximate ages of sediments, which reveal an unconformity between 3.2 and 4.7 Ma; vi) detrital neodymium isotopic compositions (ϵ_{Nd} : diamonds) and detrital strontium isotopic compositions ($^{87}Sr/^{86}Sr$: circles) for Holocene and Pliocene marine sediments ($<63\mu m$ size fraction) from DSDP Site 274 (uncertainties are smaller than data points), with depths shown to the right. Note the minimal variability in isotopic compositions between 98.65 mbsf and 7.10 mbsf, which suggests no significant change in sediment supply to the site took place between ~ 4.85 Ma and the late Pleistocene/Holocene.

terrigenous material, while facies 4 (diatom-bearing silty clays) and facies 5 (diatom-rich silty clays), contain more significant biogenic components. For the Early Pliocene section of the core, diatom valve concentrations are higher in diatom-bearing silty clays and diatom-rich silty clays deposited between 67 and 124 mbsf, and therefore are interpreted to represent intervals of enhanced biogenic opal deposition. Diatom assemblages indicate that these diatom-rich intervals were characterised by conditions warmer than today (Chapter 2). Conversely, clay-rich sediment facies have lower diatom abundances and diatom

assemblages indicating intervals of reduced productivity and cooler climatic conditions (Chapter 2). Two sampled Miocene layers at this site are characterised by facies 5 and facies 6 (nannofossil ooze, not shown in Figure 3.5)

To provide supporting regional provenance constraints, I also analysed provenance signatures of Holocene and Pliocene sediments from Deep Sea Drilling Program (DSDP) Site 274 (68°59'81"S, 173°25'64"E) which was drilled in 3326m water depth, approximately 250 km offshore of Northern Victoria Land (Figure 3.1) during DSDP Expedition 28. I focus on approximately 41m of Pliocene sediments between 59.80 and 100.70 mbsf, and one Holocene sample at 7.10 mbsf (Figure 3.6). Pliocene and Holocene sediments are composed of two lithostratigraphic facies. Above 85 mbsf, massive diatom-rich silty clay with pebbles dominate (facies A), interpreted as representing hemipelagic deposition and ice-rafting. Below 85 mbsf, silty clay with diatoms, pebbles and manganese nodules (facies B) dominate (Hayes et al. 1975), interpreted as turbidity currents. Age constraints on these Pliocene sediments are rather poor and are based on the diatom biostratigraphy of Fleming et al. (1996), which I have converted to average range model ages of Cody et al. (2008) (Figure 3.6).

Additionally, I analysed sediments from IODP Site U1358 (66°05'42"S, 143°18'76"E), which was drilled in 512m water depth on the continental shelf offshore of the Adélie Coast (Figure 3.1). Pliocene sediments were disturbed during drilling, and are composed of a single lithostratigraphic unit, a clast-rich sandy diamictite indicative of deposition in a subglacial environment, or beneath floating ice (Escutia et al. 2011). No robust age model for IODP Site U1358 exists, and diatom assemblages provide tentative constraints on a Pliocene age range between 4.4 and 5.12 Ma (*Thalassiosira inura* diatom zone; Iwai, personal communication).

3.4 Sample Selection and Methods

3.4.1 Neodymium and strontium isotopes

For this study, a total of 11 Pliocene sediment samples were selected from IODP Site U1361, between 47.25 and 73.79 mbsf, for analysis of their Nd and Sr isotopic compositions (Figure 3.5, Table 3.1). Two additional samples were selected from Miocene sediments (34X 2W 79-81cm, 313.85mbsf, ~11 Ma; 41X 1W 65-67cm, 379.05 mbsf, ~12 Ma). Pliocene samples were taken from sedimentary facies 1 (n=4), facies 2 (n=1), facies 4 (n=3) and facies

5 (n=3) (Figure 3.5, Table 3.1), with Miocene samples taken from facies 5 and 6 (nannofossil ooze; Table 3.1). For the majority of samples, a 2cm core interval was selected (~20 cm³ of material) in order to handpick individual mineral grains from >150µm fractions, and to analyse Sr and Nd isotopic compositions of <63µm detrital fractions. Two samples were taken from a smaller 1cm interval, and were analysed for bulk Nd and Sr isotopes only (7H 5W 54-55cm, 63.04 mbsf; 8H 3W 37-38cm, 69.38 mbsf) (Table 3.1)

Six samples were analysed for Nd and Sr isotopic compositions from DSDP Site 274 (Table 3.1, Figure 3.6), including one Holocene sample and five Pliocene samples (two from Late Pliocene diatom-rich silty clays, and three from Early Pliocene silty clays – see Figure 3.6). Three additional samples were selected for Nd and Sr isotopic analysis from IODP Site U1358 (Table 3.1), consisting of three Pliocene samples.

All sediment samples, except for those used for bulk analyses, were wet sieved into <63µm, 63-150µm and >150µm fractions. Splits (~500mg) of homogenised <63µm sediment were sequentially leached to remove any authigenic phases and to isolate the detrital fraction. In a first step, biogenic CaCO₃ was removed with buffered acetic acid following the method of Biscaye (1965). In a second step, ferromanganese oxides and oxyhydroxides were removed through repeated steps of leaching for 6-12 hours with a reductive solution, hydroxylamine hydrochloride (NH₂OH), following the procedure of Rutberg et al. (2000). No removal of biogenic opal was carried out, as Nd concentrations in such material are low, and mass balance calculations for Sr indicate only a minor contribution of opal to the detrital composition (Chapter 2). A representative sub-sample of 50mg of detrital sediment was dissolved by hotplate digestion using 2ml of 27M HF, 2ml of 15M HNO₃ and 0.6ml of 20M HClO₄. A secondary digestion step using 2ml of 15M HNO₃ and 1ml of 27M HF was employed if any refractory minerals remained visible after the first digestion step. Fluorides were removed in a subsequent step by fluxing samples in 6M HCl. In preparation for ion exchange chromatography, samples were then converted to nitrate form. Target analytes (Nd and Sr) were selectively separated from the sample matrix by ion chromatography on three separate columns using Eichrom Sr Spec, TRU Spec, and Ln Spec resins (*Sr-spec* resin: 100-120µm bead size, modified after Pin and Bassin [1992]; *TRU-Spec* resin: 100-120µm bead size [Pin and Zalduegui, 1997]; *Ln-spec* resin: 50 -100µm bead size, modified after Pin and Zalduegui [1997]). The entire sample was first loaded on the Sr Spec column, and the matrix elute from this column was subsequently used to first separate Nd from the sample matrix, and then from other rare earth elements.

Dried Nd cuts were taken up in ~1% HNO₃ in preparation for measurement of Nd isotopes on a Nu Instruments multi collector inductively coupled plasma mass spectrometer (MC-IPC-MS) in the MAGIC laboratories at Imperial College London. Measurements were carried out in static mode. A ¹⁴⁶Nd/¹⁴⁴Nd ratio of 0.7219 was applied to correct for instrumental mass bias following the exponential law. Tests showed that interferences from ¹⁴⁴Sm are adequately corrected if the ¹⁴⁴Sm contribution is less than 0.1% of the ¹⁴⁴Nd signal. Samarium contributions of all samples were significantly below that level. Average ¹⁴³Nd/¹⁴⁴Nd JNdi values for ten analytical sessions over a sixteen month period were: 0.511979 ± 0.000028 (n=55); 0.512079 ± 0.000011 (n=22); 0.512138 ± 0.000020 (n=40); 0.512161 ± 0.000015 (n=30); 0.512153 ± 0.000012 (n=23); 0.512110 ± 0.000017 (n=33); 0.512093 ± 0.000014 (n=28); 0.512279 ± 0.000015 (n=18); 0.512254 ± 0.000015 (n=5); 0.512220 ± 0.000018 (n=18) (2 SD). All reported ¹⁴³Nd/¹⁴⁴Nd ratios in Table 3.1 are corrected to the recommended JNdi value of 0.512115 (Tanaka et al. 2000). Inter-batch measurements of processing monitor standard BCR-1 yielded a ¹⁴³Nd/¹⁴⁴Nd of 0.512650 ± 0.000021 (n=4), compared to the recommended value of 0.512646 ± 0.000016 (Weis et al. 2006). Total procedural blanks were consistently below 10pg Nd, less than 0.01% of the total approximate Nd concentration.

Strontium was loaded in 1µl of 6M HCl onto a degassed tungsten filament followed by 1µl of tantalum chloride. Measurements were performed in a single filament assembly on a Thermo Scientific Triton thermal ionisation mass spectrometer (TIMS) in the MAGIC laboratories at Imperial College London in static mode. The measured isotopic ratios were corrected for instrumental mass bias using the exponential law and a ratio of ⁸⁸Sr/⁸⁶Sr = 8.375. Interferences from ⁸⁷Rb were corrected for using an ⁸⁷Rb/⁸⁵Rb ratio of 0.3860. Samples were analysed over the course of a thirteen-month period in five sessions. Repeated analyses of NBS987 standards over this period (n = 71) yielded ⁸⁷Sr/⁸⁶Sr ratios of 0.710260 ± 0.000015 (2 SD). As the measured value is in agreement with published values for NBS987 (0.710252 ± 0.000013; n=88) (Weis et al. 2006), no correction has been applied to sample results in Table 3.1. Repeated processing and analyses of procedural standard reference material BCR-1 yielded an ⁸⁷Sr/⁸⁶Sr ratio of 0.705025 ± 0.000018 (2 SD) (n=10), compared to the recommended value of 0.705018 ± 0.000013 (Weis et al. 2006). Procedural blanks were consistently less than 300pg, and usually less than 30pg, less than 0.01% of the total approximate Sr concentration.

3.4.2 *Clay mineralogy*

Clay mineral compositions were determined on the <2µm detrital fractions of Pliocene sediments from IODP Site U1361 and were measured on 193 discrete samples between 47.46 and 124.97 mbsf, with samples taken from all identified Pliocene sedimentary facies (Figure 3.7, Table 3.2). Sample preparation and analysis was performed at the Instituto Andaluz de Ciencias de la Tierra (Spain) by collaborators Carlota Escutia, Francisco J. Jimenez-Espejo, and Alberto Lopez Galindo, following the method of Kirsch (1991). In brief, samples were decarbonated using incrementally increasing molarities of acetic acid (0.1M to 1M). Clay was then deflocculated by successive washing with demineralised water. The <2µm fraction was separated by centrifugation at 9000 rpm for 1.3 minutes, and subsequently smeared onto glass slides for x-ray diffraction (XRD) analysis. XRD measurements were conducted with a Panalytical X-Pert Pro diffractometer using Cu Kα radiation (45 kV, 40 mA) over a 4° to 69.9928° scan range with a 0.0084° step size, measuring up to 7898 points, and 11 minutes per sample.

Data processing was performed using the X Powder® program in order to obtain quantitative mineral composition (Martín-Ramos, 2004). Analysis was carried out by the least squares method of adjustment between each experimental diffractogram and the best weighted combination of reference patterns of a database specially created for this purpose from monophasic standards analysed in the same experimental conditions as the samples (Martín-Ramos, 2004). Weighting was achieved with the standard normalised reference-intensity-ratio method described by Chung (1974). Measured fractions were converted to absolute values using scale factors normalised from the diffractogram of a standard sample with known composition using several methods: normative chemical analysis, SEM point counts and pure substances additions, with quartz used as a reference due to its high crystallochemical stability and ubiquity in all analysed samples. The percentage values obtained were corrected for absorption following Chung (1974). Clay species in Table 3.2 are expressed in relative abundances, calculated for smectite, illite, chlorite and kaolinite with uncertainties for the individual numbers ranging from 10 to 15%.

4.3 $^{40}\text{Ar}/^{39}\text{Ar}$ dating

To ensure sampling of ice-rafted material explicitly, I analysed only hornblende grains larger than 150µm in size, as smaller material can also be delivered to the deep ocean

by other means (i.e. ocean currents and aeolian processes). Hornblende grains were handpicked from Holocene marine sediments from various sites in the study area (DSDP Site 274, 1R 5N 110-111cm, n=12; IODP Site U1358B 1R 1W 18-22cm, n=25; IODP Site U1360 1R 1W 0-18cm, n=21) (see Figure 3.1 for locations). Thirteen Pliocene samples were picked for hornblende grains from 20cm³ volume samples from IODP Site U1361, as well as one Holocene sample (1H 1W 1-5cm, 0.01 mbsf) and one Miocene sample (41X 1W 65-67cm, 379.05 mbsf) (Tables 3.3 and 3.4). Sample selection was initially based on the visual count of clasts >2mm carried out on the JOIDES Resolution (Escutia et al. 2011; see Figure 3.5), focussing on peaks in clasts and intervals with fewer clasts. Selection yielded samples from sedimentary facies 2 (clay with dispersed clasts; n=3), facies 4 (diatom-bearing silty clays; n=2) and facies 5 (diatom-rich silty clays; n=10) (Tables 3.3 and 3.4).

Overall, a total of 194 hornblende grains were analysed for their ⁴⁰Ar/³⁹Ar ages from IODP Site U1361. In most samples hornblende grains were scarce in the coarse-grained sediment fractions (typically <1% abundance) resulting in low grain yields for most samples (n=1 to 25; Figure 3.8). In order to improve statistical confidence, I increased the volume of sample material processed up to 60cm³ for nine samples. Increasing sample volume produced only limited success in increasing hornblende grain yield (see Table 3.3). The difference in the amount of depositional time represented by a 2cm interval relative to a 6cm interval corresponds to a maximum integration time of ~500 to ~8,000 years, according to linear sedimentation rates calculated from the age model of IODP Site U1361 [Tauxe et al. 2012]).

Hornblende grains and monitor standards were irradiated at the TRIGA reactor at the USGS in Denver, with cadmium shielding. ⁴⁰Ar/³⁹Ar ages were obtained using single-step CO₂ laser fusion at the Lamont-Doherty Earth Observatory argon geochronology lab (AGES: Argon Geochronology for the Earth Sciences). J values used to correct for neutron flux were calculated using the co-irradiated Mmhb-1 hornblende standard with an age of 525 Ma (Samson and Alexander, 1987). Measured values were corrected for background argon with measurements from an air pipette, and were also corrected for nuclear interferences (Renne et al. 1998). Analytical errors are based on the internal precision of measurements and variation of Mmhb values and are less than 2%.

During picking for hornblende grains, it was noted that the >150µm sediment fraction of one of the Pliocene samples (U1361 10H 6W 35-37cm) contained a considerable quantity (>50%) of brown volcanic glass shards, fresh in appearance, with occasional phenocrysts of biotite and hornblende. Eight volcanic glass grains were handpicked from this sample, and analysed for ⁴⁰Ar/³⁹Ar using either one-step or two-step analysis.

3.4.3 Petrographic characterisation of ice-rafted mineral grains and lithologies of clasts in IODP Site U1361 sediments

The coarse-grained fractions (<150 μ m) of nineteen samples processed for picking of hornblende grains were also analysed, to characterise the petrographic assemblages of major mineral grains, and to identify the lithologies of ice-rafted clasts (>2mm). Petrographic mineralogical characterisation of >150 μ m sediment fractions was achieved by extrapolation of 100 to 400 randomly distributed mineral grains, whereas the lithologies of all clasts are reported.

3.5 Results

3.5.1 Neodymium and strontium isotopes: IODP Sites U1358, U1361 and DSDP Site 274

Neodymium and Sr isotope compositions of the <63 μ m fractions of Pliocene detrital sediments from IODP Site U1361 display a large range of values (ϵ_{Nd} : -6.9 to -13.2; $^{87}Sr/^{86}Sr$: 0.717 to 0.729) (Figs. 3.5 and 3.9, Table 3.1). Two bulk samples yielded ϵ_{Nd} values that fall within the same range (-9.2 and -12.8). These two bulk samples describe a slightly larger range in Sr isotopic composition, as the sample from '69.38 mbsf' yielded a slightly elevated value (0.731). In the following discussions, I include the two results on bulk samples within the ranges discussed for fine-grained sediments from IODP Site U1361.

Comparison of the Nd and Sr isotope results with the different Pliocene sedimentary facies from which the samples were extracted, reveals two sub-groups (Figure 3.9, Table 3.1). Samples analysed from clay-dominated facies 1 and 2 are characterised by ϵ_{Nd} values between -11.2 and -13.2 and $^{87}Sr/^{86}Sr$ ratios between 0.723 and 0.730, whereas samples analysed from diatom-bearing facies 4 and 5 have ϵ_{Nd} values between -6.9 and -9.9 and $^{87}Sr/^{86}Sr$ ratios between 0.716 and 0.728. The two Miocene samples analysed from IODP Site U1361 yielded ϵ_{Nd} and $^{87}Sr/^{86}Sr$ values of -7.5 and 0.711 (facies 6: nannofossil ooze) and -12.9 and 0.723 (facies 5: diatom-bearing), respectively. The former sample is unique in that it is the only sample from facies 6, a nannofossil ooze, but has a Nd and Sr isotopic composition that falls within the Pliocene sub-group composed of the diatom-bearing facies 4 and 5. The latter sample does not fall within the Nd isotope data range described for facies 4

Table 3.1. Strontium and neodymium isotopic compositions of detrital marine sediments from IODP Site U1361.

Sample name	Depth (mbsf)	$^{87}\text{Sr}/^{86}\text{Sr}$		2 SE	$^{143}\text{Nd}/^{144}\text{Nd}$		2 SE	ϵNd^a		2 SD ^b
IODP Expedition 318, Site U1361A										
Facies 1:										
6H 1W 25-27cm	47.25	0.728823	±	0.000010	0.512291	±	0.000008	-11.7	±	0.3
8H 3W 37-38cm ^c	69.38	0.730877	±	0.000008	0.511981	±	0.000018	-12.8	±	0.4
8H 3W 75-77cm	69.76	0.728736	±	0.000012	0.512060	±	0.000010	-11.2	±	0.3
8H 4W 117-119cm	71.68	0.724040	±	0.000008	0.511964	±	0.000008	-13.2	±	0.3
Facies 2:										
7H 7W 17-19cm	65.67	0.723360	±	0.000020	0.512058	±	0.000018	-11.3	±	0.4
re-analysis		0.723367	±	0.000016	-		-	-		-
Facies 4:										
7H 1W 120-122cm	57.7	0.719666	±	0.000014	0.512284	±	0.000014	-6.9	±	0.2
7H 4W 127-129cm	62.27	0.721773	±	0.000008	0.512185	±	0.000012	-8.8	±	0.2
7H 5W 54-55cm ^c	63.04	0.728100	±	0.000016	0.512164	±	0.000008	-9.2	±	0.2
Facies 5:										
8H 1W 115-117cm	67.15	0.716570	±	0.000012	0.512195	±	0.000008	-8.6	±	0.3
8H 3W 105-107cm	70.06	0.717345	±	0.000014	0.512192	±	0.000008	-8.7	±	0.3
8H 6W 27-29cm	73.79	0.724461	±	0.000022	0.512176	±	0.000012	-9.0	±	0.3
41X 1W 65-67cm	379.05	0.723114	±	0.000014	0.511975	±	0.000008	-12.9	±	0.3
Facies 6 (Miocene)										
34X 2W 79-81cm	313.85	0.720941	±	0.000014	0.512253	±	0.000010	-7.5	±	0.3
DSDP Expedition 28, Site 274										
Facies A:										
1R 5W 110-112cm	7.10	0.717592	±	0.000008	0.512506	±	0.000008	-4.6	±	0.3
7R 2W 130-132cm	59.80	0.719054	±	0.000010	0.512539	±	0.000012	-4.6	±	0.3
9R 6W 130-132cm	84.8	0.717260	±	0.000012	0.512507	±	0.000010	-4.6	±	0.3
Facies B:										
10R 3W 98-100cm	89.48	0.715900	±	0.000012	0.512523	±	0.000010	-4.3	±	0.3
11R 2W 65-67cm	98.65	0.719106	±	0.000010	0.512480	±	0.000010	-5.1	±	0.3
11R 4W 120-122cm	100.7	0.711341	±	0.000020	0.512650	±	0.000010	-1.8	±	0.3
IODP Expedition 318, Site U1358B										
1358 2R 1W 60/62	8.80	0.735730	±	0.000012	0.511687	±	0.000018	-18.6	±	0.3
1358 3R 1W 60/62	17.90	0.739112	±	0.000016	0.511607	±	0.000008	-20.1	±	0.3
1358 3R 3W 58/60	21.78	0.743243	±	0.000008	0.511573	±	0.000008	-20.8	±	0.3

^a Calculated using a present day $^{143}\text{Nd}/^{144}\text{Nd}$ (CHUR) of 0.512638 (Jacobsen and Wasserburg, 1980)^b External uncertainty (2 sigma standard deviation) is based on the standard reproducibility of the analytical session^c Bulk samples analysed, all others <63µm detrital fractions

Re-analysed values represent samples that were measured multiple times (same aliquot).

and 5. Due to a lack of further Miocene samples for this study, I omit these samples in the following discussion and focus on the Pliocene results only.

Pliocene detrital sediments analysed from DSDP Site 274 show more radiogenic and homogenous ϵ_{Nd} values between -1.8 and -5.1, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.711 and 0.719 (see Figure 3.6, Table 3.1). Samples analysed from facies A, including the uppermost Holocene sample are characterised by an ϵ_{Nd} value of -4.6, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.717 and 0.719, whereas samples from facies B yield more variable isotopic compositions. However, the ϵ_{Nd} values for all samples, apart from the oldest one (100.70 mbsf), agree within error (external uncertainty), suggesting minimal change in sediment provenance during the deposition of Pliocene and Holocene sediments at this particular site.

All Pliocene sediments analysed from IODP Site U1358B (Table 3.1) were characterised by similar Nd and Sr isotopic compositions (ϵ_{Nd} : -18.6 to -20.8; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.738 to 0.743), and have Nd isotopic signatures significantly less radiogenic and Sr isotopic signatures more radiogenic than the isotopic values described for the more distal IODP Site U1361.

3.5.2 Clay mineralogy: IODP Site U1361

Clay minerals in Pliocene sediments from IODP Site U1361 (Figure 3.7, Table 3.2) are dominated by illite (52-68%), smectite (11-33%) and kaolinite (7-16%), with smaller amounts of chlorite (5-19%). Correlation coefficients between the different clay mineral groups reveal a strong negative correlation between illite and smectite ($r^2 = -0.8$). Samples from facies 1 to 3 are characterised by less smectite and more illite, and samples from facies 4 and 5 are characterised by more smectite and less illite. This negative correlation is significant despite relatively large analytical uncertainties on the results (10-15%). A large pulse of kaolinite dominates the interval between 85.67 and 86.47 mbsf, which is accompanied by a corresponding decrease in illite. Samples from this interval have not been included in the data ranges cited above (Figure 3.7).

3.5.3 $^{40}\text{Ar}/^{39}\text{Ar}$ ages of Holocene sections of DSDP Site 274, IODP Site U1360 and U1358

Hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages in the Holocene sediment sample from DSDP Site 274 ($n=12$) (Figure 3.8, Tables 3.3 and 3.4) predominantly fall between 476 and 524 Ma (9 grains in total), with additional grains aged at 378 ± 5 Ma, 619 ± 36 Ma, and 1550 ± 9 Ma.

Table 3.2. Clay mineral relative abundances from IODP Site U1361 sediments.

Depth (mbsf)	Kaolinite	Smectite	Illite	Chlorite
Facies 1:				
50.07	10.82	15.04	63.32	10.82
50.47	9.38	13.09	66.91	10.62
50.87	10.44	21.15	59.53	8.88
51.27	11.19	13.81	65.48	9.52
51.57	13.10	15.78	58.29	12.83
51.97	12.39	20.17	56.77	10.66
52.37	9.79	17.42	64.44	8.35
54.97	8.93	17.86	64.51	8.71
55.43	10.75	17.47	62.37	9.41
55.83	10.53	21.05	59.06	9.36
56.23	9.48	19.70	61.35	9.48
69.08	9.91	13.92	66.51	9.67
69.48	11.22	15.82	61.73	11.22
70.59	9.35	21.81	60.34	8.50
70.99	9.57	21.99	58.16	10.28
71.39	10.19	18.52	62.04	9.26
71.79	9.67	19.06	59.67	11.60
72.09	11.22	27.24	54.17	7.37
Facies 2:				
60.17	8.87	21.58	59.71	9.83
60.57	11.23	16.19	60.84	11.75
60.97	11.14	15.59	62.13	11.14
61.27	15.04	19.00	52.77	13.19
63.47	11.55	18.90	59.32	10.24
63.77	8.75	15.45	68.51	7.29
64.07	9.35	20.38	62.11	8.15
65.57	13.82	21.11	53.27	11.81
65.97	11.30	18.03	61.06	9.62
77.67	9.95	25.00	54.57	10.48
78.07	13.26	16.45	58.89	11.41
78.47	7.86	19.29	64.52	8.33
78.77	8.37	17.87	65.61	8.14
80.27	12.14	20.87	52.67	14.32
80.67	11.63	16.67	61.63	10.08
81.07	10.97	20.10	56.40	12.53
81.47	9.33	16.75	62.44	11.48
81.77	12.17	17.03	59.12	11.68
82.17	11.72	20.83	58.85	8.59
82.57	10.67	20.79	57.58	10.96
82.97	16.13	11.29	53.69	18.89
83.27	12.73	18.30	57.82	11.14
83.67	12.57	17.88	56.98	12.57
84.77	12.00	20.00	55.69	12.31
85.17	9.32	21.64	60.82	8.22
85.27	13.85	19.39	54.85	11.91
85.67	33.21	23.25	34.32	9.23
86.07	29.15	26.72	35.22	8.91

86.47	32.39	21.86	34.01	11.74
86.77	33.04	17.62	39.21	10.13
87.17	11.45	19.87	58.92	9.76
87.57	13.79	19.39	53.50	13.32
87.97	12.57	20.32	57.49	9.63
88.27	11.73	16.58	58.42	13.27
88.67	12.84	17.91	55.41	13.85
89.07	11.85	19.65	56.36	12.14
89.47	13.25	18.61	56.47	11.67
89.77	13.62	19.02	58.61	8.74
90.17	10.86	19.19	59.34	10.61
90.57	9.46	22.97	57.84	9.73
90.97	12.76	24.22	49.22	13.80
95.97	11.90	16.96	58.93	12.20
96.27	9.77	18.25	63.24	8.74
96.67	10.00	21.03	57.69	11.28
97.07	14.02	19.14	54.72	12.13
97.47	11.38	20.06	58.08	10.48
97.77	13.41	16.83	58.05	11.71
98.17	11.02	22.59	57.02	9.37
98.57	12.77	21.81	54.21	11.21
98.97	13.53	19.12	55.29	12.06
99.27	10.67	26.05	53.85	9.43
99.67	10.00	22.69	56.54	10.77
106.5	9.95	21.60	60.19	8.25
106.96	7.28	40.62	47.02	5.08
107.36	10.30	21.61	60.30	7.79
107.76	9.25	21.92	60.62	8.22
107.87	11.08	24.74	55.93	8.25
108.27	11.25	22.49	57.70	8.56
108.67	12.60	22.47	55.62	9.32
110.16	10.99	28.57	49.45	10.99
110.59	11.20	26.61	52.38	9.80
111.00	9.44	23.61	57.50	9.44
111.19	9.30	19.90	61.24	9.56
113.60	9.55	27.76	54.33	8.36
113.97	11.31	22.88	57.33	8.48
114.37	10.11	21.35	58.43	10.11
114.77	9.45	26.77	55.64	8.14
115.07	11.90	25.21	52.69	10.20
115.45	12.96	25.58	50.17	11.30
115.87	11.45	25.30	53.31	9.94
116.27	11.43	22.54	53.97	12.06
116.57	14.64	23.20	49.45	12.71
116.97	11.34	21.91	55.67	11.08
117.37	11.31	23.67	55.12	9.89
117.77	10.86	26.20	52.08	10.86
118.07	12.63	20.00	55.26	12.11
118.47	12.15	19.96	55.53	12.36
118.87	13.65	20.58	57.05	8.72
119.27	11.19	17.23	59.28	12.30
119.57	12.50	27.56	49.04	10.90
119.97	11.96	25.45	53.44	9.16
124.27	11.43	23.90	54.81	9.87

124.57	10.71	24.83	55.35	9.11
124.97	9.54	24.74	57.73	7.99
Facies 3:				
66.37	9.17	21.39	58.06	11.39
66.07	10.75	22.58	55.91	10.75
66.47	8.84	21.72	60.61	8.84
66.87	10.07	19.16	63.14	7.62
67.47	11.90	13.88	62.04	12.18
68.18	10.38	22.95	56.01	10.66
68.58	12.35	12.84	65.43	9.38
68.78	12.12	24.71	52.68	10.49
74.39	9.41	22.03	60.40	8.17
74.60	11.34	16.12	62.72	9.82
75.00	11.90	20.11	55.52	12.46
Facies 4:				
47.46	11.48	16.27	62.20	10.05
47.67	11.96	23.31	56.44	8.28
48.07	12.22	14.96	60.85	11.97
48.47	13.18	18.35	57.11	11.37
48.77	11.24	21.89	51.78	15.09
49.17	10.86	19.22	60.45	9.47
49.37	11.14	18.48	58.97	11.41
49.77	9.18	15.38	66.00	9.43
52.77	9.16	17.79	63.61	9.43
53.07	10.00	24.44	53.89	11.67
53.47	11.76	21.12	58.29	8.82
53.87	9.09	16.14	64.77	10.00
54.27	9.33	24.40	56.94	9.33
54.57	14.09	17.68	55.80	12.43
56.77	8.88	19.06	57.96	14.10
57.17	12.63	25.68	52.63	9.05
57.57	13.00	23.10	52.35	11.55
57.97	10.37	20.97	58.76	9.91
58.27	10.76	20.40	56.37	12.46
58.67	11.60	19.06	60.77	8.56
59.07	11.06	15.48	60.20	13.27
59.47	9.69	21.07	58.60	10.65
59.77	7.63	17.30	65.90	9.16
61.67	13.09	18.52	57.04	11.36
62.07	9.80	19.61	59.56	11.03
62.47	11.19	17.62	60.24	10.95
62.77	9.47	18.48	60.74	11.32
64.47	11.27	16.07	61.39	11.27
64.87	12.97	23.34	48.99	14.70
Facies 5:				
65.27	13.72	19.21	54.88	12.20
69.88	11.26	18.41	58.79	11.54
70.28	12.73	24.55	51.21	11.52
72.49	12.71	17.80	55.65	13.84
72.89	12.33	20.00	55.34	12.33
73.29	12.50	21.23	53.30	12.97
73.59	10.40	21.04	58.17	10.40
73.99	11.84	18.68	59.21	10.26
75.77	13.11	20.57	50.90	15.42

76.17	10.27	29.10	50.61	10.02
76.57	12.33	22.87	55.16	9.64
76.97	10.16	20.60	57.97	11.26
77.27	10.13	18.96	59.22	11.69
79.17	10.92	17.65	63.59	7.84
79.57	12.66	19.75	48.86	18.73
79.97	11.78	19.64	54.68	13.90
84.07	11.60	16.01	61.25	11.14
84.47	11.55	20.13	55.78	12.54
91.27	13.48	23.45	46.90	16.17
91.67	10.78	19.95	56.60	12.67
92.07	15.06	21.02	52.56	11.36
92.47	12.67	25.34	49.33	12.67
92.77	11.86	27.68	48.59	11.86
93.17	9.41	27.35	53.53	9.71
93.57	13.16	23.42	51.84	11.58
93.97	12.40	30.61	43.54	13.46
94.27	13.78	21.70	47.51	17.01
94.67	11.06	20.10	55.03	13.82
94.77	11.45	18.32	57.25	12.98
95.17	15.23	15.23	52.87	16.67
95.57	12.37	20.74	54.18	12.71
100.07	8.17	20.00	63.10	8.73
100.47	8.95	25.31	54.01	11.73
100.77	10.68	22.14	54.95	12.24
101.17	13.88	25.21	48.73	12.18
101.57	10.48	33.14	45.04	11.33
101.97	11.18	22.06	55.00	11.76
102.27	12.50	24.42	51.74	11.34
102.67	10.50	20.70	59.48	9.33
103.07	10.83	24.72	54.72	9.72
103.47	14.65	20.70	51.59	13.06
103.77	10.00	23.00	55.67	11.33
104.00	9.92	26.98	52.78	10.32
104.09	8.73	21.13	58.59	11.55
104.49	8.97	17.93	62.07	11.03
104.89	8.05	18.46	62.08	11.41
105.29	7.21	17.12	65.17	10.51
105.61	8.65	16.03	63.78	11.54
105.97	9.24	20.79	59.41	10.56
109.07	10.02	31.50	48.69	9.79
109.42	11.11	24.34	55.03	9.52
109.80	10.39	31.60	47.62	10.39
120.37	9.39	31.98	46.95	11.68
120.97	13.62	22.30	52.35	11.74
121.07	15.14	23.33	48.39	13.15
121.47	10.65	26.16	54.17	9.03
121.87	11.22	21.94	55.87	10.97
122.27	12.07	30.30	47.29	10.34
122.36	10.65	25.97	52.99	10.39
123.07	12.11	25.42	52.06	10.41
123.47	12.69	25.65	49.48	12.18
123.87	11.68	26.90	51.27	10.15

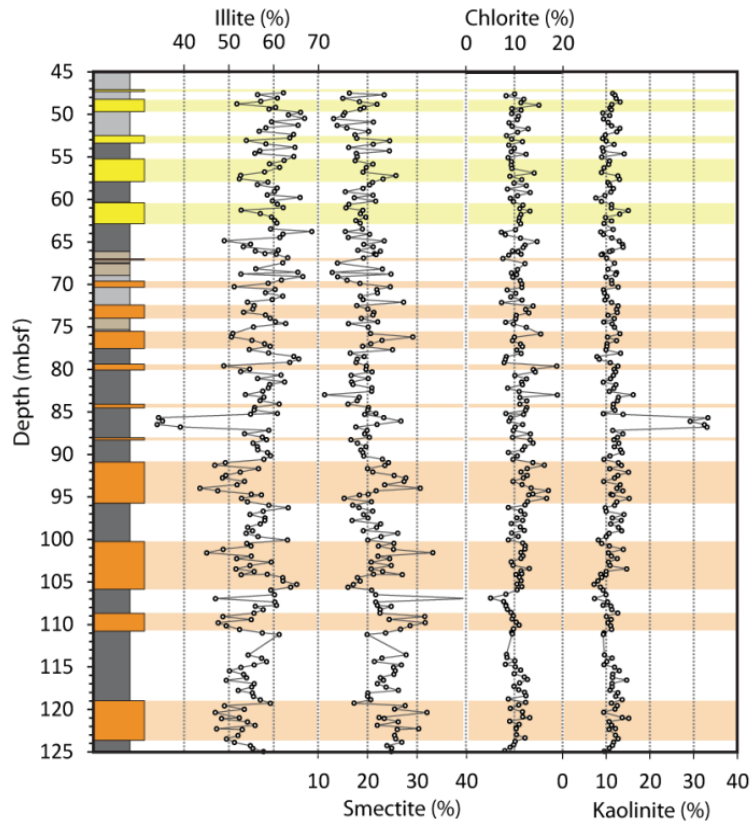


Figure 3.7. Clay mineralogy of Pliocene sediments from IODP Site U1361 between 45 and 125 mbsf, illustrating the relative abundances of illite, smectite, chlorite and kaolinite. Yellow and orange horizontal bands correspond to diatom-bearing silty clays (facies 4) and diatom-rich silty clays (facies 5) respectively, and highlight intervals of anti-correlation between relative illite and smectite abundances, particularly in diatom-rich silty clays (facies 5) below 74.00mbsf.

Hornblende grains analysed from the Holocene marine sediment sample from IODP Site U1358 show $^{40}\text{Ar}/^{39}\text{Ar}$ ages mainly between ~ 1420 and 1860 Ma (24 of 25 grains analysed), with one grain producing an older age of 2250 ± 24 Ma (Figure 3.8). Similarly, a Holocene layer sampled from IODP Site U1360 has hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages that range from 1509 to 1736 Ma (17 of 21 grains analysed), with remaining grains producing ages of 1988 ± 17 Ma, 2060 ± 9 Ma, 2514 ± 33 Ma, and 3944 ± 26 Ma (Figure 3.8, Tables 3.3 and 3.4). It is notable that hornblende grains were more abundant in sediments analysed from IODP Site U1358 and U1360 (located on the continental shelf) compared to the more distal IODP Site U1361, a pattern I discuss in more detail below.

3.5.4 Hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages from IODP Site U1361

Analyses of hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages from Pliocene (and Holocene) IODP Site U1361 sediments yielded two distinct populations: 0-50 Ma (~28%; 54 out of 194 grains analysed; Figure 3.8, Tables 3.3 and 3.4), and 440- 540 Ma (~48%; 94 out of 194 grains analysed; Figure 3.8, Tables 3.3 and 3.4). Within the youngest population, 42% of hornblende grains have ages that match the depositional age of the sediment from which they were extracted, whereas 58% of hornblende grains are older. Two sub-groups can also be identified within the 440 to 550 Ma population: one between 440 and 500 Ma (64 grains in total), and a smaller population between 500 and 540 Ma (30 grains in total) (Figure 3.8).

Remaining hornblende grains occur in minor numbers and are distributed over three broad $^{40}\text{Ar}/^{39}\text{Ar}$ age ranges (Figure 3.8, Tables 3.3 and 3.4): 90-290 Ma (~11%; 22 of 194 grains); 330-430 Ma (~6%; 11 grains of 194) and >600 Ma (~6%; 11 of 194 grains). More than half of the grains with an $^{40}\text{Ar}/^{39}\text{Ar}$ age range between 90 and 290 Ma fall between ~90 and ~130 Ma, while the remaining ages are distributed with no clear sub-grouping. The oldest $^{40}\text{Ar}/^{39}\text{Ar}$ aged grains (>600 Ma) encapsulate a wide range of ages between $\sim 641 \pm 8.7$ Ma and 2339 ± 26 Ma, with more than half of these falling within an age range of ~1000 to 1320 Ma.

During the sieving process carried out during sample processing, I furthermore recorded the weight percentage of >150 μm sediment fractions, in order to qualitatively constrain a potential correlation between amount of IRD present in each sample, and IRD provenance (i.e. $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende ages). Table 3.3 summaries these results, and reveals no obvious correlation between hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages and amount of coarse-grained material (>150 μm weight %). Furthermore, comparison of the different hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age ranges identified in individual samples with the sedimentary facies they were extracted from (Tables 3.3 and 3.4) indicates only minimal change in hornblende provenance with lithology. One potential exception to this observation is that 18 of the 22 grains with a $^{40}\text{Ar}/^{39}\text{Ar}$ age of 90 to 290 Ma occur in samples from diatom-bearing facies 4 and 5.

3.5.5 $^{40}\text{Ar}/^{39}\text{Ar}$ ages of volcanic glass from IODP Site U1361

Analyses of $^{40}\text{Ar}/^{39}\text{Ar}$ ages of volcanic glass grains at IODP Site U1361 from one particular sample (10H 6W 35-37 cm) was carried out in order to determine the absolute age

Table 3.3. Hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age ranges from IODP Site U1361 sediments.

	Depth (mbsf)	>150 μm (%)	<50 Ma	90-290 Ma	330-430 Ma	440-540 Ma	>600 Ma	Others	Total
Facies 2:									
7H 7W 17-23cm*	65.67	3	4	3	0	8	2	0	17
9H 2W 77-83cm*	77.77	4.4	7	1	2	8	0	0	18
13H 2W 46-48cm	115.47	21	4	0	0	10	0	1	15
Facies 4:									
7H 1W 120-122cm	57.70	3.7	1	5	1	16	2	0	25
7H 4W 127-131cm*	62.27	4.6	1	5	1	15	1	1	24
Facies 5:									
1H 1W 1-5cm*	0.01	0.9	5	0	1	1	0	0	7
9H 1W 57-61cm*	76.07	2.5	5	1	1	8	0	1	16
9H 1W 77-79cm	76.27	4.7	4	1	3	11	2	0	21
10H 5W 107-111cm*	92.07	21	4	2	1	8	2	0	17
10H 6W 35-37cm	92.95	10	1	0	0	0	0	0	1
10H 7W 3-5cm	94.03	1.5	3	1	0	3	0	0	7
11H 5W 27-29cm	100.75	3.3	2	0	0	0	0	0	2
11H 7W 28-30cm	103.76	3	9	2	0	2	0	0	13
12H 6W 51-53cm	109.76	4	3	1	1	3	1	0	9
44X 1W 65-67cm	379.05	0.9	0	0	0	1	1	0	2
Total			54	22	11	94	11	3	194

^a Facies corresponds to lithostratigraphy description (see text): 1:clay; 2: clay with dispersed clasts; 3: silty clay with dispersed clasts; 4: diatom-bearing silty clay; 5: diatom-rich silty clay; 6: nannofossil ooze.

*larger intervals

Table 3.4. Hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age data from DSDP Site 274, IODP Site U1358, IODP Site U1360 and IODP Site U1361.

Sample	run ID	Ca/K	Cl/K	moles ^{39}Ar	%40*	Age (Ma)	Internal error	+/- Age
IODP Expedition 318, Site U1361								
Facies 2:								
7H 7W 17-23cm	14610-06A	6.0	0.01327	0.049	53.9	3.2	0.3	0.3
7H 7W 17-23cm	13953-02	4.9	0.00938	0.068	15.6	3.9	0.3	0.2
7H 7W 17-23cm	13953-12	4.1	0.00538	0.011	51.2	4.3	1.0	1.0
7H 7W 17-23cm	14610-03A	7.4	0.0049	0.007	31	6.1	1.9	1.9
7H 7W 17-23cm	13953-01	18.3	0.08	0.001	274.7	91.9	12.9	12.9
7H 7W 17-23cm	13953-04	8.3	0.04873	0.004	100.1	100.1	3.1	2.9
7H 7W 17-23cm	13953-06	0.3	0.02435	0.003	28.9	158.1	5.8	5.6
7H 7W 17-23cm	14610-02A	8.9	0.0071	0.006	78.8	465.2	3.9	7.2
7H 7W 17-23cm	13953-15	16.6	0.06443	0.002	94.6	468.6	8.3	6.8
7H 7W 17-23cm	13953-09	7.4	0.04412	0.005	98.1	470.9	5.8	3.4
7H 7W 17-23cm	13953-08	9.7	0.03736	0.004	95.7	472.6	6.1	3.9
7H 7W 17-23cm	13953-03	7.8	0.07514	0.005	97.9	472.7	5.8	3.3
7H 7W 17-23cm	13953-07	6.3	0.05202	0.005	98.4	483.9	5.8	3.2
7H 7W 17-23cm	13953-16	10.4	0.02854	0.015	97.7	490.3	5.3	2.1
7H 7W 17-23cm	14610-05A	12.5	0.01978	0.024	98.4	501.6	1.8	6.8
7H 7W 17-23cm	14610-08A	13.2	0.03252	0.014	91.9	641.9	2.6	8.7
7H 7W 17-23cm	13953-10	4.9	0.04468	0.024	94.5	1146.5	11.9	3.1
9H 2W 77-83cm	14603-02A	5.6	0.00933	0.043	16.9	3.2	0.4	0.4
9H 2W 77-83cm	13956-03	7.5	0.01062	0.033	51.8	3.3	0.4	0.4

9H 2W 77-83cm	14603-03A	5.6	0.01034	0.055	6	7.9	1.0	1.0
9H 2W 77-83cm	14603-11A	5.6	0.00976	0.07	36.3	11.1	0.3	0.3
9H 2W 77-83cm	14603-09A	3.1	0.03147	0.055	43	11.2	0.3	0.4
9H 2W 77-83cm	14603-10A	3.9	0.03045	0.045	70.6	18.7	0.4	0.4
9H 2W 77-83cm	13956-08	3.5	0.01462	0.045	58.3	24.1	0.4	0.3
9H 2W 77-83cm	14603-04A	7.2	0.01613	0.007	79.8	124.8	1.8	2.4
9H 2W 77-83cm	13956-04	17.6	0.02376	0.005	96.7	346.3	4.5	2.9
9H 2W 77-83cm	14603-01A	3.8	-0.02327	0.001	50.8	368.5	11.8	12.8
9H 2W 77-83cm	13956-02	15.4	0.08977	0.004	72.8	441.2	6.6	4.9
9H 2W 77-83cm	13956-06	8.6	0.05532	0.001	94.4	457.6	10.7	9.7
9H 2W 77-83cm	14603-08A	10.0	0.01718	0.008	99.7	462.4	2.7	6.6
9H 2W 77-83cm	14603-06A	11.3	0.02338	0.007	85.7	473.8	3.4	7.0
9H 2W 77-83cm	14603-07A	19.2	0.02716	0.003	91.2	486.4	5.2	8.2
9H 2W 77-83cm	13956-05	7.0	0.03501	0.025	98.4	486.9	5.1	1.5
9H 2W 77-83cm	13956-07	5.9	0.04085	0.011	95.8	524.7	5.7	2.3
9H 2W 77-83cm	13956-01	5.8	0.04709	0.006	97.9	531.1	6.3	3.3
13H 2W 46-48cm	14612-16A	9.1	0.01425	0.02	46.40	5.3	0.7	0.7
13H 2W 46-48cm	14612-17A	5.6	0.01649	0.071	59.20	7.8	0.2	0.2
13H 2W 46-48cm	14612-12A	6.2	0.01456	0.085	34.90	8.1	0.2	0.2
13H 2W 46-48cm	14612-20A	9.6	0.00927	0.009	9.20	20.7	2.3	2.3
13H 2W 46-48cm	14612-19A	10.1	0.0373	0.005	64.70	381.2	4.2	5.7
13H 2W 46-48cm	14618-09A	3.6	0.01785	0.019	97.20	486.9	1.8	5.2
13H 2W 46-48cm	14612-22A	8.1	0.02237	0.082	98.60	490.2	1.0	5.0
13H 2W 46-48cm	14618-07A	4.5	0.02467	0.014	96.80	516.4	2.1	5.6
13H 2W 46-48cm	14618-08A	4.9	0.02262	0.022	98.00	521.1	1.7	5.5
13H 2W 46-48cm	14618-06A	4.7	0.01957	0.016	95.50	521.7	2.0	5.6
13H 2W 46-48cm	14618-03A	5.3	0.02919	0.022	99.10	522.3	1.7	5.5
13H 2W 46-48cm	14618-02A	4.2	0.02469	0.033	99.40	523.4	1.4	5.4
13H 2W 46-48cm	14618-01A	5.0	0.02724	0.015	97.50	525.2	1.9	5.6
13H 2W 46-48cm	14618-05A	5.0	0.02752	0.026	97.90	525.6	1.6	5.5
13H 2W 46-48cm	14618-04A	5.2	0.0224	0.032	98.40	525.7	1.6	5.5
Facies 4:								
7H 1W 120-122cm	13960-29	1.7	0.00956	0.019	56	35.9	0.8	0.7
7H 1W 120-122cm	13960-06	19.5	-0.03284	0.001	26.1	108.5	18.9	18.9
7H 1W 120-122cm	13960-08	8.6	0.0423	0.014	94.6	110.5	1.4	0.9
7H 1W 120-122cm	13960-03	14.6	0.06847	0.005	22.6	179.6	5.1	4.7
7H 1W 120-122cm	13960-11	8.5	0.01553	0.007	97.1	215.8	2.8	1.8
7H 1W 120-122cm	13960-04	7.1	0.05343	0.022	97.5	258.3	2.7	0.9
7H 1W 120-122cm	13960-17	19.0	0.06579	0.003	93.5	334.6	5.2	4.0
7H 1W 120-122cm	13960-18	19.5	0.03553	0.006	93	462.4	5.8	3.5
7H 1W 120-122cm	13960-23	7.0	0.04649	0.007	99	477.3	5.7	3.1
7H 1W 120-122cm	13960-01	11.2	0.05692	0.005	98.6	484.5	6.3	4.0
7H 1W 120-122cm	13960-13	0.1	0.00769	0.115	98.7	486.1	4.9	0.7
7H 1W 120-122cm	13960-28	7.2	0.05057	0.01	97.9	486.3	5.4	2.4
7H 1W 120-122cm	13960-27	4.5	0.02694	0.011	97.8	489.7	5.4	2.2
7H 1W 120-122cm	13960-16	4.4	0.03194	0.042	98.7	491.4	5.1	1.3
7H 1W 120-122cm	13960-02	6.9	0.03479	0.014	97.6	492.6	5.3	2.1
7H 1W 120-122cm	13960-09	6.6	0.07037	0.019	96.9	493.3	5.3	2.0
7H 1W 120-122cm	13960-30	10.6	0.03377	0.014	97.1	503.1	5.4	2.0
7H 1W 120-122cm	13960-05	7.0	0.04457	0.005	95.6	507.0	6.5	4.0
7H 1W 120-122cm	13960-25	5.6	0.04103	0.054	99.2	514.7	5.3	1.1
7H 1W 120-122cm	13960-10	5.5	0.03985	0.009	93.9	514.8	5.8	2.7
7H 1W 120-122cm	13960-22	23.8	0.09852	0.007	91.9	527.0	6.4	3.7
7H 1W 120-122cm	13960-21	4.9	0.04608	0.023	96.7	530.3	5.6	1.9
7H 1W 120-122cm	13960-26	6.7	0.04579	0.005	93.4	536.0	6.6	3.8
7H 1W 120-122cm	13960-19	4.3	0.03953	0.02	99.5	1145.5	11.9	3.1
7H 1W 120-122cm	13960-24	4.5	0.06507	0.008	99.3	1651.2	18.1	7.5
7H 4W 127-131cm	13959-02	0.0	0.00549	0.053	88.6	44.2	0.5	0.3
7H 4W 127-131cm	13959-11	9.1	0.01177	0.004	72.8	90.6	2.6	2.5
7H 4W 127-131cm	13959-03	10.7	0.0084	0.016	83.5	95.3	1.2	0.8
7H 4W 127-131cm	13959-10	10.6	0.02713	0.008	90.5	108.3	1.8	1.5
7H 4W 127-131cm	13959-08	17.1	0.01073	0.009	81.4	127.8	1.9	1.4
7H 4W 127-131cm	14611-06A	10.2	0.05302	0.016	77.6	168.4	1.2	2.5
7H 4W 127-131cm	14611-03A	21.4	0.03698	0.004	85.4	272.4	3.9	5.3
7H 4W 127-131cm	14611-10A	14.5	0.09543	0.011	71.5	321.0	2.3	4.8

7H 4W 127-131cm	13959-14	23.6	0.1155	0.001	94	457.4	12.9	12.1
7H 4W 127-131cm	13959-05	6.6	0.04383	0.012	93	462.6	5.1	2.2
7H 4W 127-131cm	13959-09	6.8	0.0264	0.001	95.1	462.9	11.2	10.2
7H 4W 127-131cm	13959-12	6.6	-0.00453	0.001	102	466.2	23.6	23.1
7H 4W 127-131cm	13959-07	9.4	0.13908	0.005	97.2	478.3	6.7	4.7
7H 4W 127-131cm	13959-13	8.0	0.05805	0.006	89	484.1	5.9	3.3
7H 4W 127-131cm	13959-01	7.1	0.0471	0.008	97.1	484.5	5.7	3.1
7H 4W 127-131cm	14611-01A	12.0	0.02957	0.006	83.9	484.9	3.6	7.2
7H 4W 127-131cm	14611-04A	9.4	0.04605	0.012	95.1	486.6	2.4	6.8
7H 4W 127-131cm	14611-12A	13.1	0.05927	0.007	98.8	495.5	3.1	7.2
7H 4W 127-131cm	14611-07A	8.0	0.04196	0.009	98.7	496.6	3.0	7.1
7H 4W 127-131cm	13959-15	13.2	0.06241	0.005	93.4	507.8	6.6	4.3
7H 4W 127-131cm	13959-04	27.5	-0.00051	0.003	77.5	508.8	8.6	6.9
7H 4W 127-131cm	14611-02A	8.4	0.03496	0.027	99.5	515.7	1.5	6.9
7H 4W 127-131cm	14611-05A	6.9	0.07841	0.011	98.5	533.6	2.9	7.5
7H 4W 127-131cm	14611-08A	9.2	0.02187	0.044	99.6	1222.6	2.4	16.1
Facies 5:								
1H 1W 3-5cm	13958-01	2.3	0.01583	0.011	-4	1.1	1.0	1.0
1H 1W 3-5cm	13958-03	3.7	0.02611	0.027	22.7	1.2	0.4	0.4
1H 1W 3-5cm	14613-02A	11.2	0.00915	0.03	57.8	3.3	0.4	0.5
1H 1W 3-5cm	13958-06	1.0	0.01716	0.009	41.5	8.2	1.3	1.3
1H 1W 3-5cm	13958-05	3.8	-0.01474	0.005	43.3	10.1	1.9	1.9
1H 1W 3-5cm	14613-03A	13.7	-0.0119	0.003	72.9	397.0	6.6	8.4
1H 1W 3-5cm	14613-05A	12.2	0.04917	0.003	90.3	481.4	5.7	8.5
9H 1W 57-61cm	13957-13	7.1	0.01467	0.006	27.1	3.1	1.7	1.7
9H 1W 57-61cm	13957-11	2.4	0.04055	0.008	8	3.7	1.7	1.7
9H 1W 57-61cm	13957-03	6.0	-0.01769	0.007	118.9	5.8	1.6	1.6
9H 1W 57-61cm	14601-02A	1.3	0.01837	0.015	27.3	8.6	0.9	0.9
9H 1W 57-61cm	13957-16	2.7	0.02578	0.029	45.5	8.8	0.4	0.4
9H 1W 57-61cm	13957-04	165.3	0.00735	0.002	51	84.9	7.2	7.2
9H 1W 57-61cm	14601-04A	4.1	0.02586	0.029	98	283.4	0.9	3.8
9H 1W 57-61cm	14601-06A	5.6	0.04427	0.007	22.9	375.3	8.8	10.1
9H 1W 57-61cm	14601-01A	11.9	0.00769	0.006	64.7	464.1	4.6	7.6
9H 1W 57-61cm	13957-17	5.0	0.065	0.007	99	473.7	5.6	3.0
9H 1W 57-61cm	13957-08	6.3	0.0318	0.028	99.1	474.2	5.0	1.5
9H 1W 57-61cm	14601-03A	10.4	0.03161	0.006	96.3	487.2	3.3	7.2
9H 1W 57-61cm	13957-10	6.9	0.0154	0.103	93.4	487.5	4.9	0.7
9H 1W 57-61cm	13957-12	4.9	0.04747	0.014	98.7	490.3	5.3	2.0
9H 1W 57-61cm	13957-09	6.3	0.01972	0.24	97.8	494.3	5.0	0.6
9H 1W 57-61cm	13957-07	5.3	0.03051	0.015	95.3	503.6	5.4	2.1
9H 1W 77-79cm	13954-05	0.1	0.02952	0.023	32	3.2	0.5	0.5
9H 1W 77-79cm	14602-10A	6.0	0.01237	0.023	14.40	3.4	0.6	0.6
9H 1W 77-79cm	14602-12A	8.0	0.01052	0.013	28.10	3.6	0.8	0.8
9H 1W 77-79cm	14602-13A	10.0	0.06932	0.004	16.00	5.5	3.1	3.1
9H 1W 77-79cm	14602-14A	7.5	0.04858	0.006	82.60	207.8	2.0	2.9
9H 1W 77-79cm	13954-03	9.2	0.0493	0.007	43	407.2	5.8	4.1
9H 1W 77-79cm	14602-11A	38.8	0.12424	0.001	38.30	414.7	10.8	11.6
9H 1W 77-79cm	14602-06A	10.2	0.1056	0.002	46.00	418.0	7.4	8.5
9H 1W 77-79cm	14602-16A	17.2	0.06031	0.002	85.20	460.2	6.2	7.7
9H 1W 77-79cm	14602-17A	13.6	0.04965	0.01	95.40	464.4	2.8	5.4
9H 1W 77-79cm	14602-05A	17.1	0.04982	0.008	95.10	470.0	2.5	5.3
9H 1W 77-79cm	14602-02A	23.4	0.03524	0.004	88.40	470.2	4.7	6.7
9H 1W 77-79cm	13954-06	10.9	0.05269	0.003	92.5	472.2	7.1	5.3
9H 1W 77-79cm	13954-04	17.6	0.03696	0.011	94.2	484.3	5.5	2.5
9H 1W 77-79cm	13954-02	7.9	0.05731	0.012	98	491.1	5.4	2.3
9H 1W 77-79cm	13954-10	5.9	0.04124	0.009	97.6	491.3	5.3	2.1
9H 1W 77-79cm	13954-07	4.2	0.01587	0.108	98.9	493.7	5.0	0.8
9H 1W 77-79cm	14602-15A	12.7	0.18022	0.007	98.40	514.1	3.1	6.0
9H 1W 77-79cm	14602-07A	15.6	0.05718	0.006	92.50	527.2	3.2	6.2
9H 1W 77-79cm	13954-11	68.3	0.12507	0.001	81.5	992.2	19.4	16.7
9H 1W 77-79cm	14602-03A	17.3	0.07465	0.005	99.00	2339.8	11.5	26.1
10H 5W 107-111cm	13955-12	7.6	0.00441	0.004	67.2	3.5	2.6	2.6
10H 5W 107-111cm	13955-16	8.0	0.02241	0.003	-4.6	3.9	3.7	3.7
10H 5W 107-111cm	13955-03	0.2	0.01576	0.084	13.6	5.1	0.3	0.2

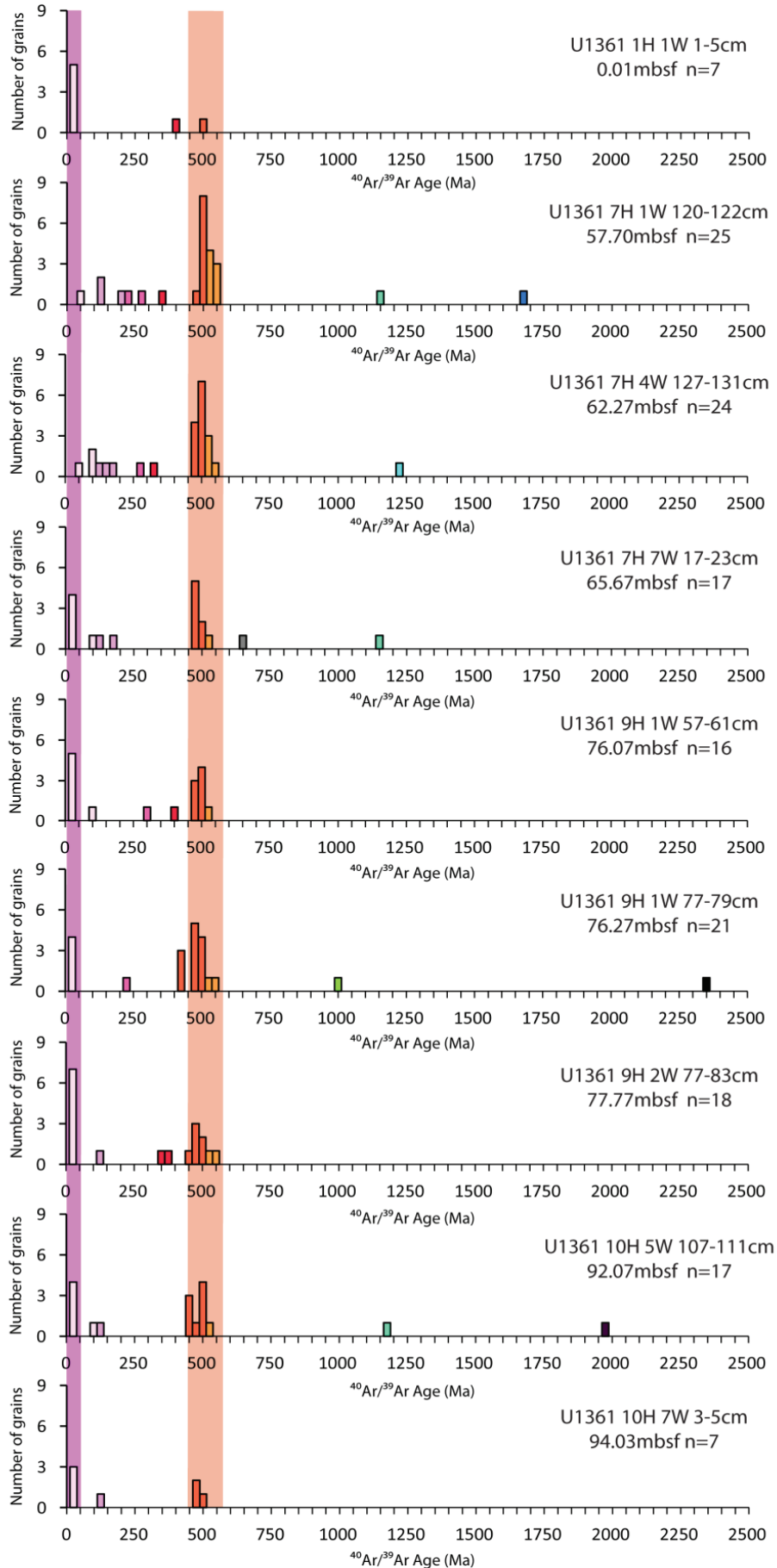
10H 5W 107-111cm	13955-01	7.1	-0.08367	0.002	-26.9	8.4	5.7	5.7
10H 5W 107-111cm	13955-10	5.1	0.04345	0.011	90.9	94.7	1.4	1.0
10H 5W 107-111cm	14609-03A	9.5	-0.02326	0.006	38.1	104.8	3.2	3.5
10H 5W 107-111cm	13955-18	1.7	-0.03053	0.001	91	429.6	16.2	15.6
10H 5W 107-111cm	13955-06	22.4	0.04786	0.004	95.9	446.2	5.9	3.9
10H 5W 107-111cm	13955-14	8.5	0.0511	0.004	96.5	448.5	5.9	3.8
10H 5W 107-111cm	14609-04A	8.2	0.06418	0.005	72.9	472.1	4.4	7.6
10H 5W 107-111cm	13955-13	6.2	0.04131	0.019	97.4	483.2	5.1	1.6
10H 5W 107-111cm	13955-15	6.4	0.03924	0.031	97.1	489.1	5.1	1.3
10H 5W 107-111cm	13955-04	14.4	-0.03148	0.002	99.4	491.2	7.9	6.2
10H 5W 107-111cm	13955-02	25.0	-0.13856	0.001	87.6	492.4	19.6	19.0
10H 5W 107-111cm	13955-05	4.5	0.05089	0.016	98	512.4	5.5	2.0
10H 5W 107-111cm	13955-11	9.8	0.03121	0.02	98.9	1161.5	12.1	3.3
10H 5W 107-111cm	13955-08	10.2	0.05041	0.011	99.7	1972.3	20.5	5.8
10H 6W 35-37cm	14607-01A	3.9	0.02056	0.012	34.30	5.3	1.0	1.0
10H 7W 3-5cm	13951-09	2.1	0.02102	0.008	251.2	4.1	1.2	1.2
10H 7W 3-5cm	13951-03	2.4	0.0229	0.005	16.5	5.9	2.2	2.2
10H 7W 3-5cm	13951-05	2.7	0.02805	0.038	55	16.7	0.4	0.4
10H 7W 3-5cm	13951-08	0.0	0.01371	0.139	97.5	104.6	1.1	0.2
10H 7W 3-5cm	13951-02	10.3	0.04797	0.007	97.1	465.9	5.5	3.0
10H 7W 3-5cm	13951-12	8.5	0.06087	0.004	98.8	467.8	6.3	4.2
10H 7W 3-5cm	13951-06	6.0	0.06304	0.009	97	492.4	5.7	2.8
1H 5W 27-29cm	14606-02A	4.4	0.00861	0.242	45.1	3.6	0.1	0.1
11H 5W 27-29cm	14606-01A	11.1	-0.01049	0.01	19.5	8.4	1.5	1.6
11H 7W 28-30cm	14617-02A	5.4	0.01416	0.137	30.10	3.8	0.1	0.1
11H 7W 28-30cm	14617-06A	5.8	0.01245	0.068	33.10	4.4	0.2	0.2
11H 7W 28-30cm	14617-03A	5.0	0.01425	0.1	28.00	4.6	0.2	0.2
11H 7W 28-30cm	14615-08A	1.6	0.01969	0.033	15.60	4.8	0.5	0.5
11H 7W 28-30cm	14617-10A	26.3	0.01583	0.007	20.20	5.1	1.5	1.5
11H 7W 28-30cm	14617-11A	8.9	0.00913	0.049	28.30	5.4	0.3	0.3
11H 7W 28-30cm	14617-13A	8.9	0.00809	0.017	11.50	5.6	0.8	0.8
11H 7W 28-30cm	14615-02A	7.5	0.01887	0.022	7.10	6.6	1.0	1.0
11H 7W 28-30cm	14617-16A	8.1	0.01292	0.043	51.70	18.1	0.3	0.4
11H 7W 28-30cm	14617-09A	8.6	0.01798	0.024	75.10	66.4	0.6	0.9
11H 7W 28-30cm	14615-06A	4.1	0.01808	0.01	41.40	96.5	1.9	2.1
11H 7W 28-30cm	14615-05A	19.4	0.02078	0.005	80.80	392.3	3.6	5.3
11H 7W 28-30cm	14617-17A	32.0	0.11642	0.003	83.90	421.9	4.5	6.2
12H 6W 51-53cm	14605-03A	10.2	0.0086	0.019	33.5	4.8	0.7	0.7
12H 6W 51-53cm	14605-04A	5.0	0.02014	0.034	21	6.3	0.5	0.5
12H 6W 51-53cm	14605-14A	12.0	0.01133	0.011	68.6	36.7	1.4	1.4
12H 6W 51-53cm	14605-15A	13.9	0.05673	0.007	56.8	100.0	2.2	2.6
12H 6W 51-53cm	14605-10A	6.5	0.03416	0.002	42	334.3	9.6	10.6
12H 6W 51-53cm	14605-13A	8.4	0.06391	0.009	88.1	481.2	2.6	6.8
12H 6W 51-53cm	14605-05A	10.2	0.02793	0.011	87	482.4	2.5	6.7
12H 6W 51-53cm	14605-11A	14.7	0.03492	0.012	97.1	536.9	2.5	7.4
12H 6W 51-53cm	14605-02A	9.0	0.04605	0.006	91.9	1069.6	5.9	15.1
41X 1W 65-67cm	14614-01A	4.3	0.00841	0.1	99.4	516.0	1.1	6.8
41X 1W 65-67cm	14614-03A	6.6	0.02071	0.041	99.5	1464.6	2.8	19.2
Sample	run ID	Ca/K	Cl/K	moles ³⁹ Ar	%40*	Corrected Age (Ma)		+/- Age
DSDP Expedition 28, Site 274								
1R 5W 110-111cm	15117-10A	9.1	0.00257	0.008	94.1	378.1		4.8
1R 5W 110-111cm	15117-06A	7.4	0.02173	0.011	98	476.3		4.0
1R 5W 110-111cm	15117-07A	32.1	-0.01303	0.002	85.3	480.1		16.4
1R 5W 110-111cm	15117-03A	16.0	0.0535	0.007	99.8	483.0		6.2
1R 5W 110-111cm	15117-02A	8.7	0.06471	0.01	100.8	491.2		4.6
1R 5W 110-111cm	15117-01A	11.3	0.01959	0.021	88.8	496.3		2.9
1R 5W 110-111cm	15117-11A	18.5	-0.00375	0.002	75.5	501.7		16.0
1R 5W 110-111cm	15117-09A	30.4	0.00037	0.002	92.8	502.7		16.5
1R 5W 110-111cm	15117-12A	21.2	0.03168	0.004	93.5	503.8		10.2
1R 5W 110-111cm	15117-04A	11.7	-0.02117	0.005	95.4	524.0		8.2
1R 5W 110-111cm	15117-08A	4.1	-0.15189	0.001	62.5	619.2		36.9
1R 5W 110-111cm	15117-05A	13.2	0.00617	0.01	96.9	1550.8		8.9

IODP Expedition 318, Site U1358

1R 1W 18-22cm	15118-01A	6.6	0.02059	0.022	98	1426.8	6.0
1R 1W 18-22cm	15118-03A	13.3	0.00968	0.034	99.6	1433.9	4.8
1R 1W 18-22cm	15118-05A	12.9	0.00491	0.042	100	1498.3	4.6
1R 1W 18-22cm	15118-06A	11.5	0.02289	0.007	99.3	1534.8	11.3
1R 1W 18-22cm	15118-07A	25.9	0.03613	0.019	99.2	1556.8	6.1
1R 1W 18-22cm	15118-08A	9.1	-0.0013	0.013	99.6	1603.0	6.9
1R 1W 18-22cm	15118-09A	12.7	0.04736	0.047	99.6	1621.7	4.1
1R 1W 18-22cm	15118-10A	24.1	0.00918	0.029	99.4	1631.6	4.8
1R 1W 18-22cm	15118-11A	8.8	0.01052	0.019	99.1	1634.2	5.8
1R 1W 18-22cm	15118-12A	15.0	0.02174	0.015	97.6	1644.4	6.9
1R 1W 18-22cm	15118-13A	12.4	0.02375	0.007	96.3	1645.2	11.1
1R 1W 18-22cm	15118-14B	7.7	0.05495	0.03	99	1651.7	5.5
1R 1W 18-22cm	15118-15B	7.2	0.04251	0.027	99.4	1654.2	5.4
1R 1W 18-22cm	15118-17B	8.2	0.00198	0.04	99.8	1671.4	4.3
1R 1W 18-22cm	15118-18B	15.1	0.01617	0.029	99.8	1675.8	4.9
1R 1W 18-22cm	15118-19B	22.2	-0.01229	0.011	99.4	1680.5	8.2
1R 1W 18-22cm	15118-20B	48.4	0.0009	0.002	98.1	1684.9	32.0
1R 1W 18-22cm	15118-21B	11.7	0.05422	0.017	99.4	1687.4	8.0
1R 1W 18-22cm	15118-22B	14.4	0.0134	0.022	99.9	1689.3	5.7
1R 1W 18-22cm	15118-23B	19.8	0.14267	0.003	98.9	1721.0	24.2
1R 1W 18-22cm	15118-24B	18.6	0.65646	0.005	100.2	1807.8	14.3
1R 1W 18-22cm	15118-25B	11.1	0.0005	0.01	99.9	1839.0	7.9
1R 1W 18-22cm	15118-26B	20.2	0.03028	0.018	99.9	1842.1	6.7
1R 1W 18-22cm	15118-27B	9.2	0.04801	0.008	100.1	1855.1	9.8
1R 1W 18-22cm	15118-28B	28.6	0.01226	0.002	99	2250.4	28.7

IODP Expedition 318, Site U1360

IR 1W 0-18cm	15115-01A	33.9	-0.03521	0.005	100.1	929.5	13.5
IR 1W 0-18cm	15115-02A	12.3	0.00045	0.165	99.8	1509.3	2.7
IR 1W 0-18cm	15115-03A	13.7	-0.00754	0.012	99.6	1533.0	9.5
IR 1W 0-18cm	15115-04A	8.4	0.05055	0.039	99.3	1544.9	5.1
IR 1W 0-18cm	15115-05A	9.7	0.05881	0.023	99.1	1566.9	6.1
IR 1W 0-18cm	15115-06A	14.1	-0.06953	0.007	96.4	1597.2	13.2
IR 1W 0-18cm	15115-07A	54.8	-0.155	0.002	97.8	1611.2	33.7
IR 1W 0-18cm	15115-08A	20.3	-0.11413	0.003	99.8	1630.9	26.4
IR 1W 0-18cm	15115-09A	55.4	-1.37802	0	101.6	1633.3	143.9
IR 1W 0-18cm	15115-10A	6.3	0.04366	0.026	99.8	1650.4	6.1
IR 1W 0-18cm	15115-11A	6.4	0.00734	0.01	99.8	1657.7	9.9
IR 1W 0-18cm	15115-12A	10.5	-0.04819	0.008	100.3	1658.7	11.7
IR 1W 0-18cm	15115-13A	12.2	-0.0059	0.003	99.6	1664.1	26.7
IR 1W 0-18cm	15115-14A	15.2	-0.01201	0.015	100	1671.5	6.4
IR 1W 0-18cm	15115-15A	17.8	0.0066	0.004	100.1	1677.6	17.9
IR 1W 0-18cm	15115-16A	9.9	-0.01331	0.011	99.7	1684.2	8.9
IR 1W 0-18cm	15115-18A	8.5	-0.03723	0.006	100	1736.6	13.4
IR 1W 0-18cm	15115-19A	18.8	0.00091	0.004	100.7	1988.4	15.7
IR 1W 0-18cm	15115-20A	8.0	0.0237	0.009	99.2	2060.8	9.7
IR 1W 0-18cm	15115-21A	8.6	0.00375	0.008	100.3	2514.9	11.9
IR 1W 0-18cm	15115-22A	11.3	-0.03047	0.008	99.6	3944.1	10.5



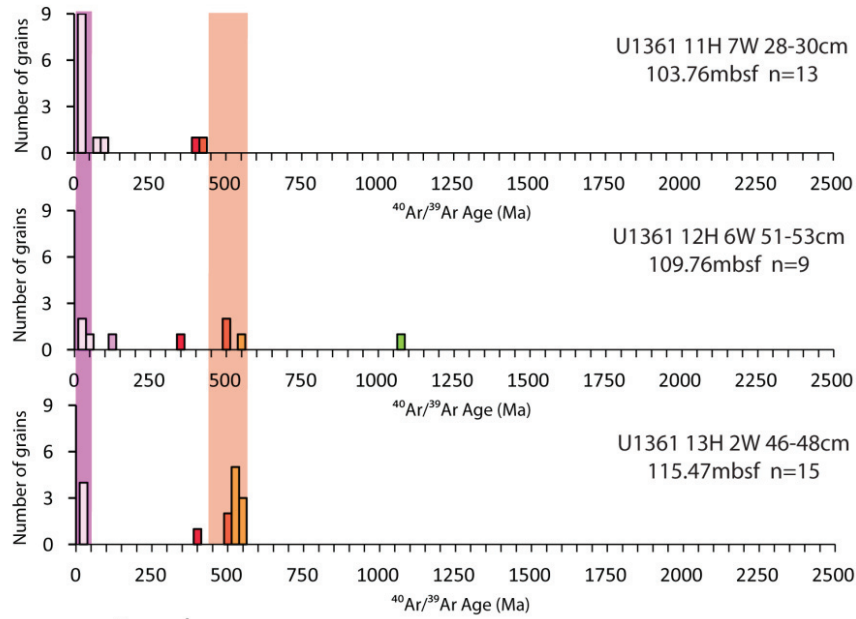
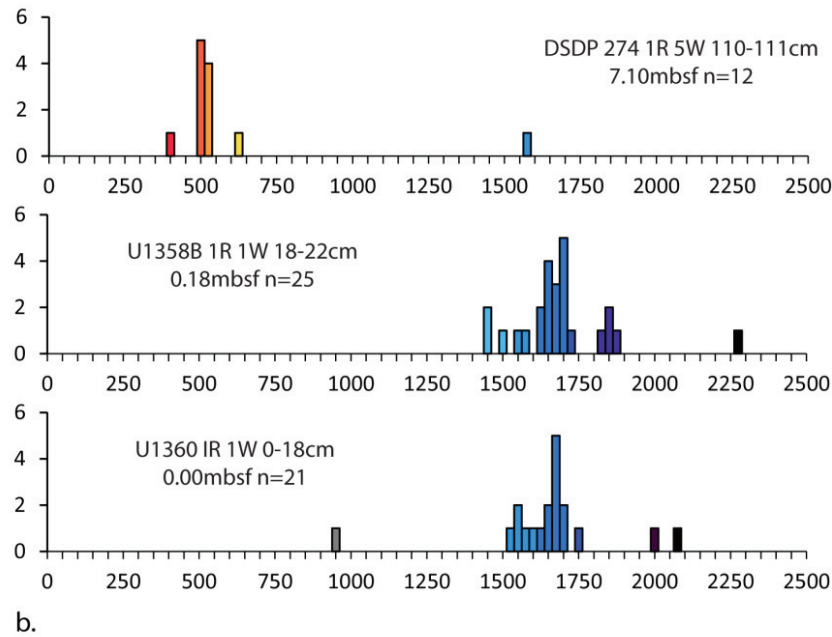


Figure 3.8. Hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age histograms, showing the distribution of grain ages between 0 and 2500 Ma, with number of grains analysed from each samples shown as 'n'. Vertical pink and orange bands highlight the two major $^{40}\text{Ar}/^{39}\text{Ar}$ age populations, 0-50 Ma and 440-540 Ma, respectively. Histogram bars are coloured according to the thermochronological scale bar shown in Figure 3.2. **a)** Histograms of samples with Holocene and Pliocene depositional ages from IODP Site U1361 (note: only samples with $n > 7$ are shown; see Table 3.3 for results on the three samples with only 1 or 2 grains analysed). **b)** Hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age histograms for Holocene marine sediments from DSDP Site 274, IODP Site U1358 and IODP Site U1360.

of volcanic events. Seven grains were analysed for $^{40}\text{Ar}/^{39}\text{Ar}$ ages in a two-step heating procedure. Only one of these grains produced consistent results for both heating steps (6.0 ± 1.1 Ma and 5.1 ± 2.8 Ma), with all others samples yielding reliable ages during the second step of analysis (2.1 ± 2.2 Ma, 3.7 ± 2.3 Ma, 4.8 ± 0.6 Ma, 4.9 ± 2.6 Ma, 5.4 ± 2.8 Ma, 7.5 ± 0.8 Ma). One additional grain was analysed by a single-step heating procedure only, and produced an age of 5.3 ± 2.8 Ma. Apart from the two glass grains with the oldest ages (6.0 ± 1.1 Ma and 7.5 ± 0.8 Ma), all remaining ages are contemporaneous within error with the estimated depositional age of the sample from which they were extracted (~ 4 Ma).

3.5.6 Petrographic and lithological characterisation of ice-rafted IODP Site U1361 fractions

Results are reported in Tables 3.5 and 3.6 and are summarised as follows. Coarse-grained fractions are dominated by quartz (up to 97.5%), feldspars (up to 18.7%), and pyroxenes (clino- and ortho) ($<6.3\%$), biotite, garnet, magnetite, and hornblende (all $<6.7\%$), with trace amounts of glauconite ($<2.7\%$). Lithic fragments are composed of siltstone, quartzose sandstone, shale, schist, basalt, granite and abundant volcanic glass. No changes in abundances of different ice-rafted components were observed between different lithological units.

3.6 Fine-grained Sediment Provenance

3.6.1 Potential neodymium and strontium isotopic endmembers

The continental provenance of fine-grained detrital sediments in IODP Site U1361 can be delineated by comparison of their measured Nd and Sr isotopic compositions with published onshore whole-rock data from known geological terranes exposed in Wilkes Land, Adélie Land, Northern and Southern Victoria Land, the Transantarctic Mountains, and Marie Byrd Land in West Antarctica (see Geological Overview; Figure 3.9). It is possible that unknown terranes hidden subglacially could contribute to the composition of IODP Site U1361 sediments. However, the study area is one of the best exposed in the Antarctic continent, and unexposed areas have been the subject of extensive ice-penetrating airborne geophysical surveying (Damaske, 2003; Ferraccioli et al. 2009; Studinger et al. 2004;

Table 3.5. Relative abundances of major detrital mineral components in 100 to 400 random counted grains >150µm in diameter from IODP Site U1361 sediments

Sample I.D.	Depth (mbsf)	Quartz (%)	Feldspar (%)	Pyroxene (%)	Garnet (%)	Biotite (%)	Magnetite (%)	Hornblende (%)	Glauconite (%)
1H 1W 3-5cm	0.03	86.5		2.7	2.7		5.4		2.7
7H 1W 120-122cm	57.7	93.5	1.1		2.2	2.2			1.1
7H 1W 122-124cm	57.76	91.9	3.0	1.0		4.0			
7H 4W 127-129cm	62.27	89.2	9.7		1.1				
7H 7W 13-15cm	65.63	83.3	6.3	6.3	2.1	2.1			
8H 3W 105-107cm	70.06	95.3	2.3					2.3	
8H 4W 117-119cm	71.68	92.4	6.5	1.1					
8H 6W 27-29cm	73.79	89.8	5.1	5.1					
8H 6W 57-59cm	74.09	94.2	4.7		1.2				
9H 1W 57-59cm	76.07	91.2	2.2	4.4	1.1				1.1
9H 1W 77-79cm	76.27	75.8	18.7	1.1		2.2	2.2		
9H 7W 45-47cm	84.95	89.6	3.1	3.1	1.0	1.0	1.0	1.0	
10H 5W 107-109cm	92.07	75.6	6.7		6.7	4.4	2.2	4.4	
10H 6W 35-37cm	92.95	90.4	2.7	1.4		4.1	1.4		
10H 7W 3-5cm	94.03	89.2	5.4	2.7	2.7				
11H 5W 25-27cm	100.75	97.5				0.7	1.8		
11H 7W 28-30cm	103.78	94.7	3.5		1.8				
12H 6W 49-51cm	109.74	88.0	8.4	0.9	0.9		0.9	0.9	
13H 2W 44-46cm	115.45	90.1	1.5	4.2			2.7	1.5	

Table 3.6. Total abundance of volcanic glass and lithologies of clasts from IODP Site U1361 sediments (>150 μ m).

Sample I.D.	Depth (mbsf)	Volcanic glass (%)	Clast characteristics
1H 1W 3-5cm	0.03	0.1	-
7H 1W 120-122cm	57.7	0.25	-
7H 1W 122-124cm	57.76	0.2	Schist, siltstone, sandstone, basalt
7H 4W 127-129cm	62.27	4	Volcanic glass
7H 7W 13-15cm	65.63	3.3	Siltstone, volcanic glass
8H 3W 105-107cm	70.06	23	Volcanic glass
8H 4W 117-119cm	71.68	4	Sandstone, siltstone, volcanic glass
8H 6W 27-29cm	73.79	35	Volcanic glass
8H 6W 57-59cm	74.09	2	Volcanic glass
9H 1W 57-59cm	76.07	8	Schist, volcanic glass
9H 1W 77-79cm	76.27	6	Schist, volcanic glass
9H 7W 45-47cm	84.95	2	Schist, basalt, siltstone, shale, granite, volcanic glass
10H 5W 107-109cm	92.07	0.5	Slate, schist, granite, basalt
10H 6W 35-37cm	92.95	56	Volcanic glass, siltstone
10H 7W 3-5cm	94.03	39	Volcanic glass, schist
11H 5W 25-27cm	100.75	5	Volcanic glass
11H 7W 28-30cm	103.78	12	Sandstone, schist
12H 6W 49-51cm	115.45	30	Basalt, volcanic glass, schist
13H 2W 44-46cm	120.55	20	Volcanic glass, basalt, schist

The total abundance of volcanic glass in each sample was calculated by counting 100 to 500 detrital mineral grains and extrapolating for the whole sample. Clast lithologies represent all clasts >2mm in diameter.

Studinger et al. 2006). Hence, I am confident that the geological terranes discussed below include the most likely continental sources for detrital marine sediments deposited offshore.

3.6.1.1 Provenance of Pliocene and Holocene DSDP Site 274 sediments

Study site DSDP Site 274 is ideally located to monitor supply of detrital material towards IODP Site U1361 from eastern sources in West Antarctica and/or the Ross Sea (Figure 3.1). The pathways of bottom waters and surface currents in the area of DSDP Site 274 are generally westwards (Orsi et al. 1999). Hence, fine-grained and ice-rafted material derived from West Antarctica and the Ross Sea would have to pass by DSDP Site 274 in order to reach IODP Site U1361.

The detrital fraction of five Pliocene sediments deposited at DSDP Site 274 after ~4.8 Ma shows very similar Nd and Sr isotopic compositions (ϵ_{Nd} : -4.3 to -5.1; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.715-0.719) to a Holocene sample analysed from the same site (ϵ_{Nd} : -4.6; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.717; Figs. 3.6 and 3.9). The same fingerprint observed in both Holocene and Pliocene sediments, suggests that Pliocene sediment delivery patterns to DSDP Site 274 were similar to today. Today, sedimentation delivery to DSDP Site 274 is controlled by turbidites (Hayes and Davey, 1975; Whittaker and Müller, 2006), supplied from the Ross Sea continental shelf and rise in the area directly adjacent to Northern Victoria Land (Figure 3.10). The Tucker and Mariner Glaciers in Northern Victoria Land (Figure 3.10) sit in close proximity to known outcrops of both Admiralty Intrusives (ϵ_{Nd} : -3 to -8) and the Cenozoic Hallet Volcanic Province of the McMurdo Volcanic Group (ϵ_{Nd} : +8.4 to -0.1; $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.703 to 0.713). Sediments supplied to the shelf downstream of these glaciers are likely to contain material derived from both terranes. In addition, it is possible that material derived from numerous Paleozoic terranes located in Northern Victoria Land (ϵ_{Nd} : -9 to -19; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.712 to 0.750; Figure 3.10) would also contribute to these shelf sediments. A likely mixture between McMurdo volcanic rocks and Paleozoic terranes would explain why sediments from DSDP Site 274 mostly overlap in isotopic space with the source field for Admiralty Intrusives, despite the limited geographic extent of this lithology.

A supply of material to DSDP Site 274 from extensive outcrops of Admiralty Intrusives in the Yule Bay area (Figure 3.10) is unlikely due to the presence of the Adare Trough, located ~100km NE of Northern Victoria Land (Müller et al. 2005; Whittaker and Müller, 2006), which would capture any sedimentary material before it reached DSDP Site

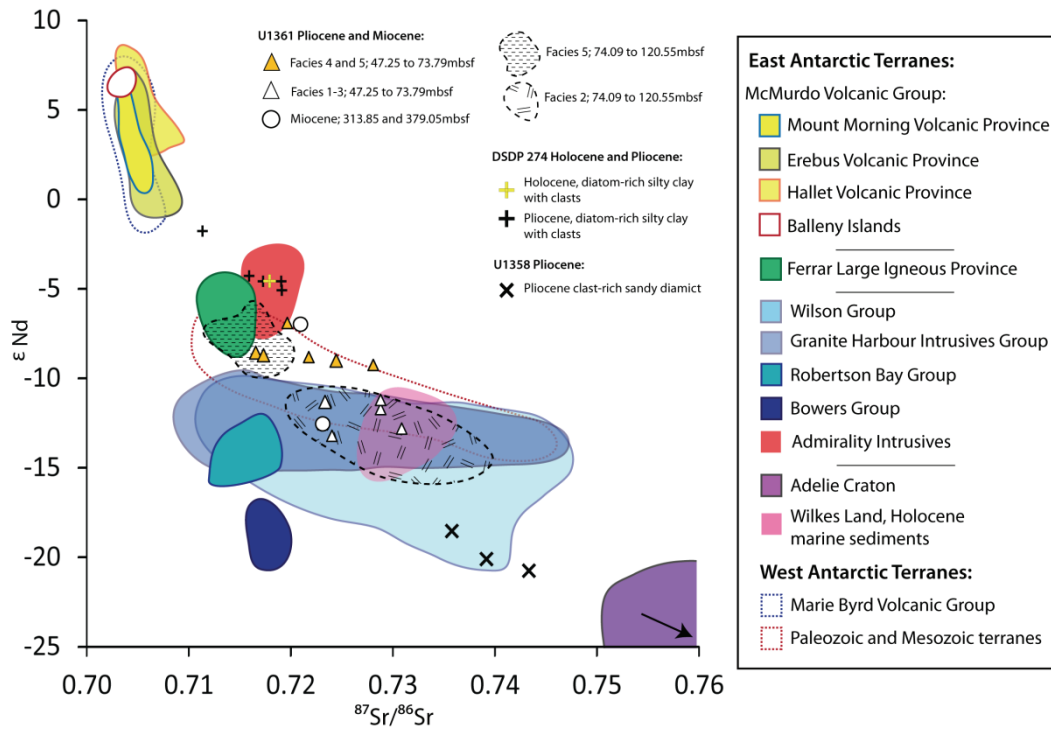


Figure 3.9. Neodymium and strontium isotopic compositions of Pliocene (47.25 to 73.79 mbsf) and Miocene (313.85mbsf and 379.05mbsf) (triangles and circles, respectively) detrital marine sediments from different sedimentary facies in IODP Site U1361, along with Holocene and Pliocene detrital marine sediments from DSDP Site 274 (horizontal crosses) and IODP Site U1358 (diagonal crosses). Errors are smaller than data points. Hatched areas represent the Nd and Sr isotopic ranges measured for samples from Holocene and Pliocene detrital sediments (0.00mbsf, and 74.09 to 120.55mbsf) taken from Chapter 2. Whole-rock Nd and Sr isotopic compositions of numerous East and West Antarctic geological terranes are compiled from the literature (see Figure 3.1 for lithologies; see Geological Overview for references on East Antarctic terranes; West Antarctic terranes: Futa et al. 1983; Hart et al. 1995; 1997; Wysoczanski et al. 1995; Panter et al. 1997; 2000; Pankhurst et al., 1998; Storey et al. 1999; Korhonen et al. 2010; Le Masurier et al. 2011).). Due to limited outcrops in Wilkes Land and hence available information on the Nd and Sr isotopic composition of the area, data from proximal Holocene marine sediments are plotted instead (Hemming et al. 2007; Roy et al. 2007; Pierce et al. 2011). The isotopic composition of the Adélie Craton (purple) primarily plots outside of the Nd and Sr isotopic space shown (ϵ_{Nd} : -20 to -28; $^{87}Sr/^{86}Sr$: 0.750 to 0.780; Borg and DePaolo, 1994; Peucat et al. 1999). Note that Pliocene IODP Site U1358 sediments, recovered from the shelf proximal to the Adélie Craton, agree well with a significant input from this old continental source in agreement with previously published proximal marine sediments from the area (Roy et al. 2007; Pierce et al. 2011).

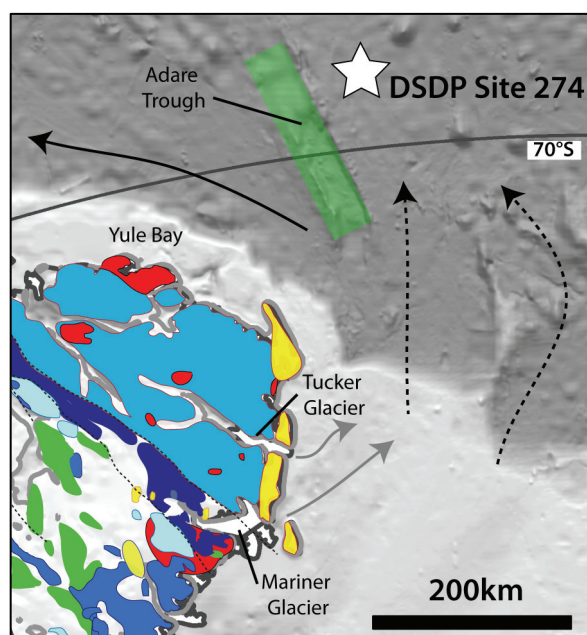


Figure 3.10. Close-up geological map of Northern Victoria Land (see Figure 3.1 for terranes and lithologies) illustrating the geographic location of the Admiralty Intrusives (red), and seafloor bathymetry of the area around DSDP Site 274. Grey arrows show likely sedimentation pathways of material source from the Mariner and Tucker Glaciers, which are located close to outcrops of the Admiralty Intrusives. Black dashed arrows indicate the direction of turbiditic flows inferred from seismic surveys (Hayes and Davis, 1975). Solid black arrow sketches the direction of flow of Antarctic Bottom Current (Orsi et al. 1999). A supply of Admiralty Intrusive material from its main outcrop area around Yule Bay to DSDP Site 274 is unlikely due to the presence of the Adare Trough (shown in green).

274 (Figure 3.10). Furthermore, fine-grained sediment delivery from Yule Bay towards DSDP Site 274 would have to flow against the direction of bottom water flow, which are today supplied from the Ross Sea and flow along the continental slope in westward direction (Figs. 3.1 and 3.10) (Orsi et al. 1999). I conclude that the Nd and Sr isotopes in DSDP Site 274 sediments are therefore best explained by a three-component mixture of material from the Admiralty Intrusives and Paleozoic terranes located along the Ross Sea margin of Northern Victoria Land, together with the more radiogenic Nd and less radiogenic Sr isotope endmember of the proximal Hallett Volcanic Group. The contribution of the latter endmember can be inferred from one Pliocene sample from DSDP Site 274, which clearly trends towards a Cenozoic volcanic signature (Figure 3.9). In summary, similarities between

Holocene and Pliocene provenance signatures of fine-grained sediments at DSDP Site 274 suggests that patterns of sediment supply from the proximal shelf have not varied through time. If detrital material from West Antarctica had reached DSDP Site 274 (and hence IODP Site U1361) during the Pliocene, it would be expected that the isotopic composition of DSDP Site 274 sediments would trend towards West Antarctic signatures. This is not observed, suggesting that little or no fine-grained material sourced from West Antarctica reached DSDP Site 274. This interpretation has important implications for constraining the provenance of sediments at IODP Site U1361, as it should not contain material derived from eastern sources not represented in DSDP Site 274 sediments.

3.6.1.2 Provenance of Pliocene IODP Site U1361 sediments

The Nd and Sr isotopic values of IODP Site U1361 Pliocene detrital sediments describe a broad negative correlation in Sr-Nd isotope space (ϵ_{Nd} : -6.9 to -13.2; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.717 to 0.729), which could represent a mixture of the most extreme potential endmembers identified regionally. These are the Cenozoic terranes of the McMurdo Volcanic Group (ϵ_{Nd} : +8.4 to -0.1; $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.703 to 0.713), and Archean and Neoproterozoic terranes of the Adélie Craton (ϵ_{Nd} : -20.0 to -29.0; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.750 to 0.780; Figs. 3.1, 3.2, 3.3 and 3.9). However, I consider this scenario very unlikely, as both Nd and Sr isotopic compositions of Pliocene sediments at IODP Site U1361 never range to very radiogenic or unradiogenic values (Figure 3.9). Furthermore, Pliocene sediments from IODP Site U1358, which is located in a more proximal location to the Adélie Craton, have more radiogenic Sr and more unradiogenic Nd isotopic compositions (ϵ_{Nd} : -18.6 to -20.8; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.738 to 0.743) than IODP Site U1361 sediments, in good agreement with proximal Holocene marine sediment analyses (ϵ_{Nd} : -17 to -24; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.730 to 0.744) (Roy et al. 2007; Hemming et al. 2007; Pierce et al. 2011; Chapter 2). If Adélie Craton terranes were an endmember for IODP Site U1361 sediments, some proportion of my samples would be expected to at least trend towards the compositional fields of IODP Site U1358 sediments (Figure 3.9), but this is not observed. Similarly, if detrital material from the McMurdo Volcanic Group was an important endmember, one would expect to see a trend towards its isotopic signature, as observed for sediments from DSDP Site 274, located in the Ross Sea.

Another potential source region which can be excluded for IODP Site U1361 is material supplied from the Neoproterozoic-aged rocks on the Wilkes Land margin (Figs. 3.1

to 3.4, and 3.9), located to the west of the Adélie Craton, as it would require transport in a direction counter to the flow of both surface and bottom ocean currents (see Figure 3.1).

Based on these considerations, it is likely that IODP Site U1361 sediments were supplied from Early Paleozoic terranes mixed with the Jurassic Ferrar Large Igneous Province (ϵ_{Nd} : -3.5 and -6.9; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.709 to 0.719) and/or the Admiralty Intrusives (Figure 3.9) located along the East Antarctic continental margin from the Mertz Shear Zone in the west to Northern Victoria Land in the east (Figure 3.1). The more unradiogenic Nd and more radiogenic Sr isotopic compositions of IODP Site U1361 sediments (ϵ_{Nd} : -11.3 to -13.2; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.728 to 0.731; Figure 3.9) approach the reported signature from terranes in north-west Northern Victoria Land and Oates Land (average ϵ_{Nd} : -14.4, $^{87}\text{Sr}/^{86}\text{Sr}$: 0.738) (Rocchi et al. 1998; Henjes-Kunst and Schussler, 2003). While such a source for Pliocene material at IODP Site U1361 is feasible, a supply of Early Paleozoic material from erosion of similarly aged granitoids by the Ninnis Glacier (Di Vincenzo et al. 2007; Goodge and Fanning, 2010) more likely, as it is more proximal to the study site. Additionally, Holocene and Pleistocene sediment pathways indicate material is supplied from bedrock near the Ninnis Glacier to the surrounding shelf, where it is transported offshore towards the study site via turbidity currents (Presti et al. 2011). While no Nd and Sr isotopic data exists for these Paleozoic granitoids, proximal Holocene shelf and offshore sediments in the vicinity of IODP Site U1361 (Goodge and Fanning, 2010; Pierce et al. 2011), are composed of detrital material with ϵ_{Nd} values between -11.0 and -14.5, signatures that match those reported for both Northern Victoria Land terranes and IODP Site U1361 sediments, confirming Early Paleozoic granitoids are a likely source for detrital sediments.

The more radiogenic Nd isotopic values obtained on IODP Site U1361 Pliocene sediments (ϵ_{Nd} : -7.5 to -9.2; Figure 3.9) appear to trend towards compositional fields of the Ferrar Large Igneous Province and the Admiralty Intrusives, with corresponding Sr isotopic values measured on the same samples generally following the same pattern. Both terranes have similarly limited geographical exposure along the Southern Ocean margin of the East Antarctic continent (Figure 3.1), with outcrops of the Admiralty Intrusives centred in Yule Bay ~1000km to the east of the study site, and two small outcrops of Ferrar Large Igneous Province at the mouth of the Wilkes Subglacial Basin. However, extensive geographical areas within the nearby low-lying Wilkes Basin have geophysical (gravity and magnetic) properties that match known Ferrar Large Igneous Province exposures (Figure 3.1) (Damaske, 2003; Studinger et al. 2004; Ferraccioli et al. 2009). A significant proportion of this inferred Ferrar Large Igneous Province material is believed to be unconsolidated sedimentary material

eroded from basalts and dolerites (Ferraccioli et al. 2009). Hence the closer proximity of this currently hidden but easily erodable Ferrar Large Igneous Province terrane to IODP Site U1361 makes it a more likely endmember than the distal granites of the Admiralty Intrusives. In conclusion, Pliocene and Miocene fine-grained sediments from IODP Site U1361 are most likely composed of material sourced from proximal Early Paleozoic granitoids and Mesozoic volcanic rocks of the Ferrar Large Igneous Province from within the Wilkes Subglacial Basin.

3.6.2 Clay mineral sources along the Wilkes Land margin

No information has been obtained on the elemental compositions of the individual clay minerals analysed from IODP Site U1361 sediments. However, illites from Quaternary and Pliocene aged channel levee sediments from various sites nearby IODP Site U1361 (between 64°17'S 143°22'E, and 64°57'S 144°23'E) have a composition that suggests they are most likely sourced from granites and granitoids found in the hinterland of the Ninnis Glacier (Figure 3.1) (Talarico and Kleinschmidt, 2003; Damiani, 2006). Detrital smectites identified in the same sediments are likely derived from the McMurdo Volcanic Group or volcanic terranes of the Ferrar Large Igneous Province (Damiani et al. 2006). Basalts of the Ferrar Large Igneous Province have been identified as a source of detrital smectite in the Ross Sea (Claridge and Campbell, 1989), whereas smectite associated with the McMurdo Volcanic Group is also authigenic in origin (Setti et al. 2000), associated with submarine weathering and hydrothermal alteration of volcanic material (Petschick et al. 1996; Setti et al. 2000). However, smectites in marine sediments nearby to IODP Site U1361 (Damiani et al. 2006) are detrital in origin, revealing no evidence of authigenic related hydrothermal alteration. Hence, it is possible to rule out the McMurdo Volcanic Group as the source of smectite in IODP Site U1361, suggesting it was indeed supplied by Ferrar Large Igneous Province terranes.

The main continental source of kaolinite for Wilkes Land sediments is most likely the sedimentary sequences of the Beacon Sandstone Supergroup (Piper and Brisco, 1975; Barrett, 1981). The most proximal known outcrops of Beacon Supergroup sediments to IODP Site U1361 lie at the mouth of the Wilkes Subglacial Basin (Bushnell and Craddock, 1970), but airborne geophysical survey data (Ferraccioli et al. 2009) suggest they may also comprise some infill of tectonic lowlands within the Wilkes Subglacial Basin proper. The pulse in kaolinite in Pliocene IODP Site U1361 sediments between 85.67 and 86.47 mbsf could

represent an interval of enhanced erosion of Beacon Supergroup sediments, but further evidence is needed to test this hypothesis.

Original clay mineral source rock signatures in marine sediments can be altered by chemical weathering and ocean current transport (e.g. Deikmann and Kuhn, 1999; Ehrmann and Mackensen, 1992; Petschick et al. 1996). However, I am confident that illites and smectites in IODP Site U1361 sediments represent the provenance signatures of Early Paleozoic granitoids and the Ferrar Large Igneous Province, respectively, as higher relative abundances of smectite in diatom-rich and diatom-bearing sedimentary facies co-vary with more radiogenic Nd isotopes, which are strongly indicative of Ferrar Large Igneous Province material. Conversely, a higher relative abundance of illite co-varies with less radiogenic Nd isotopic signatures in clays and silty-clay facies (facies 1-3), revealing that Early Paleozoic granites are a likely common source. To conclude, integration of radiogenic isotopes and clay mineralogy is useful for constraining whether provenance dominates clay mineral composition.

3.6.3 Evidence for a dynamic Pliocene East Antarctic ice sheet from lithostratigraphic variance of fine-grained sediment provenance in IODP Site U1361

Pliocene samples from facies deposited during cooler Pliocene intervals (i.e. clays [facies 1], and clays with dispersed clasts [facies 2]) have Nd and Sr isotopic signatures and clay mineralogy patterns that match an Early Paleozoic granitoid endmember (Figure 3.9), suggesting increased supply of proximal material to the study site took place during these times, similar to sediment delivery patterns today. In contrast, samples from facies deposited during warmer Pliocene intervals (diatom-bearing [facies 4] and diatom-rich silty clays [facies 5]) show isotopic compositions and clay mineralogy signatures indicative of a Ferrar Large Igneous Province endmember. Enhanced erosion of Ferrar Large Igneous Province material within the Wilkes Subglacial Basin has been proposed to explain similar isotopic compositions of diatom-rich Early Pliocene sediments from IODP Site U1361 deposited between 74 and 125 mbsf (Figure 3.9; Chapter 2). This signature has been interpreted to reflect retreat of the East Antarctic ice sheet margin several hundred kilometers inland as a result of marginal melting in response to warm ocean waters, and potential transport of Ferrar Large Igneous Province material offshore (Chapter 2). Similarities in the Nd and Sr isotopic signatures of sediments deposited between 74 and 125 mbsf (hatched areas in Figure 3.9;

Chapter 2), and between 47.25 and 73.79 mbsf (this study) suggest that these provenance patterns were maintained throughout the Pliocene.

Substantiation of the hypothesis of more dynamic ice sheet behaviour during the Pliocene is provided by the presence of Ferrar Large Igneous Province signatures in one Miocene sample from IODP Site U1361, taken from nanofossil-bearing sediments (facies 6) (Table 3.1; Figure 3.9). Ice sheet retreat into the Wilkes Basin during the Miocene, as inferred from this sample, is in agreement with evidence for fjordal open-water landscapes identified in the neighbouring low-lying Aurora Basin (Young et al. 2011), and together suggest that the East Antarctic ice sheet was likely dynamic both during the Miocene and Pliocene.

3.7 Ice-rafted Hornblende provenance

In the following section, the provenance of individual hornblende grains picked from Holocene and Pliocene ice-rafted debris fractions (>150 μm) at DSDP Site 274, and IODP Sites U1358, U1360 and U1361 is discussed in detail. Measured hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages is compared with published data from onshore outcrops and from proximal Holocene marine sediments to the East and West Antarctic continents, and the potential provenance of other coarse-grained ice-rafted mineral grains and lithic clasts in IODP Site U1361 sediments is also discussed.

3.7.1 Holocene IRD provenance at DSDP Site 274, IODP Site U1358 and IODP Site U1360

The majority of hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages of Holocene sediments at DSDP Site 274 fall within a range of 476 to 524 Ma (Figure 3.8, Table 3.3 and 3.4), which agrees well with the metamorphic age of the high-grade Late Cambrian Ross Orogeny (Stump, 1995; Boger, 2011), which spanned from 460 to 560 Ma (Goodge, 2007 and references therein) (Figure 3.11). Despite the regional prevalence of this high-grade metamorphic event (Figure 3.1; see Goodge, 2007 for review), onland thermochronology suggests that the timing of peak metamorphism of terranes in Northern Victoria Land can be identified at slightly younger ages (460-500 Ma; Dallmeyer and Wright, 1992; Goodge and Dallmeyer, 1992; Klee et al. 1990; Schussler et al. 1999) than those of Southern Victoria Land (480-550 Ma; Wysoczanski and Allibone, 2004; Goodge, 2007) and the Central Transantarctic Mountains (480-545 Ma;

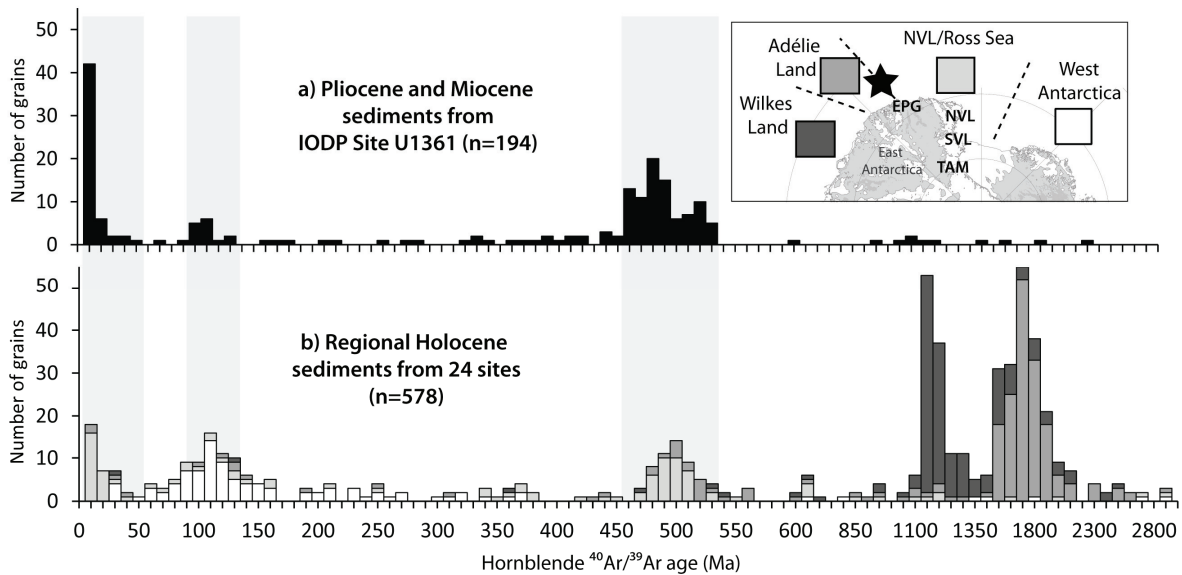


Figure 3.11. Comparison of hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages from Holocene marine sediments (bottom panel; Brachfeld et al. 2007; Roy et al. 2007; Pierce et al. 2011; this study) and Pliocene to Miocene sediments from IODP Site U1361 (top panel; this study). The scale of the x-axis in both plots changes from 10 Ma to 50 Ma per unit after 600 Ma. A) Hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages from Pliocene to Miocene IODP Site U1361 sediments (this study) are shown in black, and appear to be primarily sourced from NVL/Ross Sea, and West Antarctica. B) Holocene data are divided into four populations shown on the inset map compiled from 24 sites: dark grey corresponds to the Wilkes Land provenance sector (west of 135°E ; 7 sites in total), mid-grey represents the Adélie Land provenance sector (135°E to 142°E ; 7 sites in total), light-grey demarks Northern Victoria Land and the western Ross Sea provenance sector (142°E to 195°E ; 4 sites in total), and white stands for a West Antarctica source (east of 195°E ; 4 sites in total). NVL: Northern Victoria Land, SVL: Southern Victoria Land, TAM: Central Transantarctic Mountains, EPG: Early Paleozoic Granites (near Ninnis Glacier; see Figure 3.1 for location). Vertical grey bands corresponding to the three most significant age ranges identified in IODP Site U1361 marine sediments, 0 to 50 Ma (from NVL/Ross Sea and West Antarctica), 90-130 Ma (from West Antarctica) and 440-540 Ma (from NVL/Ross Sea) from left to right.

Goodge, 2007) (Figure 3.11). In conclusion, DSDP Site 274 potentially received IRD from all three of these geographical source areas.

Ice-rafted hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages in Holocene sediments at IODP Sites U1360 and U1358 yield ages that agree well with existing hornblende core-top data in the vicinity of the sites (Roy et al. 2007; Pierce et al. 2007), and onshore ages from the proximal Archean and Neoproterozoic Adélie Craton (Di Vincenzo et al. 2007; Duclaux et al. 2008; Goodge and Fanning, 2010; 1450-1750 Ma). As hornblende yields from IRD fractions at the IODP shelf sites U1358 and U1360 are today much higher than at the distal IODP Site U1361, I infer that

the proximal Adélie Land source areas contains more abundant hornblende grains. Ice-rafted material with such signatures was therefore likely supplied by icebergs calved from the proximal Adélie Land continental margin.

3.7.2 Provenance of ice-rafted hornblende grains in Pliocene IODP Site U1361 sediment

3.7.2.1 Ross Orogeny aged hornblendes grains

The most abundant hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age population in Pliocene IODP Site U1361 sediments has a range of 440 to 540 Ma (Figure 3.8 and 3.11). Such ages are likely to have been sourced from the high-grade Late Cambrian Ross Orogeny (Stump, 1995; Goodge, 2007 and references therein). In IODP Site U1361 sediments this population is comprised of two peaks, one between 440 and 500 Ma, and a secondary, smaller peak between 500 and 540 Ma (Figure 3.11). Northern Victoria Land, Southern Victoria Land and the Transantarctic Mountains are likely sources for grains with such ages, and are characterised by slightly different peak metamorphic conditions (460-500 Ma, 480-550 Ma and 480-545 Ma, respectively; Goodge, 2007) (Figure 3.2). In addition to these source areas, Early Paleozoic granites in the vicinity of the Ninnis Glacier could also contribute Ross Orogeny-aged grains to the study site (Figure 3.2). Holocene marine sediments located directly downstream of the Ninnis Glacier contain hornblendes with $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 480 and 560 Ma (Roy et al. 2007; Pierce et al. 2011). Hence, I propose that the older sub-group within the Ross Orogeny population is derived from icebergs sourced from the proximal Ninnis Glacier and/or Southern Victoria Land and the Transantarctic Mountains. While the younger sub-group can be partially explained by derivation from Northern Victoria Land, seven grains aged between 440 and 460 Ma cannot. Furthermore, a small number of grains have hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 330 and 430 Ma. These ages, although minor in number, can be matched to the Bowers Terrane in Northern Victoria Land (e.g. Weaver et al. 1984; Borg et al. 1987; Rocchi, 2004), which is characterised by whole-rock K-Ar ages of between 320 and 450 Ma (Adams, 2006). In summary, during the Pliocene, icebergs delivered hornblende grains to IODP Site U1361 from Northern Victoria Land, Southern Victoria Land, the Transantarctic Mountains and the local proximal coast.

3.7.2.2 Cenozoic volcanic sources for hornblende grains

The youngest and second most abundant hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age population identified in IODP Site U1361 sediments (<50 Ma) is most likely derived from the Cenozoic McMurdo Volcanic Group (Harrington, 1958; Kyle and Cole, 1974; Kyle et al. 1990; LeMasurier and Thomson, 1990) (Figs. 3.2, 3.11 and 3.12).

Comparison of the eruptive histories of the different volcanic fields that comprise the McMurdo Volcanic Group with hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages identified in IODP Site U1361 sediments may offer some insights on the geographical sources and transport modes of IRD within this age population (Figure 3.12). The Hallet Volcanic Province of the McMurdo Volcanic Group has a well-documented eruptive history spanning the last 12 million years (Müller et al. 1991; Armienti and Baroni, 1999; Acton et al. 2008; Mortimer et al. 2008; Smellie et al. 2011). The Mount Melbourne Volcanic Province's eruptive history spans from ~22 Ma to today (Rossetti et al. 2000; Giordano et al. 2012), and the Erebus Volcanic Province spans from 19 Ma to today (Dibble et al. 2008; Kelly et al. 2008; Di Vincenzo et al. 2010), respectively. However, evidence for older volcanic activity identified in volcanoclastic sediments in marine sediment cores in the western Ross Sea extends McMurdo Volcanic Group volcanism back to 26 Ma (Gamble, 1985; Barrett et al. 1987; Hambrey et al. 2002; Ross et al. 2012). The Balleny Islands (Figure 3.1) are thought to be no older than Miocene (Johnson et al. 1982), although they are inaccessible and hence poorly understood geologically. The geochemical compositions of basalts from outcrops on these islands and volcanic ash analysed from nearby marine sediments (Huang et al. 1973; Huang et al. 1975; Kyle and Seward, 1984; Shane and Froggatt, 1992) suggest an intermediate geochemical composition between that of the Hallet Volcanic Province and Erebus Volcanic Province (Kyle and Cole, 1974; Johnson et al. 1982; Green Trevor, 1992), implying similar tectonic relationships and therefore similar ages for the initiation of their formation. It is therefore feasible that the Balleny Islands may be the source of some of the volcanic ash and hornblendes younger than Miocene in age identified at IODP Site U1361.

In summary, the majority of hornblende ages that are younger than ~22 Ma could have been sourced from the Hallet Volcanic Province, the Mount Melbourne Volcanic Province, Erebus Volcanic Province or the Balleny Islands. However, grains with ages between 12 and 26 Ma are likely to have been carried to IODP Site U1361 from the southern Ross Sea by icebergs calved in the vicinity of the Mount Melbourne Volcanic Province and Erebus Volcanic Province. Three Eocene hornblende grains (35.9 ± 0.7 Ma, 36.6 ± 1.4 Ma, 44.2 ± 0.25 Ma) may be sourced from even older McMurdo Volcanic Group (Figs. 3.1, 3.2 and 3.12) volcanism that is unrecorded in the Ross Sea. However, they could also have been

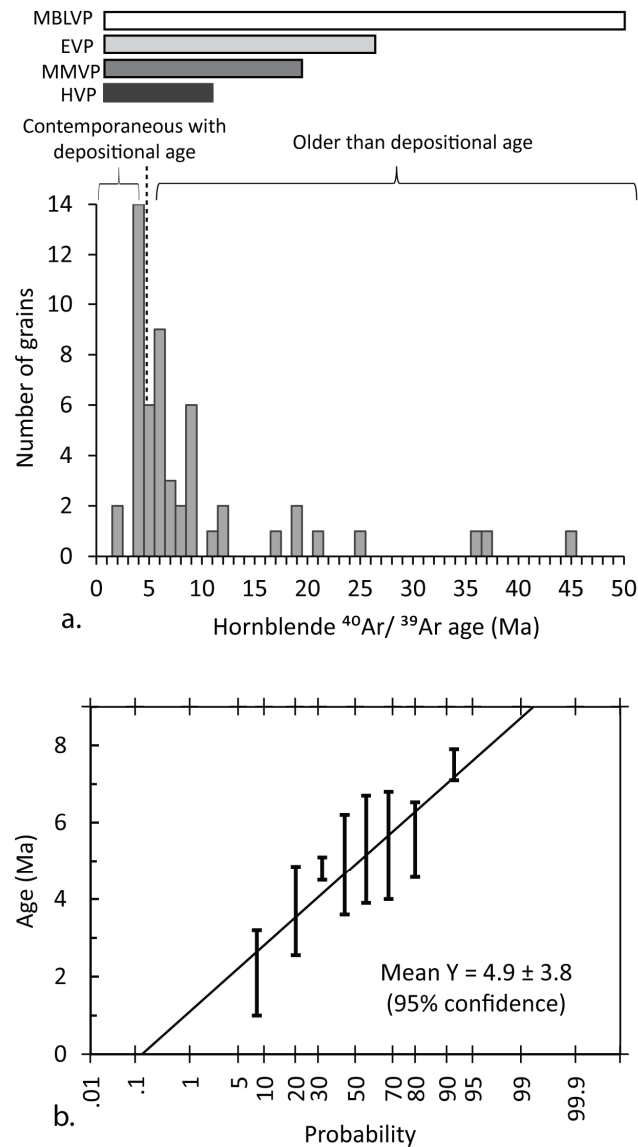


Figure 3.12. a) Histogram of the youngest Cenozoic hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age population from Pliocene IODP Site U1361 sediments. Also included are the known eruptive histories of the four main volcanic provinces in the region (see text): HVP: Hallet Volcanic Province; MMVP: Mount Melbourne Volcanic Province; EVP: Erebus Volcanic Province; MBLVP: Marie Byrd Land Volcanic Province. About half of the hornblende grains yield ages older than the deposition age, indicating that they were transported to the site by ice-rafting. **b)** Lineralised probability plot of $^{40}\text{Ar}/^{39}\text{Ar}$ ages measured on eight volcanic glass grains analysed from U1361 10H 6W 35-37 (depositional age of ~4.1 Ma). Error bars represent 1 sigma absolute uncertainties. The syn-depositional age of these volcanic glass grains points to aeolian supply to IODP Site U1361.

supplied by icebergs sourced from the Marie Byrd Land Volcanic Province (MBLVP) located to the east of the Ross Sea in West Antarctica, where Eocene volcanism has been dated to ~36 Ma, with the possibility of initial volcanism being even older (Wilch and McIntosh, 2000).

As 58% of all hornblende grains analysed from IODP Site U1361 are older than their marine sediment depositional age (Figure 3.12), it is likely that they were entrained glacially in the vicinity of their volcanic depositional centres. In contrast, most of the volcanic glass grains analysed fall within error of the depositional age of the sediment sample from which they were extracted (Figure 3.12), implying they represent contemporaneous eruptive events. Volcanic glass and phenocrysts from the McMurdo Volcanic Group have been identified in layers within existing continental ice in Northern Victoria Land and the Transantarctic Mountains (Perchiazzi et al. 1999; Smellie et al. 2011; Narcisi et al. 2012), supplied by explosive volcanism in the Hallet Volcanic Province and Mount Melbourne Volcanic Province. This observation suggests that some of the sediment load of regionally calved icebergs sourced from the continental interior adjacent to Northern Victoria Land and Southern Victoria Land may contain a volcanic glass component. An alternative source for volcanic glass could be aeolian fallout from the Balleny Islands.

3.7.2.3 Evidence for a minor population of West Antarctic sourced hornblende grains in IODP Site U1361 sediments

A minor age population in IODP Site U1361 Pliocene sediments is constituted by Late Paleozoic to Mesozoic hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Figure 3.11). However, there are no known exposed analogues in the nearby East Antarctic study area with hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages that lie between ~90 to ~290 Ma (Figure 3.2), making this age range interesting and potentially significant despite its low abundance. While it is not possible to rule out bedrock hidden within the East Antarctic continental interior as a potential source for these ages, the observed 90 to 125 Ma ages matches very well with hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age populations identified in Holocene marine sediments off of the distal West Antarctic continental margin (95 to 127 Ma; Roy et al. 2007), ~2500km away from IODP Site U1361 (Figure 3.2). Onland this hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age population is most evident in Marie Byrd Land (Figure 3.2), where calc-alkaline granodiorites and granites (Weaver et al. 1994), and mafic dykes (Storey et al. 1999) were intruded into metasedimentary basement rocks between 95 and 125 Ma (Weaver et al. 1994; Luyendyk et al. 1996; Storey et al. 1999; Siddoway et al. 2005).

3.7.2.4 Sources for other minor hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age ranges in IODP Site U1361 sediments

Four hornblende grains from IODP Site U1361 sediments have $^{40}\text{Ar}/^{39}\text{Ar}$ ages that match the proximal Archean and Neoproterozoic Adélie Craton, which has a well-constrained age population between 1450 and 1750 Ma (Di Vincenzo et al. 2007; Roy et al. 2007; Pierce et al. 2011; this study) (Figs. 3.2 and 3.11). A lack of such ages could indicate limited iceberg supply to IODP Site U1361 from this area during the Pliocene.

A small Mesoproterozoic hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age population between 1000 and 1300 Ma can be seen in Pliocene sediments at IODP Site U1361, as well as in other sediments offshore of Adélie Craton (Roy et al. 2007; Pierce et al. 2011; this study) and in Ross Sea sediments (Roy et al. 2007; Pierce et al. 2011). Similar to in Holocene sediments, these ages occur in minor numbers in IODP Site U1361 (6 grains in total). This age range has no known exposed analogues in East and West Antarctica to the east of the Adélie Craton. It does, however, match significant populations of Proterozoic hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages in Holocene marine sediments offshore of the Wilkes Land margin to the west of the Adélie Craton (Roy et al. 2007; Pierce et al. 2011) (Figure 3.2) and thermochronological ages for proximal onland exposures (Sheraton et al. 1992; Post et al. 1996, 2000; Möller et al. 2002; Fitzsimons, 2003). This tectono-metamorphic age is inferred to be related to the Grenvillian Orogeny (Dalziel, 1991; Fitzsimons, 2000a, 2000b; Boger, 2011). However, a supply of icebergs to IODP Site U1361 from areas of the west of the Adélie Craton is unlikely, as this would be counter to the direction icebergs are transported around the continent (Figure 3.1). The possibility of a Grenvillian-aged igneous body, or at least crustal material with remnant Grenvillian signatures, located beneath the East Antarctic ice sheet to the west of the Transantarctic Mountains, has been proposed in accordance with the SWEAT hypothesis (South-Western US and East Antarctica) (Moores, 1991; Goodge et al. 2008, 2010), as Grenvillian U-Pb zircon ages have been identified in glacial sediments in the Ross Sea area (Goodge et al. 2010). It is hence possible that Mesoproterozoic aged hornblende grains in IODP Site U1361 may be related to a similar continental interior source currently obscured by the ice sheet.

While assigning unproven sources to minor hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age occurrences is difficult due to the possibilities of partial resetting and alteration of source rocks, comparison to available onshore and marine sediment information suggests that Pliocene icebergs were

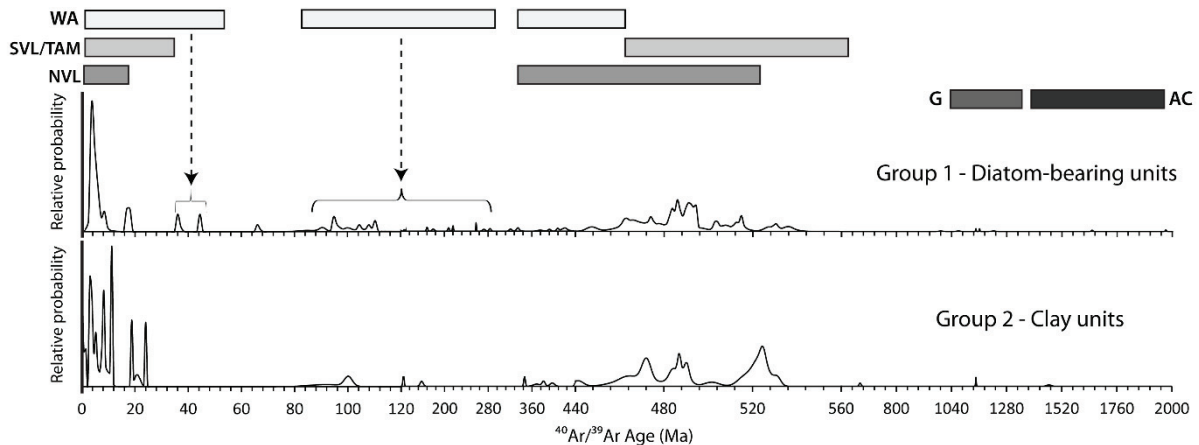


Figure 3.13. Probability diagrams of $^{40}\text{Ar}/^{39}\text{Ar}$ ages for all hornblende grains between 0 to 2000 Ma from Pliocene IODP Site U1361 sediments, separated into two groups according to their lithology: Group 1 (top panel) consists of sedimentary facies 4 (diatom-bearing silty clays) and facies 5 (diatom-rich silty clays), and Group 2 (bottom panel) consists of facies 1 to 3 (clays; clays with dispersed clasts; silty clay with dispersed clasts, respectively). Also included are the known thermochronological age ranges of major geographical source areas. AL: Adélie Land, NVL: Northern Victoria Land, SVL/TAM: Southern Victoria Land/Transantarctic Mountains, MBL: Marie Byrd Land; G: Grenville. Dashed arrows indicate West Antarctic derived hornblendes, and highlight an increase in West Antarctic IRD delivery to IODP Site U1361 during times of enhanced biological productivity and warmth (see Chapter 2). Note the scale change of the x-axis at 440 Ma and 560 Ma.

supplied to IODP Site U1361 from the proximal East Antarctic Coast, Northern Victoria Land, Southern Victoria Land, the Transantarctic Mountains and West Antarctica (Figure 3.1). Finally, it is important to note that it is unlikely that icebergs sourced from ice shelves contain much detrital subglacial material, as most debris melts out to form sub-ice shelf deposits where the base of the ice shelf is in contact with the ocean before calving (e.g. Alley et al. 1989). Therefore, most ice-rafted grains in IODP Site U1361 sediments were probably supplied from multiple marine-terminating glaciers located in the above mentioned areas. The majority of the ice streams supplying these glaciers are topographically constrained, either lying within deep sub-basins, as is the case for the ice streams that drain the Ninnis and Cook glaciers at the mouth of the Wilkes Subglacial Basin, which sit in ~2km deep sub-basins (Ferraccioli et al. 2009), or are confined to flow in valleys running through mountain ranges in Southern and Northern Victoria Land or the Transantarctic Mountains. These observations offer strength to the Pliocene provenance constraints provided by Holocene marine

sediments, as it suggests IRD provenance patterns in this region will have changed minimally since the Pliocene.

3.8 Increased West Antarctic IRD in IODP Site U1361 during Pliocene Warmth

Provenance constraints on hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age populations in IODP Site U1361 sediments suggest that IRD supply from East Antarctic sources to the site remained relatively consistent throughout the Pliocene, regardless of changing environmental conditions inferred from lithostratigraphy and diatom assemblages (Chapter 2). The only exception to this pattern is the delivery of West Antarctic IRD, which although present as a minor number of hornblende grains in IODP Site U1361 sediments, primarily occurs within diatom-bearing and diatom-rich sedimentary facies, inferred to have been deposited during intervals of warmer-than-present conditions (Chapter 2) (Figure 3.13).

Iceberg pathways are regionally constrained to follow an anti-clockwise direction around the East Antarctic continent (Figure 3.1), although it is not very well understood to what extent wind stress and hence coastal currents would be affected by a smaller continental ice mass (e.g. DeConto et al. 2007). Large modern tabular icebergs sourced from ice shelves have lifetimes of several years, as observed from satellites (e.g. Antarctic Iceberg Tracking Database; available at <http://www.scp.byu.edu/data/iceberg/database1.html>). This means that smaller icebergs, calved from glacier fronts, will likely melt more rapidly and closer to their source areas than tabular icebergs. For paleo-reconstructions, it is important to consider that sea surface temperatures of ocean waters near the Antarctic continent during the Pliocene were warmer than today. Silicoflagellate assemblages (Whitehead and Bohaty, 2003; Escutia et al. 2009) and paleothermometry indicators (TEX_{86} ; McKay et al. 2012a) suggest temperatures up to 6°C warmer than today during interglacials and prolonged warm intervals spanning up to 200,000 years in duration (Whitehead and Bohaty, 2003; Escutia et al. 2009; Bart and Iwai, 2012; McKay et al. 2012a, see Chapter 2). Constraints on iceberg survivability in warm Pliocene ocean waters (Chapter 5) lends support to the interpretation that the presence of West Antarctic IRD in IODP Site U1361 sediments, although minor in abundance, is significant, considering the amount of icebergs that must have been produced from glacial calving fronts in order to travel over 2500km without completely melting on their westward journey to IODP Site U1361. This suggests that the largely marine-based West Antarctic ice sheet may have been more sensitive to warm conditions (Naish et al.

2009; Pollard and DeConto, 2009) than the numerous East Antarctic marine-terminating glaciers that supplied IRD to IODP Site U1361 during the Pliocene.

3.9 Fine-grained Sediment Provenance Versus IRD Provenance: Insights into Mineralogical Bias in Glaciomarine Sediments

Ice-rafted debris often comprises a considerable proportion of fine-grained detrital material (Andrews, 2000). However, direct comparison of Nd and Sr isotopic compositions of <63 μ m fractions in IODP Site U1361 sediments with hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age populations identified in the >150 μ m fractions of the same samples reveals that IRD provenance does not follow the range of variability observed in fine-grained sediments (Figure 3.14). In fact, IRD provenance patterns differ considerably from fine-grained sediment provenance patterns (Figure 3.14). For example, the provenance of fine-grained sediments suggest that retreat of the East Antarctic ice sheet margin into the Wilkes Subglacial Basin took place during warmer Pliocene conditions, but there is a marked absence of evidence for these sources in sand-size IRD provenance signatures. Conversely, comparison of the provenance signatures of finer sediment fractions, in this case, the Nd and Sr isotopic composition of <63 μ m detrital sediments and the abundance of detrital smectite in clay mineral assemblages, converge to suggest an increase in the supply of Wilkes Subglacial Basin derived material took place during warm intervals.

The striking disparity between fine-grained sediment provenance and ice-rafted hornblende provenance patterns in IODP Site U1361 can be explained by the mineralogical composition of continental source rocks. Initial bedrock composition ultimately determines the final composition of eroded terrigenous products, and the rock types within a drainage catchment area determine the suitability of single mineral thermochronometers to provide the most appropriate provenance information (e.g. see Hodges, 2003 for a review). For example, some minerals utilised in thermochronological studies (e.g. zircon, feldspar, biotite, hornblende) are preferentially found in certain lithologies (e.g. Moecher and Samson, 2006), potentially leading to bias in the detrital sediment record. In this case study, the dominant bedrock sources supplying fine-grained sediments to IODP Site U1361 are granites (from proximal Early Paleozoic terranes [Talarico and Kleinschmidt, 2003; Goodge and Fanning, 2010]), and dolerites and fine-grained basalts (Elliot and Fleming, 2008) from Ferrar Large Igneous Province bedrock and recycled Ferrar Large Igneous Province sediments within the Wilkes Subglacial Basin (Studinger et al. 2004; Ferraccioli et al. 2009).

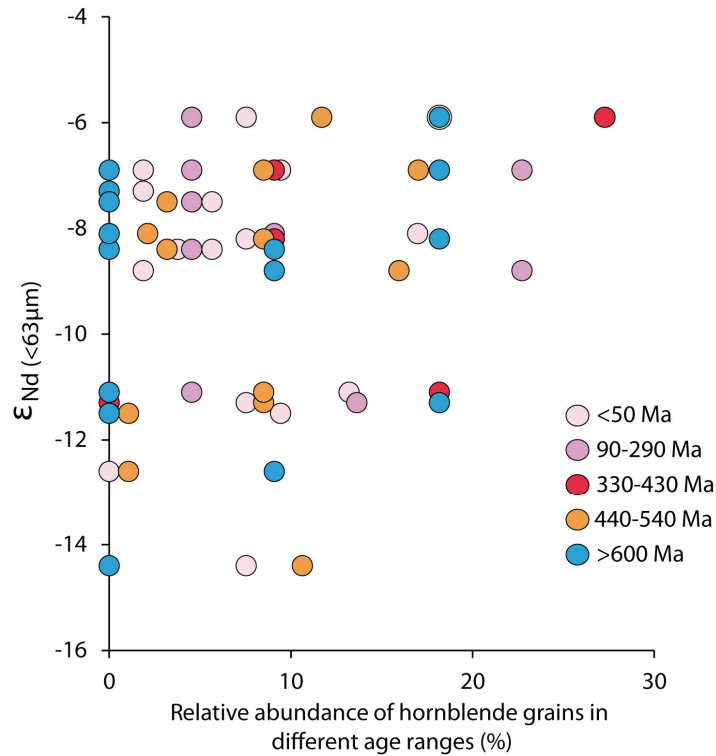


Figure 3.14. Neodymium isotopic compositions of detrital $<63\mu\text{m}$ size fractions from Holocene (taken from Chapter 2), Pliocene (taken from Chapter 2; this study) and Miocene (this study) sediments from IODP Site U1361 (errors are the same size or smaller than data points) plotted versus the relative abundance of hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age ranges from the same samples, illustrating a lack of correlation between fine-grained sediment provenance and IRD provenance. This mismatch is most readily explained by a lithological bias in the IRD provenance, as investigated hornblende grains are not abundant in some of the key lithologies identified from the fine-grained sediment provenance.

However, hornblendes are rare in mafic Ferrar Large Igneous Province lithologies (DeMarchi et al. 2010; Hauptvogel and Passchier, 2012). This explains why no hornblendes with $^{40}\text{Ar}/^{39}\text{Ar}$ ages that match the well constrained emplacement age of the Ferrar Large Igneous Province at ~ 178 Ma (Foland et al. 1993; Heimann et al. 1994; Duncan et al. 1997; Minor and Mukasa, 1997) have been found in IODP Site U1361 sediments. It is however important to note that despite the absence of hornblende grains in coarse-grained IRD from IODP Site U1361 sediments, the petrography of ice-rafted clasts reveals significant quantities of clino- and ortho-pyroxenes (up to 4.3% of total detrital fraction $>150\mu\text{m}$). In contrast to hornblendes, these minerals are characteristic of the Ferrar Large Igneous Province (e.g. Demarchi et al. 2001; Hauptvogel and Passchier, 2012) confirming supply of this material.

This interpretation is validated by the presence of clasts of basalt in the same Pliocene sediments. Furthermore, Ferrar basalts are often associated with Beacon sandstones (Elliot and Fleming, 2008), lithologies of which are dominated by K-feldspar and quartz - these minerals along with clasts of sandstone are abundant in IODP Site U1361 sediments, lending additional support to the interpretation that icebergs were sourced from within the Wilkes Subglacial Basin during the Pliocene, but did not carry any hornblende grains.

Alternative thermochronological provenance information on a Ferrar Large Igneous Province source, in place of hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ data, could be gained by K-Ar analyses on bulk sediments or $^{40}\text{Ar}/^{39}\text{Ar}$ analyses on detrital plagioclase feldspar, similar to existing thermochronological analyses of whole rock basalts and mineral grains from Ferrar and related flood basalts (Foland et al. 1993; Heimann et al. 1994; Fleming et al. 1997; Duncan et al. 1997).

3.10 Conclusions

The Nd and Sr isotopic composition and clay mineralogy of fine-grained Pliocene and Miocene IODP Site U1361 sediments reveals supply of detrital material from Early Paleozoic granitoids located upslope from the drill site, and Mesozoic volcanic and sedimentary terranes of the Ferrar Large Igneous Province and Beacon Supergroup, located at the mouth and within the Wilkes Subglacial Basin. In contrast, according to $^{40}\text{Ar}/^{39}\text{Ar}$ dating of ice-rafted hornblende grains, Holocene, Pliocene and Miocene IRD at IODP Site U1361 is sourced from multiple regions including the proximal coast, Northern Victoria Land, Southern Victoria Land, the Transantarctic Mountains and Marie Byrd Land, in West Antarctica.

Fine-grained sediment provenance parallels lithostratigraphic variations associated with changing paleoenvironmental conditions, with enhanced erosion of Mesozoic terranes within the Wilkes Subglacial Basin taking place during warmer climatic intervals, and delivery of Early Paleozoic material from the proximal coast during cooler intervals, a pattern similar to today. In contrast, provenance changes of East Antarctica sand-size IRD do not vary between different lithostratigraphic units. Accordingly, no evidence for retreat of the East Antarctic ice sheet within the Wilkes Subglacial Basin can be seen in ice-rafted hornblende ages in IODP Site U1361. This mismatch can be explained by a lithological bias in the hornblende-based IRD provenance, as the major bedrock source supplying detrital

material from within the Wilkes Subglacial Basin is the Ferrar Large Igneous Province, mainly a predominantly basaltic lithology which contains very few hornblende grains.

My data demonstrate that selection of appropriate provenance tools requires a priori knowledge of source rock lithology, but integration of more than one mineral-based thermochronological system with fine-grained radiogenic isotope analyses and clay mineralogy can minimise the potential of mineralogical bias, and provide novel information on continental geology and ice sheet dynamics.

CHAPTER 4

The provenance fingerprint of Marine
Isotope Stage 31 in marine sediments
from IODP Site U1359, Wilkes Land

Chapter Summary

This chapter presents the results of provenance analyses on Pleistocene IODP Site U1359 sediments, deposited between ~0.9 and ~1.2 Ma. Investigation of fine-grained (<63µm) detrital neodymium and strontium isotopes and $^{40}\text{Ar}/^{39}\text{Ar}$ ages of ice-rafted hornblende grains (>150µm) unravel the provenance of sediments deposited during Pleistocene ‘super-interglacial’ Marine Isotope Stage (MIS) 31 (~1.06 to ~1.08 Ma). Marine Isotope Stage 31 has been suggested to coincide with major collapse of the West Antarctic ice sheet (WAIS) which may have produced a marine sediment provenance fingerprint detectable at the distal IODP Site U1359, located offshore the Wilkes Subglacial Basin, East Antarctica.

The $^{40}\text{Ar}/^{39}\text{Ar}$ ages of individual hornblende grains extracted from carbonate-bearing Pleistocene layers, which likely correspond to Pleistocene interglacials (potentially including MIS 31), indicate a small but significant amount of ice-rafted detritus (IRD) delivered from the Ross Sea and West Antarctica. These data represent encouraging pilot data that may provide a framework to decipher potential collapse of the West Antarctic ice sheet in future detailed analyses.

In contrast, results from fine-grained detrital Nd and Sr isotopes on the same samples match modern provenance patterns. This finding is interesting when compared to previously analysed Pliocene sediments from IODP Site U1361, which indicated large fluctuations in fine-grained sediment provenance associated with retreat of the East Antarctic ice sheet during times of climatic warmth. This in turn implies that the local margin of the East Antarctic ice sheet did not retreat during the studied Pleistocene interglacial intervals, and hence expanded significantly between the late Pliocene and the mid-Pleistocene (i.e. between ~2.8 to 0.9 Ma). One clear difference from modern provenance signatures is the occurrence of a significant amount of IRD sourced from the local Adélie Coast at IODP Site U1359, hinting at an increase in iceberg production from this margin during Pleistocene interglacials compared to today.

4.1 Introduction

Low-lying marine-based areas of Antarctica’s ice sheets are potentially sensitive to climatic warmth (Mercer, 1978), but their behaviour during such conditions is poorly understood. One of the warmest intervals of the Pleistocene in Antarctica has been identified

as the ‘super-interglacial’ MIS 31 (~1.06 to ~1.08 Ma) (Scherer et al. 2008; Naish et al. 2009). This event was contemporaneous with orbital configurations with high eccentricity and obliquity, which resulted in intervals of strong high latitude insolation anomalies at ~1.06 Ma and ~1.08 Ma. These intervals coincide with a minimum in benthic $\delta^{18}\text{O}$ records (Lisiecki and Raymo, 2005), indicating retreat of high latitude ice sheets. Marine sediments in the Ross Sea (Scherer et al. 2008; Naish et al. 2009; McKay et al. 2012b), and off the Antarctic Peninsula (Vautravers and Hillenbrand, 2008) and in Prydz Bay (Villa et al. 2008) all record evidence for elevated warmth during this event, with diatom assemblages in the Ross Sea implying sea surface temperatures of 3 to 5°C warmer than today (Scherer et al. 2008). Open ocean conditions in the Ross Sea (Naish et al. 2009; McKay et al. 2012b) have been inferred by deposition of diatomite, with ice sheet models suggesting retreat of the Ross Ice Shelf and potential collapse of marine-based areas of the West Antarctic ice sheet may have taken place (Pollard and DeConto, 2009; DeConto et al. 2012). Coincidence of the timing of MIS 31 with the paleomagnetic Jaramillo subchron (0.988 to 1.072 Ma) means identification of this interglacial interval in marine sediments can be achieved (e.g. Scherer et al. 2008). However, due to the presence of a short interval of reverse polarity recorded globally between ~1.05 and 1.07 Ma (e.g. Singer et al. 1999; Channell and Kleiven, 2000; Guo et al. 2002), there remains some controversy as to the timing of the base of the Jaramillo subchron (Biswas et al. 1999; Channell et al. 2002) and hence the timing of MIS 31 in marine sediments.

This study aims to test whether a potential collapse of the West Antarctic ice sheet during MIS 31 created a provenance fingerprint that delivered West Antarctic and Ross Sea-sourced ice rafted detritus (IRD) over 2500km to the Adélie Coast margin of East Antarctica. The proxies utilised in this study are neodymium (Nd) and strontium (Sr) isotopic compositions of fine-grained (<63 μm) detrital marine sediments, and the $^{40}\text{Ar}/^{39}\text{Ar}$ ages of individual hornblende grains handpicked from ice-rafted detritus (>150 μm). The parent and daughter elements of the long-lived radioactive decay systems of rubidium-strontium (Rb-Sr) and samarium-neodymium (Sm-Nd) are separated during mantle melting due to their different compatibilities, meaning bedrocks with different ages and lithologies will have different radiogenic isotope characteristics (e.g. in continental crust, higher Rb/Sr ratios and lower Sm/Nd ratios lead to more radiogenic Sr isotopes and less radiogenic Nd isotopes relative to the mantle). In glaciomarine sediments, both isotope systems can be used to derive an integrated bedrock signature from bedrock sources eroded by the ice (e.g. Hemming et al. 1998; Roy et al. 2007; Hemming et al. 2007; Colville et al. 2011). However, Sr isotopes are additionally prone to alteration by weathering and grain-size selective sedimentary sorting

(Blum and Erel, 1997). Hence, when integrating both radiogenic isotope systems in detrital marine sediments, they can provide information on an array of processes, including continental weathering, erosional patterns, and transport by ocean currents.

In addition, ice-rafting can deliver continental detritus to the ocean floor. In proximal Antarctic marine sediments, a number of studies have focussed on individual mineral grains greater than 150µm for IRD provenance analyses (e.g. $^{40}\text{Ar}/^{39}\text{Ar}$ ages of ice-rafted hornblende grains have been used to detect iceberg provenance; Roy et al. 2007; Williams et al. 2010; Pierce et al. 2011). Hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages are particularly useful for IRD provenance tracing in areas with complex tectono-metamorphic histories such as Antarctica, as the argon measured in hornblende grains reflects the age when the grain cooled below ~500°C (Hodges, 2003).

In the search for a potential fingerprint of MIS 31, here I present provenance patterns of Pleistocene sediments deposited from ~0.9 to ~1.2 Ma from Integrated Ocean Drilling Program (IODP) Site U1359 (64°54'S, 143°57'E). These new Pleistocene results will be compared to results from Pliocene sediment layers at a neighbouring site IODP Site U1361 (64°24'S, 143°53'E; Chapters 2 and 3), located approximately 50km to the north of IODP Site U1359 (Figure 4.1), and with Holocene sediment provenance patterns in the region.

4.2 IODP Site U1359

Integrated Ocean Drilling Program Site U1359 is located down-current of the Ross Sea and the marine-based West Antarctic ice sheet, and offshore of the Wilkes Subglacial Basin, where large areas of the East Antarctic ice sheet lie below sea level (Figure 4.1). The site was drilled in 3020m water depth, approximately 265 km offshore of the Adelie Coast, during IODP Expedition 318 (Escutia et al. 2011). A total of ~194m of sediment was drilled at this site, covering Miocene to Holocene-aged strata (Escutia et al. 2011; Tauxe et al. 2012). Detrital sediments are today supplied to the site by ice sheet driven turbidity currents (Escutia et al. 2011) which carry shelf sediments downslope in submarine channels orientated perpendicular to the coast (Busetti et al. 2003; Donda et al. 2003; Escutia et al. 2000, 2003). In addition to turbidity deposition, ice-rafting also supplies detrital material to the area (Pierce et al. 2011). Pleistocene sediments at IODP Site U1359 (Figure 4.2) are composed of two main facies, diatom and foraminifera-bearing muds (facies 1), interpreted to represent a hemipelagic depositional settling during interglacial conditions, and fine-grained muds

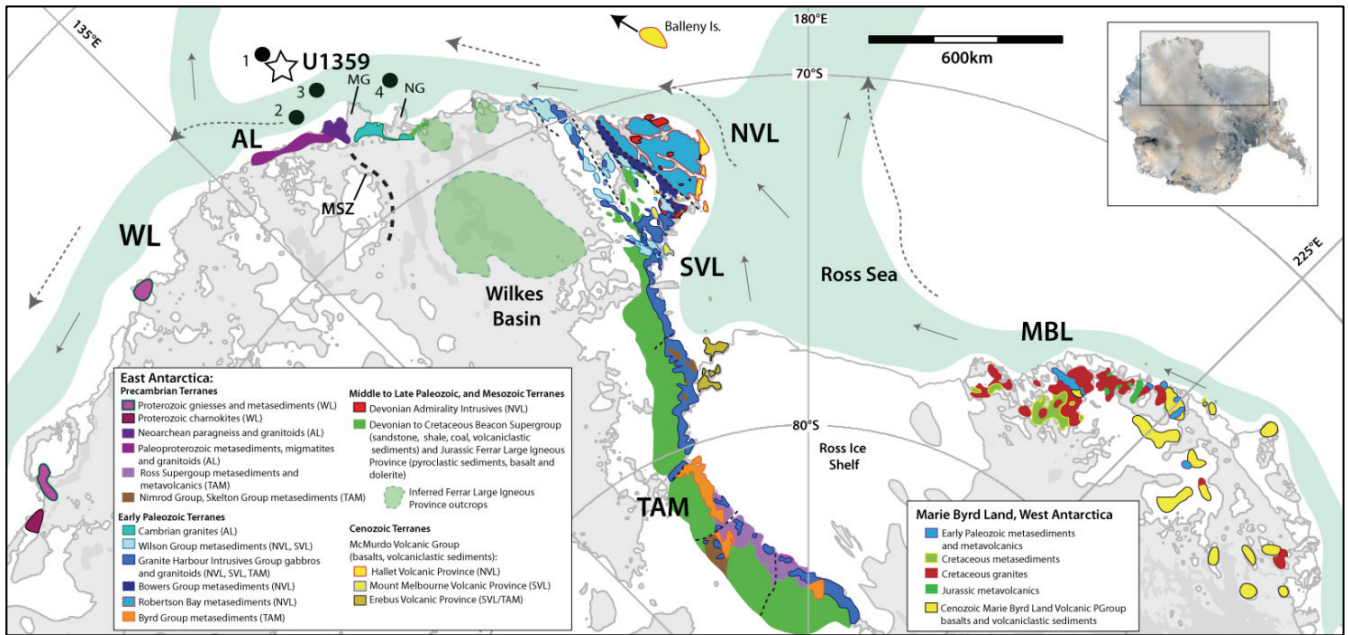


Figure 4.1. Geological map of the study area illustrating the diverse range of bedrock ages and lithologies (modified from Bushnell and Craddock, 1970). Also shown is the continental subglacial topography (BEDMAP 2; Fretwell et al. 2013) with continental regions below sea level in light grey, and of more than 2000m below sea level in darker grey. Dashed lines refer to major structural features (Flottmann et al. 1993; Ferraccioli et al. 2009). Star (offshore) indicates the location of IODP Site U1359. Sites 1, 2, 3 and 4 refer to IODP Sites U1361, U1358, and ELT37-06 and DF79-47, respectively. Blue shading offshore represents the approximate transport region of icebergs in the modern ocean (Antarctic Iceberg Tracking Database [1978–2012]; available at <http://www.scp.byu.edu/data/iceberg/database1.html>) with direction of movement shown with small grey arrows. Larger dashed arrows indicate the approximate location of major flow of Antarctic Bottom Water (Orsi et al. 1999). AL: Adélie Land, NVL: Northern Victoria Land, SVL: Southern Victoria Land, TAM: Transantarctic Mountains, MBL: Marie Byrd Land, NG: Ninnis Glacier, MG: Mertz Glacier, MSZ: Mertz Shear Zone.

interbedded with mm-scale silt laminae (facies 2), interpreted to represent deposition by turbidity currents, triggered by sediment overloading via glacial advance to the continental shelf edge (Escutia et al. 2011). Facies 1 sediments are characterised by higher abundances of coarse-grained detrital material ($>150\mu\text{m}$; Figure 4.2), implying an increase in ice-rafting during presumably warmer conditions, with increased biogenic production. An interval of deformed bedding has been identified between approximately 26.50 and 26.80 mbsf (Figure 4.2).

The age model for IODP Site U1359 is based on paleomagnetic inclination measurements, substantiated by biostratigraphic diatom and radiolarian datums (Tauxe et al.

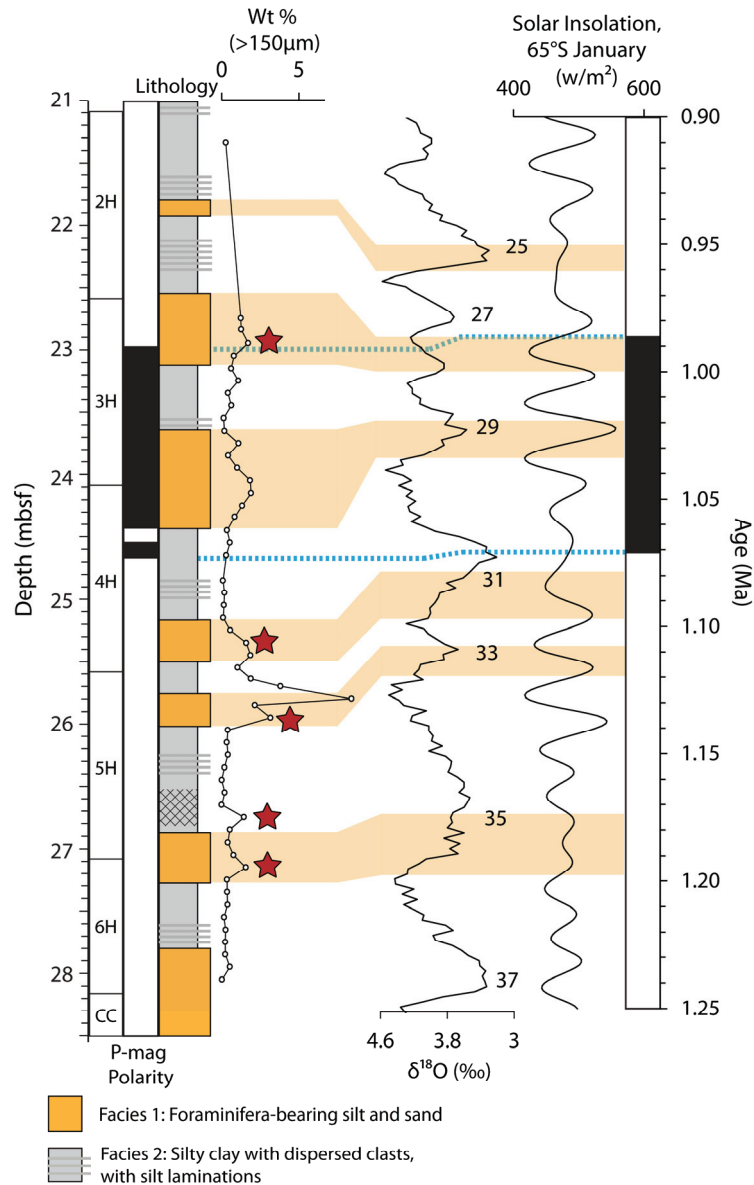


Figure 4.2. Downcore section of Pleistocene sediments recovered at IODP Site U1359, including the studied time interval around MIS 31. From left to right: i) depth in meters below sea floor; ii) core intervals; iii) paleomagnetic chron boundaries (Tauxe et al. 2012); iv) lithostratigraphy (modified from Escutia et al. 2011), with sediments composed of alternating units of foraminifera-bearing silts and sands (facies 1), with silty clays with laminations (facies 2), hatched interval denotes disturbance; v) relative abundance of the weight of detrital material >150µm: stars indicate the locations of samples analysed in this study; vi) benthic $\delta^{18}\text{O}$ stack from Lisiecki and Raymo (2005), with glacial-interglacial transitions and peak interglacial intervals highlighted in pink to indicate possible contemporaneous deposition of carbonate-bearing facies at IODP Site U1359, with Marine Isotopes Stages numbered sequentially; vii) modelled solar insolation for 65°S at January (monthly average) from Laskar et al. (2001); viii) paleomagnetic chron boundaries after Gradstein et al. (2012), with dashed blue line indicating age correlations with IODP Site U1359 magnetic reversals.

2012). The studied Plesitocene interval contains the Jaramillio subchron (C1r.1n), which spans from 0.988 to 1.072 Ma (Gradstein et al. 2012). The top of this subchron is well constrained at 23.00 mbsf, but there is some uncertainty about where the base of this subchron lies (24.54 to 24.75 mbsf) (Tauxe et al. 2012) (Figure 4.2).

4.3 Sampling and Methods

A total of five sediment samples were selected from IODP Site U1359 for provenance analysis (Figure 4.2, Tables 4.1 and 4.2). Four samples were selected from facies 1 (22.95 mbsf, 25.35 mbsf, 25.95 mbsf and 27.15 mbsf), all of which correspond to peaks in coarse grained detrital material. One sample was analysed from facies 2, at 26.75 mbsf. Samples were chosen from the top and below the Jaramillio subchron in order to reconstruct environmental conditions around MIS 31. While the base of the Jaramillio subchron has not yet clearly been defined at IODP Site U1359 (i.e. inferred to lie at either 24.54 or 24.71 mbsf; Figure 4.2), paleomagnetic inclination data (Tauxe et al. 2012) suggest that the facies 1 interval between ~25.20 and ~25.50 mbsf may correspond to peak warmth of MIS 31, and that the sample from 25.35 mbsf was deposited during this interglacial (see discussion below).

4.3.1 *Neodymium and strontium isotopes*

Bulk sediment samples were wet sieved into <63 μ m, 63-150 μ m and >150 μ m fractions. Splits (~500mg) of homogenised <63 μ m sediment were sequentially leached to remove biogenic carbonate and authigenic ferromanganese oxides and hydroxides. Removal of CaCO₃ was achieved by leaching of dried sediments repeatedly with buffered acetic acid following the method of Biscaye et al. (1965). Ferromanganese oxides and oxyhydroxides were removed through repeated steps of leaching for 6-12 hours with a reductive solution, hydroxylamine hydrochloride (NH₂OH), following the method of Rutberg et al. (2000). No removal of biogenic opal was carried out. A representative sub-sample of 50mg of detrital sediment was dissolved by hotplate digestion using 2ml of 27M HF, 2ml of 15M HNO₃ and 0.6ml of 20M HClO₄. A secondary digestion step using 2ml of 15M HNO₃ and 1ml of 27M HF was employed if any refractory minerals remained visible after the first step. Fluorides were removed in a subsequent step by fluxing samples in 6M HCl. In preparation for ion exchange chromatography, samples were then converted to nitrate form. Target analytes (Nd

and Sr) were selectively separated from the sample matrix by ion chromatography on three separate columns. The entire sample was first loaded on a Sr Spec column (*Sr-spec* resin: 100-120 μ m bead size, modified after Pin and Bassin [1992]). The matrix elute from this column was subsequently used to first separate Nd from the sample matrix (*TRU-Spec* resin: 100-120 μ m bead size, Pin and Zalduegui [1997]), and then from the other rare earth elements (*Ln-spec* resin: 50-100 μ m bead size, modified after Pin and Zalduegui [1997]).

Dried Nd cuts were taken up in ~1% HNO₃ in preparation for measurement of Nd isotopes on a Nu Instruments multi collector inductively coupled plasma mass spectrometer (MC-IPC-MS) in the MAGIC laboratories at Imperial College London, and results are shown in Table 4.1. Measurements were carried out in static mode. A ¹⁴⁶Nd/¹⁴⁴Nd ratio of 0.7219 was applied to correct for instrumental mass bias following the exponential law. Tests showed that interferences from ¹⁴⁴Sm are adequately corrected if the ¹⁴⁴Sm contribution is less than 0.1% of the ¹⁴⁴Nd signal. Samarium contributions of all the samples were significantly below that level. Average ¹⁴³Nd/¹⁴⁴Nd JNdi values for two analytical sessions over two days were: 0.512115 $\pm$ 0.000030 (n=12) and 0.512079 $\pm$ 0.000011 (n=22). All ¹⁴³Nd/¹⁴⁴Nd ratios in Table 4.1 are corrected to the recommended JNdi value of 0.512115 (Tanaka et al. 2000). Inter-batch measurements of processing monitor standard BCR-1 yielded ¹⁴³Nd/¹⁴⁴Nd ratios of 0.512645 $\pm$ 0.000016 and 0.512659 $\pm$ 0.000016, compared to the recommended value of 0.512646 $\pm$ 0.000016 (Weis et al. 2006). Total procedural blanks were consistently below 10pg Nd, less than 0.01% of the total approximate Nd concentration.

Strontium was loaded in 1 μ l of 6M HCl onto a degassed tungsten filament followed by 1 μ l of tantalum chloride. Measurements were performed in a single filament assembly on a Thermo Scientific Triton thermal ionisation mass spectrometer (TIMS) in the MAGIC laboratories at Imperial College London in static mode. The measured isotopic ratios were corrected for instrumental mass bias using the exponential law and a ratio of ⁸⁸Sr/⁸⁶Sr = 8.375. Interferences from ⁸⁷Rb were corrected for using a ⁸⁷Rb/⁸⁵Rb ratio of 0.3860. Samples were analysed in one session. Repeated analyses of NBS987 standards (n = 13) yielded ⁸⁷Sr/⁸⁶Sr ratios of 0.710260 $\pm$ 0.000016 (2 SD). As the measured value is in agreement with published values for NBS987 (0.710252 $\pm$ 0.000013; n=88) (Weis et al. 2006), no correction has been applied to sample results in Table 4.1. Repeated processing and analyses of procedural standard reference material BCR-1 yielded an ⁸⁷Sr/⁸⁶Sr ratio of 0.705021 $\pm$ 0.000012 and 0.705023 $\pm$ 0.00008 (2 SD), compared to 0.705018 $\pm$ 0.000013 (Weis et al. 2006). Procedural blanks were consistently below 30pg, less than 0.01% of the total approximate Sr concentration.

4.3.2 *Hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages*

As fine-grained detrital material can be supplied to the ocean floor by currents and wind, as well as by ice-rafting, only hornblende grains larger than 150 μm in size were analysed as they can only be ice-rafted in origin. The >150 μm fraction of five samples were handpicked from IODP Site U1359 for hornblende grains. A total of 80 hornblende grains were analysed (up to 29 grains per sample) and results are reported in Tables 4.2 and 4.3.

Hornblende grains and monitor standards were irradiated at the TRIGA reactor at the USGS in Denver, with cadmium shielding. $^{40}\text{Ar}/^{39}\text{Ar}$ ages were obtained using single-step CO_2 laser fusion at the Lamont-Doherty Earth Observatory argon geochronology lab (AGES: Argon Geochronology for the Earth Sciences). J values used to correct for neutron flux were calculated using the co-irradiated Mmhb-1 hornblende standard with an age of 525 Ma (Samson and Alexander, 1987). Measured values were corrected for background argon with measurements from an air pipette, and were also corrected for nuclear interferences (Renne et al. 1998). Analytical errors are based on the internal precision of measurements and variation of Mmhb values and are less than 2%.

4.4 Results

Measurements of Nd and Sr isotopic compositions of five Pleistocene detrital sediments from IODP Site U1359 display a small range of values (ϵ_{Nd} : -11.4 to -13.3; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.720 to 0.725) (Figure 4.3).

Analyses of hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages from the same five Pleistocene sediments from IODP Site U1359 (Figs. 4.4 and 4.5) yield two distinct populations: 0 to 50 Ma (~30%; 24 grains in total) (Figure 4.4), and 1400 to 1950 Ma (~23%; 18 grains in total). Within the youngest $^{40}\text{Ar}/^{39}\text{Ar}$ ages population, 96% of hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages are older than the depositional age of the sediment from which they were extracted (Figure 4.6), with 80% lying between 3 and 11 Ma. The remaining hornblende grains occur in minor numbers and are distributed into three broad $^{40}\text{Ar}/^{39}\text{Ar}$ age ranges: 80 to 290 Ma (~13%; 10 grains in total), 440 to 510 Ma (~14%; 11 grains in total), and 1100 to 1240 Ma (~10%; 8 grains in total). Approximately half of the grains within the 80 to 290 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ age population fall between ~90 and ~130 Ma (Figure 4.5).

Table 4.1. Neodymium and strontium isotopic compositions of Pleistocene detrital sediments (<63µm) from IODP Site U1359.

Sample	Depth (mbsf)	⁸⁷ Sr/ ⁸⁶ Sr	2 SE	¹⁴³ Nd/ ¹⁴⁴ Nd	2 SE	εNd†	2 SD^
U1359 1H CC 1-3cm*	0.01	0.717393 ± 0.000008		0.512066 ± 0.000004		-12.9 ± 0.3	
U1359 4H 3W 35-37cm	22.95	0.720363 ± 0.000008		0.512052 ± 0.000007		-11.4 ± 0.2	
re-analysis		0.720370 ± 0.000010					
U1359 4H 4W 125-127cm	25.35	0.723514 ± 0.000012		0.512049 ± 0.000008		-11.5 ± 0.2	
U1359 4H 5W 35-37cm	25.95	0.721720 ± 0.000010		0.512059 ± 0.000007		-11.3 ± 0.2	
U1359 4H 5W 115-117cm	26.75	0.725660 ± 0.000010		0.511976 ± 0.000009		-12.9 ± 0.3	
U1359 4H 6W 5-7cm	27.15	0.721711 ± 0.000012		0.511954 ± 0.000007		-13.3 ± 0.2	

Re-analysed values represent samples that were measured multiple times (same aliquot).

† Calculated using a present day ¹⁴³Nd/¹⁴⁴Nd (CHUR) of 0.512638 (Jacobsen and Wasserburg, 1980)

^ External uncertainty (2 sigma standard deviation) is based on the standard reproducibility of the analytical session

*data from Chapter 2

Table 4.2. ⁴⁰Ar/³⁹Ar hornblende populations (>150µm) from Pleistocene sediments from IODP Site U1359.

Sample	0-50 Ma	80-290 Ma	440-510 Ma	1100-1240 Ma	1400-1950 Ma	Others	Total
U1359 4H 3W 35-37cm	2	1	0	1	2	1	7
U1359 4H 4W 125-127cm	14	3	1	1	3	2	24
U1359 4H 5W 35-37cm	3	3	6	3	11	3	29
U1359 4H 5W 115-117cm	0	0	1	2	2	1	6
U1359 4H 6W 5-7cm	5	3	3	1	0	2	14
Total	24	10	11	8	18	9	80
% U1359 Pleistocene	30	13	14	10	23	10	-
% U1361 Pliocene ^a	25	11	50*	3	2	9	-
Various sites, Holocene ^b	8	8	23†	4	56	0	-
% U1361 Holocene	71	0	14	0	0	14	-

^a Data from Chapter 2

^b Taken from closest available sites: U1358, ELT37-06, DF79-47 (Roy et al. 2007; Pierce et al. 2011)

*U1361 range: 440-540 Ma

† Holocene range: 440-580 Ma

Table 4.3. Results of individual hornblende ⁴⁰Ar/³⁹Ar ages from sediments from IODP Site U1359.

Sample	run ID	Ca/K	Cl/K	moles ³⁹ Ar	%40*	Age (Ma)	+/- Age	Internal error
1359 4H 3W 35-37cm	14318-04	1.58461	0.03318	0.004	95.2	14.07	2.90535	2.92
1359 4H 3W 35-37cm	14318-09	-0.01783	-0.01111	0.002	37.9	26.48	6.77971	6.80
1359 4H 3W 35-37cm	14318-08	9.03463	0.02525	0.003	87.9	287.40	3.72822	6.85
1359 4H 3W 35-37cm	14318-01	47.57798	0.02673	0.003	90.8	314.74	5.01541	8.05
1359 4H 3W 35-37cm	14318-05	6.36236	0.07674	0.005	99.8	1225.42	7.19878	25.54
1359 4H 3W 35-37cm	14318-07	10.41497	0.05183	0.007	99.6	1447.69	6.32131	29.64
1359 4H 3W 35-37cm	14318-02	9.93577	0.08461	0.005	99.4	1520.34	9.01213	31.71
1359 4H 4W 125-127cm	14319-07	2.78496	0.01074	0.029	32.9	0.77	0.35777	0.36
1359 4H 4W 125-127cm	14319-09	0.63076	0.00626	0.012	75.9	3.01	0.91129	0.91
1359 4H 4W 125-127cm	14319-04	2.70153	0.00682	0.018	52	3.37	0.56836	0.57

1359 4H 4W 125-127cm	14319-11	2.35339	0.00543	0.016	54.1	3.51	0.58308	0.59
1359 4H 4W 125-127cm	14319-03	2.14912	0.0096	0.02	90.6	3.74	0.49886	0.50
1359 4H 4W 125-127cm	14319-01	2.60008	0.01019	0.011	44.3	4.26	0.99	0.99
1359 4H 4W 125-127cm	14319-08	2.53846	0.01367	0.045	55	4.35	0.2343	0.25
1359 4H 4W 125-127cm	14319-10	0.3009	0.01965	0.005	64.6	4.70	2.0181	2.02
1359 4H 4W 125-127cm	14319-19	2.17267	0.01445	0.065	59.9	4.81	0.16678	0.19
1359 4H 4W 125-127cm	14319-23	3.1144	0.02728	0.009	63.9	7.60	1.12203	1.13
1359 4H 4W 125-127cm	14319-21	1.04222	0.02283	0.005	50.2	7.76	1.94233	1.95
1359 4H 4W 125-127cm	14319-02	1.60031	0.01344	0.01	34	8.00	1.13915	1.15
1359 4H 4W 125-127cm	14319-16	2.10666	0.00663	0.012	47.6	8.97	0.96392	0.98
1359 4H 4W 125-127cm	14319-13	13.53583	-0.0229	0.002	65.7	43.80	4.15044	4.24
1359 4H 4W 125-127cm	14319-05	0.58852	0.03212	0.003	85.9	85.18	3.14201	3.57
1359 4H 4W 125-127cm	14319-25	7.2575	0.02547	0.005	77.7	89.85	2.45905	3.05
1359 4H 4W 125-127cm	14319-15	2.19332	0.03118	0.01	98.3	181.18	1.39071	3.88
1359 4H 4W 125-127cm	14319-12	14.9673	0.01095	0.003	96.4	472.01	4.53545	10.47
1359 4H 4W 125-127cm	14319-24	8.39064	0.05783	0.015	98.2	1127.51	4.18563	22.94
1359 4H 4W 125-127cm	14319-06	10.63006	0.04134	0.013	99.6	1323.40	4.52062	26.85
1359 4H 4W 125-127cm	14319-22	7.49025	0.0754	0.005	99.9	1374.33	8.00483	28.63
1359 4H 4W 125-127cm	14319-14	11.47955	0.08463	0.005	99.6	1438.69	8.65197	30.05
1359 4H 4W 125-127cm	14319-20	2.15279	0.10449	0.004	96.5	1469.48	10.6045	31.24
1359 4H 4W 125-127cm	14319-17	7.56016	0.03151	0.034	99.9	1666.19	3.53332	33.51
1359 4H 5W 35-37cm	14320-28	8.19113	0.02077	0.015	46.4	3.87	0.69553	0.70
1359 4H 5W 35-37cm	14320-20	2.68549	0.00862	0.027	82	6.89	0.39446	0.42
1359 4H 5W 35-37cm	14320-19	10.33768	-0.01989	0.003	41.3	27.82	3.99281	4.03
1359 4H 5W 35-37cm	14320-04	14.66576	0.03438	0.003	88.9	102.43	3.33006	3.91
1359 4H 5W 35-37cm	14320-09	1605.26403	-0.93419	0.001	35.8	133.87	34.26971	34.37
1359 4H 5W 35-37cm	14320-17	10.96807	0.03898	0.022	93.1	152.20	0.80327	3.15
1359 4H 5W 35-37cm	14320-22	12.81417	0.10185	0.005	94.6	368.67	2.80352	7.89
1359 4H 5W 35-37cm	14320-27	13.16105	0.07251	0.012	95.3	449.99	2.18883	9.26
1359 4H 5W 35-37cm	14320-34	25.37037	0.02856	0.002	97.4	475.07	7.71122	12.24
1359 4H 5W 35-37cm	14320-24	17.03071	0.22595	0.002	100	487.14	8.34987	12.83
1359 4H 5W 35-37cm	14320-02	20.01106	0.05554	0.004	95.6	488.99	4.21121	10.65
1359 4H 5W 35-37cm	14320-16	10.80344	0.12658	0.004	94.1	492.33	4.08593	10.66
1359 4H 5W 35-37cm	14320-29	8.89765	0.04427	0.009	98.8	509.90	2.97519	10.62
1359 4H 5W 35-37cm	14320-03	17.87521	0.11233	0.001	92.5	659.16	11.27486	17.35
1359 4H 5W 35-37cm	14320-21	15.21551	0.14917	0.001	100.7	757.25	13.86041	20.53
1359 4H 5W 35-37cm	14320-31	67.23803	0.05757	0.003	93.3	1098.24	9.33038	23.86
1359 4H 5W 35-37cm	14320-30	18.07853	0.02561	0.014	97.7	1135.64	3.80545	23.03
1359 4H 5W 35-37cm	14320-10	12.73055	0.02492	0.019	98.8	1235.88	3.73446	25.00
1359 4H 5W 35-37cm	14320-01	13.62674	0.10939	0.003	97.7	1584.86	10.41782	33.37
1359 4H 5W 35-37cm	14320-15	6.52042	0.14082	0.006	99.1	1609.57	7.98206	33.17
1359 4H 5W 35-37cm	14320-05	10.13967	0.05099	0.008	99.6	1617.99	7.3627	33.19
1359 4H 5W 35-37cm	14320-13	9.35452	0.07887	0.003	99.2	1628.59	11.04528	34.39
1359 4H 5W 35-37cm	14320-14	8.76102	0.06925	0.02	99.7	1664.77	4.39029	33.58
1359 4H 5W 35-37cm	14320-07	31.79495	0.08749	0.002	96.8	1669.58	13.03126	35.84
1359 4H 5W 35-37cm	14320-11	7.68908	0.10766	0.006	99.3	1734.71	8.44012	35.71
1359 4H 5W 35-37cm	14320-32	6.94154	0.10063	0.003	99.4	1806.40	9.80254	37.43
1359 4H 5W 35-37cm	14320-33	7.58842	0.05844	0.012	99.5	1860.33	5.26658	37.58
1359 4H 5W 35-37cm	14320-06	7.58837	0.05597	0.05	99.5	1862.07	3.03001	37.36
1359 4H 5W 35-37cm	14320-12	7.33959	0.08993	0.009	99.3	1871.60	7.15753	38.11
1359 4H 5W 115-117cm	14321-01	338.9512	-0.18396	0.001	63.6	54.12	9.34517	9.41
1359 4H 5W 115-117cm	14321-02	47.9407	0.11776	0.002	83.7	439.42	7.4405	11.52
1359 4H 5W 115-117cm	14321-04	11.02827	0.07408	0.003	97.8	1124.68	9.53622	24.43
1359 4H 5W 115-117cm	14321-05	21.62862	0.00614	0.001	94.3	1205.01	26.70092	35.97
1359 4H 5W 115-117cm	14321-07	11.73977	0.05329	0.005	99.3	1392.46	7.54597	28.85
1359 4H 5W 115-117cm	14321-03	10.54656	0.02785	0.01	99.5	1420.24	5.35058	28.90
1359 4H 6W 5-7cm	14322-11	9.30565	0.01285	0.016	34	2.07	0.6322	0.63
1359 4H 6W 5-7cm	14322-09	9.35525	0.01393	0.03	73.1	2.90	0.37116	0.38

1359 4H 6W 5-7cm	14322-13	11.01929	0.0184	0.009	56.4	4.24	1.15924	1.16
1359 4H 6W 5-7cm	14322-02	6.07702	0.01308	0.003	47.6	10.28	3.26688	3.27
1359 4H 6W 5-7cm	14322-06	11.00902	-0.00443	0.009	96.6	10.64	1.14577	1.17
1359 4H 6W 5-7cm	14322-01	0.37127	0.01391	0.017	74.6	72.59	0.83719	1.68
1359 4H 6W 5-7cm	14322-04	5.31803	0.04286	0.013	28.7	99.79	2.41708	3.13
1359 4H 6W 5-7cm	14322-14	20.69296	0.01125	0.003	61.5	190.00	4.07745	5.57
1359 4H 6W 5-7cm	14322-15	11.89873	0.06969	0.003	98.5	396.85	5.20922	9.49
1359 4H 6W 5-7cm	14322-03	14.46845	0.04248	0.004	95.8	447.61	3.923	9.77
1359 4H 6W 5-7cm	14322-08	9.38346	0.02646	0.009	98.5	479.29	2.43284	9.89
1359 4H 6W 5-7cm	14322-05	7.67965	0.02926	0.023	99.8	488.72	1.62234	9.91
1359 4H 6W 5-7cm	14322-10	9.82359	0.0115	0.072	99.8	1137.71	2.15193	22.86
1359 4H 6W 5-7cm	14322-12	0.1493	0.07682	0.004	96	3007.00	15.43108	62.09

4.5 Discussion

4.5.1 Provenance of fine-grained sediments

The Nd and Sr isotopic compositions of Pleistocene detrital sediments from IODP Site U1359 (ϵ_{Nd} : -11.4 to -13.3; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.720 to 0.725) overlap with those of Pliocene detrital sediments analysed from IODP Site U1361 (Figure 4.3), where the source has been identified as **Early Paleozoic granitoids** (see Chapters 2 and 3 for a detailed geological overview of the region) exposed in the hinterland of the *Ninnis and Mertz Glaciers* (Talarico and Kleinschmidt, 2003; Goodge and Fanning, 2010) (Figure 4.1). No Nd isotopic information is available for these particular granites, but sedimentary patterns indicate that detrital material supplied by these two glaciers (Roy et al. 2007; Goodge and Fanning, 2010; Pierce et al. 2011; Chapter 2) is conduited offshore to the study site via turbidites (Escutia et al. 2011; Presti et al. 2011). The range of Nd isotopic compositions measured for Pleistocene sediments agrees with those obtained for Holocene sediments from IODP Site U1359 (ϵ_{Nd} : -12.9; Chapter 2), nearby IODP Site U1361 (ϵ_{Nd} : -11.5; Chapter 2) and DF79-47 (ϵ_{Nd} : -12.4; Pierce et al. 2011). This suggests that fine-grained Pleistocene sediments are derived from the same sources area as Holocene sediments, i.e. local Early Palaeozoic granitoids.

4.5.2 Ice-rafted detritus provenance

The youngest and most abundant hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age population identified in IODP Site U1359 sediments (<50 Ma) is most likely derived from the Cenozoic **McMurdo Volcanic Group** (Figure 4.6; Chapter 3), located in the *Ross Sea and South Pacific*

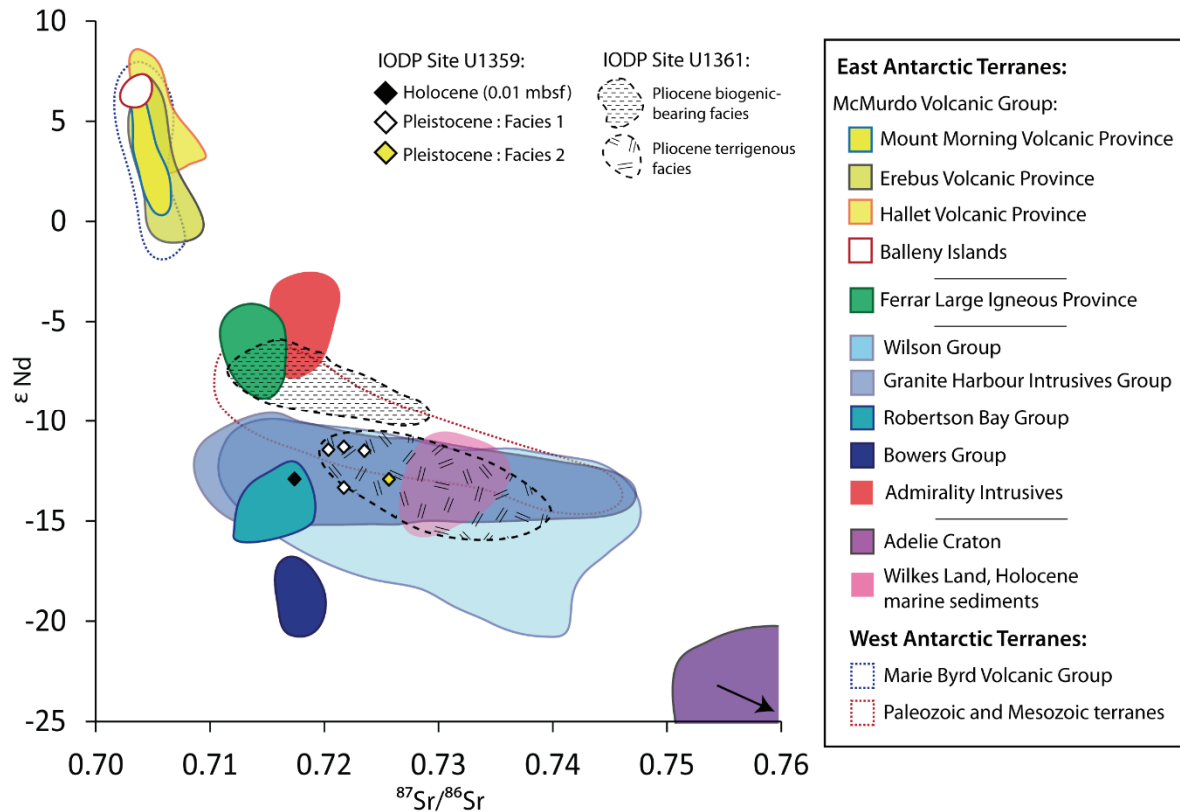


Figure 4.3. Neodymium and strontium isotopic composition of Pleistocene detrital sediments from IODP Site U1359 (errors are smaller than data points) and potential East and West Antarctic source terranes (see Chapters 2 and 3). See Figure 4.2 for lithologies and sample locations. East Antarctic terranes are presented in groups according to their age, with Cenozoic volcanic in yellow, Mesozoic basalts in green, Palaeozoic granitic source areas in blue and red, and Proterozoic to Archean terranes in purple and pink (see Figure 4.1). Hatched areas represent the Nd and Sr isotopic ranges measured for samples from Pliocene detrital sediments (data from Chapters 2 and 3). Note that all Pleistocene samples from IODP Site U1359 fall within the field of the Pliocene terrigenous facies, which in turn has been interpreted to be derived from the local Paleozoic source areas in the hinterland of the Ninnis Glacier (Chapters 2 and 3).

(Harrington, 1958; Kyle and Cole, 1974; Kyle et al. 1990; LeMasurier and Thomson, 1990), and/or from the **Marie Byrd Land Volcanic Province** located to the east of the Ross Sea in *West Antarctica* (Hole and Lemausier, 1994; Wilch and Mackintosh, 2000) (Figure 4.1). As most of hornblende grains analysed produced $^{40}\text{Ar}/^{39}\text{Ar}$ ages that were older than the depositional age of the sediment from which they were extracted (Figure 4.6), these hornblende grains were likely subglacially entrained in close proximity to the eruptive centres of the McMurdo Volcanic Group and/or the Marie Byrd Land Volcanic Province, as opposed

to being representative of explosive eruptive events that occurred contemporaneously with deposition of marine sediments.

The second largest, and oldest hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age population (1400 to 1950 Ma) in IODP Site U1359 sediments, is most likely sourced from the proximal Archean and Neoproterozoic **Adélie Craton**, which has a well constrained hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age population between 1450 and 1950 Ma (Di Vincenzo et al. 2007; Roy et al. 2007; Pierce et al. 2011; Chapter 3).

The Mesozoic to Late Paleozoic hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age population (80 to 290 Ma) identified in Pleistocene sediments from IODP Site U1359 is minor, but may be significant as it has no exposed analogue on the proximal East Antarctic continent. Whilst this age range may be associated with a currently unknown source from within the East Antarctic interior, it matches well with $^{40}\text{Ar}/^{39}\text{Ar}$ ages of detrital hornblendes in Holocene marine sediments offshore of Marie Byrd Land in West Antarctica (95 to 280 Ma; Roy et al. 2007). Supporting evidence for a Marie Byrd Land source is also provided by an excellent match with onland hornblende, muscovite and biotite $^{40}\text{Ar}/^{39}\text{Ar}$ ages and zircon U-Pb ages from Marie Byrd Land (95 to 125 Ma; Weaver et al. 1994; Luyendyk et al. 1996; Storey et al. 1999; Siddoway et al. 2005) (see Chapter 3 for a more detailed overview of a Marie Byrd Land source).

The 440 to 510 Ma aged hornblende grains identified in Pleistocene marine sediments at IODP Site U1359 corresponds to the Late Cambrian **Ross Orogeny** (460-560 Ma; Goodge, 2007 and references therein), a metamorphic overprint signature that is ubiquitous throughout most of Northern Victoria Land, Southern Victoria Land and the Transantarctic Mountains (Goodge, 2007). Onland geochronological studies based on $^{40}\text{Ar}/^{39}\text{Ar}$ ages of hornblendes and biotites, and U-Pb ages of zircons and monazites suggest that metasedimentary terranes in Northern Victoria Land (Goodge and Dallmeyer, 1992; Klee et al. 1990; Dallmeyer and Wright, 1992; Schussler et al. 1999) show slightly younger cooling histories (460-500 Ma) than those of Southern Victoria Land (480-550 Ma [Wysoczanski and Allibone, 2004; Goodge, 2007]) and the Central Transantarctic Mountains (480-545 Ma; Goodge, 2007). In addition, Early Paleozoic granites in the vicinity of the Ninnis Glacier can also contribute Ross Orogeny aged grains, as intrusive emplacement ages fall within the age range reported above (Goodge and Fanning, 2010). Holocene marine sediments located directly downstream of the Ninnis Glacier contain hornblende grains characterised by $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 480 and 560 Ma (Roy et al. 2007; Pierce et al. 2011). The youngest ages within the 440 to 510 Ma age population in IODP Site U1359 sediments (i.e. 440-460

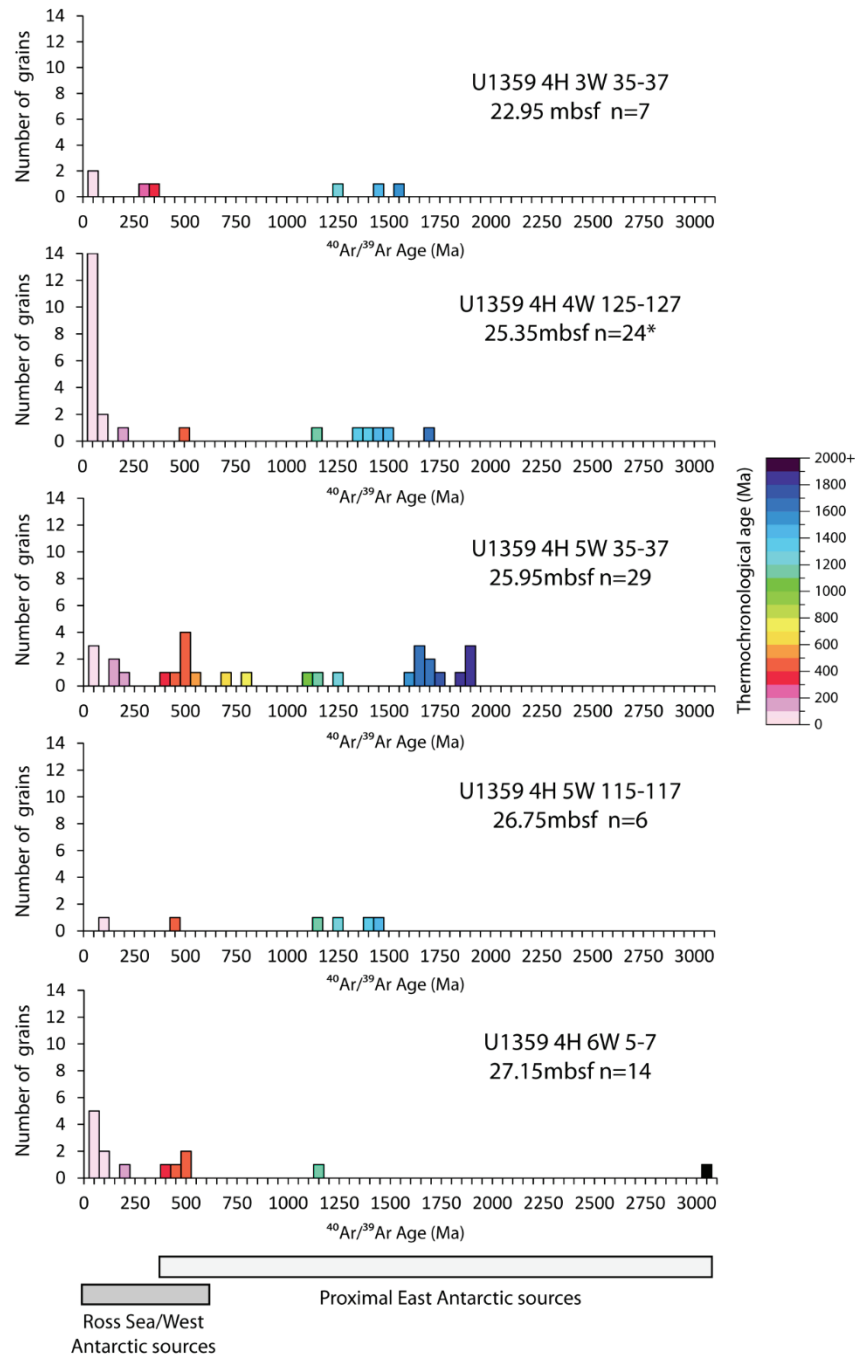


Figure 4.4. Histograms of $^{40}\text{Ar}/^{39}\text{Ar}$ age populations for ice-rafted hornblende grains analysed from five specific layers at IODP Site U1359 (see Figure 4.2). ‘n’ indicates the number of grains analysed, with age ranges coloured according to the scale bar to the right. Second sample from top (*) was potentially deposited during MIS 31, but could also be slightly older. Shown at the bottom is the approximate thermochronological age range of the two main sources for IRD supply: dark grey indicates ages that are most likely delivered from West Antarctica and the Ross Sea area (i.e. from the east), and light grey indicates ages that can be delivered from the continental margin proximal to IODP Site U1359.

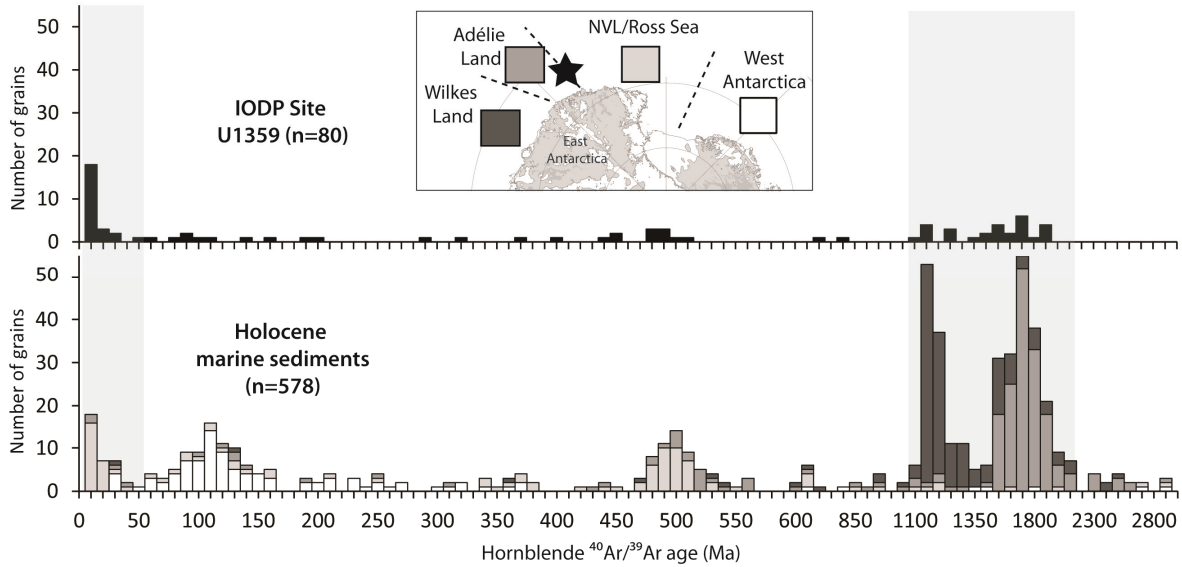


Figure 4.5. Comparison of hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age populations from Holocene marine sediments across the study area (Brachfeld et al., 2007; Roy et al., 2007; Pierce et al., 2011; Chapter 3), and Pleistocene sediments from IODP Site U1359 (this study). Holocene data are divided into four populations shown on the inset map: dark grey corresponds a Wilkes Land provenance sector (west of $\sim 135^\circ\text{E}$), mid-grey represents the Adélie Land provenance sector (135°E to 142°E), light-grey a Northern Victoria Land and western Ross Sea provenance sector (142°E to 195°E), and white a West Antarctica source (east of $\sim 200^\circ\text{E}$). IODP Site U1359 Pleistocene sediments (five individual samples; 80 hornblende grains analysed) are shown in black (top panel). The grey shading highlights the most abundant population within the Pleistocene samples, the Cenozoic population (0-50 Ma), and a more scattered age range from 1100 to 1900 Ma, representing Adélie Land.

Ma) represent a signature that is too young for the Ross Orogeny (Goodge, 2007), and may be instead associated with the Ordovician-Silurian Robertson Bay-Swanson Orogen proposed to comprise areas of Marie Byrd Land and the allochthonous Robertson Terrane in Northern Victoria. In summary, during the Pleistocene time interval around MIS 31, icebergs likely supplied Ross-aged hornblende grains to IODP Site U1359 from Northern Victoria Land, Southern Victoria Land, the Transantarctic Mountains and the local proximal coast.

Mesoproterozoic hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages (1000-1300 Ma) detected in low numbers in Pleistocene sediments at IODP Site U1359 have no known exposed analogue to the east of the Adélie Craton. However, this age range matches the $^{40}\text{Ar}/^{39}\text{Ar}$ ages of hornblende grains in Holocene marine sediments offshore of the *Wilkes Land margin* to the west of the Adélie Craton (Roy et al. 2007; Pierce et al. 2011). This metamorphic signature is thought to be related to the Mesoproterozoic **Grenville Orogeny** (Dalziel, 1991; Fitzsimons, 2000). It is

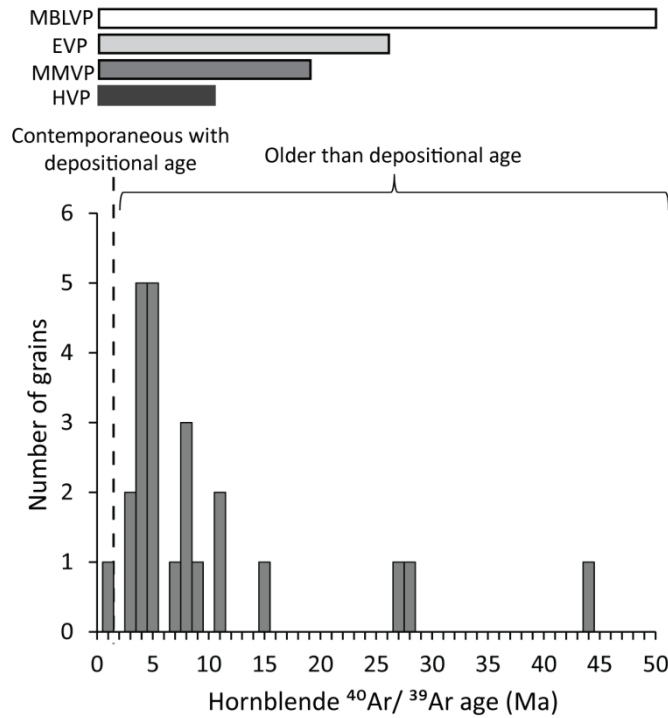


Figure 4.6. Histogram for the youngest hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age population from Pleistocene IODP Site U1359 sediments. Shown at the top are the known eruptive histories of the four main volcanic provinces of the McMurdo volcanic group: HVP: Hallet Volcanic Province; MMVP: Mount Melbourne Volcanic Province; EVP: Erebus Volcanic Province; MBLVP: Marie Byrd Land Volcanic Province. Not that the majority of all hornblende grains yield older ages than the depositional age, pointing to an ice-rafted origin of the hornblende grains.

possible that Mesoproterozoic aged hornblende grains in IODP Site U1359 may have been sourced from a currently hidden terrane within the continental interior of East Antarctica (Moores, 1991; Goodge et al. 2008, 2010) (see Chapter 3 for more detailed discussion of Grenville-aged hornblendes in Wilkes Land sediments).

4.6 Evidence for a More Stable and Potentially Larger Pleistocene East Antarctic Ice Sheet Relative to the Pliocene

Holocene sediments from four sites (IODP Sites U1361, U1358, and ELT37-06 and DF79-47, Roy et al. 2007; Pierce et al. 2011; Chapter 2), located in a proximal location to IODP Site U1359, were selected to compare Holocene (four sites cited above), Pleistocene (from IODP Site U1359, this study) and Pliocene (from IODP Site U1361, Chapter 3) IRD

provenance patterns through time (see Figure 4.7). These sites were selected due to their proximity to IODP Site U1359. Two of these sites are located on the continental shelf (IODP Site U1358, ELT37-06), and show provenance signatures dominated by material from the proximal Adélie Craton (1400-1950 Ma). Hence, when Holocene IRD provenance patterns from the above sites are combined, they may be biased towards an Adélie Craton source. This bias is further supported by a lack of old ages indicative of an Adélie Craton source at IODP Site U1361, the only distal site in a location adjacent to IODP Site U1359 (see Chapter 3). Despite this, ages within this Proterozoic age range occur in higher abundances in Pleistocene (19%) sediments, in contrast to Pliocene marine sediments in nearby IODP Site U1361 (2%). This increase in IRD supplied from the proximal Adélie Land margin could be explained by growth of ice volume through time, from a scenario of a margin retreated from its current location during the Pliocene (Chapters 2 and 3) to one more similar to the modern extent during the Pleistocene. Such a scenario is in contrast to the lack of Adélie Land derived IRD in Holocene sediments at IODP Site U1361. A potential mechanism to explain this discrepancy would be increased local erosion during MIS 31, potentially associated with a more dynamic local ice margin.

Evidence for advance of the East Antarctic ice sheet between ~1.2 and ~2.8 Ma can also be inferred from fine-grained sediment provenance patterns (Figure 4.3). The narrow range of Nd and Sr isotopic compositions for Holocene (Hemming et al. 2007; Roy et al. 2007; Pierce et al. 2011; Chapters 2 and 3) and Pleistocene sediments at IODP Site U1359 (ϵ_{Nd} : -11.4 to -13.3; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.720 to 0.725) is in contrast to the much larger Pliocene range of isotopic compositions at neighbouring IODP Site U1361 (ϵ_{Nd} : -5.9 to -14.7, $^{87}\text{Sr}/^{86}\text{Sr}$: 0.712-0.738) (Figure 4.3; Chapters 2 and 3). Pliocene sediment composition was likely controlled by alternations in the downslope supply of proximal Early Paleozoic material, and Mesozoic-aged material sourced from the Ferrar Large Igneous Province, supplied by meltwater plumes from within the low-lying Wilkes Subglacial Basin (Chapter 2). Pliocene sediments that trended towards this latter Jurassic endmember were deposited during periods of enhanced climatic warmth, which drove inland retreat of the East Antarctic ice sheet margin into the Wilkes Subglacial Basin (Chapter 2).

Pleistocene sediments at ODP Site U1359 are characterised by increased amounts of carbonate, possibly related to warmer interglacial conditions. However, in contrast to the Pliocene, interglacial warmth appears to have been insufficient to drive significant retreat of the East Antarctic ice sheet into the Wilkes Subglacial Basin. Hence, I infer that large-scale retreat of the East Antarctic ice sheet into the Wilkes Subglacial Basin did not occur during

the studied Pleistocene interval, and ended sometime between 1 Ma and 2.8 Ma. Interestingly, the lack of evidence for retreat into the Wilkes Subglacial Basin appears to be in contrast to ice sheet model results, which show a small amount of retreat of the East Antarctic ice sheet during MIS 31, similar in extent to retreat inferred for the warm Pliocene (Pollard and DeConto, 2009; DeConto et al. 2012).

Reconstructions of atmospheric CO₂ concentrations (Kurschner et al. 1996; Pagani et al. 2010; Seki et al. 2010; Bartoli et al. 2011) show a gradual decline by ~100 ppm from 4.1 to 2 Ma, coincident with the onset and intensification of Northern Hemisphere glaciation at ~2.75 Ma (Shackleton et al. 1984; Maslin et al. 1998; Kleiven et al. 2002; Haug et al. 2005; Mudelsee and Raymo, 2005; Lunt et al. 2008). This ‘Pliocene-Pleistocene transition’ (Ravelo et al. 2004) saw global ice volume increase by 22m of eustatic sea level equivalent (Sosdian and Rosenthal, 2009), a cooling of deep water masses by 2°C (Sosdian and Rosenthal, 2009) and intensification of glacial/interglacial cycles (Lisiecki and Raymo, 2005), with clear implications for the volumetric change of Antarctica’s ice sheets. Sedimentary records from the Ross Sea reveal evidence for major ice sheet expansion onto the continental shelf after 3.3 Ma (Naish et al. 2009), and evidence from proximal marine sediments for ice sheet growth in low-lying regions have been identified in the Prydz Bay area in the late Pliocene (e.g. O'Brien et al. 2007; see Chapters 5 and 6). Thus I infer that growth of the East Antarctic ice sheet along the Wilkes Land Margin took place between ~1.2 and ~2.8 Ma, likely associated with the Pliocene-Pleistocene transition.

4.7 Evidence for West Antarctic Ice Sheet changes during the Pleistocene?

Ice-rafted detritus in Pleistocene and Pliocene sediments is characterised by higher abundances of ice-rafted hornblende grains with Cenozoic ⁴⁰Ar/³⁹Ar ages (~3 to 50 Ma; Figure 4.7) than observed in Holocene sediments, indicating a source from the McMurdo Volcanic Group, or even the Marie Byrd Volcanic Province (Figure 4.1). These areas encompass the distal Ross Sea area and/or West Antarctica. The increase in far-travelled IRD at OPD Site U1359 is accompanied by a higher abundance of hornblende grains with Mesozoic to Late Paleozoic ⁴⁰Ar/³⁹Ar ages, likely sourced from Marie Byrd Land in West Antarctica. This observation is significant in the context of ice-sheet changes inferred for warm intervals during the Pleistocene. Sedimentary records from the Ross Sea provide evidence for retreat of the Ross Ice Shelf margin south of its current location during Pleistocene interglacials (Naish et al. 2009). In particular, MIS 31 may have seen larger-scale

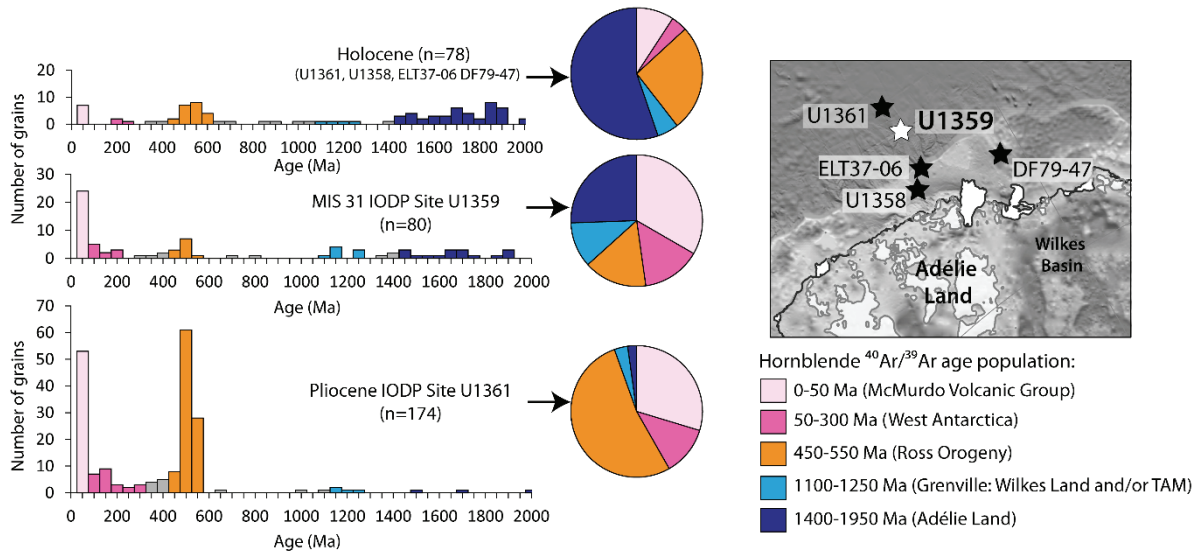


Figure 4.7. Histograms and pie charts illustrating hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age populations in margin sediments offshore the Adélie Coast through time (see text for information on selection of sites), coloured according to the colour bar on the right. Inset map shows the location of sites used for comparison. Note that the Holocene panel (top) comprises shelf and deep sea sites at the same time, while the MIS 31 and Pliocene panels (middle and bottom) are based on distal sites only. This distinction matters as all of the $>1400\text{Ma}$ ages in Holocene sediments are confined to the shelf area and none are found at IODP Site U1361 (Chapters 2 and 3).

collapse of the West Antarctic ice sheet (Naish et al. 2009; Pollard and DeConto, 2009; DeConto et al. 2012; McKay et al. 2012b).

There are some uncertainties as to where exactly the base of the Jaramillo subchron is located in IODP Site U1359 (somewhere between 24.54 to 24.71 mbsf; Figure 4.2). However, the carbonate-bearing unit from which the sample at 25.35 mbsf was taken is the first below the depth at which the chron boundary is inferred to be located, and it is therefore possible that this sample was deposited during MIS 31. Other samples were also derived from carbonate-bearing intervals, which can be interpreted to relate to neighbouring interglacials. In detail, the uppermost sample at 22.95 mbsf, which is associated with the top of the Jaramillo subchron (C1r.1n), can be correlated to MIS 27. The lower two samples from carbonate-bearing units, likely correspond to MIS 33 and 35, but these age assignments are less certain.

If the carbonate-bearing unit from which the sample at 25.35 mbsf was extracted does indeed correspond to MIS 31, it would be expected to see an increase in ice-rafted material

from the Ross Sea and Marie Byrd Land, as collapse of the West Antarctic ice sheet has been modelled for this time (e.g. Pollard and DeConto, 2009; DeConto et al. 2012). Intriguingly, of all the Pleistocene so far samples analysed from IODP Site U1359, this sample contains the highest abundance of ice-rafted hornblendes sourced from the McMurdo Volcanic Group (Ross Sea) and Marie Byrd Land volcanic (West Antarctica). This observation is particularly significant considering that sea surface temperatures in the Ross Sea during MIS 31 were up to 5°C warmer than today, as constrained by diatom assemblages (Scherer et al. 2008). These elevated temperatures suggest that in order for debris-laden icebergs from West Antarctica to survive transport over 2500km to the East Antarctic margin, West Antarctic iceberg production rates must have been significantly higher than today (see Chapter 5). Our new provenance constraints therefore provide possible evidence for dynamic behaviour of the West Antarctic ice sheet during MIS 31, but refinement of the age model by orbital tuning is required to support this interpretation.

4.8 Conclusion

Analyses of the provenance of Pleistocene marine sediments deposited around the time of super-interglacial MIS 31 at IODP Site U1359 offshore the Adélie Land margin of East Antarctica hint at potential evidence for large-scale dynamic behaviour of the West Antarctic ice sheet. Although the age model for this site requires refinement, and more provenance analyses are desirable, existing $^{40}\text{Ar}/^{39}\text{Ar}$ age data on ice-rafted hornblende grains point to prominent far-travelled IRD from the Ross Sea and West Antarctica during MIS 31. Fine grained sediment provenance signatures, in contrast, indicate sediment supply patterns similar to those of the modern day, which argues against significant retreat of the East Antarctic ice sheet during interglacials. Taken together with the Pliocene results presented in Chapter 2, expansion of the East Antarctic ice sheet probably took place between ~2.8 and ~1 Ma. An interesting puzzle in this regard is the increased abundance of local IRD from the Adélie Land margin, a feature which is neither observed during the warm Pliocene nor during the Holocene at IODP Site U1361, located very proximal to IODP Site U1359. Future studies on additional core top samples in the region, as well as on more samples from around MIS 31, and improvement of the age model of IODP Site U1359 are needed to substantiate the interpretations presented here.

CHAPTER 5

Increased iceberg production and growth of the East Antarctic Ice Sheet during the Late Pliocene

Chapter Summary

Investigations into the provenance of ice-rafted detritus (IRD) in Southern Ocean marine sediments can provide vital information about the locations of dynamic ice sheet behaviour in the geological past. The Pliocene Epoch, from 2.58 to 5.33 Ma, was characterised by a long term global cooling trend punctuated by several intervals of enhanced climatic warmth with global temperatures and pCO₂ levels similar to those predicted for the near future. However, the response of the East Antarctic ice sheet (EAIS) to these variable climatic conditions is poorly understood, even though low lying regions, such as the Aurora Subglacial Basin, located in Wilkes Land, East Antarctica, may have played a significant role in contributing to elevated Pliocene sea level.

In this chapter, I present a detailed IRD provenance study of 21 individual IRD layers from ODP Site 1165 (64°22'77"S, 67°13'14"E; Prydz Bay, East Antarctica) that span the Pliocene. By comparing ⁴⁰Ar/³⁹Ar ages of ice-rafted hornblende grains (>150µm) to known thermochronological ages from outcrops, I can identify two distinct IRD sources. Prior to ~3.27 Ma, hornblende grains indicate a predominant supply from the local Prydz Bay region (⁴⁰Ar/³⁹Ar ages of 455 to 575 Ma). After ~3.27 Ma, IRD supply from the distal Wilkes Land margin significantly increases (⁴⁰Ar/³⁹Ar ages of 1035 to 1315 Ma), with the highest amounts of this distally sourced material found between ~2.65 and ~3.27 Ma (up to 55% of all ice-rafted hornblende grains). Levels of Wilkes Land IRD deposited during the Pleistocene remain high compared to the Early Pliocene, although Pleistocene sample resolution is low.

Initially, these results appear counter-intuitive, as increased iceberg supply from the Aurora Subglacial Basin, in Wilkes Land, may be expected as a result of destabilisation of the EAIS during the warm Early Pliocene, and not during the cooler conditions of the Late Pliocene. ODP Site 1165 is however located over 1500 km to the west of the Wilkes Land margin, suggesting any changes in sea surface temperatures (SST) may have had an impact on the survivability of Early Pliocene icebergs supplied from this distal location.

To better constrain the role of SST on changing IRD provenance patterns, I collaborated with colleagues from Leeds University to develop an iceberg drift model. The model generates icebergs from multiple glaciers along the East Antarctic margin and predicts both their trajectory in the Southern Ocean under modern wind fields, and how far they will travel before melting. Sensitivity tests were run for a range of SST scenarios between 1 and 8°C warmer than pre-industrial levels. Results suggest that a modest warming of up to 2°C in local SSTs may result in an increase in the number of icebergs sourced from the distal Wilkes

Land margin melting over ODP Site 1165. In contrast, temperatures above 2°C drive a decrease in the amount of Wilkes Land icebergs melting at IODP Site 1165, implying shorter iceberg survival rates. These general trends are in agreement with observed Pliocene IRD provenance patterns, as our data indicate an increase in distally sourced Wilkes Land IRD in conjunction with regionally declining SST after ~3.3 Ma.

Some Pliocene intervals are however characterised by higher provenance variability than SST sensitivity tests can account for (~3.1 Ma, ~3.2 Ma and between ~4.6 Ma and ~4.75 Ma). This observation hints at the influence of additional factors, such as glacial-interglacial variations in SSTs and iceberg flux, and iceberg sediment loading. In detail, between ~4.6 to ~4.75 Ma, IRD provenance patterns appear to closely match the global benthic oxygen isotopes stack and hence global ice volume. Marine Isotope Stages N7, N9 and NS1 (interglacials) are seemingly characterised by increased supply of Wilkes Land IRD, suggesting the EAIS margin produced large quantities of icebergs, possibly due to ice sheet destabilisation in the Aurora Subglacial Basin in response to climatic warmth during interglacials. The younger layers (~3.1 and ~3.2 Ma) appear to correspond to the Late Pliocene interglacials KM1 (~3.08 Ma) and KM5 (~3.19 Ma), when SSTs were cooler and the EAIS was larger compared to the Early Pliocene, leading to an even more pronounced Wilkes Land provenance signal at ODP Site 1165.

5.1 Introduction

The Cenozoic evolution of the Antarctic ice sheet since its inception ~34 million years ago has been well-documented using benthic oxygen isotope records (e.g. Shackleton, et al. 1984; Zachos et al. 2001; Pekar and DeConto, 2006; Miller et al. 2005, 2012), sea level estimates (e.g. Dowsett and Cronin, 1990; Miller, 1996, 1998; Naish and Wilson, 2009), and ice sheet modelling (e.g. DeConto and Pollard, 2003; DeConto et al. 2007, 2008; Golledge et al. 2012).

While ice volume on Antarctica changed throughout the Cenozoic, the Pliocene Epoch has emerged as a time interval of particular interest, due to its potential similarity to expected climatic conditions for the next century (Jansen et al. 2007). The Early Pliocene (3.60 to 5.33 Ma) was characterised by mean global temperatures 2 to 4°C higher than today (Haywood et al. 2009; Pagani et al. 2010; Fedorov et al. 2013), with estimates for pCO₂ between 250 and 450 ppm (Seki et al. 2010; Pagani et al. 2010, Bartoli et al. 2011). Eustatic sea level estimates for highstands during this time have been reconstructed from

paleoshorelines (Naish and Wilson, 2009; Raymo et al. 2011) and benthic oxygen isotope records (Dwyer and Chandler, 2009; Miller et al. 2012), and range between 5 and 40 metres higher than today, with a current best estimate of $22 \pm 10\text{m}$ (Miller et al. 2012). These estimates imply that complete melting of West Antarctica's and Greenland's ice sheets (i.e. $\sim 12\text{m}$ of global sea level equivalent [Houghton et al. 2001; Fretwell et al. 2013]) during the most extreme highstands may have been accompanied by significant retreat of the much larger EAIS ($\sim 54\text{m}$ of global sea level equivalent [Fretwell et al. 2013]). The warmth of the Early Pliocene ended around $\sim 3.3\text{ Ma}$ and was followed by a long term cooling trend, accompanied by Antarctic ice growth and global sea level fall, ultimately leading into the high-amplitude climate variability characteristic of the Late Pleistocene (Lisiecki and Raymo, 2005).

Proximal evidence for the response of Antarctica's ice sheets to Early Pliocene warmth is recorded in Ross Sea sediments (Naish et al. 2009), which suggest that repeated collapse of the Ross Ice Shelf and retreat of the West Antarctic ice sheet (WAIS) took place during this time (DeConto and Pollard, 2009). Early Pliocene destabilisation of the WAIS was accompanied by repeated retreat events of the EAIS into the nearby Wilkes Subglacial Basin, as inferred from sediment provenance patterns in nearby offshore marine sediments (Chapters 2 and 3). Further evidence for contemporaneous retreat of the EAIS in Prydz Bay is derived from marine sediments of the Pagodroma Group, deposited south of the modern Amery Ice Shelf front (Hambrey and McKelvey, 2000; McKelvey et al. 2001; Whitehead et al. 2004), along with Early Pliocene deposition of the marine sediment Sørsdal Formation inland at the Vestfold Hills to the east of Prydz Bay (Quilty, 1992; Adamson and Pickard, 1993; Harwood et al. 2000). The end of the Early Pliocene warmth and the beginning of Late Pliocene cooling in proximal East Antarctic marine sediments is characterised by major ice sheet advance in the Ross Sea and Prydz Bay regions after 3.3 Ma (O'Brien et al. 2007; Naish et al. 2009; Passchier, 2011; Chapter 6).

Recently, Williams et al. (2010a) published a pilot study on the $^{40}\text{Ar}/^{39}\text{Ar}$ ages of individual ice-rafted hornblende grains ($>150\mu\text{m}$) from 11 IRD layers at Ocean Drilling Program Site 1165 ($64^{\circ}22'77''\text{S}$, $67^{\circ}13'14''\text{E}$; offshore of Prydz Bay, East Antarctica; Figure 5.1), in order to constrain Pliocene to Miocene ice dynamics in the region. Five IRD layers from this study were retrieved from Pliocene sediments (one at $\sim 3.5\text{ Ma}$, and four between ~ 4.6 and $\sim 4.75\text{ Ma}$), and their provenance patterns were interpreted to represent major iceberg armada events, released from the vicinity of the low-lying Aurora Subglacial Basin (see Figure 5.1 for location) into the Southern Ocean during episodes of EAIS destabilisation.

The massive Aurora Subglacial Basin, located inland of the Wilkes Land margin, extends ~1000km from the coast to the continental interior, and is ~287,000 km² in area (Young et al. 2011; Wright et al. 2012). The EAIS today sits within the Aurora Subglacial Basin, reaching in places up to 4.5 km in thickness (Young et al. 2011; Wright et al. 2012). At the mouth of the basin is the Totten Glacier, which is notable in modern observations for being one of the fastest accelerating glacier systems in East Antarctica (Rignot, 2006). More than 20% of the EAIS within the Aurora Subglacial Basin lies at least 1km below sea level, but 400 to 700km inland from the Wilkes Land margin, in the immediate vicinity of the Totten Glacier, the basin reaches up to 2.4 km below sea level (Young et al. 2012). It seems very likely that this large basin was therefore a likely location for EAIS retreat in the past (e.g. Young et al. 2012), similar to the Wilkes Subglacial Basin (Chapters 2 and 3), but no direct records exist to reveal the behaviour of the ice sheet in this region. However, ice sheet modelling suggests that the EAIS retreated within the Aurora Subglacial Basin during Pliocene warmth, from between ~200 km inland of the current ice margin (~3m contribution to global sea level rise; Pollard and DeConto, 2009) to ~800km inland of the current ice margin (~16m of global sea level rise from the EAIS; Dolan et al. 2011; see also Hill et al. 2007). Additionally, recent airborne geophysical surveys indicate that the subglacial topography of the Aurora Subglacial Basin was formed by a retreated ice sheet margin (Young et al. 2012).

In this chapter I present a new high-resolution IRD provenance record, based on ⁴⁰Ar/³⁹Ar ages of individual ice-rafted hornblende grains (>150µm) from 21 Pliocene sediment layers deposited at ODP Site 1165. This new data set is the first of its resolution, and provides unprecedented insights into Pliocene EAIS stability in the Prydz Bay and the Wilkes Land area in proximity to the Aurora Subglacial Basin. Climatic interpretation of the provenance record is furthermore substantiated by results derived from iceberg trajectory modelling under various sea surface temperature (SST) conditions.

5.2 Geological Overview

A necessary prerequisite for any provenance interpretation of detrital marine sediments is a detailed understanding of the geological characteristics of potential continental source areas. The overview presented here builds upon the review presented in Williams et al. (2010a), and provides an outline of the lithologies and thermochronological histories of

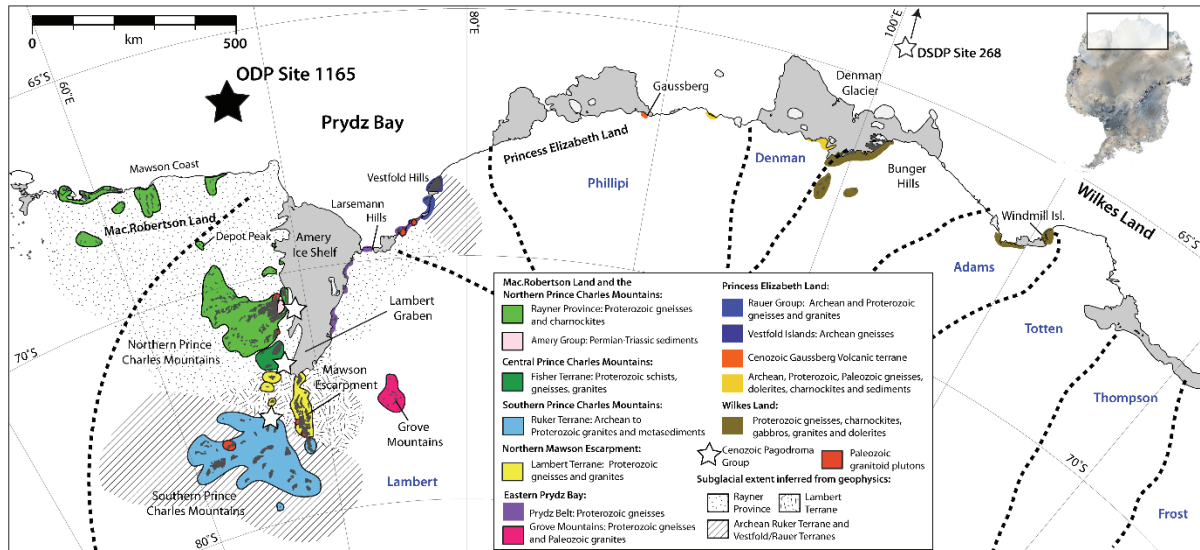


Figure 5.1. Geological map of the Prydz Bay and Wilkes Land regions (modified from Mikhalsky, 2010; Boger, 2011), showing the locations of ODP Site 1165 and DSDP Site 268 in the Southern Ocean. Black areas represent outcrops. Inferred subglacial extent of terranes is from McLean et al. (2009). Ice shelves are shown in dark grey. For more details on geology see text. Blue dashed lines represent the drainage basins of major glacier systems regionally, with corresponding glacier names in blue (from Rignot et al. 2011).

known bedrock terranes with the Prydz Bay and Wilkes Land regions of East Antarctica, compiled from published information on outcrops, along with their potential subglacial extents as inferred from tectonic conjugate correlatives, and crustal gravity and magnetic anomalies provided by airborne geophysics (see Figure 5.1). Wherever possible, individual mineral grain $^{40}\text{Ar}/^{39}\text{Ar}$ ages are presented, and where this information is unavailable, zircon U-Pb ages are given (Figure 5.2). Areas to the west of Prydz Bay are not included in this review as they are unlikely to contribute to sediment provenance signatures at ODP Site 1165, as discussed in more detail in Section 5.6.4.

Overall, the East Antarctic shield in the area of Prydz Bay and Wilkes Land is comprised of several Archean to Cambrian-aged crustal blocks and pervasive high-grade metamorphic belts, produced during the formation and break-up of Rodinia and Gondwana: the Proterozoic Grenville orogeny identified in the Rayner Province (900-990 Ma) in the Prydz Bay region, and in the Wilkes Land region (1130-1310 Ma), and the Paleozoic Pan-African orogeny in the Prydz Bay region (400-600 Ma) (e.g. Moores, 1991; Dalziel, 1991; Fitzsimons et al. 1997; Fitzsimons, 2000a, 2000b, 2003; Goodge, 2003; Meert, 2003; Mikhalsky et al. 2007; Veveers et al. 2008; Boger et al. 2011).

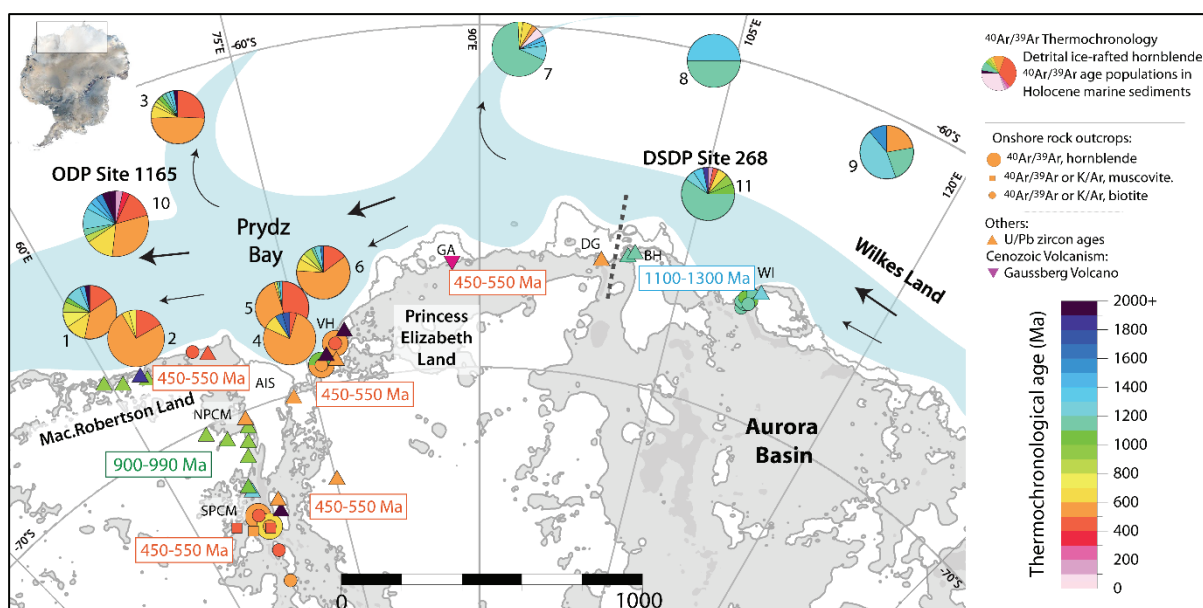


Figure 5.2. Map of study area, highlighting the general agreement between onshore (symbols) and offshore (pie charts) IRD thermochronology. Onshore data are based on $^{40}\text{Ar}/^{39}\text{Ar}$ ages of individual hornblende and mica grains and U-Pb dating of zircons (different symbols). Data sources: Black et al. (1991), Young and Black (1991), Sheraton et al. (1992, 1993), Takigami et al. (1992), Post et al. (1996), Young et al. (1997), Carson et al. (2000), Boger et al. (2000, 2001), Möller et al. (2002), Tong et al. (2002), Halpin et al. (2005), Liu et al. (2006, 2007a), Wilson et al. (2007), Phillips et al. (2007), Corvino et al. (2008, 2011). Values shown in boxes represent the age ranges for the most recent major tectonic event in different areas. The stipple line around 100°E marks the geological boundary between older overprint ages to the east (i.e. Wilkes Land), and younger ages in the Prydz Bay area to the west. Shading on the continent outlines the subglacial topography from BEDMAP 2 (Fretwell et al., 2013) with white areas marking highlands and grey areas marking areas below sea floor. Offshore data are based on $^{40}\text{Ar}/^{39}\text{Ar}$ ages of individual hornblende grains from Holocene marine sediments: 1 – RC17-15 (Roy et al. 2007), 2 – JPC 34 (Brachfeld et al. 2007), 3 – ELT47-14 (Roy et al. 2007), 4 – JPC 25 (Brachfeld et al. 2007), 5 – ODP Site 1166 (Roy et al. 2007), 6 – ELT 47-07 (Roy et al. 2007), 7 – ELT49-30 (Pierce et al. 2011), 8 – ELT50-13 (Roy et al. 2007), 9 – ELT50-16 (Roy et al. 2007), 10 – ODP Site 1165 (this study), 11 – DSDP Site 268 (Williams et al. 2010a). Blue shading offshore represents the approximate transport regions and pathways of icebergs (Antarctic Iceberg Tracking Database [1978–2012]; available at <http://www.scp.byu.edu/data/iceberg/database1.html>). Larger arrows represent the highest concentration of icebergs, along trajectories where surface currents are stronger. NPCM: Northern Prince Charles Mountains, SPCM: Southern Prince Charles Mountains, AIS: Amery Ice Shelf, VH: Vestfold Hills, GA: Gaussberg Volcanic field, DG: Denman Glacier, BH: Bunger Hills, WI: Windmill Islands.

The Rayner Province of Mac.Robertson Land and the Northern Prince Charles Mountains

Exposed bedrock units along the *Mac.Robertson Land* (MRL) coast and inland are part of the regionally extensive high-grade Neoproterozoic **Rayner Province** (e.g. Black et al. 1987a; Young et al. 1997; Boger et al. 2000; Fitzsimons, 2000b). Outcrops are composed of Proterozoic gneisses and charnockites (Young and Black, 1991; Boger et al. 2000; Carson et al. 2000; Kelly et al. 2002), with Neoproterozoic intrusions and associated high-grade metamorphism recorded with peak conditions between 910 and 990 Ma (zircon U-Pb) (Young and Black, 1991; Boger et al. 2000; Carson et al. 2000; Kelly et al. 2002; Halpin et al. 2007). Only limited $^{40}\text{Ar}/^{39}\text{Ar}$ data are available for this terrane, with whole rock $^{40}\text{Ar}/^{39}\text{Ar}$ ages of charnokites of ~475 Ma, and K-feldpars ages between 443 and 450 Ma (Takigami et al. 1992). Evidence for high-grade Paleozoic overprinting is corroborated by zircon U-Pb ages in granites between 500 and 550 Ma (Manton et al. 1992; Takigami and Funaki, 1991; Takigami et al. 1992).

Consistent with the sparse onland thermochronology, marine sediments deposited in continental shelf areas along MRL contain ice-rafted hornblende grains with predominant $^{40}\text{Ar}/^{39}\text{Ar}$ ages of 490 to 550 Ma (Brachfeld et al. 2007; Roy et al. 2007) (Figure 5.2). Similar Paleozoic hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages can be found in the Eastern Ghats of India (~500 Ma, Mezger and Cosca, 1999), which is inferred to be the Rodinia conjugate margin to Mac.Robertson Land (e.g. Merger and Cosca. 1999; Boger et al. 2000; Fitzsimons, 2000a; Boger et al. 2011),

Bedrock in the *Northern Prince Charles Mountains* (NPCM) (~70-72°S, ~60-70°E), in the western region of Prydz Bay, also comprises the Rayner Province, here consisting of a Late Mesoproterozoic sequence of gneisses and charnockites with a pervasive Neoproterozoic overprint signature (900-990 Ma, zircon U-Pb) (Young and Black, 1991; Manton et al. 1992; Kinny et al. 1997; Boger et al. 2000; Carson et al. 2000; Mikhalsky et al. 1999), similar to bedrock in MRL. In fact, the Rayner Province is inferred from magnetic anomaly patterns to extend from MRL to the NPCM, west to ~64°E from the NPCM, and south to the Southern Prince Charles Mountains (SPCM) (Golynsky et al. 2002; McLean et al. 2009) (Figure 5.1). Bedrock in the NPCM's appears to have been only minimally overprinted by the Paleozoic Pan-African tectonic event, evidence for which has been identified in high-strain zones and limited granite intrusions (Manton et al. 1992; Zhou and Hensen 1995; Carson et al. 1996; Hensen et al. 1997; Scrimgeour and Hand, 1997; Fitzsimons et al. 1997; Zhao et al. 1997; Boger et al. 2002). In addition to Precambrian

bedrock, Permian and Triassic-aged strata of the Amery Group (Webb and Fielding, 1993) are also present in the most easterly region of the NPCM, along with Cretaceous and Cenozoic-aged marine and glaciomarine sediments of the Pagodroma group (McKelvey et al. 2001; Whitehead et al. 2004).

The central Prince Charles Mountains

To the south of the NPCM, in the *central Prince Charles Mountains* (CPCM) lies the **Fisher Terrane**, a ~300km wide southwest trending domain consisting of Proterozoic schists, gneisses and granitoids (Mikhalsky et al. 1996). Zircon U-Pb ages record crystallisation of intrusive rocks between ~1200 Ma and 1300 Ma (Beliatsky et al. 1994; Kinny et al. 1997; Mikhalsky et al. 2001), and a later stage of alteration associated with intrusions emplaced between ~1020 and 1050 Ma (Boger et al. 2000; Carson et al. 2000; Mikhalsky et al. 2001a, 2001b). Only limited Paleozoic signatures have been identified in the Fisher Terrane, associated with granites intruded between 530 and 550 Ma (zircon U-Pb, Mikhalsky et al. 2007).

The Southern Prince Charles Mountains and the Mawson Escarpment

The *Southern Prince Charles Mountains* (SPCM), along with the southern-most region of the *Mawson Escarpment* (Figure 5.1) are composed of the **Ruker Terrane**, an Archean felsic crystalline basement unit intruded by granites (~3160 Ma, zircon U-Pb; Boger et al. 2001), and subsequently metamorphosed in the Late Archean (2780-2800 Ma, zircon U-Pb; Boger et al. 2006, Phillips et al. 2006, 2007, 2009; Mikhalsky et al. 2006, 2010). In addition, Late Archean pegmatites (~2650 Ma, zircon U-Pb; Boger et al. 2006) and Archean to Mesoproterozoic-aged metasedimentary rocks comprise parts of this terrane, which was affected by medium-grade overprint of Early Paleozoic age (Boger and Wilson, 2005; Phillips et al. 2007, 2009). This final metamorphic event is well recorded by hornblende, biotite and muscovite $^{40}\text{Ar}/^{39}\text{Ar}$ ages to have taken place between 486 and 530 Ma (Phillips et al. 2007).

The **Lambert Terrane** lies in the northern region of the *Mawson Escarpment* between 72.3°S and 73.3°S, and is composed of Paleoproterozoic gneisses (2420-2480 Ma, zircon U-Pb; Phillips et al. 2006, Mikhalsky et al. 2006) characterised by a later high-grade recrystallisation event possibly associated with emplacement of numerous pegmatitic dykes

(2100-2180 Ma, Mikhalsky et al. 2006, 2007, 2010). The Lambert Terrane was subsequently affected by multiple cross-cutting granite dykes and high-grade deformation between 900-940 Ma, associated with formation of the Rayner Province (zircon U-Pb, Corvino et al. 2008, 2011; monazite U-Pb, Phillips et al. 2009). Lastly, the Lambert Terrane shows signs of a pervasive Paleozoic high-grade deformation, as recorded by $^{40}\text{Ar}/^{39}\text{Ar}$ ages of micas (495-585 Ma: Phillips et al. 2007) and granitic dykes (470-590 Ma; Mikhalsky et al. 2006; Corvino and Henjes-Kunst, 2007; Boger et al. 2001, 2008).

The Grove Mountains and Eastern Prydz Bay area

A Paleozoic overprint event has also been recognised in the *Grove Mountains* to the south-east of Prydz Bay (Liu et al. 2007a) (Figure 5.1), where bedrock has been proposed to be geologically analogous to the Rayner Province in the NPCM (Hensen and Zhou, 1995; Harley et al. 1998; Wang et al. 2008). The Grove Mountains are composed of Mesoproterozoic orthogneiss basement overlain by high-grade paragneiss, with zircon crystallisation U-Pb ages of 910 to 1170 Ma (Kinny et al. 1993; Liu et al. 2007a), and also contain abundant orogenic Paleozoic granitoids and metamorphic signatures related to the Pan-African Orogeny (~500 Ma, zircon U-Pb, Liu et al. 2006).

The **Prydz Belt** is exposed along the eastern flank of the *Lambert Graben* and the Amery Ice Shelf, and is comprised of Mesoproterozoic orthogneiss (zircon U-Pb, ~1100 Ma; Hensen and Zhou, 1995; Zhao et al. 2003) and Neoproterozoic paragneiss (930-990 Ma, zircon U-Pb; Zhao et al. 1995; Liu et al. 2007b), a similar age range to the Rayner Province of the NPCM (Stuwe and Hand, 1992; Mikhalsky et al. 2001b; McLean et al. 2009). However, evidence for major high-grade Paleozoic metamorphism and intrusions of granites is also present, inferred to have taken place between 490 and 550 Ma (Carson et al. 1996; Hensen and Zhou, 1995; Fitzsimons et al. 1997; Liu et al. 2007b, 2009). Sampling of early structural features for $^{40}\text{Ar}/^{39}\text{Ar}$ ages of hornblende grains record a Proterozoic age of 1036 Ma (Tong et al. 1998), whereas $^{40}\text{Ar}/^{39}\text{Ar}$ ages of biotites from later and more predominant structural features show Early Palaeozoic ages (485-500 Ma) (Zhao et al. 1992; Tong et al. 2002).

Princess Elizabeth Land (73 to 89°E)

Similar to the Rayner Province, the **Rauer Group** (Harley, 2003), located to the east of the Prydz Belt in *Princess Elizabeth Land*, represents a region of high-grade metamorphic rocks that were potentially part of the same Neoproterozoic high-grade orogenic terrane of the Rayner Province with a peak metamorphic age range of 900-990 Ma (Kinny et al. 1993; Carson et al. 2000; Fitzsimons, 2000b; Boger et al. 2000). The Rauer Group also consists of Archean gneisses (2800-2850 Ma, >3300 Ma, zircon U-Pb; Harley et al. 1998), which were intruded by Mesoproterozoic mafic dykes and a Neoproterozoic paragneiss (~1000 Ma, zircon U-Pb and plagioclase $^{40}\text{Ar}/^{39}\text{Ar}$; Tong et al. 2002; Tong and Wilson 2006). It was later intruded by granites and affected by high-grade metamorphic overprint associated with the Pan-African tectonic event ($^{40}\text{Ar}/^{39}\text{Ar}$ hornblendes and biotites, 500-510 Ma; Wilson et al. 2007). Importantly, while marine sediments offshore of the Amery Ice Shelf and Princess Elizabeth Land show two peaks in U-Pb ages of detrital zircons of 512 to 540 Ma and 800 to 1100 Ma (Tochilin et al. 2012), hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages date between 450 and 550 Ma, with a distinct lack of 1000 to 1300 Ma aged grains (Roy et al. 2007; van de Flierdt et al. 2008; Tochilin et al. 2012; Figure 5.2). This observation suggests that metamorphism associated with the Pan-African orogeny dominates the thermochronological $^{40}\text{Ar}/^{39}\text{Ar}$ age spectrum in the Prydz Bay area.

The **Vestfold Hills**, to the east of the Rauer Group, represent a basement unit dominated by Archean high-grade gneisses intruded by Mesoproterozoic mafic dikes (Black et al. 1991; Dirks et al. 1994), with U-Pb zircon ages ranging between 2475 and 2526 Ma (Black et al. 1991; Zhao et al. 1992; Wilson et al. 2007), and 490 to 550 Ma (Hensen and Zhou, 1995). Geophysical surveys suggest that the tectonic block that contains both the Rauer Group and Vestfold Hills extends some 200km south from their coastal exposures into the continental interior (Golynsky et al. 2002; McLean et al. 2009).

To the east of the Vestfold Hills and adjacent to the Philippi Glacier (Figure 5.1), sits the extinct and isolated **Cenozoic Gaussberg Volcano** (67°48'S, 89°11'E), consisting of highly potassic leucites and lamproites (Sheraton and Condari, 1980; Murphy et al. 2002).

Wilkes Land (90-160°E)

Outcrops along the coast of East Antarctica along *Wilkes Land* are very sparse, with only limited exposure in the vicinity of the *Denman Glacier* (~100°E), the nearby *Bunger Hills*, and the *Windmill Islands* (~110°E). Outcrops within the vicinity of the Denman Glacier

consist of Archean gneisses, Neoproterozoic charnockite and dolerite intrusions, and later Paleozoic plutons (~515 Ma, zircon U-Pb; Black et al. 1992), sandstones and siltstones (Black et al. 1992). The most easterly extent of Paleozoic (Pan-African) tectonic deformation is inferred to lie between the Denman Glacier and the Bunger Hills (Black et al. 1992). This interpretation is supported by the presence of a linear crustal magnetic anomaly that lies between the Bunger Hills and the Denman Glacier (Golynsky et al. 2002). This feature possibly represents the continuation of the Darling Fault in SW Australia, which marks the western boundary of the Proterozoic Albany-Fraser Orogeny (Clarke et al. 1995; Clark et al. 2000; Boger, 2011) (Figure 5.2).

Exposures in the Bunger Hills are primarily composed of Proterozoic high-grade gneisses, with U-Pb zircons recording peak metamorphism at ~1190 Ma (Stuwe and Powell, 1989; Black et al. 1992; Sheraton et al. 1990, 1993). The gneisses were subsequently intruded by granites and minor gabbros (1150-1170 Ma) and dolerite dykes (~1140 Ma; Sheraton et al. 1993).

Similarly, the Windmill Islands area consists of Proterozoic gneisses intruded by charnockites, and by later dolerite dykes and gabbro (Paul et al. 1995; Post et al. 1996, 2000; Möller et al. 2002; Zhang et al. 2012). Bedrock here represents part of a Mesoproterozoic orogenic belt characterised by zircon U-Pb ages of two distinct deformation events at 1180 to 1258 Ma and 1300 to 1372 Ma, respectively (Post 1996, 2000). These ages correspond with U-Pb zircon ages from the Albany-Fraser Orogeny of SW Australia (two stages of orogenesis: 1140 to 1215 Ma, and 1260 to 1340 Ma; Clarke et al. 1995; Nelson et al. 1995; Duebendorfer, 2002).

Despite sparse outcrops, detrital zircons from moraine sediments along the Wilkes Land margin are dominated by U-Pb ages between 1107 and 1368 Ma (Zhang et al. 2012), indicating that inland areas have subglacial rock compositions similar to those of exposed bedrock at the Windmill Island, with no evidence for significant Pan-African tectonism or magmatism. This is confirmed by modern marine sediments offshore of the Wilkes Land margin, which are dominated by hornblende grains with $^{40}\text{Ar}/^{39}\text{Ar}$ ages of 1100 to 1300 (Roy et al. 2007, Pierce et al. 2011) (Figure 5.2).

Summary

In summary, a detailed review of published geological information from bedrock exposed in the area from ~60°E to 120°E reveals two distinct tectono-metamorphic signatures

with characteristic $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende ages: (i) Paleozoic Pan-African signatures of the MRL coast, the Prydz Bay area (which consists of the CPCM, SPCM, the Mawson Escarpment, the Grove Mountains and the Eastern flank of the Lambert Graben) and the Princess Elizabeth Land coast, and (ii) Proterozoic signatures of the Wilkes Land margin to the east of Denman Glacier (1100 to 1300 Ma) (Figure 5.2).

5.3 Study Sites

Ocean Drilling Program (ODP) Site 1165 was drilled in 3537m water depth from the West Wind Drift, ~400km northwest of Prydz Bay (Figs. 5.1 and 5.2) during Expedition 188. It contains 999m of near continuous sediment strata, a record spanning the last 21 Myrs (Florindo et al. 2003). The top ~50mbsf contain a stratigraphic record of Pliocene and Pleistocene terrigenous and hemipelagic deposition (Warnke et al. 2004) (Figure 5.3). The lithostratigraphy of this interval consists of alternating green and grey diatom-bearing silty clays, diatom-rich clay and diatom ooze, with dispersed sand grains and dropstones (Warnke et al. 2004) (Figure 5.3). Sediments between 33 and 50 mbsf are relatively silt-rich and characterised by 2-5m fluctuations in terrigenous grain-size (Passchier, 2011) and low sedimentation rates (<2.2 cm/kyr), interpreted to represent suspension settling from turbidity plumes and contourites (Passchier, 2011). A significant change in sedimentation has been identified between 35 and 33 mbsf (Warnke et al. 2004), with an increase in sedimentation rates up to 5.5 cm/kyr at 35 mbsf and a tenfold increase in ice rafted mass accumulation rates (IRD MAR) (Passchier, 2011) at 33 mbsf, representing an increase in deposition of ice-rafted material at the site (Figure 5.3).

The age model for ODP Site 1165 (Figure 5.3) is based on magnetostratigraphic datums supported by biostratigraphy (after Florindo et al. 2003; Grützner et al. 2005; Villa et al. 2008; see Chapter 6). For the Pliocene time interval (17.95 to 49.15 mbsf; ~2.65 to ~4.99 Ma), I adapted the age model used by Grützner et al. (2005) and Passchier (2011), converted to the Gradstein et al. (2012) timescale. It is important to note that between ~15 and 17 mbsf (~1.8 to ~3.0 Ma) a condensed unit has been identified, which potentially contains several hiatuses (Florindo et al. 2003; Villa et al. 2008). I hence refrain from exact age-related interpretations for this section of the core.

In addition to ODP Site 1165, sediments from Deep Sea Drilling Project (DSDP) Site 268 (63°56'99"S, 105°09'34"E) (Figure 5.2), located offshore of the Bunger Hills (Wilkes Land margin), were studied. The site was drilled in 3544m water depth, but only ~66m of

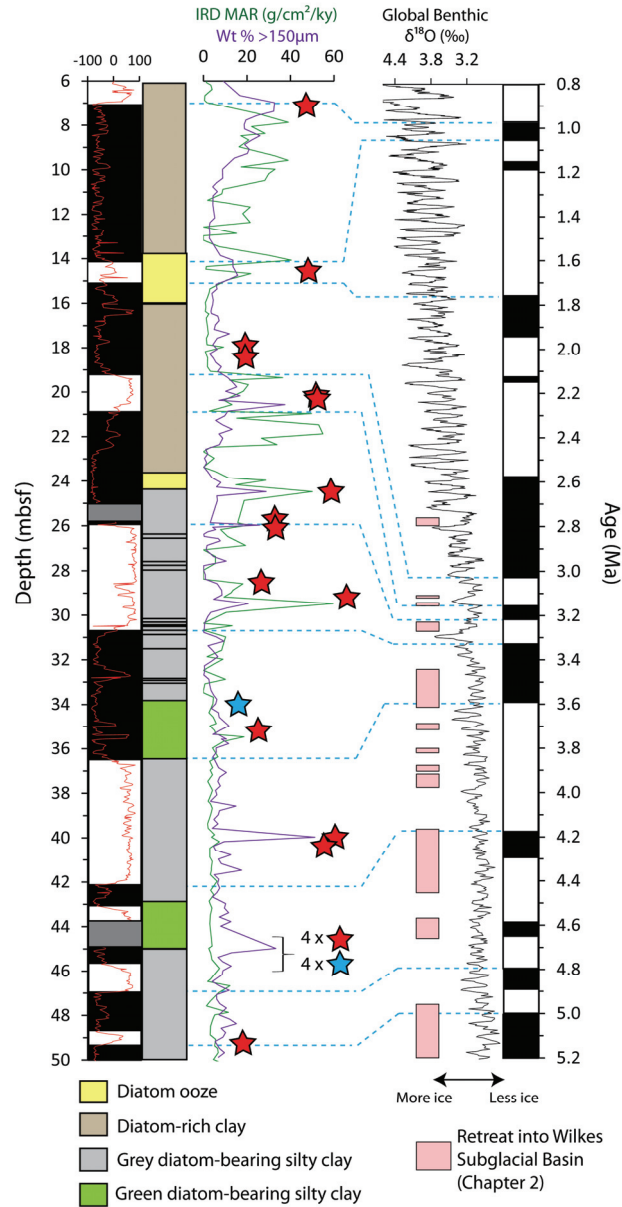


Figure 5.3. Downcore summary of Pliocene sediments from ODP Site 1165. From left to right: (i) depth in meters below sea floor; (ii) paleomagnetic chron boundaries (Florindo et al. 2003) with inclination data shown in red, and grey shading indicating areas with no data; (iii) lithostratigraphy (modified after Passchier, 2011); (iv) grain size records: green represents ice rafted mass accumulation rates calculated for detrital fractions ($>125\mu\text{m}$) ($\text{IRD MAR} = \% >125\mu\text{m} \times \text{terrigenous fraction} \times \text{bulk density} \times \text{linear sedimentation rate}$; from Passchier [2011]), and purple represents the relative abundance of material $>150\mu\text{m}$ in size, from Warnke et al. (2004), (v) red stars indicate the samples analysed for $>150\mu\text{m}$ hornblende grain $^{40}\text{Ar}/^{39}\text{Ar}$ ages from this study, whereas blue stars represent results published by Williams et al. (2010a); (vi) pink bands indicate timing of intervals when retreat of the EAIS into the Wilkes Subglacial Basin is inferred to have taken place (Chapter 2); (vii) global benthic stable oxygen isotope stack (Lisiecki and Raymo, 2004); paleomagnetic chron boundaries from Gradstein et al. (2012).

Oligocene to Quaternary sediments were recovered from ~474m of penetration (14% recovery; Hayes et al. 1975). Sediments above ~160m are composed of diatom oozes, silty clays and clays with abundant sand and pebbles throughout (Hayes et al. 1975; Piper and Brisco, 1975), interpreted to represent hemipelagic and terrigenous turbidity related deposition with common iceberg rafting. The age model of DSDP Site 268 has been constrained by silicoflagellate assemblages (Escutia, personal communication), and suggests sediments deposited between 113.66 mbsf and 116.38 mbsf are aged between ~4.2 and ~5.5 Ma, ~ 3.3 Ma between 84.81 and 86.84 mbsf, and ~ 2.5 Ma between 56.51 and 58.24 mbsf. Grain size records (Hayes et al. 1975) suggest coarse-grained detrital material (>150 μ m) comprises a significant proportion of bulk sediment weight (typically >5% and up to 50%), and occurs in similarly high abundances throughout all studied intervals.

5.4 Sampling and Methods

A total of 21 sediment samples from ODP Site 1165 were selected from all lithostratigraphic units (Figure 5.3, Tables 5.1 and 5.2). Eighteen samples are Pliocene in age, two samples correspond to IRD layers deposited in the Pleistocene (7.00 mbsf, ~1.00 Ma; 14.75 mbsf, ~1.60 Ma), and one sample was taken from the core-top. Grain size (Warnke et al. 2004) and IRD mass accumulation records (MAR) (Passchier et al. 2011) (Figure 5.3) were used as guidance to sample intervals of high and low delivery of coarse-grained iceberg-rafted material to ODP Site 1165.

Bulk sediment samples (20cm³) were wet sieved into <63 μ m, 63-150 μ m, >150 μ m fractions. Hornblende grains were subsequently handpicked from the >150 μ m fractions of each sample. For five samples, hornblende grains were separated into two size fractions, <1mm and >1mm, in order to investigate the effect of grain size on provenance signatures (Table 5.2). A total of 549 grains were analysed for ⁴⁰Ar/³⁹Ar ages, with grain counts for individual samples typically ranging between 19 and 43 (Figure 5.4, Table 5.1). The exceptions are one sample, which yielded only four hornblende grains (49.15 mbsf, ~4.99 Ma), two samples with 12 grains (45.64 mbsf, ~4.62 Ma; 45.90 mbsf, ~4.68 Ma), and one sample containing 16 grains (25.86 mbsf, ~3.20 Ma). In addition, 107 hornblende grains were analysed from two Pliocene samples from DSDP Site 268 (Figure 5.4, Tables 5.2 and 5.4).

Hornblende grains and monitor standards were irradiated at the TRIGA reactor at the USGS in Denver, with cadmium shielding. ⁴⁰Ar/³⁹Ar ages were obtained using single-step

CO₂ laser fusion at the Lamont-Doherty Earth Observatory argon geochronology lab (AGES: Argon Geochronology for the Earth Sciences). J values used to correct for neutron flux were calculated using the co-irradiated Mmhb-1 hornblende standard 525 Ma (Samson and Alexander, 1987). Measured values were corrected for background argon with measurements from an air pipette, and were also corrected for nuclear interferences (Renne et al., 1998). Analytical errors are based on the internal precision of measurements and variation of Mmhb values and are less than 2%.

5.5 Results

Hornblende grains analysed from ODP Site 1165 yielded two distinct ⁴⁰Ar/³⁹Ar age populations (Tables 5.1 and 5.2, Figure 5.4). The first ranges from 455 to 575 Ma, and is comprised of 253 grains (out of a total of 549; ~46%), with 207 of these grains (~90%) dated between 480 and 550 Ma. The second age population ranges between 1035 and 1315 Ma, and is comprised of 139 grains (~25%), with 77 grains (~60%) between 1120 and 1175 Ma. Hornblende grains of the two different separated grain sizes (<1mm and >1mm) yielded ⁴⁰Ar/³⁹Ar ages that occur in both of these age bins, and show no particular preference for either age range (Table 5.2). This observation suggests that IRD grain size introduced no bias to obtained ⁴⁰Ar/³⁹Ar ages at ODP Site 1165.

Outside of these two main populations, remaining hornblende grains from ODP Site 1165 yielded ⁴⁰Ar/³⁹Ar ages from 10 to 410 Ma (6 grains, ~1%), 580 to 735 Ma (78 grains in total, ~14%), 740 to 1035 Ma (29 grains in total, ~5%), and >1325 Ma (44 grains in total, ~8%). Within the >1325 Ma age range, 22 grains (~70%) fall within 1325-1670 Ma (Tables 5.1 and 5.2, Figure 5.4).

In a previous study, Williams et al. (2010a) analysed ice-rafted hornblende grains for ⁴⁰Ar/³⁹Ar ages from five Pliocene layers (34.10 mbsf, ~3.48 Ma; 45.50 mbsf, 45.70 mbsf, 45.80 mbsf, 46.00 mbsf, ~4.6-4.75 Ma) from ODP Site 1165 (included in Table 5.1 and Figure 5.4). Similar to my results, this study found two predominant hornblende ⁴⁰Ar/³⁹Ar age populations in Pliocene sediments, the largest between 450 and 600 Ma, and a secondary one between 1100 to 1300 Ma (Figure 5.4). Henceforth, data from samples analysed in Williams et al. (2010a) are included in discussion within this chapter.

The abundance of the two main hornblende grain ⁴⁰Ar/³⁹Ar age populations (455-575 Ma, and 1035-1315 Ma) in Pliocene ODP Site 1165 sediments varies through time. On

Table 5.1. Hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age ranges from ODP Site 1165 (>150 μm).

	Depth (mbsf)	Age (Ma)	0-410 Ma	455-575 Ma	580-735 Ma	740 -1035 Ma	1040-1315 Ma	>1315 Ma	Total
1H 1W 1-3cm	0.01	0.00	2	12	5	0	5	4	28
2H 2W 20-22cm	7.00	1.00	0	20	3	1	10	0	34
2H 6W 45-47cm	14.75	1.60	0	12	1	1	10	3	27
3H 2W 15-17cm	17.95	2.7	0	18	2	1	7	4	32
3H 2W 45-47cm	18.25	2.80	1	9	4	1	11	1	27
3H 3W 109-112cm	20.39	3.09	1	4	4	2	12	1	24
3H 3W 130-132cm	20.60	3.11	0	8	4	5	8	1	26
3H 6W 70-73cm	24.50	3.19	0	7	3	0	12	6	28
4H 1W 6-9cm	25.86	3.205	0	8	2	1	3	2	16
4H 1W 15-17cm	25.95	3.207	0	21	4	2	11	4	42
4H 2W 109-112cm	28.39	3.27	0	26	7	4	3	2	42
4H 3W 70-72cm	29.50	3.30	0	24	4	1	8	4	41
4H 6W 80-82cm*	34.10	3.48	0	14	10	2	10	3	39
4H 7W 20-22cm	35.00	3.53	0	18	7	1	9	0	35
5H 4W 20-22cm	40.00	3.96	0	17	4	2	6	3	32
5H 4W 60-62cm	40.40	4.01	1	7	7	1	7	1	24
6H 1W 15-17cm	44.95	4.55	0	16	4	3	0	1	24
6H 1W 70-72cm*	45.50	4.60	3	19	5	3	5	4	39
6H 1W 84-86cm	45.64	4.62	0	5	0	1	5	1	12
6H 1W 90-92*	45.70	4.63	0	31	14	7	5	9	66
6H 1W 94-96cm	45.74	4.64	1	6	4	0	5	3	19
6H 1W 100-102cm*	45.80	4.65	0	14	2	6	4	15	41
6H 1W 104-106cm	45.84	4.655	0	9	5	2	3	1	20
6H 1W 110-112cm	45.90	4.665	0	2	4	0	4	2	12
6H 1W 121-123cm*	46.00	4.75	1	16	3	3	2	2	27
6H 3W 135-137cm	49.15	4.99	0	4	0	0	0	0	4
Total			9	347	112	50	139	77	761

*from Williams et al. 2010a

Table 5.2. Hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age data from IODP Site 1165 (>150 μm).

Sample	Depth	Run ID	Ca/K	Cl/K	Mol ^{39}Ar	% ^{40}Ar *	Age (Ma)	$\pm$ Age
ODP Site 1165								
1H 1W 1-3cm	0.01	14604-22A	4.02	0.03193	0.012	76.2	290.2	4.3
1H 1W 1-3cm	0.01	14604-28A	3.01	0.03438	0.014	97.3	405.1	5.6
1H 1W 1-3cm	0.01	14604-24A	65.26	0.01387	0.003	72.4	487.4	8.7
1H 1W 1-3cm	0.01	14604-20A	5.64	0.0142	0.022	99	493.7	6.6
1H 1W 1-3cm	0.01	14604-25A	6.55	0.05872	0.013	96	496.4	6.9
1H 1W 1-3cm	0.01	14604-27A	7.12	0.05393	0.008	98.4	505.5	7.1
1H 1W 1-3cm	0.01	14604-05A	21.63	0.47601	0.01	94.9	505.8	7.0
1H 1W 1-3cm	0.01	14604-02A	19.31	0.04576	0.015	98.1	510.7	7.0
1H 1W 1-3cm	0.01	14604-01A	5.98	0.02364	0.022	99.8	526.3	7.1
1H 1W 1-3cm	0.01	14604-16A	5.21	0.20722	0.013	98.2	527.3	7.3
1H 1W 1-3cm	0.01	14604-12A	12.46	0.01991	0.054	97.9	529.2	7.0

1H 1W 1-3cm	0.01	14604-26A	6.1	0.00973	0.029	96.5	536.8	7.2
1H 1W 1-3cm	0.01	14604-07A	7.99	0.01866	0.012	99.2	538.7	7.4
1H 1W 1-3cm	0.01	14604-14A	9.66	0.04553	0.008	95.4	543.4	8.0
1H 1W 1-3cm	0.01	14604-29A	10.47	0.04881	0.018	93.6	606.6	8.2
1H 1W 1-3cm	0.01	14604-19A	7.86	0.02264	0.02	96.4	615.0	8.3
1H 1W 1-3cm	0.01	14604-06A	6.99	0.01179	0.027	96.5	622.9	8.3
1H 1W 1-3cm	0.01	14604-18A	7.46	0.06036	0.01	96.3	688.8	9.7
1H 1W 1-3cm	0.01	14604-11A	17.14	0.02562	0.085	98.5	703.8	9.3
1H 1W 1-3cm	0.01	14604-13A	16.44	0.08513	0.003	98.4	1033.7	16.0
1H 1W 1-3cm	0.01	14604-17A	8.96	0.03192	0.029	99.4	1137.6	15.1
1H 1W 1-3cm	0.01	14604-09A	8.45	0.01677	0.032	99.6	1160.1	15.4
1H 1W 1-3cm	0.01	14604-03A	10.99	0.05647	0.007	99.2	1169.7	16.2
1H 1W 1-3cm	0.01	14604-21A	8.86	0.07385	0.004	96.6	1231.4	18.7
1H 1W 1-3cm	0.01	14604-23A	7.97	0.01944	0.017	99.3	1306.9	17.4
1H 1W 1-3cm	0.01	14604-10A	14.34	0.02077	0.012	99.4	1459.5	19.7
1H 1W 1-3cm	0.01	14604-15A	10.35	0.01019	0.101	99.6	2406.4	31.4
1H 1W 1-3cm	0.01	14604-04A	28.72	0.02397	0.013	98	3193.8	42.1
2H 2W 20-22cm	7.00	13648-01	9.36912	0.05115	0.509	98.8	584.0	8.2
2H 2W 20-22cm	7.00	13648-14	9.65291	0.07248	0.062	97	472.8	7.5
2H 2W 20-22cm	7.00	13648-05	22.22444	0.03522	0.127	95.4	482.3	7.5
2H 2W 20-22cm	7.00	13648-17	9.83941	0.01017	0.211	99.1	499.2	7.1
2H 2W 20-22cm	7.00	13648-24	11.92436	0.01318	0.19	97.8	499.5	7.4
2H 2W 20-22cm	7.00	13648-15	8.15877	0.03219	0.349	98.2	501.0	7.2
2H 2W 20-22cm	7.00	13648-36	21.98455	0.10294	0.033	97.9	502.7	8.8
2H 2W 20-22cm	7.00	13648-21	5.50115	0.02626	0.098	100.1	504.6	7.3
2H 2W 20-22cm	7.00	13648-16	12.35819	0.00539	0.098	97.3	504.9	7.7
2H 2W 20-22cm	7.00	13648-02	6.08886	0.015	1.103	98.9	505.2	7.1
2H 2W 20-22cm	7.00	13648-20	18.50698	0.04115	0.076	93.6	505.2	8.4
2H 2W 20-22cm	7.00	13648-32	5.5752	0.0922	0.134	99.3	506.8	7.3
2H 2W 20-22cm	7.00	13648-35	10.61881	0.03392	0.081	97.9	507.7	7.7
2H 2W 20-22cm	7.00	13648-03	8.26744	0.01015	0.561	93.8	507.9	8.0
2H 2W 20-22cm	7.00	13648-06	6.26123	0.01516	0.358	99.2	509.3	7.2
2H 2W 20-22cm	7.00	13648-34	6.55584	0.03508	0.162	98.8	511.8	7.4
2H 2W 20-22cm	7.00	13648-04	21.83517	0.02803	0.346	95.7	517.1	7.8
2H 2W 20-22cm	7.00	13648-28	7.04246	0.04137	0.136	99.6	517.5	7.4
2H 2W 20-22cm	7.00	13648-12	7.25592	0.16613	0.219	98.4	523.3	7.6
2H 2W 20-22cm	7.00	13648-29	16.97777	0.00687	0.21	96.3	546.6	8.2
2H 2W 20-22cm	7.00	13648-13	43.27581	0.44407	0.005	75.7	553.8	27.6
2H 2W 20-22cm	7.00	13648-10	8.59625	0.03114	0.23	93.4	597.2	9.4
2H 2W 20-22cm	7.00	13648-23	6.24371	0.07502	0.197	99.7	659.4	9.2
2H 2W 20-22cm	7.00	13648-30	9.92797	0.01173	0.193	96.8	811.8	11.6
2H 2W 20-22cm	7.00	13648-07	20.37574	0.03437	0.126	96.8	1076.6	15.1
2H 2W 20-22cm	7.00	13648-25	6.62682	0.01324	0.253	99.1	1130.7	14.9
2H 2W 20-22cm	7.00	13648-18	8.5781	0.00956	0.155	98.4	1132.5	15.2
2H 2W 20-22cm	7.00	13648-19	6.00082	0.01662	0.104	99.1	1136.2	15.3
2H 2W 20-22cm	7.00	13648-22	9.90677	0.00701	0.083	99	1142.1	15.5
2H 2W 20-22cm	7.00	13648-09	7.25972	0.01314	0.445	99.7	1151.7	15.0
2H 2W 20-22cm	7.00	13648-11	14.75199	0.02301	0.129	98.2	1159.0	15.7
2H 2W 20-22cm	7.00	13648-26	6.59859	-0.00053	0.096	99.8	1166.1	15.6
2H 2W 20-22cm	7.00	13648-08	7.01853	0.01646	0.202	98.6	1197.4	15.9
2H 2W 20-22cm	7.00	13648-27	7.89252	0.00823	0.533	99.2	1244.1	16.2
2H 2W 20-22cm	7.00	13648-33	1.30454	0.1275	0.01	99	4011.3	53.7
2H 6W 45-47cm	14.75	13650-15	14.35718	-0.00713	0.062	91.7	486.6	8.4
2H 6W 45-47cm	14.75	13650-11	7.23411	-0.00017	0.152	98.1	491.0	7.3
2H 6W 45-47cm	14.75	13650-08	8.70921	-0.00189	0.131	97.5	499.1	7.4
2H 6W 45-47cm	14.75	13650-16	16.39091	-0.01107	0.073	92.1	504.2	8.6
2H 6W 45-47cm	14.75	13650-23	7.44953	0.00878	0.103	98.6	505.4	7.4
2H 6W 45-47cm	14.75	13650-22	10.72418	0.00416	0.106	97	506.7	7.7
2H 6W 45-47cm	14.75	13650-10	11.52615	0.02331	0.222	97.8	508.3	7.4

2H 6W 45-47cm	14.75	13650-29	7.07948	0.02292	0.058	96.9	513.4	8.1
2H 6W 45-47cm	14.75	13650-09	5.16247	0.11714	0.546	99.1	520.3	7.3
2H 6W 45-47cm	14.75	13650-19	5.73068	-0.00266	0.178	98	536.1	7.8
2H 6W 45-47cm	14.75	13650-25	10.09532	0.03757	0.119	99.4	537.5	7.7
2H 6W 45-47cm	14.75	13650-07	6.23369	0.03138	0.147	98.8	546.2	7.9
2H 6W 45-47cm	14.75	13650-04	9.34803	0.01906	0.414	97.1	666.6	9.6
2H 6W 45-47cm	14.75	13650-28	11.49335	0.03556	0.036	97.9	802.4	12.6
2H 6W 45-47cm	14.75	13650-24	29.60235	0.00314	0.038	98.8	1099.9	15.9
2H 6W 45-47cm	14.75	13650-21	43.12063	0.02328	0.02	94.6	1100.4	18.7
2H 6W 45-47cm	14.75	13650-03	49.14695	0.02751	0.039	95.7	1121.3	17.1
2H 6W 45-47cm	14.75	13650-17	22.06966	-0.02043	0.047	98	1131.8	16.4
2H 6W 45-47cm	14.75	13650-14	9.92728	-0.00543	0.049	100	1145.0	15.8
2H 6W 45-47cm	14.75	13650-31	5.72683	0.01705	0.091	99.5	1145.4	15.4
2H 6W 45-47cm	14.75	13650-06	6.1666	0.00528	0.261	97.2	1168.6	15.8
2H 6W 45-47cm	14.75	13650-18	27.17769	-0.00414	0.088	88.1	1171.3	19.2
2H 6W 45-47cm	14.75	13650-26	16.25161	0.0104	0.038	99.4	1233.4	17.8
2H 6W 45-47cm	14.75	13650-30	7.42141	-0.00553	0.067	97.4	1269.6	17.7
2H 6W 45-47cm	14.75	13650-01	40.60616	0.04367	0.066	87.1	1327.9	21.6
2H 6W 45-47cm	14.75	13650-02	10.38275	0.03242	0.11	99.3	1465.7	19.0
2H 6W 45-47cm	14.75	13650-32	6.44101	0.00314	0.077	99.4	1472.4	19.1
3H 2W 15-17cm	17.95	13428-18	5.85028	0.02095	0.135	99.7	495.7	5.3
3H 2W 15-17cm	17.95	13428-28	33.5835	0.00574	0.068	90.5	495.7	5.9
3H 2W 15-17cm	17.95	13428-02	9.6567	0.00216	0.293	98.6	496.3	5.7
3H 2W 15-17cm	17.95	13428-21	8.36802	-0.00493	0.086	99.6	496.9	5.4
3H 2W 15-17cm	17.95	13428-30	7.54102	0.00832	0.436	99	498.0	5.1
3H 2W 15-17cm	17.95	13428-13	12.92322	0.05003	0.192	99	501.6	5.2
3H 2W 15-17cm	17.95	13428-19	25.15087	0.02725	0.097	97.7	504.9	5.4
3H 2W 15-17cm	17.95	13428-11	13.8127	0.07765	0.483	99	508.5	5.2
3H 2W 15-17cm	17.95	13428-32	6.34569	0.03924	0.169	96.7	514.5	6.1
3H 2W 15-17cm	17.95	13428-17	10.8411	0.099	0.039	100.6	517.6	6.4
3H 2W 15-17cm	17.95	13428-20	6.91291	0.01905	0.275	99.4	519.2	5.3
3H 2W 15-17cm	17.95	13428-31	12.1926	0.03756	0.047	94.4	519.5	8.1
3H 2W 15-17cm	17.95	13428-15	9.09941	-0.00044	0.156	95.8	522.7	5.4
3H 2W 15-17cm	17.95	13428-23	8.73466	-0.00236	0.081	100.1	524.6	7.0
3H 2W 15-17cm	17.95	13428-29	6.29805	0.00449	0.094	87.3	533.8	5.8
3H 2W 15-17cm	17.95	13428-25	10.58511	0.00368	0.144	99	543.2	5.8
3H 2W 15-17cm	17.95	13428-06	9.65677	0.0558	0.283	99.6	544.4	6.3
3H 2W 15-17cm	17.95	13428-24	7.29453	0.02035	0.178	96.7	545.6	5.6
3H 2W 15-17cm	17.95	13428-22	9.00429	-0.00349	0.087	98.9	591.5	6.4
3H 2W 15-17cm	17.95	13428-09	16.58741	-0.00713	0.058	99.4	611.0	10.0
3H 2W 15-17cm	17.95	13428-01	7.91737	0.00143	0.288	100.4	753.8	8.7
3H 2W 15-17cm	17.95	13428-04	12.36456	-0.00313	0.104	99.8	1083.6	14.3
3H 2W 15-17cm	17.95	13428-12	6.41575	0.01738	0.138	99.5	1137.8	11.7
3H 2W 15-17cm	17.95	13428-08	12.49802	-0.02288	0.092	99.5	1150.8	14.2
3H 2W 15-17cm	17.95	13428-16	12.74576	0.01382	0.283	99.3	1155.9	11.8
3H 2W 15-17cm	17.95	13428-05	5.99879	0.01669	0.421	99.8	1163.7	12.7
3H 2W 15-17cm	17.95	13428-27	8.94952	0.00243	0.274	99.4	1174.4	13.0
3H 2W 15-17cm	17.95	13428-26	13.81268	0.00054	0.18	98.8	1270.8	13.1
3H 2W 15-17cm	17.95	13428-03	8.31992	-0.00255	0.292	100	1388.0	14.8
3H 2W 15-17cm	17.95	13428-07	8.13335	-0.00285	0.136	100	1498.5	17.1
3H 2W 15-17cm	17.95	13428-10	8.88082	-0.00666	0.129	100.5	1499.7	17.3
3H 2W 15-17cm	17.95	13428-14	31.60819	-0.1212	0.005	70.3	2251.2	45.7
3H 2W 45-47cm	18.25*	13543-01	9.14525	0.02594	2.539	99.5	1135.2	12.3
3H 2W 45-47cm	18.25*	13543-02	7.34591	0.06204	2.144	99.2	1266.3	13.9
3H 2W 45-47cm	18.25	13544-01	8.46969	0.01649	0.55	98.3	541.6	5.7
3H 2W 45-47cm	18.25	13544-02	19.30035	0.01133	0.268	98.2	543.1	5.6
3H 2W 45-47cm	18.25	13544-03	8.16346	0.02414	0.329	99.3	1127.0	11.5
3H 2W 45-47cm	18.25	13544-04	23.6687	0.0097	0.314	98.3	558.9	5.7
3H 2W 45-47cm	18.25	13544-05	20.83277	0.01459	0.225	94.2	872.9	8.9

3H 2W 45-47cm	18.25	13547-15	1.28549	0.10648	0.007	48.7	406.6	21.3
3H 2W 45-47cm	18.25	13547-02	9.94852	0.00655	0.123	93.8	489.7	5.8
3H 2W 45-47cm	18.25	13547-06	13.14128	0.00093	0.139	97	494.1	5.8
3H 2W 45-47cm	18.25	13547-20	12.62853	-0.00817	0.118	96.8	498.9	6.5
3H 2W 45-47cm	18.25	13547-19	32.25737	-0.05103	0.017	95.4	503.4	13.3
3H 2W 45-47cm	18.25	13547-17	8.23847	0.02173	0.045	100.6	515.9	9.0
3H 2W 45-47cm	18.25	13547-11	11.27503	-0.00309	0.132	98.8	534.9	5.6
3H 2W 45-47cm	18.25	13547-14	18.37177	0.05319	0.062	94.4	587.8	6.5
3H 2W 45-47cm	18.25	13547-03	6.28305	0.05556	0.197	98.4	660.6	6.9
3H 2W 45-47cm	18.25	13547-13	16.96553	0.03005	0.062	93.4	675.6	7.7
3H 2W 45-47cm	18.25	13547-09	18.95145	0.01126	0.119	97	693.0	7.3
3H 2W 45-47cm	18.25	13547-07	7.02757	0.01648	0.081	98.8	1051.6	13.0
3H 2W 45-47cm	18.25	13547-01	24.3577	0.01745	0.079	95.2	1081.1	11.4
3H 2W 45-47cm	18.25	13547-04	12.06145	0.00941	0.09	98.4	1093.2	12.0
3H 2W 45-47cm	18.25	13547-16	8.09501	0.00796	0.112	98.7	1128.9	11.7
3H 2W 45-47cm	18.25	13547-08	8.11989	0.02038	0.086	98.6	1136.5	12.1
3H 2W 45-47cm	18.25	13547-05	9.29902	0.00435	0.109	98.5	1139.6	12.0
3H 2W 45-47cm	18.25	13547-12	9.55644	0.00824	0.082	96.9	1212.9	12.7
3H 2W 45-47cm	18.25	13547-18	8.72588	0.00537	0.078	98.2	1231.6	14.9
3H 2W 45-47cm	18.25	13547-10	26.6418	0.05277	0.053	98.7	1652.9	17.8
3H 3W 109-112cm	20.39 *	13545-01	6.50028	0.00779	0.431	98.1	499.9	5.1
3H 3W 109-112cm	20.39 *	13545-02	7.48248	0.01667	0.657	99.3	503.5	5.3
3H 3W 109-112cm	20.39 *	13545-03	22.46636	-0.00459	0.228	94.3	578.1	6.6
3H 3W 109-112cm	20.39 *	13545-04	15.25589	0.01556	0.436	98.5	1121.9	11.4
3H 3W 109-112cm	20.39 *	13545-05	17.44161	0.00973	0.481	98.1	1151.9	11.8
3H 3W 109-112cm	20.39	13546-08	14.42715	0.00236	0.193	27.5	11.2	0.6
3H 3W 109-112cm	20.39	13546-03	12.47766	-0.0067	0.091	96.1	493.3	6.2
3H 3W 109-112cm	20.39	13546-18	6.48664	0.02224	0.188	99.1	563.1	6.7
3H 3W 109-112cm	20.39	13546-12	5.58641	0.01861	0.256	97.8	575.7	6.4
3H 3W 109-112cm	20.39	13546-13	12.81666	0.00947	0.163	97	606.0	7.1
3H 3W 109-112cm	20.39	13546-04	24.29161	-0.0094	0.107	95.3	679.4	7.9
3H 3W 109-112cm	20.39	13546-17	11.44752	0.00784	0.056	98.7	771.9	8.8
3H 3W 109-112cm	20.39	13546-07	9.6559	0.06838	0.349	87	978.0	10.0
3H 3W 109-112cm	20.39	13546-19	6.49249	0.02926	0.165	98.4	1112.7	11.4
3H 3W 109-112cm	20.39	13546-15	9.16529	0.00166	0.106	96.9	1115.7	12.9
3H 3W 109-112cm	20.39	13546-14	5.13419	0.02467	0.502	99.1	1117.2	11.7
3H 3W 109-112cm	20.39	13546-01	18.79876	-0.00931	0.201	98.1	1117.3	11.4
3H 3W 109-112cm	20.39	13546-06	10.16784	0.01317	0.264	99.2	1121.0	12.3
3H 3W 109-112cm	20.39	13546-02	9.22223	-0.00193	0.132	99.4	1132.7	11.8
3H 3W 109-112cm	20.39	13546-05	8.78061	0.00257	0.241	99.4	1135.3	12.5
3H 3W 109-112cm	20.39	13546-09	12.61794	0.00973	0.076	99.5	1138.4	12.1
3H 3W 109-112cm	20.39	13546-11	8.62442	0.01509	0.197	98.7	1161.7	11.9
3H 3W 109-112cm	20.39	13546-10	6.66891	0.01225	0.597	99.1	1238.9	12.7
3H 3W 109-112cm	20.39	13546-16	11.17192	0.00063	0.057	98.6	1314.3	14.4
3H 3W 130-132cm	20.60	13429-15	5.53171	0.05576	1.097	99.4	475.9	4.8
3H 3W 130-132cm	20.60	13429-19	7.86199	0.00946	0.518	98.3	486.7	5.2
3H 3W 130-132cm	20.60	13429-06	5.5321	0.02468	0.169	99.8	497.4	5.6
3H 3W 130-132cm	20.60	13429-07	7.27768	0.03233	0.145	100.3	502.6	6.1
3H 3W 130-132cm	20.60	13429-18	13.31188	0.02056	0.268	98.1	509.8	5.3
3H 3W 130-132cm	20.60	13429-25	9.00598	0.01208	0.09	101.4	521.9	5.8
3H 3W 130-132cm	20.60	13429-16	18.64246	0.02427	0.47	98.5	530.7	5.7
3H 3W 130-132cm	20.60	13429-08	8.47735	0.03033	0.125	100.6	547.2	7.1
3H 3W 130-132cm	20.60	13429-22	7.70404	0.03526	0.25	98.3	611.8	6.7
3H 3W 130-132cm	20.60	13429-17	42.93991	0.01023	0.197	96.3	613.3	6.9
3H 3W 130-132cm	20.60	13429-05	16.73287	0.00614	0.178	97	632.9	7.6
3H 3W 130-132cm	20.60	13429-27	14.43559	-0.009	0.06	101.3	639.7	7.3
3H 3W 130-132cm	20.60	13429-13	10.01837	0.02559	0.458	99.5	727.6	7.8
3H 3W 130-132cm	20.60	13429-03	11.18809	0.02119	0.161	100.5	801.4	9.6

3H 3W 130-132cm	20.60	13429-04	49.02765	0.01852	0.03	102.6	848.2	14.8
3H 3W 130-132cm	20.60	13429-09	8.37015	0.03141	0.117	99.8	902.6	9.5
3H 3W 130-132cm	20.60	13429-01	20.44097	0.0123	0.127	99.6	1011.7	10.7
3H 3W 130-132cm	20.60	13429-14	19.60739	0.00261	0.517	97.9	1081.5	11.0
3H 3W 130-132cm	20.60	13429-26	9.70223	-0.0112	0.093	100.3	1135.4	13.8
3H 3W 130-132cm	20.60	13429-20	10.90308	-0.00228	0.157	99.1	1138.0	11.9
3H 3W 130-132cm	20.60	13429-23	9.00433	0.00071	0.423	99.5	1143.7	11.7
3H 3W 130-132cm	20.60	13429-24	5.89125	0.02395	0.231	99.8	1144.0	12.6
3H 3W 130-132cm	20.60	13429-11	5.9722	0.01052	0.088	101	1161.6	15.0
3H 3W 130-132cm	20.60	13429-10	7.01586	0.01004	0.09	100.4	1172.2	14.8
3H 3W 130-132cm	20.60	13429-02	6.96164	0.02321	0.123	100.4	1208.9	14.0
3H 3W 130-132cm	20.60	13429-21	13.60872	0.00993	0.239	98.7	1488.8	15.3
3H 6W 70-73cm	24.50	13430-08	5.81778	0.06625	0.374	100.5	504.4	5.6
3H 6W 70-73cm	24.50	13430-04	7.63426	0.02622	0.603	99.6	507.5	5.5
3H 6W 70-73cm	24.50	13430-03	13.72975	0.0214	0.081	95.9	508.0	7.3
3H 6W 70-73cm	24.50	13430-07	6.89216	0.00321	0.105	99.5	512.3	6.7
3H 6W 70-73cm	24.50	13430-17	9.79565	0.01767	0.334	94.6	545.1	5.7
3H 6W 70-73cm	24.50	13430-05	9.49478	0.04296	0.118	96.6	546.7	7.9
3H 6W 70-73cm	24.50	13430-11	40.93927	-0.0161	0.031	105.6	567.7	10.6
3H 6W 70-73cm	24.50	13430-19	11.71143	0.03208	0.191	99.2	588.9	6.1
3H 6W 70-73cm	24.50	13430-09	181.61777	0.01687	0.02	57.1	674.8	11.5
3H 6W 70-73cm	24.50	13430-06	47.29965	-0.03455	0.017	102.4	711.2	10.9
3H 6W 70-73cm	24.50	13430-02	7.34287	0.01039	0.231	99.2	1046.9	11.5
3H 6W 70-73cm	24.50	13430-01	281.84984	-0.10373	0.028	65.9	1048.8	22.5
3H 6W 70-73cm	24.50	13430-18	19.01793	-0.01434	0.031	95.8	1066.6	13.7
3H 6W 70-73cm	24.50	13430-24	13.22385	0.00963	0.18	98.8	1071.0	12.0
3H 6W 70-73cm	24.50	13430-23	8.02226	0.0229	0.116	97.1	1121.2	13.2
3H 6W 70-73cm	24.50	13430-14	6.14221	0.03465	0.367	99.2	1125.1	11.4
3H 6W 70-73cm	24.50	13430-28	6.31316	0.04002	0.049	99	1127.9	14.5
3H 6W 70-73cm	24.50	13430-20	31.39783	0.00989	0.027	99	1142.6	13.6
3H 6W 70-73cm	24.50	13430-27	18.46659	0.0353	0.05	99	1148.9	13.1
3H 6W 70-73cm	24.50	13430-26	8.0236	0.01363	0.109	99.3	1171.7	12.2
3H 6W 70-73cm	24.50	13430-21	10.30219	0.02189	0.125	98.3	1240.1	12.9
3H 6W 70-73cm	24.50	13430-10	9.13393	0.01196	0.324	99.6	1292.7	14.1
3H 6W 70-73cm	24.50	13430-25	15.91133	0.02368	0.045	99.6	1331.2	19.2
3H 6W 70-73cm	24.50	13430-15	204.563	-0.02287	0.005	40.7	1362.1	66.6
3H 6W 70-73cm	24.50	13430-22	14.06833	-0.00786	0.211	98.4	1568.7	16.4
3H 6W 70-73cm	24.50	13430-16	10.16458	0.01774	0.561	99.5	1607.9	17.1
3H 6W 70-73cm	24.50	13430-12	67.51405	0.00666	0.057	97.2	1615.0	19.4
3H 6W 70-73cm	24.50	13430-13	45.3005	0.03719	0.005	92	2149.7	54.5
4H 1W 6-9cm	25.86	13580-04	6.99433	0.0067	0.503	98.1	457.4	4.6
4H 1W 6-9cm	25.86	13580-03	7.19398	0.02904	0.473	97.6	505.4	5.2
4H 1W 6-9cm	25.86	13580-05	6.39913	0.01159	0.26	97.3	506.7	5.6
4H 1W 6-9cm	25.86	13580-12	6.99161	-0.00285	0.149	98.7	508.6	5.4
4H 1W 6-9cm	25.86	13580-08	15.33212	0.01304	0.251	95.7	511.6	5.3
4H 1W 6-9cm	25.86	13580-13	10.0305	0.01671	0.141	99.5	525.0	5.5
4H 1W 6-9cm	25.86	13580-15	12.18158	0.04469	0.109	97.4	534.0	6.6
4H 1W 6-9cm	25.86	13580-01	5.71299	0.11436	0.97	98.3	549.2	5.7
4H 1W 6-9cm	25.86	13580-11	8.79686	0.02652	0.131	95.1	659.7	8.1
4H 1W 6-9cm	25.86	13580-02	7.81916	0.04432	0.321	98.9	696.8	7.5
4H 1W 6-9cm	25.86	13580-14	19.30214	0.03468	0.115	94.5	898.7	9.5
4H 1W 6-9cm	25.86	13580-07	6.168	0.0452	0.79	98.6	1066.5	10.9
4H 1W 6-9cm	25.86	13580-16	7.34611	0.01195	0.085	98.5	1134.0	12.0
4H 1W 6-9cm	25.86	13580-10	16.53772	0.02077	0.12	96.4	1153.3	12.0
4H 1W 6-9cm	25.86	13580-06	13.41729	0.0075	0.264	96.9	1621.8	16.6
4H 1W 6-9cm	25.86	13580-09	11.06206	0.02018	0.122	99	2457.0	25.3
4H 1W 15-17cm	25.95	13431-35	27.94715	0.00487	0.031	100.2	481.7	6.7
4H 1W 15-17cm	25.95	13431-20	7.17598	0.03409	0.061	98.7	482.8	5.7

4H 1W 15-17cm	25.95	13431-31	16.40389	-0.00423	0.059	97.1	497.3	5.8
4H 1W 15-17cm	25.95	13431-18	5.78567	0.01478	0.191	99.7	508.5	5.2
4H 1W 15-17cm	25.95	13431-23	6.45276	0.03822	0.29	99.8	509.0	5.5
4H 1W 15-17cm	25.95	13431-34	6.91166	0.00709	0.352	99.4	510.5	5.2
4H 1W 15-17cm	25.95	13431-38	12.30177	0.0488	0.043	99.8	510.6	6.5
4H 1W 15-17cm	25.95	13431-24	7.43749	0.01691	0.089	101.5	511.3	5.6
4H 1W 15-17cm	25.95	13431-39	13.54873	0.01773	0.08	97.5	511.6	5.8
4H 1W 15-17cm	25.95	13431-21	6.55295	0.01459	0.136	99.4	519.1	6.2
4H 1W 15-17cm	25.95	13431-09	5.77517	0.03356	0.081	101	519.7	7.0
4H 1W 15-17cm	25.95	13431-05	9.82468	0.00564	0.17	100.7	521.7	6.8
4H 1W 15-17cm	25.95	13431-07	7.60656	0.04585	0.095	97.6	523.2	5.8
4H 1W 15-17cm	25.95	13431-14	7.57989	0.04186	0.108	98.5	532.1	5.7
4H 1W 15-17cm	25.95	13431-22	13.55629	-0.00726	0.113	97.6	532.5	6.6
4H 1W 15-17cm	25.95	13431-27	10.11825	0.02353	0.122	93.1	537.3	6.4
4H 1W 15-17cm	25.95	13431-30	13.88871	0.00278	0.143	98.4	551.9	5.8
4H 1W 15-17cm	25.95	13431-15	6.40333	0.06956	0.238	90.9	558.4	5.8
4H 1W 15-17cm	25.95	13431-10	6.06079	0.01617	0.095	101.1	568.2	7.4
4H 1W 15-17cm	25.95	13431-03	5.83538	0.12221	0.203	99.3	605.1	6.9
4H 1W 15-17cm	25.95	13431-32	11.95387	0.27325	0.149	99	646.8	7.3
4H 1W 15-17cm	25.95	13431-33	8.78052	0.06993	0.12	96.7	662.1	7.1
4H 1W 15-17cm	25.95	13431-36	9.11931	0.03398	0.062	97.9	664.6	7.5
4H 1W 15-17cm	25.95	13431-13	18.50956	0.02329	0.027	97.1	732.6	13.4
4H 1W 15-17cm	25.95	13431-17	32.28616	0.12602	0.017	94.3	757.4	17.1
4H 1W 15-17cm	25.95	13431-01	6.74177	0.00869	0.14	98.3	1108.7	13.2
4H 1W 15-17cm	25.95	13431-12	9.80625	0.00907	0.089	99.4	1120.9	12.2
4H 1W 15-17cm	25.95	13431-19	5.4772	0.01641	0.118	99.8	1126.9	11.7
4H 1W 15-17cm	25.95	13431-37	5.83754	0.03854	0.072	100.4	1168.8	15.2
4H 1W 15-17cm	25.95	13431-28	13.70108	0.00761	0.111	97.1	1174.8	12.3
4H 1W 15-17cm	25.95	13431-25	7.29473	0.00868	0.486	99.7	1184.2	12.5
4H 1W 15-17cm	25.95	13431-02	6.41943	0.00449	0.138	99.8	1206.6	14.3
4H 1W 15-17cm	25.95	13431-29	6.16668	0.00338	0.129	99.5	1212.6	12.7
4H 1W 15-17cm	25.95	13431-26	5.21617	0.009	0.475	99.5	1266.7	12.8
4H 1W 15-17cm	25.95	13431-06	61.72669	0.00918	0.014	95.4	1309.0	27.0
4H 1W 15-17cm	25.95	13431-08	7.33893	0.04461	0.046	100.8	1310.0	19.2
4H 1W 15-17cm	25.95	13431-04	76.51176	0.00584	0.021	98	1377.3	25.7
4H 1W 15-17cm	25.95	13432-01	48.7137	0.01448	0.187	97.1	1191.4	12.3
4H 1W 15-17cm	25.95 *	13432-02	7.72878	0.00614	0.432	99.6	1310.2	13.4
4H 1W 15-17cm	25.95 *	13432-03	7.79466	0.00737	0.875	99.7	1857.0	18.8
4H 1W 15-17cm	25.95 *	13432-04	5.33592	0.08885	0.776	99.1	1053.3	11.3
4H 1W 15-17cm	25.95 *	13432-05	8.56219	0.0746	0.329	95.7	494.9	5.7
4H 1W 15-17cm	25.95 *	13432-06	6.28632	0.04038	0.354	100.1	500.4	5.5
4H 2W 109-112cm	28.39	13581-11	6.97138	0.02155	0.076	98.3	464.9	5.3
4H 2W 109-112cm	28.39	13581-10	9.81259	0.01989	0.124	84.4	475.6	5.7
4H 2W 109-112cm	28.39	13581-40	8.64106	0.09181	0.018	99.2	480.7	9.5
4H 2W 109-112cm	28.39	13581-03	4.57261	0.06922	0.623	99.2	487.1	5.1
4H 2W 109-112cm	28.39	13581-29	8.51102	-0.01095	0.063	97	490.7	5.9
4H 2W 109-112cm	28.39	13581-31	6.969	0.06758	0.085	98.6	494.7	5.3
4H 2W 109-112cm	28.39	13581-28	9.67038	0.00474	0.173	98.8	500.3	5.9
4H 2W 109-112cm	28.39	13581-15	8.13249	0.00761	0.124	97.6	501.5	5.2
4H 2W 109-112cm	28.39	13581-14	5.51428	0.01855	0.287	99.1	501.8	5.2
4H 2W 109-112cm	28.39	13581-19	6.11345	0.0072	0.143	98.5	503.3	5.3
4H 2W 109-112cm	28.39	13581-42	9.108	0.01774	0.103	98.7	504.1	5.4
4H 2W 109-112cm	28.39	13581-25	7.95468	-0.00096	0.073	95.1	504.2	5.7
4H 2W 109-112cm	28.39	13581-26	12.74683	0.00899	0.028	94.5	504.4	8.0
4H 2W 109-112cm	28.39	13581-18	7.69175	0.02773	0.097	98.3	509.4	6.2
4H 2W 109-112cm	28.39	13581-21	5.55877	0.02473	0.065	98.5	510.5	6.0
4H 2W 109-112cm	28.39	13581-35	8.23178	0.01342	0.14	96.4	512.4	6.2
4H 2W 109-112cm	28.39	13581-27	10.68288	0.02527	0.137	98.1	512.5	5.5
4H 2W 109-112cm	28.39	13581-24	6.72064	-0.00465	0.05	95.2	514.2	6.3
4H 2W 109-112cm	28.39	13581-02	8.89711	0.04556	0.197	97.4	524.3	5.4

4H 2W 109-112cm	28.39	13581-39	5.19258	0.05609	0.117	98.5	524.7	5.5
4H 2W 109-112cm	28.39	13581-32	25.79625	0.00892	0.027	92.4	525.0	6.8
4H 2W 109-112cm	28.39	13581-22	8.96272	0.01083	0.119	97	526.8	6.4
4H 2W 109-112cm	28.39	13581-09	12.45506	0.00697	0.06	98.5	545.6	7.4
4H 2W 109-112cm	28.39	13581-38	5.65883	0.01298	0.067	97.9	548.7	6.3
4H 2W 109-112cm	28.39	13581-41	37.21768	0.02858	0.032	95	568.5	7.4
4H 2W 109-112cm	28.39	13581-05	25.90672	0.03235	0.053	95.9	574.2	6.3
4H 2W 109-112cm	28.39	13581-08	8.06368	0.00853	0.137	97.9	596.5	6.3
4H 2W 109-112cm	28.39	13581-01	11.49558	0.01791	0.143	93.3	614.4	6.4
4H 2W 109-112cm	28.39	13581-16	3.30852	0.28733	0.154	99.6	620.6	6.4
4H 2W 109-112cm	28.39	13581-07	17.95893	0.13728	0.011	97.7	626.2	11.5
4H 2W 109-112cm	28.39	13581-17	24.68061	0.00975	0.063	95.3	628.5	9.5
4H 2W 109-112cm	28.39	13581-04	11.9085	0.04376	0.111	98.5	685.5	7.2
4H 2W 109-112cm	28.39	13581-23	14.93482	-0.00694	0.015	102	720.3	16.0
4H 2W 109-112cm	28.39	13581-13	5.8452	0.1349	0.237	98.7	772.6	7.9
4H 2W 109-112cm	28.39	13581-36	6.02934	0.00177	0.119	98.1	794.5	9.2
4H 2W 109-112cm	28.39	13581-37	36.05434	0.06405	0.024	91.7	889.7	11.6
4H 2W 109-112cm	28.39	13581-12	45.39326	0.05085	0.044	96.4	931.1	13.3
4H 2W 109-112cm	28.39	13581-34	22.3384	-0.05687	0.019	88	1076.3	19.7
4H 2W 109-112cm	28.39	13581-06	7.50546	-0.00992	0.078	98.3	1122.3	12.0
4H 2W 109-112cm	28.39	13581-20	9.17894	0.01898	0.045	99.5	1143.6	14.8
4H 2W 109-112cm	28.39	13581-30	6.84657	0.07969	0.124	99.4	1309.7	13.7
4H 2W 109-112cm	28.39	13581-33	15.98747	0.01482	0.02	97.9	1442.5	17.4
4H 3W 70-72cm	29.50	13434-12	4.65189	0.0612	0.141	99.1	480.7	5.5
4H 3W 70-72cm	29.50	13434-02	15.01492	0.08092	0.474	99.7	483.6	5.1
4H 3W 70-72cm	29.50	13433-02	6.68902	0.02949	0.332	99.5	495.2	5.5
4H 3W 70-72cm	29.50	13434-24	11.81885	0.00095	0.118	96.6	495.5	6.2
4H 3W 70-72cm	29.50	13434-06	7.41454	0.02856	0.66	99.3	503.0	5.4
4H 3W 70-72cm	29.50	13434-23	7.94415	0.01647	0.161	97.6	506.2	5.4
4H 3W 70-72cm	29.50	13433-12	12.06183	0.02574	0.051	100.6	506.4	6.0
4H 3W 70-72cm	29.50	13434-28	7.16496	0.01524	0.068	98.4	508.2	7.5
4H 3W 70-72cm	29.50	13434-01	9.51299	0.01134	0.457	100.2	508.3	5.7
4H 3W 70-72cm	29.50	13434-26	9.9692	0.03236	0.077	98.3	508.4	5.8
4H 3W 70-72cm	29.50	13433-10	10.22038	0.02696	0.111	88.9	513.3	7.1
4H 3W 70-72cm	29.50	13434-25	7.44675	-0.00264	0.061	100.6	515.4	7.7
4H 3W 70-72cm	29.50	13434-14	6.02555	0.05907	0.331	99.7	515.7	5.5
4H 3W 70-72cm	29.50	13434-10	8.69445	0.01847	0.172	99	519.1	6.1
4H 3W 70-72cm	29.50	13434-17	6.93709	0.03722	0.11	100.7	519.3	5.6
4H 3W 70-72cm	29.50	13433-09	5.67935	0.06154	0.285	101	521.9	5.8
4H 3W 70-72cm	29.50	13434-22	5.70067	0.02643	0.231	99.1	527.6	5.4
4H 3W 70-72cm	29.50	13433-01	6.35447	0.0287	0.392	99.9	534.2	5.5
4H 3W 70-72cm	29.50	13434-04	9.58578	0.00368	0.347	100.3	538.3	5.9
4H 3W 70-72cm	29.50	13434-16	21.24515	-0.00183	0.049	97	538.3	7.8
4H 3W 70-72cm	29.50	13434-29	5.95195	0.05394	0.063	102.1	539.1	6.2
4H 3W 70-72cm	29.50	13433-06	7.49325	0.10178	0.071	99.9	540.6	6.1
4H 3W 70-72cm	29.50	13434-13	9.48026	0.01971	0.149	98.7	544.1	5.7
4H 3W 70-72cm	29.50	13434-19	5.45486	0.02025	0.275	98.6	547.5	5.6
4H 3W 70-72cm	29.50	13434-05	12.12558	0.00801	0.295	98.9	617.6	6.3
4H 3W 70-72cm	29.50	13434-21	17.07013	0.05117	0.028	98.1	634.7	9.2
4H 3W 70-72cm	29.50	13434-15	6.51937	0.01138	0.178	99.3	643.5	6.6
4H 3W 70-72cm	29.50	13434-27	17.36249	0.00584	0.075	98.7	702.5	7.7
4H 3W 70-72cm	29.50	13433-03	8.65392	0.01443	0.102	99.8	827.6	10.6
4H 3W 70-72cm	29.50	13433-11	10.24487	0.02059	0.082	101.6	1131.5	14.1
4H 3W 70-72cm	29.50	13433-07	6.06085	0.02874	0.293	100.1	1134.2	12.5
4H 3W 70-72cm	29.50	13433-04	6.54835	0.00266	0.212	100.3	1141.6	13.3
4H 3W 70-72cm	29.50	13434-08	7.3807	0.01341	0.209	99.6	1147.9	12.5
4H 3W 70-72cm	29.50	13434-07	6.70376	0.00964	0.41	99.1	1152.0	12.1
4H 3W 70-72cm	29.50	13434-09	6.31794	0.0143	0.169	99.5	1152.7	11.9
4H 3W 70-72cm	29.50	13434-20	7.99392	-0.00369	0.096	99.6	1162.7	12.4
4H 3W 70-72cm	29.50	13433-05	12.49933	0.01219	0.194	100.1	1202.8	14.5

4H 3W 70-72cm	29.50	13434-03	45.00068	0.12699	0.107	99.9	1322.3	17.9
4H 3W 70-72cm	29.50	13434-11	9.00424	0.01865	0.2	99.7	1539.4	16.8
4H 3W 70-72cm	29.50	13434-18	15.24398	0.01079	0.103	99.1	1667.7	17.5
4H 3W 70-72cm	29.50	13433-08	11.52916	0.03292	0.161	100	2510.8	25.9
4H 7W 20-22cm	35.00	13435-15	11.83705	0.01854	0.078	97.2	478.9	5.3
4H 7W 20-22cm	35.00	13435-14	5.70303	0.03224	0.559	99.4	487.8	5.0
4H 7W 20-22cm	35.00	13435-10	6.10639	0.0209	0.063	100.6	500.0	7.1
4H 7W 20-22cm	35.00	13435-04	15.00321	0.02721	0.079	101.1	500.7	7.6
4H 7W 20-22cm	35.00	13435-18	9.4632	0.01104	0.096	97.5	500.8	6.5
4H 7W 20-22cm	35.00	13435-19	7.75895	0.01055	0.069	99.9	503.0	6.7
4H 7W 20-22cm	35.00	13435-28	7.84849	-0.00685	0.099	96.5	511.7	5.5
4H 7W 20-22cm	35.00	13435-30	6.27653	0.0438	0.161	98	512.3	5.3
4H 7W 20-22cm	35.00	13435-29	8.83865	0.03123	0.1	99.1	521.6	5.5
4H 7W 20-22cm	35.00	13435-25	9.36829	-0.01341	0.09	96.6	522.7	6.3
4H 7W 20-22cm	35.00	13435-05	8.41273	0.02322	0.152	101.8	528.8	6.8
4H 7W 20-22cm	35.00	13435-09	8.4132	0.03432	0.17	99.9	549.6	6.8
4H 7W 20-22cm	35.00	13435-27	7.72194	0.02201	0.19	96.5	559.4	5.8
4H 7W 20-22cm	35.00	13435-02	7.09894	0.05684	0.241	99.3	561.0	6.2
4H 7W 20-22cm	35.00	13435-21	5.84311	0.03772	0.613	99.1	563.8	5.9
4H 7W 20-22cm	35.00	13435-03	40.04572	-0.00158	0.049	101.6	564.7	9.8
4H 7W 20-22cm	35.00	13435-11	13.52625	0.0129	0.09	99.9	568.6	6.3
4H 7W 20-22cm	35.00	13435-07	11.76236	-0.00489	0.148	99.3	595.6	7.3
4H 7W 20-22cm	35.00	13435-06	6.86506	0.02301	0.11	98.2	599.4	7.2
4H 7W 20-22cm	35.00	13435-26	2.68648	0.03763	0.2	98.7	638.5	6.6
4H 7W 20-22cm	35.00	13435-23	9.51944	0.00566	0.08	97.8	654.9	7.1
4H 7W 20-22cm	35.00	13435-16	5.64953	0.00657	0.271	98.3	660.7	7.2
4H 7W 20-22cm	35.00	13435-12	5.89135	0.09657	0.578	99.3	661.0	6.7
4H 7W 20-22cm	35.00	13435-31	6.54502	0.00962	0.112	98.1	807.4	8.5
4H 7W 20-22cm	35.00	13435-24	11.01637	-0.00468	0.09	97.5	1118.1	11.7
4H 7W 20-22cm	35.00	13435-13	33.28719	0.01682	0.086	97.3	1118.7	12.0
4H 7W 20-22cm	35.00	13435-22	7.22823	0.01154	0.17	99.3	1123.9	11.5
4H 7W 20-22cm	35.00	13435-01	6.24407	0.01572	0.174	98.4	1136.5	12.8
4H 7W 20-22cm	35.00	13435-08	7.42167	0.01473	0.112	100.6	1137.8	12.1
4H 7W 20-22cm	35.00	13435-17	5.27633	0.02961	0.535	99.6	1139.8	12.0
4H 7W 20-22cm	35.00	13435-20	5.78448	0.01107	0.103	99.8	1140.3	11.9
4H 7W 20-22cm	35.00 *	13436-01	8.10049	0.01504	0.407	96.7	723.7	8.1
4H 7W 20-22cm	35.00 *	13436-02	10.07389	0.00024	0.485	98.4	1297.7	13.2
4H 7W 20-22cm	35.00 *	13436-03	8.1436	0.00411	0.475	100.1	1138.1	11.9
4H 7W 20-22cm	35.00 *	13436-04	12.82688	0.04677	0.154	100.6	568.2	7.1
5H 4W 20-22cm	40.00	13437-14	24.27093	0.00912	0.034	96.6	457.0	6.9
5H 4W 20-22cm	40.00	13437-03	14.2513	0.04686	0.039	97.4	462.7	5.8
5H 4W 20-22cm	40.00	13437-24	8.0202	0.04102	0.072	97	479.9	5.5
5H 4W 20-22cm	40.00	13437-18	21.16245	0.03062	0.069	96.7	485.1	5.6
5H 4W 20-22cm	40.00	13437-21	7.84913	0.00652	0.148	97.7	490.7	5.1
5H 4W 20-22cm	40.00	13437-13	6.04813	0.15678	0.253	98.7	493.3	5.1
5H 4W 20-22cm	40.00	13437-17	13.37244	0.01604	0.105	98	509.0	6.0
5H 4W 20-22cm	40.00	13437-25	7.55853	0.01914	0.14	94.8	509.5	6.2
5H 4W 20-22cm	40.00	13437-02	22.72464	-0.00475	0.085	99.2	511.9	6.9
5H 4W 20-22cm	40.00	13437-07	8.47291	0.04272	0.165	99.6	513.6	6.0
5H 4W 20-22cm	40.00	13437-16	23.445	0.00683	0.069	94.4	518.6	6.1
5H 4W 20-22cm	40.00	13437-01	9.13301	0.00811	0.164	100.6	523.8	6.4
5H 4W 20-22cm	40.00	13437-22	18.75719	0.00187	0.053	94.8	532.5	6.0
5H 4W 20-22cm	40.00	13437-28	11.09866	0.0117	0.22	98.3	533.2	6.1
5H 4W 20-22cm	40.00	13437-30	10.70566	0.00877	0.166	94.5	535.2	6.4
5H 4W 20-22cm	40.00	13437-12	7.43679	0.00248	0.452	98.4	593.7	6.0
5H 4W 20-22cm	40.00	13437-06	7.00368	0.01698	0.073	95.6	613.8	9.2
5H 4W 20-22cm	40.00	13437-27	10.3588	0.0001	0.088	95.3	634.0	6.8
5H 4W 20-22cm	40.00	13437-08	5.5818	0.09861	0.116	97.2	712.4	9.1
5H 4W 20-22cm	40.00	13437-26	14.16847	0.01209	0.1	97.4	726.1	8.8

5H 4W 20-22cm	40.00	13437-04	38.02655	-0.00803	0.036	93.1	809.5	14.5
5H 4W 20-22cm	40.00	13437-11	30.65236	-0.02177	0.025	99	1063.7	14.1
5H 4W 20-22cm	40.00	13437-10	12.86683	0.05809	0.033	100.1	1068.4	13.1
5H 4W 20-22cm	40.00	13437-15	10.73139	-0.00492	0.061	95.5	1103.3	12.1
5H 4W 20-22cm	40.00	13437-29	6.8078	0.01301	0.128	99.6	1138.9	11.9
5H 4W 20-22cm	40.00	13437-09	20.24755	0.01375	0.064	99.8	1151.5	14.5
5H 4W 20-22cm	40.00	13437-23	22.15308	0.24254	0.037	99.3	1303.0	14.7
5H 4W 20-22cm	40.00	13437-19	44.88111	-0.02547	0.036	98	1614.3	23.0
5H 4W 20-22cm	40.00	13437-05	14.49731	0.00641	0.196	98.4	2697.1	29.5
5H 4W 20-22cm	40.00 *	13438-01	8.07053	0.00885	0.497	99.7	1222.5	13.1
5H 4W 20-22cm	40.00 *	13438-02	15.41888	0.01203	0.586	98.9	500.0	5.3
5H 4W 20-22cm	40.00 *	13438-03	6.57913	0.04117	0.51	98.8	501.1	5.4
5H 4W 60-62cm	40.40	13582-20	0.04447	0.01459	0.16	74.6	34.7	0.7
5H 4W 60-62cm	40.40	13582-25	28.11341	-0.10359	0.013	80.3	450.6	12.4
5H 4W 60-62cm	40.40	13582-02	4.8559	0.13263	0.549	99.3	490.6	5.2
5H 4W 60-62cm	40.40	13582-04	5.25181	0.0087	0.415	99.4	495.0	5.3
5H 4W 60-62cm	40.40	13582-03	5.99303	0.07446	0.174	98.8	509.8	5.3
5H 4W 60-62cm	40.40	13582-19	15.91514	0.03489	0.063	97.5	518.2	7.8
5H 4W 60-62cm	40.40	13582-09	6.94865	0.00098	0.132	96.4	535.0	6.6
5H 4W 60-62cm	40.40	13582-05	13.92717	0.01043	0.128	97.8	561.0	6.4
5H 4W 60-62cm	40.40	13582-06	5.57662	0.03896	0.252	98.2	591.2	6.1
5H 4W 60-62cm	40.40	13582-18	5.80013	0.01507	0.29	99.2	592.9	6.0
5H 4W 60-62cm	40.40	13582-15	11.25045	0.01	0.208	98.7	605.5	6.2
5H 4W 60-62cm	40.40	13582-11	8.37235	-0.00896	0.127	96.5	618.4	6.6
5H 4W 60-62cm	40.40	13582-16	7.61027	0.00737	0.257	98	663.6	7.3
5H 4W 60-62cm	40.40	13582-08	4.55317	0.00538	0.273	99	679.1	6.9
5H 4W 60-62cm	40.40	13582-22	9.26595	0.03432	0.022	96.1	716.3	10.1
5H 4W 60-62cm	40.40	13582-14	15.39067	0.02209	0.157	97.1	726.9	7.6
5H 4W 60-62cm	40.40	13582-17	29.23116	0.10023	0.025	96.4	1073.0	13.1
5H 4W 60-62cm	40.40	13582-10	5.43952	0.04748	0.162	99.3	1097.0	12.5
5H 4W 60-62cm	40.40	13582-12	6.66491	0.02115	0.25	97.1	1099.7	11.8
5H 4W 60-62cm	40.40	13582-07	5.59632	0.00325	0.115	99.1	1137.9	11.8
5H 4W 60-62cm	40.40	13582-23	7.10788	-0.01422	0.064	99.1	1140.6	11.9
5H 4W 60-62cm	40.40	13582-01	24.4663	0.06892	0.032	94.9	1157.4	17.6
5H 4W 60-62cm	40.40	13582-24	11.24901	-0.01176	0.029	99.5	1167.5	19.3
5H 4W 60-62cm	40.40	13582-21	76.31694	0.08238	0.006	89.6	3941.7	51.2
6H 1W 15-17cm	44.95	13439-18	7.99416	0.05482	0.283	99.2	475.9	4.9
6H 1W 15-17cm	44.95	13439-07	7.72614	0.01638	1.149	98.7	479.1	4.8
6H 1W 15-17cm	44.95	13439-19	6.49164	0.00252	1.187	99.5	488.9	5.0
6H 1W 15-17cm	44.95	13439-24	10.2298	0.03562	0.152	95.1	492.6	5.1
6H 1W 15-17cm	44.95	13439-15	43.09195	0.00923	0.175	92.7	497.7	5.2
6H 1W 15-17cm	44.95	13439-08	7.27069	0.04615	0.295	96.3	498.0	5.1
6H 1W 15-17cm	44.95	13439-16	34.55521	0.03953	0.376	92.5	500.2	5.1
6H 1W 15-17cm	44.95	13439-14	5.95374	0.04349	0.422	98.3	501.6	5.1
6H 1W 15-17cm	44.95	13439-21	7.20331	0.01803	0.331	99.4	504.3	5.5
6H 1W 15-17cm	44.95	13439-02	11.61882	0.04655	0.334	94.8	506.5	5.8
6H 1W 15-17cm	44.95	13439-20	5.2694	0.02026	0.37	99	516.6	5.3
6H 1W 15-17cm	44.95	13439-01	6.21979	0.0521	0.118	92	521.4	5.6
6H 1W 15-17cm	44.95	13439-03	7.2327	0.03983	0.207	100.2	525.7	6.4
6H 1W 15-17cm	44.95	13439-23	6.45109	0.00745	0.312	97.5	525.8	5.7
6H 1W 15-17cm	44.95	13439-10	6.66732	0.01346	0.542	99.7	550.2	5.6
6H 1W 15-17cm	44.95	13439-11	10.12618	0.02696	1.011	94.1	550.9	5.7
6H 1W 15-17cm	44.95	13439-17	8.86583	0.01295	0.42	98.5	604.1	6.2
6H 1W 15-17cm	44.95	13439-04	25.59683	0.06505	0.025	94.1	608.3	9.0
6H 1W 15-17cm	44.95	13439-13	5.45653	0.01943	0.498	94.7	630.2	6.4
6H 1W 15-17cm	44.95	13439-09	20.73213	0.02451	0.141	94.3	634.8	6.7
6H 1W 15-17cm	44.95	13439-05	20.73428	0.01417	0.521	94.9	733.1	8.0
6H 1W 15-17cm	44.95	13439-22	38.97733	0.00065	0.284	88.4	821.1	8.4
6H 1W 15-17cm	44.95	13439-12	12.73448	0.03855	0.189	84.8	842.7	8.8

6H 1W 15-17cm	44.95	13439-06	27.55624	0.00172	0.086	98.7	1481.5	15.6
6H 1W 84-86cm	45.64	13482-05	8.81747	0.00561	0.241	100.5	478.5	2.0
6H 1W 84-86cm	45.64	13482-02	26.6647	0.00838	0.092	98.3	489.1	6.2
6H 1W 84-86cm	45.64	13482-12	5.60735	0.06128	0.219	99	508.9	2.4
6H 1W 84-86cm	45.64	13482-13	6.12765	0.04185	0.035	98.4	509.9	2.2
6H 1W 84-86cm	45.64	13482-15	10.3279	0.0145	0.024	97.2	519.9	1.5
6H 1W 84-86cm	45.64	13482-21	21.9239	0.02395	0.021	98.5	531.8	1.6
6H 1W 84-86cm	45.64	13482-01	6.82941	0.00954	1.977	99.9	539.5	2.0
6H 1W 84-86cm	45.64	13482-09	7.96593	0.02964	0.161	99.7	547.6	2.9
6H 1W 84-86cm	45.64	13482-20	12.61632	-0.0112	0.006	96.4	640.0	3.6
6H 1W 84-86cm	45.64	13482-17	30.03107	-0.32994	0	85.2	678.2	32.0
6H 1W 84-86cm	45.64	13482-23	22.56624	0.01932	0.098	95.7	698.8	1.9
6H 1W 84-86cm	45.64	13482-04	13.46817	0.02417	0.42	98.2	896.6	3.8
6H 1W 84-86cm	45.64	13482-07	8.16158	-0.00655	0.051	99.7	1092.2	9.9
6H 1W 84-86cm	45.64	13482-22	7.01826	0.02215	0.086	99.6	1108.2	2.8
6H 1W 84-86cm	45.64	13482-11	7.06323	0.01267	0.433	99.8	1114.5	4.5
6H 1W 84-86cm	45.64	13482-08	13.42312	-0.00426	0.365	99.4	1117.1	3.8
6H 1W 84-86cm	45.64	13482-10	10.69392	-0.00578	0.084	99.9	1119.8	6.0
6H 1W 84-86cm	45.64	13482-18	6.82823	0.04858	0.009	99.3	1125.2	4.5
6H 1W 84-86cm	45.64	13482-19	35.92711	-0.03262	0.003	97.9	1137.7	8.1
6H 1W 84-86cm	45.64	13482-16	7.79609	0.00525	0.017	99.9	1172.9	5.8
6H 1W 84-86cm	45.64	13482-06	12.84223	0.0074	0.207	99.3	1192.2	2.9
6H 1W 84-86cm	45.64	13482-14	597.76553	-0.14897	0.001	74.2	1491.6	22.9
6H 1W 84-86cm	45.64	13482-03	7.28054	0.01035	0.972	99.5	1811.7	5.2
6H 1W 94-96cm	45.74	13481-13	0.00605	-0.00257	0.244	84.1	56.6	2.0
6H 1W 94-96cm	45.74	13481-09	2.66657	0.49811	0.001	27.8	302.8	333.6
6H 1W 94-96cm	45.74	13481-12	6.10327	0.02684	0.082	100	467.5	6.1
6H 1W 94-96cm	45.74	13481-18	5.83873	0.09894	0.46	99.8	486.7	1.2
6H 1W 94-96cm	45.74	13481-16	9.38918	0.04257	0.207	99.6	496.6	2.4
6H 1W 94-96cm	45.74	13481-24	14.01213	0.01102	0.01	97.6	511.2	2.2
6H 1W 94-96cm	45.74	13481-01	7.86427	0.0031	0.26	99.2	513.9	2.0
6H 1W 94-96cm	45.74	13481-11	15.85569	0.03331	0.075	98.7	519.7	5.6
6H 1W 94-96cm	45.74	13481-10	11.35659	0.01008	0.488	100	527.5	2.0
6H 1W 94-96cm	45.74	13481-22	9.7295	0.01909	0.007	100.4	537.3	2.5
6H 1W 94-96cm	45.74	13481-20	13.8093	0.02551	0.069	99	574.9	6.3
6H 1W 94-96cm	45.74	13481-21	7.02095	0.05049	0.036	99.4	593.5	3.0
6H 1W 94-96cm	45.74	13481-14	8.99911	0.064	0.338	99.7	600.9	1.6
6H 1W 94-96cm	45.74	13481-04	21.88017	0.01051	0.099	99	692.4	4.6
6H 1W 94-96cm	45.74	13481-19	24.24528	-0.01353	0.056	98.7	701.0	10.1
6H 1W 94-96cm	45.74	13481-23	12.23844	0.01615	0.009	98.2	736.1	3.2
6H 1W 94-96cm	45.74	13481-08	8.23428	0.01171	0.308	99	1063.4	4.7
6H 1W 94-96cm	45.74	13481-07	13.21429	0.00451	0.39	99.1	1090.8	2.6
6H 1W 94-96cm	45.74	13481-05	6.87671	0.03163	0.12	99.4	1136.8	4.5
6H 1W 94-96cm	45.74	13481-17	9.45931	0.02861	0.098	100	1147.6	5.7
6H 1W 94-96cm	45.74	13481-03	17.36446	0.012	0.073	99.8	1148.0	6.9
6H 1W 94-96cm	45.74	13481-02	21.14915	0.00494	0.232	99.6	1392.6	3.3
6H 1W 94-96cm	45.74	13481-15	36.89571	-0.03061	0.069	98.3	1946.8	17.0
6H 1W 94-96cm	45.74	13481-06	17.28017	-0.00231	0.069	99.7	2845.0	10.7
6H 1W 104-106cm	45.84	13479-18	13.3723	0.00116	0.735	94.3	474.5	1.6
6H 1W 104-106cm	45.84	13479-16	5.35384	0.04145	1.016	99.2	481.2	1.5
6H 1W 104-106cm	45.84	13479-01	6.79553	0.02676	0.752	99.8	483.2	0.9
6H 1W 104-106cm	45.84	13479-19	8.95958	0.02095	0.246	99.1	487.3	2.8
6H 1W 104-106cm	45.84	13479-17	4.89205	0.04425	1.554	99.6	487.4	1.5
6H 1W 104-106cm	45.84	13479-05	11.34314	0.00372	0.184	99.2	499.7	2.6
6H 1W 104-106cm	45.84	13479-03	12.06513	-0.00402	0.435	99.4	512.9	1.3
6H 1W 104-106cm	45.84	13479-22	9.39988	0.00268	0.031	99.7	520.3	2.1
6H 1W 104-106cm	45.84	13479-10	16.30926	0.00918	0.107	99.3	523.3	5.2
6H 1W 104-106cm	45.84	13479-15	41.74596	-0.0072	0.046	97.5	544.3	9.0

6H 1W 104-106cm	45.84	13479-07	10.54733	0.00778	0.525	99.4	566.1	1.2
6H 1W 104-106cm	45.84	13479-21	8.82226	0.02759	0.015	98.7	594.5	3.9
6H 1W 104-106cm	45.84	13479-11	20.76854	0.0539	0.328	96.4	668.1	1.9
6H 1W 104-106cm	45.84	13479-02	23.99345	-0.00359	0.141	98.9	671.3	3.4
6H 1W 104-106cm	45.84	13479-06	27.96411	-0.0092	0.334	94	673.2	3.4
6H 1W 104-106cm	45.84	13479-13	30.52615	0.01262	0.126	97.5	683.5	3.8
6H 1W 104-106cm	45.84	13479-14	23.40237	0	0.121	96.6	801.0	4.3
6H 1W 104-106cm	45.84	13479-09	20.97384	0.057	0.057	98.2	843.9	7.9
6H 1W 104-106cm	45.84	13479-23	7.77198	0.0184	0.014	99.4	900.0	2.9
6H 1W 104-106cm	45.84	13479-04	9.5687	0.00241	0.157	99	1045.7	7.0
6H 1W 104-106cm	45.84	13479-08	9.61577	0.00181	0.085	99	1050.2	5.9
6H 1W 104-106cm	45.84	13479-24	14.1319	0.00793	0.014	99.6	1059.4	3.4
6H 1W 104-106cm	45.84	13479-20	7.62191	0.01137	0.095	98.8	1109.9	5.6
6H 1W 104-106cm	45.84	13479-12	6.69613	0.07015	0.326	99.3	2189.7	9.4
6H 1W 110-112cm	45.90	13478-13	4.40738	0.02908	0.017	89.1	489.3	4.0
6H 1W 110-112cm	45.90	13478-01	7.06443	0.01703	1.089	99.8	489.9	1.3
6H 1W 110-112cm	45.90	13478-14	28.85948	-0.00358	0.014	92.8	494.4	1.8
6H 1W 110-112cm	45.90	13478-17	7.9238	0.00478	0.055	96	517.0	0.8
6H 1W 110-112cm	45.90	13478-15	6.24821	0.04887	0.025	99.1	517.4	1.3
6H 1W 110-112cm	45.90	13478-07	16.14715	-0.00722	0.075	99.5	519.6	5.8
6H 1W 110-112cm	45.90	13478-23	14.55595	0.00843	0.032	99.5	530.4	1.3
6H 1W 110-112cm	45.90	13478-16	8.41937	0.01229	0.022	98	537.2	3.1
6H 1W 110-112cm	45.90	13478-19	11.5332	0.00492	0.005	88.9	553.3	7.7
6H 1W 110-112cm	45.90	13478-24	27.09227	0.04789	0.002	96.2	598.4	5.8
6H 1W 110-112cm	45.90	13478-06	31.18937	-0.0095	0.129	97.3	599.4	5.7
6H 1W 110-112cm	45.90	13478-12	16.73199	-0.01699	0.08	97.7	606.2	5.4
6H 1W 110-112cm	45.90	13478-10	48.25251	-0.00789	0.045	97.9	641.9	9.6
6H 1W 110-112cm	45.90	13478-02	7.68663	0.00184	0.253	97.4	655.0	3.4
6H 1W 110-112cm	45.90	13478-09	9.69399	0.00063	0.139	99.5	1108.1	7.6
6H 1W 110-112cm	45.90	13478-20	6.53314	0.00736	0.184	99.6	1130.5	1.9
6H 1W 110-112cm	45.90	13478-08	11.84711	0.00483	0.256	98.4	1131.0	6.4
6H 1W 110-112cm	45.90	13478-11	34.56316	-0.05662	0.053	100.3	1173.9	9.3
6H 1W 110-112cm	45.90	13478-21	9.2889	0.00919	0.016	96	1174.6	3.6
6H 1W 110-112cm	45.90	13478-04	20.31973	-0.00439	0.04	100.2	1215.6	11.6
6H 1W 110-112cm	45.90	13478-22	42.66258	0.13567	0.004	99.5	1340.7	16.7
6H 1W 110-112cm	45.90	13478-03	12.40343	0.0124	0.678	99.7	1389.1	4.9
6H 1W 110-112cm	45.90	13478-05	20.047	-0.01177	0.071	99	1561.8	8.3
6H 1W 110-112cm	45.90	13478-18	49.84658	-0.03974	0.005	99.8	2489.8	11.4
6H 3W 135-137cm	49.15	13583-01	4.60348	0.00725	0.235	99.6	517.4	5.7
6H 3W 135-137cm	49.15	13583-03	4.57562	0.00843	0.169	98.8	522.2	5.9
6H 3W 135-137cm	49.15	13583-04	5.10618	0.00671	0.2	99.8	522.9	5.4
6H 3W 135-137cm	49.15	13583-02	4.57656	0.00855	0.148	100.3	528.7	5.5

* Hornblendes >1mm in diameter, all others <1mm

Table 5.3. Hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age ranges from DSDP Site 268 (>150 μm).

	Depth (mbsf)	Age (Ma)	0-660 Ma	660-675 Ma	675-1100 Ma	1100-1280 Ma	1280-1840 Ma	Total
1R 1W 72-74cm*	0.72		3	1	4	21	3	32
3R 2W 81-82cm	57.81	2.3	1	8	3	45	6	63
5R 1W 88-89cm	114.38	4.2	1	0	2	35	6	44
Total			5	9	9	101	15	139

* from Williams et al. 2010a

Table 5.4. Hornblende grain $^{40}\text{Ar}/^{39}\text{Ar}$ age data from DSDP Site 268 (>150 μm).

Sample	Depth	Run ID	Ca/K	Cl/K	Mol 39Ar	%40Ar*	Age (Ma)	$\pm$ Age
DSDP Site 268								
3R 2W 81-82cm	57.81	15119-54A	4.34277	0.0156	0.021	95.2	468.8	2.6
3R 2W 81-82cm	57.81	15119-14A	6.89222	0.0533	0.006	97.4	657.6	7.3
3R 2W 81-82cm	57.81	15119-35A	6.89121	0.0653	0.019	99	660.3	3.3
3R 2W 81-82cm	57.81	15119-16A	5.94190	0.0118	0.097	99.9	662.8	1.7
3R 2W 81-82cm	57.81	15119-59A	6.47832	0.0924	0.021	98	663.5	3.1
3R 2W 81-82cm	57.81	15119-12A	6.79540	0.0394	0.01	98.4	665.0	4.9
3R 2W 81-82cm	57.81	15119-03A	6.56015	0.0472	0.048	99.6	665.1	2.1
3R 2W 81-82cm	57.81	15119-18A	6.08326	0.0221	0.01	98.4	673.8	4.6
3R 2W 81-82cm	57.81	15119-40A	6.64512	0.0595	0.015	98.4	674.9	4.3
3R 2W 81-82cm	57.81	15119-46A	6.49786	0.0397	0.019	99.1	888.3	4.2
3R 2W 81-82cm	57.81	15119-55A	5.02140	0.0073	0.024	99.5	900.4	3.6
3R 2W 81-82cm	57.81	15119-56A	7.01417	0.0075	0.034	99.2	987.3	3.5
3R 2W 81-82cm	57.81	15119-04A	9.23064	-0.0428	0.001	93.5	1075.8	29.2
3R 2W 81-82cm	57.81	15119-39A	0.00332	0.0067	0.165	99.8	1075.9	1.9
3R 2W 81-82cm	57.81	15119-21A	7.00298	0.0121	0.046	99.5	1108.3	3.1
3R 2W 81-82cm	57.81	15119-64A	9.90123	0.0194	0.028	99.4	1110.1	4.2
3R 2W 81-82cm	57.81	15119-43A	8.42304	0.0105	0.015	99.3	1114.6	5.2
3R 2W 81-82cm	57.81	15119-11A	6.03527	0.0465	0.031	98.7	1114.6	3.8
3R 2W 81-82cm	57.81	15119-02A	11.11740	-0.0030	0.022	98.5	1119.8	4.4
3R 2W 81-82cm	57.81	15119-36A	10.59580	0.0108	0.028	99.7	1122.5	4.2
3R 2W 81-82cm	57.81	15119-44A	14.99360	0.0167	0.02	98.7	1123.0	4.9
3R 2W 81-82cm	57.81	15119-31A	6.98475	0.0150	0.02	99.3	1123.3	4.4
3R 2W 81-82cm	57.81	15119-22A	5.67697	0.0282	0.036	99.8	1123.8	3.9
3R 2W 81-82cm	57.81	15119-26A	5.13004	0.0515	0.024	99.8	1124.0	4.9
3R 2W 81-82cm	57.81	15119-08A	7.52779	0.0095	0.033	100.1	1125.6	3.7
3R 2W 81-82cm	57.81	15119-60A	9.11089	0.0128	0.032	99.6	1125.6	3.7
3R 2W 81-82cm	57.81	15119-23A	11.88169	0.0123	0.009	99.5	1126.1	7.5
3R 2W 81-82cm	57.81	15119-53A	6.94684	0.0031	0.015	99.6	1128.0	5.0
3R 2W 81-82cm	57.81	15119-30A	6.13149	0.0136	0.082	99.1	1128.7	2.6
3R 2W 81-82cm	57.81	15119-62A	15.40450	0.0362	0.015	100.2	1130.0	5.2
3R 2W 81-82cm	57.81	15119-25A	7.81741	0.0070	0.04	100	1130.1	3.2
3R 2W 81-82cm	57.81	15119-50A	7.69168	0.0047	0.036	99.8	1131.7	3.8
3R 2W 81-82cm	57.81	15119-52A	12.36697	-0.0228	0.007	99.1	1132.7	8.8
3R 2W 81-82cm	57.81	15119-34A	7.35896	0.0071	0.056	99.7	1134.4	3.1
3R 2W 81-82cm	57.81	15119-19A	7.15850	0.0015	0.024	99.9	1142.7	4.5
3R 2W 81-82cm	57.81	15119-10A	8.46549	0.0099	0.023	99.6	1143.1	4.0
3R 2W 81-82cm	57.81	15119-24A	7.32210	0.0177	0.029	99.9	1143.6	3.9
3R 2W 81-82cm	57.81	15119-48A	7.96545	-0.0027	0.018	99.1	1144.4	4.7
3R 2W 81-82cm	57.81	15119-06A	22.97095	0.0416	0.012	99.1	1149.1	6.4
3R 2W 81-82cm	57.81	15119-29A	27.10155	-0.0182	0.013	98.7	1149.1	6.1
3R 2W 81-82cm	57.81	15119-41A	7.22340	0.0385	0.05	99.4	1153.5	3.1
3R 2W 81-82cm	57.81	15119-63A	8.33921	0.0257	0.01	99.7	1156.3	6.9
3R 2W 81-82cm	57.81	15119-45A	11.16260	0.0036	0.032	99.3	1157.1	3.5
3R 2W 81-82cm	57.81	15119-42A	7.56623	0.0164	0.02	99.8	1162.6	4.5
3R 2W 81-82cm	57.81	15119-33A	8.29671	0.0040	0.009	98.5	1164.0	8.9
3R 2W 81-82cm	57.81	15119-05A	30.19864	0.0164	0.009	94.3	1167.0	7.2
3R 2W 81-82cm	57.81	15119-01A	17.05865	-0.0048	0.038	97.8	1174.1	3.4
3R 2W 81-82cm	57.81	15119-61A	8.44763	0.0099	0.012	97.8	1181.3	6.4
3R 2W 81-82cm	57.81	15119-47A	10.60100	0.0045	0.016	99.4	1183.0	5.3
3R 2W 81-82cm	57.81	15119-49A	8.14613	-0.0018	0.069	99.8	1184.0	2.9
3R 2W 81-82cm	57.81	15119-51A	20.86062	-0.0142	0.026	98.9	1191.6	4.7
3R 2W 81-82cm	57.81	15119-37A	23.77114	0.0404	0.007	99.4	1195.7	8.4
3R 2W 81-82cm	57.81	15119-13A	10.63966	0.0130	0.015	99.6	1197.5	5.1
3R 2W 81-82cm	57.81	15119-38A	16.75281	0.0088	0.021	98.9	1208.7	4.6
3R 2W 81-82cm	57.81	15119-28A	35.12976	-0.0199	0.006	99	1216.8	10.0
3R 2W 81-82cm	57.81	15119-32A	14.39944	-0.0084	0.013	99.5	1222.0	6.6
3R 2W 81-82cm	57.81	15119-07A	13.74542	-0.0068	0.014	96.3	1229.3	6.7

3R 2W 81-82cm	57.81	15119-58A	23.01768	0.0591	0.003	93.3	1276.1	19.0
3R 2W 81-82cm	57.81	15119-20A	9.19349	0.0077	0.016	99.9	1276.8	6.6
3R 2W 81-82cm	57.81	15119-15A	22.28298	0.0156	0.011	99.8	1434.6	8.0
3R 2W 81-82cm	57.81	15119-17A	8.67190	0.0112	0.03	99.7	1439.8	4.3
3R 2W 81-82cm	57.81	15119-57A	10.90280	0.0272	0.017	99.5	1541.5	6.0
3R 2W 81-82cm	57.81	15119-27A	18.53110	-0.0603	0.005	99	1670.3	14.3
5R 1W 88-89cm	114.38	15116-32A	6.49707	0.0778	0.008	93	313.3	5.0
5R 1W 88-89cm	114.38	15116-31A	6.33401	0.0235	0.005	100	1003.1	10.4
5R 1W 88-89cm	114.38	15116-34A	5.26090	0.0124	0.01	95.6	1022.2	6.9
5R 1W 88-89cm	114.38	15116-03A	15.15757	-0.0413	0.011	98.1	1096.9	6.3
5R 1W 88-89cm	114.38	15116-46A	8.42417	0.0526	0.006	99.6	1100.9	10.3
5R 1W 88-89cm	114.38	15116-37A	9.50119	-0.0203	0.006	84.3	1106.1	10.2
5R 1W 88-89cm	114.38	15116-11A	6.93022	0.0081	0.008	98.4	1119.1	9.0
5R 1W 88-89cm	114.38	15116-42A	6.37414	0.0114	0.008	99	1119.2	7.3
5R 1W 88-89cm	114.38	15116-39A	6.00282	-0.0395	0.008	98.8	1120.5	8.5
5R 1W 88-89cm	114.38	15116-14A	7.03711	-0.0376	0.006	100.1	1122.2	9.0
5R 1W 88-89cm	114.38	15116-43A	7.80858	0.0309	0.007	98.3	1123.0	8.4
5R 1W 88-89cm	114.38	15116-22A	12.93653	0.0077	0.005	100.2	1127.7	11.4
5R 1W 88-89cm	114.38	15116-02A	7.28756	-0.0522	0.006	99	1132.6	9.7
5R 1W 88-89cm	114.38	15116-05A	19.15782	0.0203	0.005	100.3	1135.0	11.3
5R 1W 88-89cm	114.38	15116-27A	10.08061	-0.0113	0.016	99.9	1139.1	5.3
5R 1W 88-89cm	114.38	15116-20A	15.91427	-0.0389	0.004	98.8	1142.0	14.0
5R 1W 88-89cm	114.38	15116-24A	10.60115	0.0248	0.003	101.1	1142.1	18.0
5R 1W 88-89cm	114.38	15116-17A	6.67011	0.0129	0.01	100.2	1147.8	7.4
5R 1W 88-89cm	114.38	15116-30A	8.14719	-0.0091	0.013	100.2	1148.4	6.0
5R 1W 88-89cm	114.38	15116-47A	10.00245	0.0298	0.008	100	1149.2	7.6
5R 1W 88-89cm	114.38	15116-19A	8.72584	0.0096	0.01	99.5	1151.8	7.8
5R 1W 88-89cm	114.38	15116-09A	7.66568	-0.0076	0.008	97.7	1153.9	9.1
5R 1W 88-89cm	114.38	15116-06A	6.98844	0.0500	0.007	101	1157.5	9.5
5R 1W 88-89cm	114.38	15116-13A	10.36771	-0.0473	0.007	100.1	1157.9	9.9
5R 1W 88-89cm	114.38	15116-29A	35.23624	0.1242	0.002	100.9	1158.5	22.4
5R 1W 88-89cm	114.38	15116-38A	13.51986	-0.0199	0.024	99.7	1159.3	4.4
5R 1W 88-89cm	114.38	15116-36A	24.26515	-0.1809	0.002	98	1164.2	21.5
5R 1W 88-89cm	114.38	15116-12A	8.19718	-0.0118	0.01	100.5	1167.2	7.6
5R 1W 88-89cm	114.38	15116-41A	10.65467	0.0304	0.005	99.2	1174.2	11.3
5R 1W 88-89cm	114.38	15116-21A	8.89505	-0.0031	0.015	100	1180.5	5.5
5R 1W 88-89cm	114.38	15116-15A	13.24917	0.0221	0.003	102.1	1184.3	18.5
5R 1W 88-89cm	114.38	15116-40A	16.63772	0.0857	0.001	84.5	1185.8	76.5
5R 1W 88-89cm	114.38	15116-18A	8.72645	0.0097	0.016	99.9	1222.2	5.7
5R 1W 88-89cm	114.38	15116-26A	10.34072	-0.0454	0.004	100.2	1227.3	12.6
5R 1W 88-89cm	114.38	15116-04A	18.38673	0.0520	0.004	100.2	1236.5	13.8
5R 1W 88-89cm	114.38	15116-28A	76.03539	-0.0673	0.001	98.4	1248.8	33.2
5R 1W 88-89cm	114.38	15116-23A	12.20222	-0.0191	0.011	99.9	1260.7	6.7
5R 1W 88-89cm	114.38	15116-35A	13.83020	0.0314	0.006	99.9	1458.6	10.1
5R 1W 88-89cm	114.38	15116-10A	7.54520	-0.0160	0.008	100.2	1492.4	9.4
5R 1W 88-89cm	114.38	15116-08A	8.16721	-0.0203	0.005	100.3	1493.0	14.2
5R 1W 88-89cm	114.38	15116-33A	11.16160	0.0761	0.006	99	1509.4	12.1
5R 1W 88-89cm	114.38	15116-16A	21.29930	0.0681	0.001	99.7	1555.6	37.8
5R 1W 88-89cm	114.38	15116-25A	7.45436	0.0406	0.011	97.3	1607.5	8.8
5R 1W 88-89cm	114.38	15116-07A	9.83166	0.0472	0.007	99.3	1836.0	11.0

average, ~66% of all analysed hornblende grains deposited between ~3.27 and 4.99 Ma have $^{40}\text{Ar}/^{39}\text{Ar}$ ages that fall within the younger population (455-575 Ma). Grains with $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 1035 and 1315 Ma make up only ~17% of the total of all hornblende grains. In contrast, hornblendes with these $^{40}\text{Ar}/^{39}\text{Ar}$ ages display up to a two-fold increase in

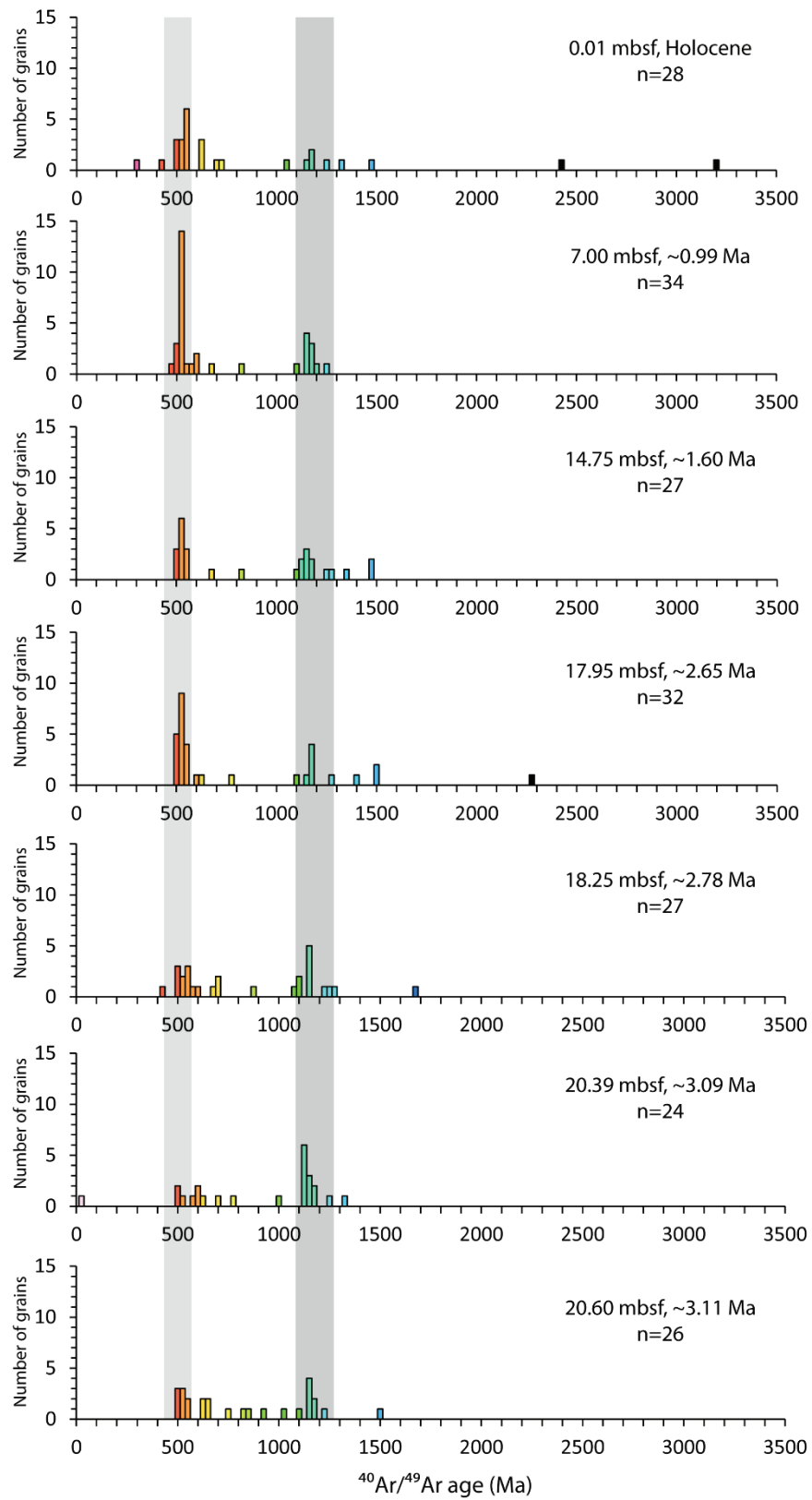
abundance between ~2.7 Ma and ~3.207 Ma, making up on average 33% of all grains analysed. The core-top sample shows a hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age distribution similar to sediments deposited before 3.27 Ma, with the younger population dominating (~67%).

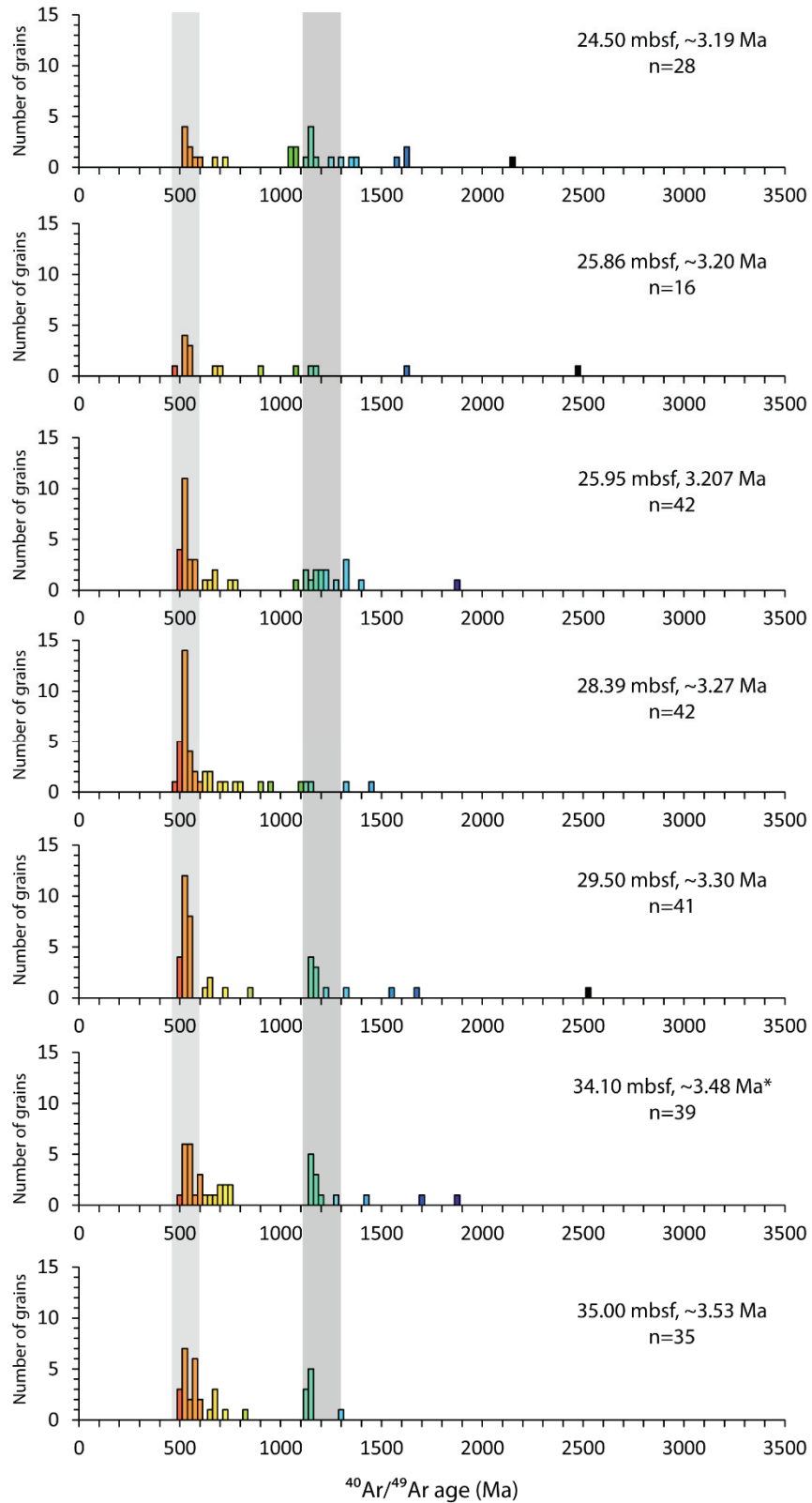
To better identify variability of these two main hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age populations through time, their combined abundances were set to 100% (i.e. excluding all other age populations) and a ratio was calculated by calculating the percentage of one population relative to the other (Figure 5.5). Values that approach one indicate increased relative abundance of the older $^{40}\text{Ar}/^{39}\text{Ar}$ age population (1035-1315 Ma), and values that approach zero contain more of the younger $^{40}\text{Ar}/^{39}\text{Ar}$ age population (455-575 Ma). Ratios between the two end members vary between 0 and 0.55 and show a clear increase in the older age population after ~3.207 Ma, with an average ratio value of 0.21 before ~3.207 Ma, and an average ratio of 0.40 after ~3.207 Ma (Figure 5.5). The highest ratio can be observed in two Late Pliocene samples, deposited at ~3.09 Ma (ratio: 0.57) and ~3.19 Ma (ratio: 0.55). Calculated ratios for the Pleistocene (~2.7 to 0.99 Ma) produce an average of 0.37, but Pleistocene samples are limited in number and there are considerable uncertainties about their stratigraphic ages (see Section 3). The core-top sample is characterised by a ratio of 0.21, similar to the average value for the Early Pliocene.

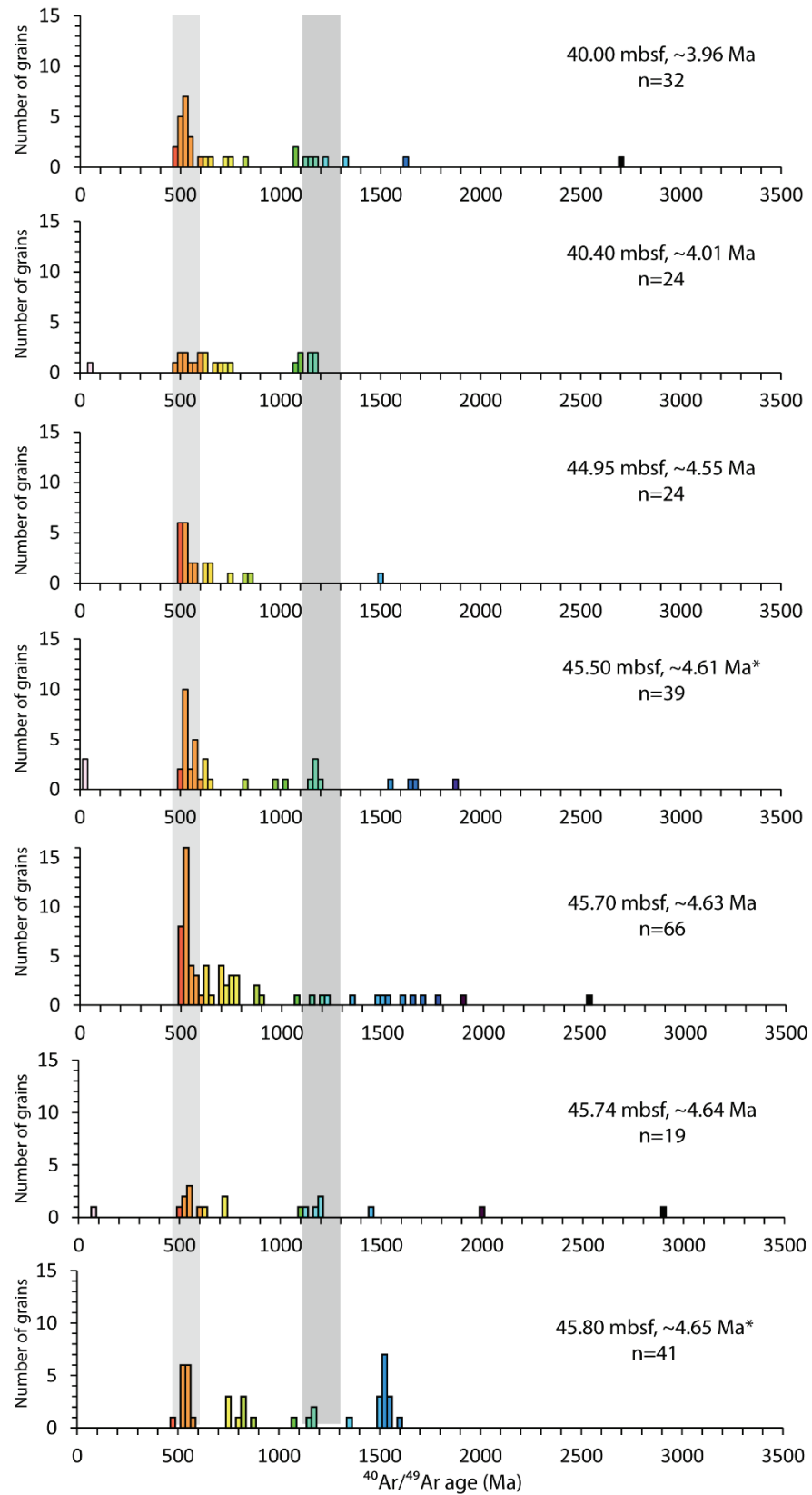
An interesting feature of the downcore record shown in Figure 5.5 is that high resolution sampling produced a large degree of variability in the provenance signature. For example, within an Early Pliocene interval between ~4.6 Ma and ~4.75 Ma (eight samples analysed; four from Williams et al. [2010a], and four from this study), two large ‘pulses’ of the older population (1035 to 1315 Ma) are evident (ratio: 0.50, at ~4.62 Ma; ratio: 0.40 at ~4.68 Ma), although it is important to note that these samples have somewhat low hornblende grain counts (12 grains each).

Hornblende grains extracted from Pliocene DSDP Site 268 sediments are dominated by $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 1100 and 1280 Ma, with 79 grains of 107 in total (~73%) falling within this age range (Tables 5.3 and 5.4, Figure 5.4). Sixty of these 79 grains analysed (~76%) yielded a more narrowly defined hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age range (1115 to 1185 Ma). Remaining hornblende grains showed $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 660 and 675 Ma (8 grains of 107, 7.4%); 675 and 1100 Ma (7 grains, 6.5%); 1280-1840 Ma (11 grains of 107, 10.2%), and 313 ± 4 and 468 ± 2 Ma (two grains).

A. ODP Site 1165







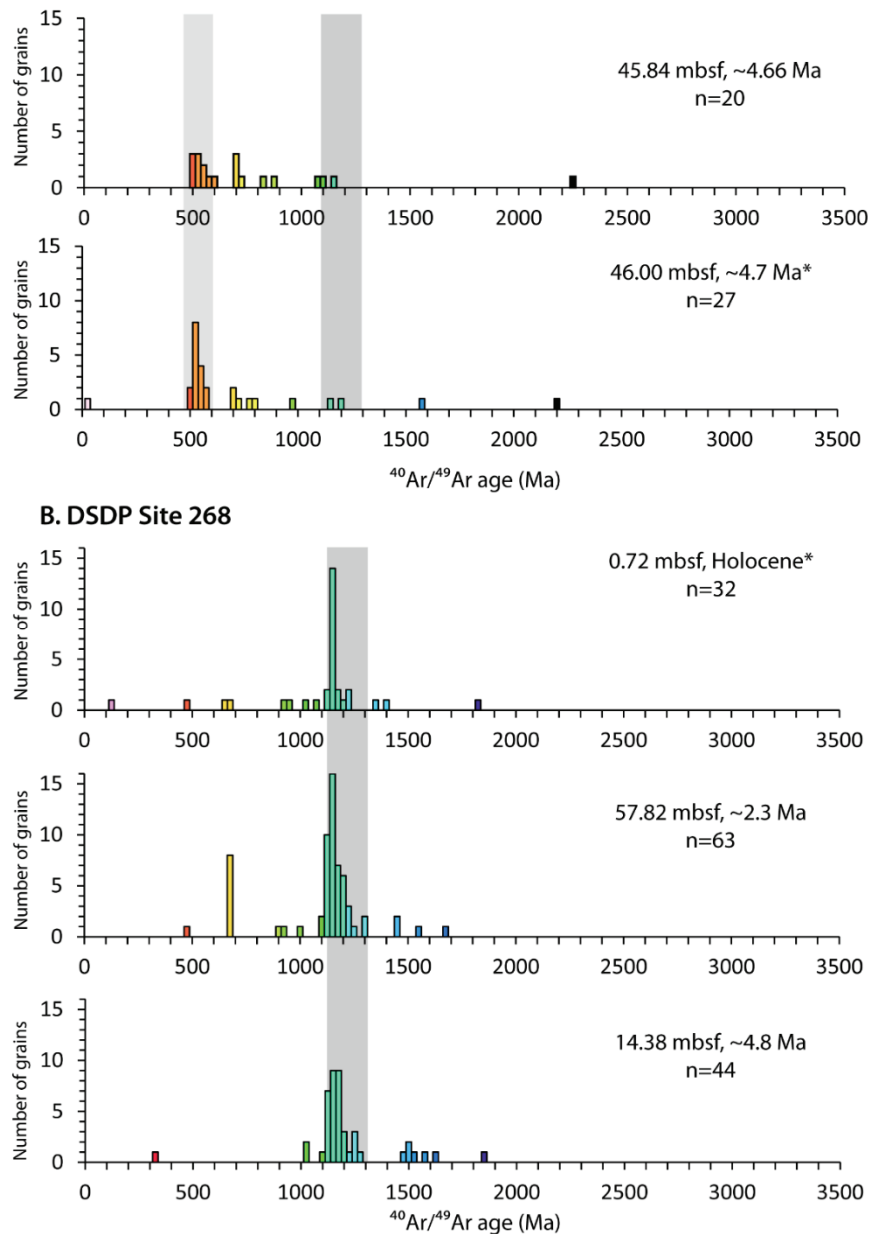


Figure 5.4. Hornblende grain $^{40}\text{Ar}/^{39}\text{Ar}$ age histograms, showing the distribution of grain ages between 0 and 3500 Ma, with number of grains analysed from each sample shown as 'n'. Histogram bars are coloured according to the thermochronological scale bar in Figure 5.2. **a)** Histograms of samples analysed from Holocene and Pliocene ODP Site 1165 sediments where 'n' is greater than 16. Sample 6H 1W 110-112cm [n=12], 6H 1W 84-86cm [n=12] and 6H 3W 135-137cm [n=4] are not plotted due to low grain counts. Samples with stars are from Williams et al. (2010a). Vertical light grey and dark grey bands highlight the two major $^{40}\text{Ar}/^{39}\text{Ar}$ age populations in ODP Site 1165 sediments: 455-575 Ma and 1035-1315 Ma, respectively. **b)** Hornblende grain $^{40}\text{Ar}/^{39}\text{Ar}$ age histograms of Holocene (Williams et al. 2010a) and Pliocene (this study) marine sediments from DSDP Site 268.

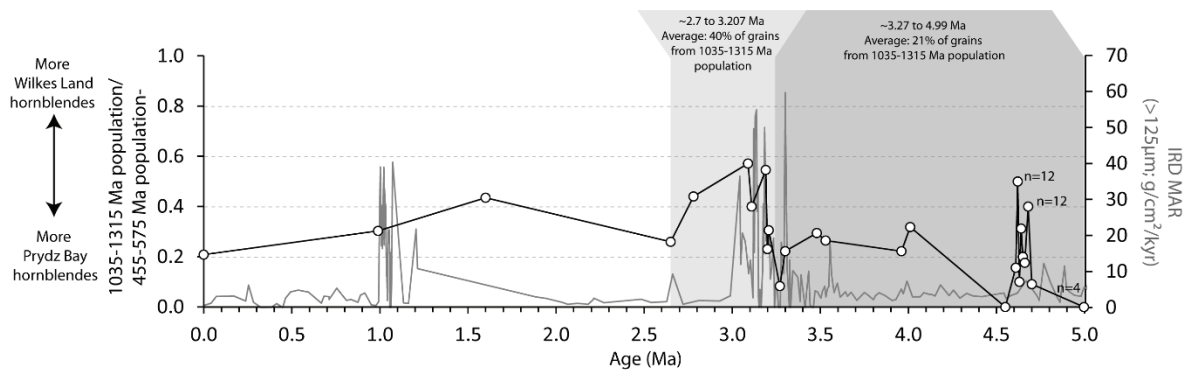


Figure 5.5. Ratio of the relative abundance of hornblendes with $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 1035 and 1315 Ma (Wilkes Land sector) versus those with $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 455 and 575 Ma (Prydz Bay sector) in marine sediments from ODP Site 1165. In order to calculate these fractions their sum has been set to 100% of all grains in each sample (e.g. small age populations of different ages are omitted; see text for further explanation). Samples with low grain counts are annotated with the number of grains analysed. Superimposed is the IRD mass accumulate rate record published by Passchier (2011) for the same site. Note the significant increase in IRD accumulation after ~3.3 Ma.

5.6 Provenance of Pliocene Ice-Rafted Hornblende Grains from ODP Site 1165

Comparison of measured hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages from core-top (Holocene) and Pliocene ODP Site 1165 sediments with published ages from onshore outcrops (Figure 5.2), and other marine sediments proximal to the East Antarctic continent (Figure 5.6), provides insights into the geographical sources of ice-rafted sediments.

5.6.1 Prydz Bay as a source for Paleozoic $^{40}\text{Ar}/^{39}\text{Ar}$ ages of hornblende grains in ODP Site 1165 sediments

The majority of hornblende grains in ODP Site 1165 sediments reveal $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 480 and 550 Ma (Figure 5.6), an age range that matches very well with the most recent major metamorphic event to have affected the nearby East Antarctic continent, the Pan-African Orogeny (450-600 Ma) (Fitzsimons, 2000a; Mikhalsky, 2007; Boger, 2011). Evidence for this pervasive event is manifested as Early Paleozoic granite intrusions and high to medium-grade metamorphism identified in numerous terranes throughout the Prydz Bay region and Princess Elizabeth Land (Zhao et al. 1992, 1997; Hensen and Zhou, 1995; Carson et al. 1996; Fitzsimons et al. 1997; Tong et al. 1998, 2002; Mikhalsky et al. 2006; Corvino

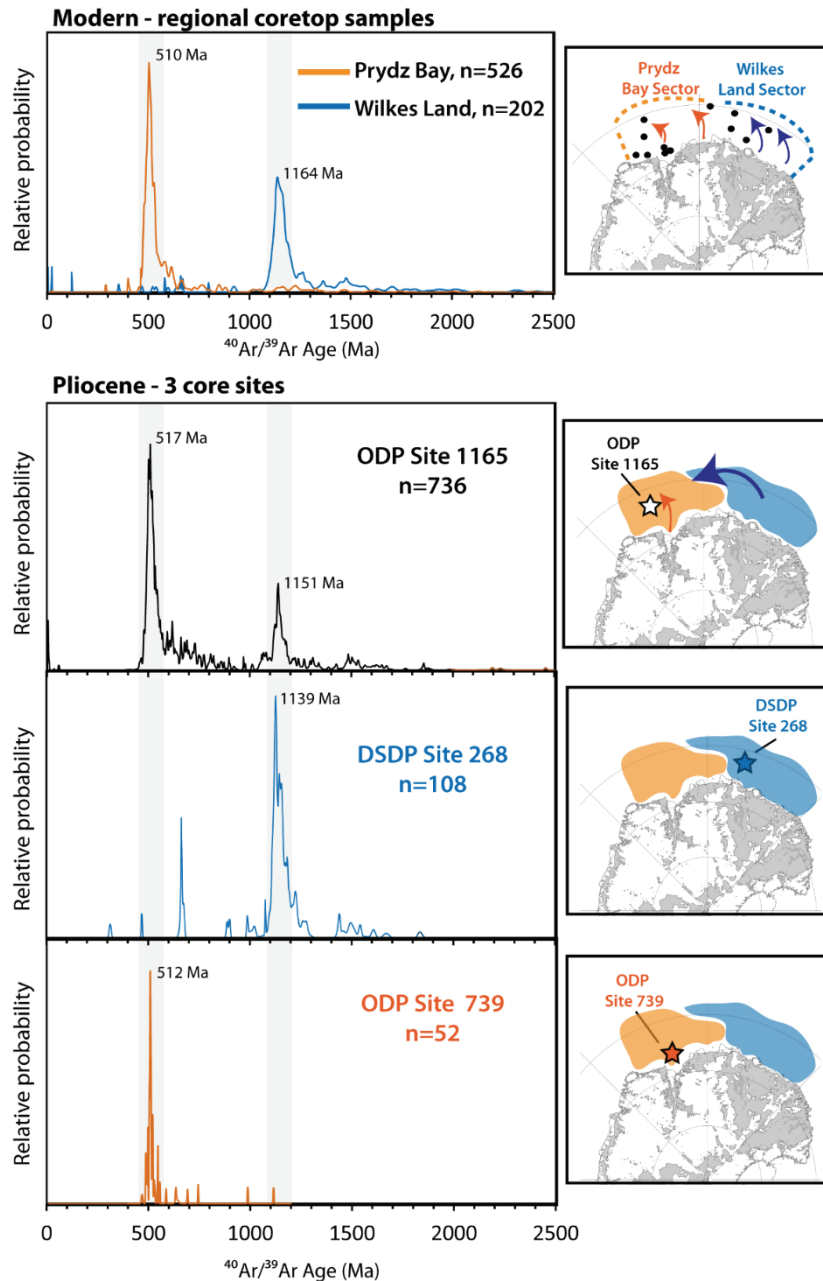


Figure 5.6. Comparison of modern and Pliocene provenance fingerprints offshore Prydz Bay and Wilkes Land. The top panel shows the modern day situation as derived from 12 core locations and their ice-rafted hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Brachfeld et al. 2007; Roy et al. 2007; Pierce et al. 2011; this study). The lower panel shows Pliocene results for three different sites: top - ODP Site 1165 (this study and Williams et al. [2010a]), middle - DSDP Site 268 (this study), bottom - ODP Site 739 (Tochilin et al. 2012). Note the absence of $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 1100 and 1300 Ma in modern Prydz Bay sediments and Pliocene sediments from ODP Site 739. In contrast this population is significant in Pliocene sediments from ODP Site 1165, and in Holocene and Pliocene sediments from DSDP Site 268 (offshore of Wilkes Land). All relative probability and weighted means of the $^{40}\text{Ar}/^{39}\text{Ar}$ age distributions of individual $>150\mu\text{m}$ hornblende grains were calculated using ISOPLLOT (Ludwig, 2003).

and Henjes-Kunst, 2007; Phillips et al. 2007; Liu et al. 2007a, 2009; Wilson et al. 2007; Boger et al. 2001, 2008) (Figs. 5.2 and 5.6). This age signature also regionally dominates ice-rafted hornblende grains in modern marine sediments (Brachfeld et al. 2007; Roy et al. 2007; Pierce et al. 2011; van de Flierdt et al. 2008; Figure 5.2) and in Pliocene sediments from ODP Site 739 (67°16'87"S, 75°04'91"E), located more proximal to the continent than ODP Site 1165 (Tochilin et al. 2012) (Figure 5.6). In summary, this Pan-African IRD signature is likely supplied by icebergs calved into the ocean from the Mac.Robertson Land margin, the Lambert Glacier, and individual glaciers along Princess Elizabeth Land (Figure 5.2).

5.6.2 Wilkes Land as a source for Proterozoic $^{40}\text{Ar}/^{39}\text{Ar}$ ages of hornblende grains in ODP Site 1165 sediments

The second prominent hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ age population identified in ODP Site 1165 sediments shows a Proterozoic age range between 1035 and 1315 Ma (Figure 5.5). Despite numerous terranes in MRL, the Prydz Bay area, and Princess Elizabeth Land showing evidence for Proterozoic formation or overprinting, the exact age range has almost no known analogues in these regions (Figure 5.2). For example, the Rayner Province, exposed in MRL and in the NPCM, and similar terranes exposed in the eastern Prydz Bay region (e.g. the Lambert Terrane, Prydz Belt), show Proterozoic ages between 900 and 990 Ma (Young and Black, 1991; Manton et al. 1992; Kinny et al. 1997; Boger et al. 2000; Boger et al. 2000; Carson et al. 2000; Kelly et al. 2002; Halpin et al. 2007), an age range too young to account for hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages found in Pliocene sediments at ODP Site 1165.

Two terranes could potentially serve as source areas for the specific $^{40}\text{Ar}/^{39}\text{Ar}$ age range (1035-1315 Ma): the Fisher Terrane in the CPCM, and the Rauer Group in Princess Elizabeth Land. Both contain limited evidence for U-Pb zircon ages in the range of 900 to 1300 Ma (Kinny et al. 1993, 1997; Beliatsky et al. 1994; Mikhalsky et al. 1999; Boger et al. 2000, Carson et al. 2000; Fitzsimons, 2000a; Mikhalsky et al. 2001; Tong et al. 2002; Tong and Wilson 2006). Insights into whether the Fisher Terrane could have served as a source for Proterozoic-aged hornblende grains in Pliocene ODP Site 1165 sediments can be gained from the provenance of Pliocene IRD in marine sediments deposited ~200km offshore of the modern front of the Amery Ice Shelf at ODP Site 739 (Tochilin et al. 2012) (Figure 5.6). Hornblende grains in these Pliocene marine sediments are almost exclusively characterised by Paleozoic $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 470 and 560 Ma (Tochilin et al. 2012) (Figure 5.6). As

any icebergs laden with IRD sourced from glaciers near the Fisher Terrane would have had to pass the location of ODP Site 739 in order to reach ODP Site 1165, I render an inland source for Proterozoic aged hornblende grains from the Prince Charles Mountains area as unlikely.

The second potential source region within the Prydz Bay area for Proterozoic $^{40}\text{Ar}/^{39}\text{Ar}$ ages is the Rauer Group in Princess Elizabeth Land, to the east of ODP Site 1165. The Rauer Group exhibits Proterozoic ages in geographically limited high-strain structural features, while surrounding rocks are overprinted with a predominant Paleozoic thermochronological signature (Tong et al. 2002; Tong and Wilson, 2006). Since ice-rafted hornblende grains in Holocene marine sediments deposited offshore Princess Elizabeth Land are dominated by Paleozoic $^{40}\text{Ar}/^{39}\text{Ar}$ ages (Roy et al. 2007, Pierce et al. 2012) (Figure 5.2), it seems unlikely that the Rauer Terrane was a significant source for hornblende grains with Proterozoic $^{40}\text{Ar}/^{39}\text{Ar}$ ages in Pliocene ODP Site 1165 sediments. However, no thermochronological information is available for limited outcrops and Holocene marine sediments in the eastern region of Princess Elizabeth Land (Figure 5.2), and very limited airborne geophysical data is available for areas inland of this region (Figure 5.1; Golynsky et al. 2002). Hence it is not possible to fully exclude unexposed subglacial bedrock inland of Princess Elizabeth Land as a source for the Proterozoic $^{40}\text{Ar}/^{39}\text{Ar}$ aged hornblende grains found at ODP Site 1165.

However, a $^{40}\text{Ar}/^{39}\text{Ar}$ age range between 1050 and 1315 Ma matches very well with the thermochronological ages of bedrock exposures located along the Wilkes Land margin, at the Bunger Hills and the Windmill Islands (Black et al. 1992; Sheraton et al. 1993; Paul et al. 1995; Post et al. 1997, 2000; Möller et al. 2002; Zhang et al. 2012) (Figs. 5.2 and 5.6). Marine sediments deposited offshore of the Wilkes Land margin contain hornblende grains with $^{40}\text{Ar}/^{39}\text{Ar}$ ages dominated by these same Proterozoic signatures (Roy et al. 2007; Williams et al. 2010a; Pierce et al. 2011; Figs. 5.2 and 5.6). Furthermore, ice-rafted hornblende grains in Pliocene marine sediments deposited offshore the Wilkes Land margin, at DSDP Site 268 (Figs. 5.4 and 5.6), are dominated by $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 1100 and 1280 Ma as well. This observation confirms icebergs laden with hornblendes with Proterozoic $^{40}\text{Ar}/^{39}\text{Ar}$ ages were indeed supplied from this margin, not only today but also during the Pliocene. Therefore the Wilkes Land margin is a viable source of Proterozoic-aged hornblende grains. This IRD would have been transported by icebergs over a distance of ~1500km from Wilkes Land, to Prydz Bay, where they were deposited in Pliocene sediments at ODP Site 1165.

5.6.3 Sources of minor $^{40}\text{Ar}/^{39}\text{Ar}$ age ranges in ODP Site 1165 sediments

Eight hornblende grains from six Pliocene sediment layers in ODP Site 1165 (deposited at ~2.8 Ma, ~3.09 Ma, ~4.01 Ma, ~4.6 Ma, ~4.64 Ma, and ~4.75 Ma) yield Cenozoic $^{40}\text{Ar}/^{39}\text{Ar}$ ages ranging between ~6 Ma and 35 Ma (Figure 5.4). These grains are probably sourced from the isolated Cenozoic Gaussberg Volcanic field, located in the vicinity of the Philippi Glacier (Sheraton and Condari, 1980; Murphy et al. 2002) (Figure 5.1). Volcaniclastic material has been identified as clasts in glacier debris in this region (Murphy et al. 2002) suggesting icebergs calved from the Philippi Glacier reached the study site during the Pliocene. The Kerguelen Plateau, located in the Southern Ocean north of Princess Elizabeth Land (Coffin and Eldhom, 1994), can be excluded as a source of Cenozoic $^{40}\text{Ar}/^{39}\text{Ar}$ ages, as Cenozoic volcanic activity is limited to the northern islands of this large igneous province (Nicolaysen et al. 2000). Modern iceberg pathways (see Figure 5.2) render a supply of icebergs from these islands to ODP Site 1165 as highly unlikely.

Hornblende grains with $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 590 and 1035 Ma are not unique to the Pliocene but match similar thermochronological ages in Holocene marine sediments proximal to the Princess Elizabeth Land and offshore of Prydz Bay, including in the core-top of ODP Site 1165, suggesting they were derived from these areas (Brachfeld et al. 2007; Roy et al. 2007; Pierce et al. 2011; this study) (Figs. 5.2 and 5.6).

The oldest group of hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages found at ODP Site 1165 falls mainly in the age range of 1325 to 1670 Ma (44 grains in total). Such ages are typical in modern sediments offshore of the Archean and Proterozoic Adélie Craton (~135°E to 142°E) (zircon U-Pb, 1600-1740 Ma; 2450-2500 Ma; Oliver and Fanning, 1997; Peucat et al. 1999; Menot et al. 2005; Duclaux et al. 2007) located to the east of the Wilkes Land margin. Due to the westward transport of icebergs by ocean currents, some ages of this range are also found offshore Wilkes Land (Roy et al. 2007; Pierce et al. 2011; this study) (Figure 5.6). Two Pliocene IRD layers in ODP Site 1165 (45.70 mbsf, 4.63 Ma; 45.80 mbsf, 4.65 Ma) previously analysed by Williams et al. (2010a) contained a significant population of hornblende grains with $^{40}\text{Ar}/^{39}\text{Ar}$ ages that match those in sediments offshore of the Adélie Craton (1400 to 1700 Ma; Roy et al. 2007; Pierce et al. 2011; see also Chapter 3). However, as this age population does not occur in significant quantities in IRD deposited in stratigraphically similar ODP Site 1165 sediments, as presented in this study, I omit any further discussion of a potential role of far-travelled IRD sourced from the Adélie Craton.

Summary

Comparison of $^{40}\text{Ar}/^{39}\text{Ar}$ ages of ice-rafted hornblende grains extracted from Pliocene ODP Site 1165 sediments with known onshore and offshore thermochronological ages reveals two main source regions for Pliocene icebergs. The first is comprised of the proximal MRL coast, the Prydz Bay area and Princess Elizabeth Land, and supplied hornblende grains with $^{40}\text{Ar}/^{39}\text{Ar}$ ages of 455 to 575 during the Pliocene and today. I henceforth describe this IRD source as the ‘Prydz Bay sector’. The second provenance area is the distal Wilkes Land margin, which was the source of ice-rafted hornblende grains in Pliocene ODP Site 1165 sediments with $^{40}\text{Ar}/^{39}\text{Ar}$ ages between 1035 and 1315 Ma – it is henceforth described as the ‘Wilkes Land sector’.

5.6.4 IRD sources to the west of Prydz Bay?

The provenance discussion above considers potential IRD sources within the context of modern day iceberg transport pathways. These trajectories are largely determined by the westward flowing coastal current, within which icebergs are entrained in an anti-clockwise direction around East Antarctica (Antarctic Iceberg Tracking Database [1978–2012]; available at <http://www.scp.byu.edu/data/iceberg/database1.html>) (Figure 5.2), unless they become grounded on the continental shelf. The East Wind drift (e.g. Tchernia and Jeannin, 1980) is a product of cold air masses (katabatic winds) that flow from the higher continental interior of the EAIS towards the Southern Ocean. Hence, these wind fields could potentially have been affected by changes in the geometry and volume of the ice sheet (DeConto et al. 2007). In fact, it is not well constrained as to whether the coastal current would be maintained during significant ice volume loss (Hill, personal communication), and our new data may offer some insights into whether this took place during the Pliocene.

If the coastal current would have slowed down significantly or stopped altogether during the Pliocene, icebergs sourced from regions to the west of Prydz Bay could feasibly have reached our study site. Such a westerly source could furthermore become more important in case of a shift in the location of the southern boundary of the westwind-driven (i.e. eastward flowing) Antarctic Circumpolar Current (Orsi et al. 1995; Meijers et al. 2010), which today is located close to the latitude of ODP Site 1165 (Bindoff et al. 2000) (Figure 5.2). A southward shift of the polar fronts has indeed been suggested to have taken place under warmer than present climates (e.g. Toggweiler et al. 2006; Hemming et al. 2007;

Brierley et al. 2009; Kemp et al. 2010). However, bedrock terranes in Enderby Land (Black and James, 1983; Sandiford, 1985; Black and McColluch, 1987b) to the west of Prydz Bay and MRL (Fig. 2), are characterised by Archean (>2450 Ma; Black et al. 1983; Harley and Black, 1997; Kelly and Harley, 2005) and Proterozoic (1030-1100 Ma; Jacobs et al. 1998; 2003; Fitzsimons, 2000a, 2000b) thermochronological ages that show only a small overlap with the Proterozoic $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende ages observed in ODP Site 1165 sediments (i.e. 1050-1315 Ma, but centred around 1120 to 1175 Ma). Hence, we exclude Pliocene supply of Proterozoic hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages from sources to the west to ODP Site 1165, and take our data as indication that surface currents and iceberg transport pathways followed similar routes during the Pliocene and today.

5.7 Controls on the Delivery of IRD from the Wilkes Land Margin and Associated Aurora Subglacial Basin to ODP Site 1165 During the Pliocene

The data presented here reveal that Pliocene IRD at ODP Site 1165 was predominantly derived from two sources, the Prydz Bay area and the distal Wilkes Land margin. The latter has previously been suggested to be the site of major ice sheet destabilisation during the Pliocene (Hill et al. 2007; Williams et al. 2010a; Dolan et al. 2011), associated with warmer SSTs (Whitehead and Bohaty, 2003; Escutia et al. 2009; McKay et al. 2012a) and ice sheet retreat in the Prydz Bay area (Harwood et al. 2000; Hambrey and McKelvey, 2000; McKelvey et al. 2001; Whitehead et al., 2001; Fordyce et al. 2002; Whitehead et al. 2004). Today, warm deep water masses, upwelling onto continental shelves, drive retreat of ice shelves and marine-terminating glaciers in the Amundsen Sea sector of West Antarctica by basal melting, where the ice-stream grounding lines are in contact with ocean waters (Rignot and Jacobs, 2002; Jenkins et al. 2010; Joughin et al. 2010; Jacobs et al. 2011; Pritchard et al. 2012; Steig et al. 2012). Marginal areas of the EAIS in the vicinity of the Aurora Subglacial Basin lie up to 2.4 km below sea level in direct contact with the Southern Ocean (Young et al. 2012). Geophysical surveys (Young et al. 2012; Wright et al. 2012) reveal a fjordal-type geometry of the subglacial topography of the Aurora Subglacial Basin, suggesting that the EAIS was retreated significantly within the basin in the past compared to today (Figure 5.7). They also reveal the presence of a highland area between 400 and 750 km south of the Totten Glacier, suggesting that it may have acted as a pinning point for a retreated ice margin (Young et al. 2012) (Figure 5.7).

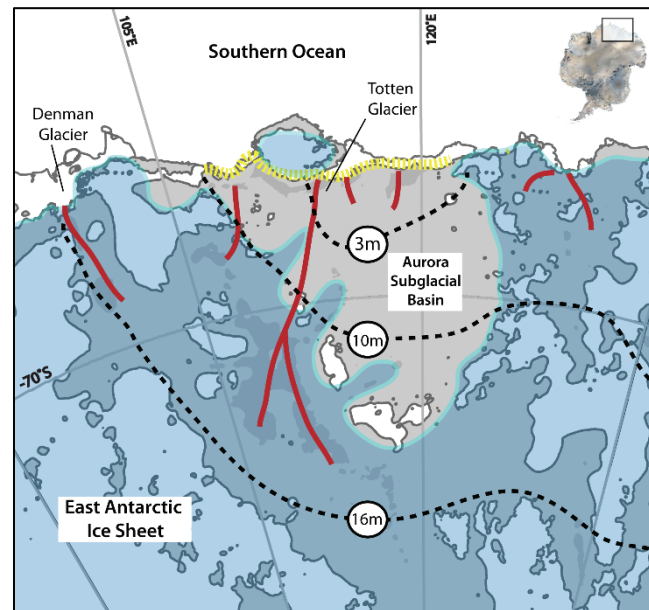


Figure 5.7. Map of the Aurora Subglacial Basin, illustrating: i) the subglacial topography (base map, with areas above sea level lighter than areas below sea level; Fretwell et al. 2013); ii) the current positions of ice streams (red lines; Rignot et al. 2011); iii) the position of the current EAIS grounding line (yellow dashed line); iv) the approximate positions of the EAIS margin within the Aurora Subglacial Basin in three different Pliocene ice sheet modelling scenarios (black dashed lines), with numbers in circles representing the total contribution of the EAIS to global sea level rise (3m: Pollard and DeConto, 2009; 10m: Hill et al. 2007; 16m: Dolan et al. 2011); (v) the approximate position of a retreated Neogene EAIS margin as inferred from subglacial topography (blue shading with light blue line; Young et al. 2012).

These topographic features and observations make it likely that the Aurora Subglacial Basin was a location of mass loss of the EAIS in the past, supplying icebergs carrying IRD with a Wilkes Land provenance signature to ODP Site 1165. This line of reasoning, however, suggests that a Wilkes Land IRD provenance signature should be more prevalent during the warm Early Pliocene, in comparison to the relatively colder temperatures of the Late Pliocene. This prediction stands in contrast to the results of the IRD provenance data, which show a significant increase in Wilkes Land IRD at ODP Site 1165 after ~3.27 Ma. This change is contemporaneous with cooler sea surface temperatures and major ice sheet expansion in Antarctica (~3.3 Ma) as evidenced by the first major Pliocene advance of the Lambert Glacier in Prydz Bay (O'Brien et al. 2007), and by a dramatic increase in the amount of coarse-grained ice-rafted material deposited after the Marine Isotope Stage M2 glacial (Warnke et al. 2004; Passchier, 2011) (Figs. 5.3 and 5.6).

Table 5.5. Compilation of regional ocean temperatures for the Pliocene.

Age (Ma)	Temperature above modern (°C)	Proxy	Location	Source
2.5-3	0-2	TEX ₈₆ ^L ; upper ocean summer/spring	Ross Sea	McKay et al. 2012a
3.2-3.3	1	Silicoflagellate assemblage; mean annual SST	ODP Site 1165	Whitehead and Bohaty, 2003
3.3-3.6	1-2	Silicoflagellate assemblage; mean annual SST	ODP Site 1165	Whitehead and Bohaty, 2003
3.3-4.5	2-5	TEX ₈₆ ^L ; upper ocean summer/spring	Ross Sea	M McKay et al. 2012a
3.5	2.5	Silicoflagellate assemblage; summer SST	ODP Site 1165	Escutia et al. 2009
3.6	2.7-4	Silicoflagellate assemblage; summer SST	ODP Site 1165	Escutia et al. 2009
3.6	>4	Silicoflagellate assemblage; mean annual SST	Kerguelen Plateau	Bohaty and Harwood, 1998
3.6-3.75	2-6	Silicoflagellate assemblage; mean annual SST	ODP Site 1165	Whitehead and Bohaty, 2003
3.7	>5.6	Silicoflagellate assemblage; summer SST	ODP Site 1165	Escutia et al. 2009
3.8-4.3	1-2.5	Silicoflagellate assemblage; mean annual SST	ODP Site 1165	Whitehead and Bohaty, 2003
4.1-4.5	1.5-3	Diatom assemblages; mean annual SST	Sørsdal Formation	Whitehead et al. 2001
4.2	>4	Silicoflagellate assemblage; mean annual SST	Kerguelen Plateau	Bohaty and Harwood, 1998
4.3	>4	Silicoflagellate assemblage; mean annual SST	Kerguelen Plateau	Bohaty and Harwood, 1998
4.3-4.4	3-4	Silicoflagellate assemblage; mean annual SST	ODP Site 1165	Whitehead and Bohaty, 2003
4.4-4.5	1-3	Silicoflagellate assemblage; mean annual SST	ODP Site 1165	Whitehead and Bohaty, 2003
4.5	>4	Silicoflagellate assemblage; mean annual SST	Kerguelen Plateau	Bohaty and Harwood, 1998
4.6	4	Silicoflagellate assemblage; mean annual SST	ODP Site 1165	Whitehead and Bohaty, 2003
4.65-4.8	3-4	Silicoflagellate assemblage; mean annual SST	ODP Site 1165	Whitehead and Bohaty, 2003
4.8-5	3	Silicoflagellate assemblage; mean annual SST	ODP Site 1165	Whitehead and Bohaty, 2003

How can these observations be reconciled? At this point it is important to reiterate that ODP Site 1165 is located more than 1500 km away from the mouth of the Aurora Subglacial Basin. Hence any sediment-laden icebergs produced from this distal area would have had to travel a significant distance before melting. It therefore seems plausible to invoke a role for sea surface temperatures (SSTs) in IRD provenance patterns, which could have affected survival rates of sediment-laden icebergs (e.g. icebergs would travel further during colder Late Pliocene than the warm Early Pliocene). Importantly, while regional SST records after 3.3 Ma are very limited (see Bohaty and Harwood, 1998), TEX₈₆^L data from the Ross Sea (McKay et al. 2012a) appear to show a decline in summer and spring temperatures from 2 to 5°C above modern during the Early Pliocene to 0 to 2°C after ~3.2 to 3.3 Ma (see Table 5.5 for a review of regional SST estimates). This cooling is in line with the increase in distally source IRD deposited at ODP Site 1165, and a significant increase in IRD mass accumulation rates at ~3.3 Ma (Passchier, 2011). Hence, it is feasible that in addition to volumetric changes in the EAIS and resulting iceberg flux, changing Pliocene SSTs, as well as changes in sediment loading, may have had an effect on observed IRD provenance patterns at ODP Site 1165, and therefore may have obscured a direct link between my new IRD record and ice sheet stability in the Aurora Subglacial Basin.

5.8 Sensitivity test on the effect of sea surface temperatures on iceberg melting patterns

To better understand Pliocene IRD provenance patterns in the context of variable climatological conditions, constraints must be placed on the relative importance of iceberg transport pathways (see Section 6.4), the sediment-loading of icebergs, iceberg flux to the Southern Ocean, and iceberg survivability. IRD deposition is ultimately a complex function of all of these processes. While sediment loading and iceberg fluxes are intrinsically difficult to constrain, iceberg survivability is largely a function of iceberg volume, current speed and melting rates, which in turn is controlled by prevailing SSTs.

5.8.1 Iceberg trajectory modelling framework, and comparison of results from modelled pre-industrial iceberg melting patterns and observed core-top IRD provenance patterns

In order to investigate the role of SSTs on iceberg trajectories and to allow for comparison to observed Pliocene IRD patterns, an iceberg survivability model developed with colleagues Daniel Hill (University of Leeds, BGS), Aisling Dolan, and Alan Haywood

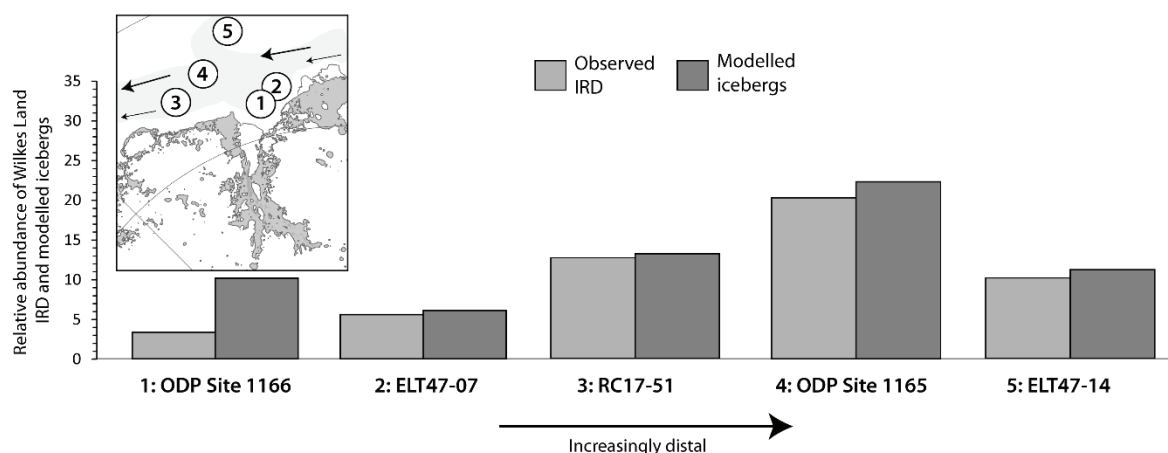


Figure 5.8. Histogram illustrating the data-model comparison for Wilkes Land IRD relative to Prydz Bay IRD deposited (light grey boxes), and Wilkes Land icebergs relative to Prydz Bay icebergs melted (dark grey boxes) at four sites located in the Prydz Bay region during the Holocene. Observed IRD provenance is inferred from $^{40}\text{Ar}/^{39}\text{Ar}$ age distributions of hornblende grains (Brachfeld et al, 2007; Roy et al. 2007; this study).

(University of Leeds), following previous work by Gladstone et al. (2001) and Bigg et al. (1997). After Gladstone et al. (2001), the model injects 100 icebergs of 10 different size classes (ranging from 40x40x60m to 250x1467x2200m in volume) into the Southern Ocean from seven distinct drainage basins located in the Prydz Bay area (represented by the Lambert, Philippi and Denman Glaciers) and at the Wilkes Land margin (represented by the Adams, Totten, Thompson and Frost Glaciers) (see Figure 5.1 for locations of drainage basins), and subsequently records their trajectories and location of melting. Icebergs were released monthly over a 12 month period (i.e. 1200 from each glacier in total) with seasonally changing wind fields and surface currents taken from a pre-industrial global climate model scenario (HadCM3). Annually averaged modelled iceberg trajectories derived from this model set-up match well with those observed by satellites today (Antarctic Iceberg Tracking Database [1978–2012]; available at <http://www.scp.byu.edu/data/iceberg/database1.html>), with icebergs travelling in an anti-clockwise direction upon entrainment into the westward-flowing coastal current (Figure 5.2).

To evaluate this iceberg trajectory modelling framework, iceberg melting patterns were modelled over five core sites (ELT47-07, ELT47-14, ODP Site 1166, ODP Site 1165, and RC17-51; core-top data from Brachfeld et al. 2007; Roy et al. 2007; this study; Figure 5.8), all located in the Prydz Bay area, under pre-industrial climate conditions. Importantly, modelled icebergs did not contain IRD, rather their site of melting was modelled, with each

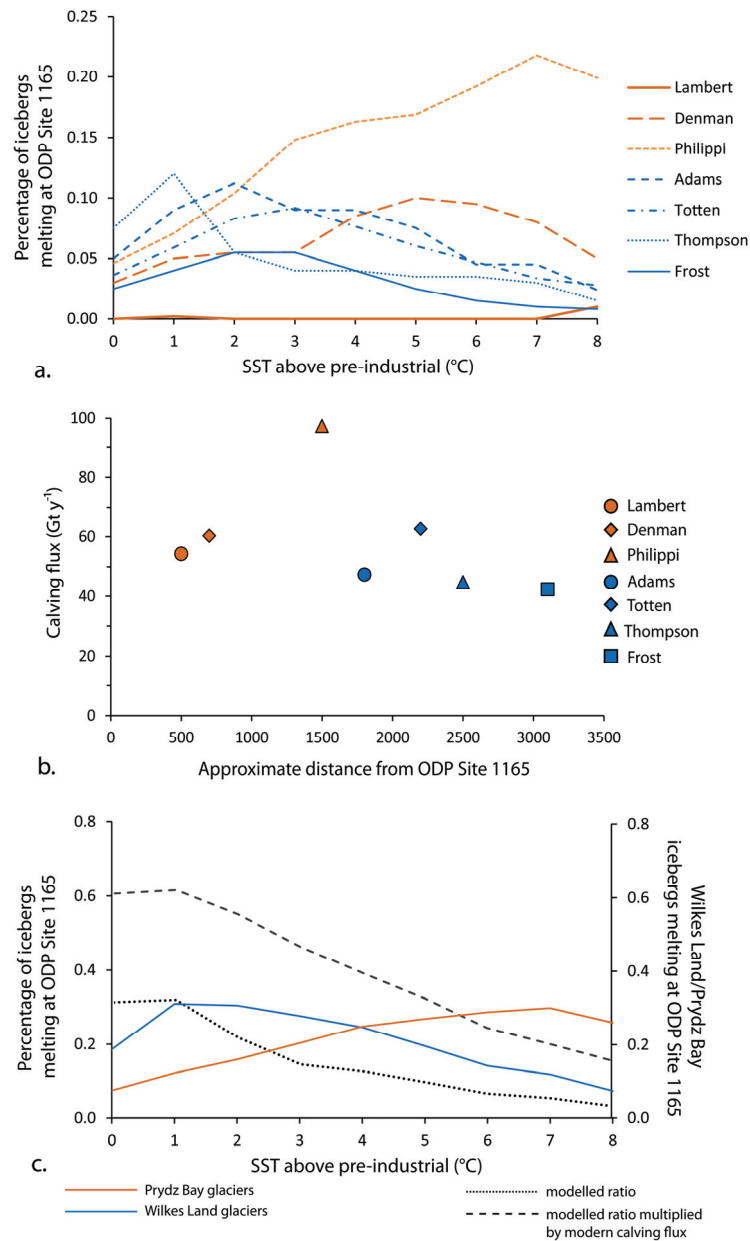


Figure 5.9. a) Percentage of icebergs produced from Prydz Bay glaciers (in orange) and Wilkes Land glaciers (in blue) that melt over ODP Site 1165 in different SST scenarios. b) Calving flux (Gladstone et al. 2001) and approximate distance from ODP Site 1165 of Prydz Bay glaciers (orange data points) and Wilkes Land glaciers (blue data points). c) Combined percentage of icebergs from Prydz Bay (orange line) and Wilkes Land (blue line) glaciers (left y-axis) that melt at ODP Site 1165 ratio under different SSTs (x-axis). The modelled ratio of Wilkes Land icebergs to Prydz Bay icebergs is shown as dotted line (right y-axis), and has been multiplied by the calving flux for each glacier (dashed line; right y-axis).

of the seven glacier systems mentioned above was assigned a provenance sector (Prydz Bay sector: Lambert, Philippi and Denman glaciers; Wilkes Land sector: Adams, Totten, Thompson and Frost glaciers; Figure 5.1). From this, the proportion of icebergs that melt at each site sourced from either sector was calculated and multiplied by modern day calving fluxes (Gladstone et al. 2001), allowing for comparison with published and new IRD provenance data from core-top sediments at these sites (Brachfeld et al. 2007; Roy et al, 2007; this study).

Results are presented in Figure 5.8, where modelled and measured provenance data are expressed as ratios of Wilkes Land icebergs/IRD over Prydz Bay icebergs/IRD and show an excellent agreement for four of the five sites. This good agreement indicates that even though IRD loading is not taken into account, and wind field strengths were unchanged, we can be confident that the model is capturing the physical process that today govern the distribution of melting icebergs (and therefore their provenance at a given location) around the East Antarctic continent. The key factor controlling the proportion of melting icebergs supplied to any individual site is its location relative to source glaciers. For example, sites RC17-51 and ODP Site 1166 (Sites 1 and 3; Figure 5.8) are located down-current of the Lambert Glacier and as such the majority of icebergs that melt at these sites are sourced from this glacier system. Conversely, icebergs that melt over ELT47-17, ELT47-07 and ODP Site 1165 are mainly supplied from the Denman and Philippi Glaciers. One interesting observation when comparing modelled and observational data in the Prydz Bay area is that even though the amount of Wilkes Land-derived icebergs melting over ODP Site 1165 is low for the modern day, it is still higher than in any of the other sites (Figure 5.8). This observation can be explained by the more proximal locations of sites ODP Site 1166, ELT47-07 and RC17-51 to the continent, and the comparatively more distal setting of Site ELT47-14. The iceberg trajectory model hence reveals a zone of maximum westward transport, which is matched by the highest abundance of icebergs transported today (Antarctic Iceberg Tracking Database [1978–2012]; available at <http://www.scp.byu.edu/data/iceberg/database1.html>). Of all sites shown in Figure 5.8, ODP Site 1165 is located the closest to this region of maximum iceberg transport (indicated by the thicker arrows in Figure 5.8), implying it is ideally placed to study far-field IRD supply back in time.

The only site to show any significant disparity between modelled iceberg melting patterns and observed IRD provenance patterns is ODP Site 1166. The unrealistically high Wilkes Land iceberg contribution obtained from the model run may be an artefact of small

scale ocean circulation features that occur at the front of the modelled Amery Ice Shelf and are not well captured within the employed global circulation model.

In summary, the excellent agreement between the overall results in iceberg melting and IRD provenance suggest that the model successfully replicates the most important features that control modern iceberg trajectories and influence the ratio of Wilkes Land to Prydz Bay IRD delivered to ODP Site 1165, i.e. the location and direction of the coastal current.

5.8.2 Elevated sea surface temperatures and iceberg melting patterns

To test the effect of increased SSTs on modelled iceberg melting patterns, sensitivity experiments were performed with the same pre-industrial ocean currents and wind patterns as described above, but with uniformly increased SSTs. These results are then compared to observed Pliocene IRD provenance in order to monitor Pliocene iceberg melting patterns at ODP Site 1165 under warmer ocean temperatures. In multiple runs, SSTs were increased in 1°C increments up to 8°C above pre-industrial values (Figure 5.9a). Overall, the pattern of icebergs derived from all glaciers to melt above ODP Site 1165 (apart from the Lambert Glacier, see above) shows the same general trend with increasing temperature: an initial increase with increasing temperatures, followed by a subsequent decrease with further increasing temperatures (Figure 5.9a). This result suggests that as SSTs increase, iceberg melt rates over the site increase, before a temperature threshold is reached and a significant fraction of icebergs melt before they can reach ODP Site 1165. It would be expected that the distance of each glacier from ODP Site 1165 would therefore play an important role in how many icebergs could survive before melting over the site, and that if this was the case, icebergs from more distal sites would reach their peak melt rate at a lower temperature than icebergs produced from more proximal glaciers. This pattern is exactly what is observed in the modelled melting patterns of icebergs produced from each glacier, apart from the Thompson Glacier, which produces the highest melt percentages at ODP Site 1165 for similar to present day temperatures of all Wilkes Land glaciers (Figure 5.9a).

Converting the modelled iceberg melting rates for all combined Prydz Bay glaciers and Wilkes Land glaciers with increasing SSTs to the ratio of Wilkes Land icebergs over Prydz Bay icebergs (i.e. comparable to the IRD provenance data in Figure 5.5), shows there is a clear trend, whereby more Wilkes Land icebergs are observed to melt over ODP Site 1165 at colder temperatures between 0°C and 2°C than at warmer temperatures (3 to 8°C)

(Figure 5.9c). These results can explain to a large extent why the Late Pliocene decline in SST around ~3.3 Ma (Table 5.5) was accompanied by a shift in the observed IRD provenance pattern, to a more distally sourced Wilkes Land-bearing assemblage.

5.9 Evidence for Increased Iceberg Flux from EAIS Destabilisation Events During Interglacials

There are features in my new IRD dataset (and the model results) that cannot be completely explained by changing SSTs. It is plausible that factors not captured by model runs such as millennial scale changes in iceberg calving rates and/or sediment loading and/or changes in wind field strength (and therefore surface current strength) may play a role in IRD provenance patterns, particularly where the resolution of the provenance data is sub-orbital.

The processes that govern iceberg calving rates on annual to decadal timescales, such as ice stream velocity and calving front erosion, are relatively well understood (Benn et al. 2007). For example, to recreate more realistic ratios as predicted by our iceberg survivability model, fractional melts from the different glaciers must be multiplied by the relevant glacier calving fluxes (e.g. Gladstone et al. 2001; Figure 5.9b). This exercise shows that the ratio of Wilkes Land to Prydz Bay icebergs now approaches values calculated for Pliocene IRD patterns, although it is unrealistic to assume that calving fluxes have not changed through time.

Controls on iceberg production rates on longer millennial timescales are less well known, primarily due to a lack of orbitally resolved IRD records in the Southern Ocean. Available high resolution records (Passchier, 2011) do however suggest that orbital-scale fluctuations in ice volume and/or SST were a major control on IRD flux to the Southern Ocean during the Pliocene, despite uncertainties about iceberg loading and current patterns. In fact, ice sheet modelling and observational data such as globally averaged oxygen isotope records suggest that large-scale advance and retreat of high latitude ice sheets (and hence iceberg production rates), are most likely modulated by changes in summer insolation (e.g. Ruddiman, 2003) following the beat of precessional (~23 kyr) cycles (Laskar et al. 1993; Raymo et al. 1996). Due to the inherent difficulties in constraining loading and surface current strength in the past, and the obvious importance of orbital-scale flux of IRD, below I focus on how the latter may have affected Pliocene IRD provenance patterns.

Major growth of global ice volume was contemporaneous with the Marine Isotope Stage M2 glacial (~3.3 Ma; Lisiecki and Raymo, 2005), and has been documented in multiple

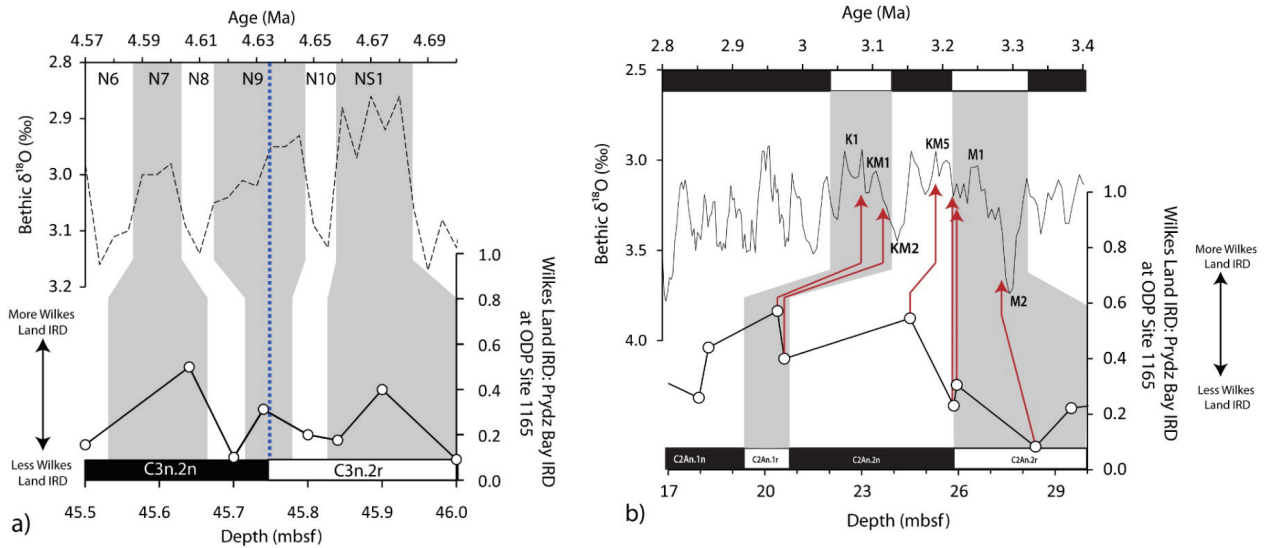


Figure 5.10. IRD provenance records from ODP Site 1165, highlighting two well dated intervals containing the highest amounts of far travelled IRD. a) Global benthic oxygen isotope stack (top) (Lisiecki and Raymo, 2005) and ratio of Wilkes Land IRD to Prydz Bay IRD (bottom) between ~ 4.57 and ~ 4.69 Ma. Grey bands: inferred interglacial intervals. b) Global benthic oxygen isotope stack (top) (Lisiecki and Raymo, 2005) and ratio of Wilkes Land IRD to Prydz Bay IRD between 2.5 and 3.5 Ma, illustrating the transition to increased delivery of Wilkes Land IRD after 3.3 Ma, and the timing of the two most significant Wilkes Land IRD depositional events at ODP Site 1165.

locations around the Antarctic perimeter (O'Brien et al. 2007; Naish et al. 2009; Chapter 6). This ice growth was accompanied by cooler Southern Ocean SSTs (Table 5.5), suggesting that more distally sourced icebergs could have reached ODP Site 1165 before melting. This interpretation is supported by a large increase in IRD deposition at this time (Passchier, 2011; Figure 5.5) and increased supply of Wilkes Land IRD to ODP Site 1165 after ~ 3.3 Ma (this study). This climatic shift was also characterised by an increase in the amplitude of benthic $\delta^{18}\text{O}$ variability between glacial and interglacial cycles (Lisiecki and Raymo, 2005), pointing towards retreat of Antarctica's ice sheets during Late Pliocene interglacials (Dwyer and Chandler, 2009). Due to the proximity of the samples at 20.39 and 24.50 mbsf to paleomagnetic chron boundaries (C2An.1r and C2An.2n, respectively; Gradstein et al. 2012) these IRD intervals can be attributed to interglacials MIS K1 (3.08 Ma) and KM5 (3.19 Ma), respectively (Lisiecki and Raymo, 2005) (Figure 5.10). These two interglacials are characterised by the highest amount of Wilkes Land IRD (Wilkes Land IRD/Prydz Bay IRD = 0.55 at 3.08 Ma; Wilkes Land IRD/Prydz Bay IRD = 0.50 at 3.19 Ma) for any IRD layer

analysed at ODP Site 1165. Late Pliocene IRD provenance results indicate a significant increase in the flux of icebergs from the Wilkes Land margin during interglacials, which accompany overall increases in IRD MAR (Passchier, 2011), potentially related to ice sheet retreat. A potential mechanism for increased IRD flux during an ice sheet destabilization event involves the penetration of warm ocean waters into the low lying region at the mouth of the Aurora Subglacial Basin (Young et al. 2012), driving large-scale ice-bed decoupling (Hughes, 2011) where areas of the EAIS became ungrounded, and icebergs calved into the Southern Ocean. However, ultimate confirmation of this interpretation would have to come from IRD mass accumulation records from sites closer to the Aurora Subglacial Basin.

In contrast to the colder Late Pliocene, the EAIS was probably at times retreated to the pinning point formed by the highlands in the middle region of the Aurora Subglacial Basin during the warmer Early Pliocene (Figure 5.7; Young et al. 2012) (see also Chapter 2). It is curious to note in this context that high resolution IRD provenance results between ~4.6 and ~4.75 Ma also appear to show increases in Wilkes Land IRD during interglacials. The layer at 45.75 mbsf ODP Site 1165 corresponds to the paleomagnetic chron boundary between C3n.2r (4.631 Ma to 4.799 Ma) and C3n.2n (4.300 to 4.631 Ma), assigning it an exact age of 4.631 Ma (Figure 5.10a), suggesting it corresponds to interglacial Marine Isotope Stage (MIS) N9 (Lisiecki and Raymo, 2005) (Figure 5.10). Estimated ages for neighboring samples imply that interglacial samples in general show a higher ratio, indicating more Wilkes Land IRD (MIS interglacials N7, ~4.62 Ma, ratio: 0.5; NS1, ~4.665 Ma, ratio: 0.4), while samples deposited during glacial periods are more dominated by IRD with a Prydz Bay signature (MIS N6, ratio: 0.16; N8, ratio: 0.1; N10, ratio: 0.18). The IRD provenance data appear to contradict modelling results, which suggest that when SSTs are more than 4°C higher than current temperatures (Table 5.5), the ratio of Wilkes Land icebergs versus Prydz Bay icebergs melting at ODP Site 1165 should not be higher than 0.18 (Figure 5.9c), i.e. most Wilkes Land icebergs would melt before reaching the Prydz Bay area. In order to survive transport over 1500 km in very warm SSTs, an extremely large quantity of icebergs and/or larger sized icebergs possibly with a higher detritus loading must have been repeatedly produced. Larger icebergs, similar to tabular icebergs produced from ice shelves, but laden with IRD, would take longer to melt than smaller ones released by marine-terminating glaciers (Antarctic Iceberg Tracking Database [1978–2012]; available at <http://www.scp.byu.edu/data/iceberg/database1.html>). However, this interpretation remains speculative as little is known about the dynamics of large-scale ice sheet disintegration (Hughes, 2011) and more proximal complete drill cores to test this idea do not yet exist.

5.10 Conclusions

Analyses of the provenance of ice-rafted hornblende grains deposited at ODP Site 1165 throughout the Pliocene by interpreting their $^{40}\text{Ar}/^{39}\text{Ar}$ ages reveals that icebergs were sourced from two predominant areas: (i) outlet glaciers in the local Prydz Bay region, and (ii) the distal Wilkes Land margin located at the mouth of the low-lying Aurora Subglacial Basin. Ice-rafted sediments deposited during the warmer Early Pliocene are dominated by local sources, while sediments deposited during the cooler part of the Pliocene are characterised by more distally sourced IRD. The EAIS was likely retreated along the Wilkes Land margin between ~ 3.27 and 5 Ma, and changing IRD provenance patterns after ~ 3.27 Ma are probably a result of cooler SSTs, in combination with an increase in the volume of the EAIS. The interpretation of this long-term evolution of IRD provenance is supported by results from an iceberg trajectory model run for different SST scenarios, implying that only during colder Late Pliocene temperatures, icebergs from the distant Wilkes Land coast could survive the journey to ODP Site 1165 in significant numbers. However other parameters such as iceberg flux and sediment loading may also have played a role for the observed provenance patterns. Prominent outliers are samples that correspond to the Early Pliocene interglacials N7, N9 and NS1, and the Late Pliocene interglacials K1 and KM5, which seem to indicate increased IRD production from the Wilkes Land margin during Pliocene interglacials. Potential explanations for such variability invoke in both cases destabilisation in the low-lying Aurora Subglacial Basin, an interpretation that will have to be tested by future drilling in this sector of the Southern Ocean.

CHAPTER 6

Retreat and advance of the East
Antarctic ice sheet during
global Pliocene climate change
revealed by provenance analysis of
fine-grained sediments from
ODP Site 1165, Prydz Bay

Chapter Summary

The Lambert Glacier-Amery Ice Shelf in Prydz Bay, is outlet to the largest ice sheet drainage system in East Antarctica. However, its behaviour during past global climate change is poorly constrained. New insights can be gained by studying its evolution during two distinct climatic periods: (i) the warm Early Pliocene (~3.5 to ~5.3 Ma), when global temperatures and atmospheric CO₂ concentrations were similar to those predicted for the near future, and (ii) the cooler Late Pliocene (~2.5 to ~3.5 Ma). Investigation of the strontium and neodymium isotopic compositions of fine-grained (<63µm) detrital sediments, deposited offshore of Prydz Bay, has the potential to reveal their provenance and thereby offer new insights into the response of the Lambert Glacier-Amery Ice Shelf system to these changing environmental conditions, and its potential contribution to global climate change during the Pliocene.

In this chapter, I present results from 39 Quaternary and Pliocene marine sediment samples from Ocean Drilling Program (ODP) Site 1165 (64°22'77"S, 67°13'14"E; Prydz Bay), located on a sediment drift on the East Antarctic continental rise. Comparison of the detrital neodymium isotope fingerprint of the sediments with potential continental (and oceanic) source areas indicates that sediments at ODP Site 1165 were primarily supplied from the local Prydz Bay region. Strontium isotopic compositions of detrital marine sediments at this particular site are variable, due to the poly-metamorphic nature of source terranes in the region, which result in a large range of bedrock ⁸⁷Sr/⁸⁶Sr ratios. Additionally, analyses of clay and silt separates from three Pliocene samples indicate that a grain size effect may have distorted ⁸⁷Sr/⁸⁶Sr provenance signatures. Hence, provenance interpretations in this chapter are based on neodymium isotopes only.

Sediments deposited before ~3.48 Ma were most likely sourced from the flanks of the Lambert Graben, while sediments deposited after ~3.42 Ma were likely sourced from the proximal Mac.Robertson Land coast with an accompanying increase in Wilkes Land supplied ice-rafted detritus. In addition, comparison of a high resolution interval of 13 samples deposited between ~4.6 and ~4.75 Ma with global benthic oxygen isotopes reveals obliquity-paced fluctuations in sediment provenance between these two endmembers.

Regional paleoclimate records suggests that an interpretation of a supply of detrital material from within the Lambert Graben agrees well with retreat of the Amery Ice Shelf-Lambert Glacier several hundreds of kilometres south of its current position during the Early Pliocene. Global records and modelling suggest ice shelf retreat in the low-lying Lambert

Graben was possibly in response to upwelling of warm deep ocean water masses onto the continental shelf in a climate warmer than today. The change in sediment provenance around ~3.42 Ma indicates an increase in supply of nearby continental shelf sediments, likely deposited by an advancing ice margin and/or by export of dense shelf waters. According to the age model of ODP Site 1165, regional growth of the EAIS in the Prydz Bay area was contemporaneous with ice growth in West Antarctica and declining sea surface temperatures regionally, and together with increased sea ice cover, may have led to increased production of Antarctic Bottom Water. In turn, increased supply of southern component water from East Antarctica into the Atlantic Ocean have played a vital role in driving global cooling, ultimately contributing to the onset of Northern Hemisphere glaciation.

6.1 Introduction

The Lambert Glacier-Amery Ice Shelf (LG-AIS) system and its numerous tributary glaciers, located in Prydz Bay, represents the largest ice sheet catchment area in East Antarctica (Hambrey, 1991), draining ~14% of the East Antarctic ice sheet (EAIS) (Rignot and Thomas, 2002). Satellite observations suggest the EAIS is today experiencing mass loss in Wilkes Land, associated with the Totten Glacier, and along Princess Elizabeth Land in the vicinity of the Philippi Glacier (see Figure 5.1 in Chapter 5 for locations) (Chen et al. 2009; Rignot et al. 2011). However, the overall mass balance of the EAIS is closer to zero (Sheppard et al. 2012), although considerable uncertainties exist about long-term satellite monitoring of ice sheet change (Wouters et al. 2013). Studies into the mass balance of the LG-AIS have produced conflicting estimates of both negative and positive mass balances over the past 15 years (e.g. Wingham et al. 1998; Fricker et al. 2000; Rignot et al. 2002; Davis et al. 2006; Yu et al. 2010). Insights into the response of the LG-AIS to changing environmental conditions can be gained from studying its behaviour in the geological past. This chapter therefore focuses on the Pliocene Epoch (2.58 to 5.33 Ma), as it was a time of significant climatic fluctuations that are well preserved in the marine sediment record around Antarctica.

The Early Pliocene (3.60 to 5.33 Ma) is recognised as a period of global warmth, with mean global temperatures 2 to 4°C higher than today (Haywood et al. 2004; Fedorov et al. 2013), and estimates for atmospheric CO₂ between 250 and 450ppm (Raymo et al. 1996; Tripathi et al. 2009; Pagani et al. 2010; Seki et al. 2010; Bartoli et al. 2011). A low latitudinal gradient of global temperatures indicates amplification of atmospheric and oceanic

temperatures in polar regions during this time (Haywood et al. 2009; Ballantyne et al. 2010; Robinson et al. 2011; McKay et al. 2012a; Brigham-Grette et al. 2013). Marine sediments deposited offshore of the Wilkes Subglacial Basin in East Antarctica (Chapters 2 and 3), and in the Ross Sea (e.g. Naish et al. 2009; McKay et al. 2012a), along with numerous onshore deposits in the Prydz Bay region (Quilty et al. 1999, 2000; Harwood et al. 2000; Hambrey and McKelvey, 2000; McKelvey et al. 2001; Whitehead and McKelvey, 2001; Fordyce et al. 2002; Whitehead et al. 2004), and ice sheet modelling (Hill et al. 2007; Pollard and DeConto, 2009; Dolan et al. 2010) suggest that Antarctica's ice sheets responded to Early Pliocene warmth with mass loss in low-lying areas (Chapters 2 and 5) and retreat of large ice shelves.

The warmth of the Early Pliocene was followed by a long term cooling transition throughout the Late Pliocene (2.53 to 3.60 Ma) into the large amplitude and higher frequency climate variability of Pleistocene glacial/interglacial intervals (e.g. Haywood et al. 2009). Areas of the EAIS, in combination with the marine-based West Antarctic ice sheet, saw an increase in ice volume during this time, as inferred from global benthic oxygen isotope records and sea level estimates (e.g. Lisiecki and Raymo, 2005; Miller et al. 2012). Such distal records are supplemented by proximal records that show evidence for expansion of the Lambert Glacier in Prydz Bay (O'Brien et al. 2007), growth of the Ross Ice Shelf in West Antarctica (Naish et al., 2009) and a significant increase in ice-rafted deposition in Prydz Bay (Passchier, 2011). Continued cooling ultimately led to the initiation of major Northern Hemisphere glaciation around 2.7 Ma (e.g. Ravelo et al. 2004). While declining atmospheric CO₂ concentrations (Lunt et al. 2008; Seki et al. 2010), closure of oceanic gateways (Cane et al. 2001; Schneider and Schmittner, 2006), sea surface temperature fluctuations in the equatorial Pacific (Fedorov et al. 2006; Brierley et al. 2009), and orbital variability (Maslin et al. 1998) are some of the processes invoked to explain continued Late Pliocene cooling, the role played by major ice growth in Antarctica during this time is poorly constrained (e.g. Paillard and Parrenin, 2004; McKay et al. 2012a).

In this chapter I focus on reconstructing the evolution of the EAIS during the Pliocene by constraining the provenance of fine-grained (<63µm) detrital sediments deposited offshore of Prydz Bay from Ocean Drilling Program (ODP) Site 1165 (64°22'77"S, 67°13'14"E; see Figure 6.1 for location), through analysis of their strontium (⁸⁷Sr/⁸⁶Sr) and neodymium isotopic compositions (¹⁴³Nd/¹⁴⁴Nd, expressed as ε_{Nd}, which describes the deviation of measured ¹⁴³Nd/¹⁴⁴Nd ratios from the Chondritic Uniform Reservoir in parts per 10,000). Improved understanding of the response of the LG-AIS and EAIS to Early Pliocene warmth

and Late Pliocene cooling, as constrained by regional erosional and depositional patterns, may offer new insights into the response and role of the EAIS to past climate change.

6.2 Geological Overview

Constraining the provenance of marine sediments at ODP Site 1165 requires an understanding of the geological characteristics of potential source areas. A detailed overview of bedrock terranes in the Prydz Bay and Wilkes Land regions, including their locations, lithologies and metamorphic histories, is provided in Chapter 5 (Figs. 5.1 and 5.2). In Table 6.1 and Figures 6.1 and 6.2, I summarise available published Nd and Sr isotopic information for these terranes and other potential oceanic source areas, along with published Nd and Sr isotope compositions of Holocene marine sediments proximal to the East Antarctic continent.

While Sr isotopic analyses are regionally sparse and variable in their results, I here use the Nd isotopic composition of bedrock terranes (Figure 6.1 and Table 6.1) to delineate eight isotopically distinct provenance sectors (from west to east; Figure 6.1): 1) Enderby Land, 2) Mac.Robertson Land (MRL) and the northern region of the Northern Prince Charles Mountains (NPCM), 3) the southern region of the NPCM, and the Central Prince Charles Mountains (CPCM), 4) the Southern Prince Charles Mountains (SPCM) and the Mawson Escarpment, 5) the eastern flank of the Lambert Graben including the Grove Mountains, 6) Princess Elizabeth Land, 7) the Kerguelen Plateau, and 8) Wilkes Land. Due to their geographical location, sectors two to five are henceforth described as occurring within the ‘Prydz Bay area’.

6.3 Study Sites

This chapter focusses on Pliocene and Pleistocene sediments from ODP Site 1165 (64°22'77"S, 67°13'14"E), situated on the continental rise to the northwest of Prydz Bay. The site was drilled in 3537m water depth from the central Wild Drift, and is located approximately 200 km north of MRL (O'Brien et al. 2001) (Figure 6.3). The Wild Drift is an elongate sediment mound orientated obliquely to the continental margin in a NW-SE direction, with geometrical features interpreted from reflection seismic surveys that imply it was formed by a combination of deposition from downslope channel focussed turbidity currents and westerly-directed bottom water movement (Kuvaas and Leitchenkov, 1992; Kuvaas et al. 2004), an interpretation confirmed by later seismic surveys and drilling

Table 6.1. Onshore whole-rock Nd and Sr isotope data for bedrock terranes, and offshore Holocene marine sediments in the Prydz Bay and Wilkes Land regions. Offshore data from Brachfeld et al. (2007), Hemming et al. 2007, Roy et al. (2007), Pierce et al. (2011), and this study.

Provenance Sector	Region (from West to East)	Terrane	Major whole-rock range ϵ_{Nd}	Major whole-rock range $^{87}Sr/^{86}Sr$	Refs.	Offshore ϵ_{Nd}	Offshore $^{87}Sr/^{86}Sr$
1	Enderby Land	Napier Complex	-25.0 to -47.0 (n=18)	0.725 to 0.889 (n=20)	1-3	None available	None available
2	Mac.Robertson Land, Mawson Coast	Rayner Province	-16 to -21.6 (n=18)	0.715 to 0.757 (n=18)	4	-18.9, -19.2 (n=2)	0.728, 0.741 (n=2)
2 and 3	Northern Prince Charles Mountains	Rayner Province	-10.5 to -18.6 (n=29)	0.709 to 0.758 (n=16)	5-8		
3	Central Prince Charles Mountains	Fisher Terrane	-7.7 to -15.4 (n=12)	0.706 to 0.717 (n=3)	7, 9		
4	Southern Prince Charles Mountains	Ruker Terrane	-18.8 to -38.8 (n=113)	None available	9, 10		
4	The Mawson Escarpment	Lambert Terrane	-16.5 to -36.7 (n=25)	0.739 to 0.775 (n=5)	9-11		
5	Eastern Prydz Bay	Grove Mountains	-16.0 to -19.7 (n=17)	0.714 to 0.747 (n=17)	12, 13	Offshore Prydz Bay: -17.7 to -21.3 (n=3)	Offshore Prydz Bay: 0.737, 0.7231 (n=2)
5 and 6	Eastern Prydz Bay and Princess Elizabeth Land	The Prydz Belt	-5.0 to -21.1 (n=20)	None available	14-16		
6	Princess Elizabeth Land	Vestfold Hills	-27.4 to -38.7 (n=3)	0.702 to 0.711 (n=3)	17		
6	Princess Elizabeth Land	Gaussberg Volcanic Terrane	-12.1 to -14.9 (n=23)	0.7092 to 0.7098 (n=23)	18		
7	Southern Ocean	Kerguelen Plateau	+5.9 to -5.5 (n=166)	0.703 to 0.707 (n=166)	19-30		
8	Wilkes Land	Bunger Hills	-14.8 to -23.9 (n=6)	0.717 to 0.719 (n=2)	31	Offshore Wilkes Land (100°E to 120°E): -11 to -14.8 (n=4)	Offshore Wilkes Land (100°E to 120°E): 0.727 to 0.734 (n=3)
8	Wilkes Land	Windmill Islands	-11.2 to -26.0 (n=19)	None available	32, 33		

1: DePaolo et al. 1982	12: Liu et al. 2006	23: Weis et al. 1989
2: Black et al. 1987	13: Liu et al. 2007a	24: Weis et al. 2001
3: Black and McColluch, 1987	14: Liu et al. 2007b	25: Weis et al. 2002
4: Young et al. 1997	15: Hensen and Zhou, 1995	26: Salters et al. 1992
5: Manton et al. 1992	16: Grew et al. 2012	27: Ingle et al. 2002
6: Zhao et al. 1997	17: Black et al. 1991	28: Neal et al. 2002
7: Mikhalsky et al. 1999	18: Murphy et al. 2002	29: Frey et al. 2002
8: Mikhalsky et al. 2008	19: Clarke et al. 1983	30: Kieffer et al. 2002
9: Mikhalsky et al. 2007	20: Barling et al. 1990	31: Sheraton et al. 1990
10: Mikhalsky et al. 2010	21: Barling et al. 1994	32: Möller et al. 2002
11: Boger et al. 2008	22: Davies et al. 1989	33: Zhang et al. 2012

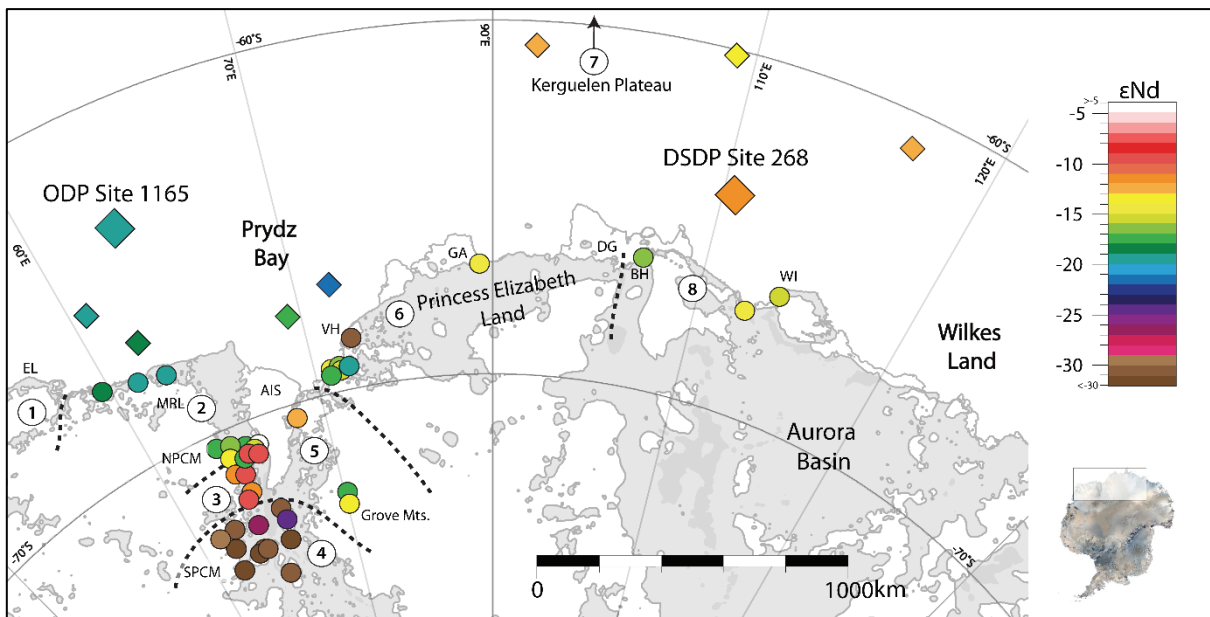


Figure 6.1. Onshore whole-rock (circles) and offshore marine sediment (diamonds) neodymium isotope provenance map of study area. Each onshore data point represents up to 25 individual whole-rock measurements. Numbers refer to provenance sectors separated according to their Nd isotopic compositions: 1) Enderby Land (EL; data plots just off map); 2) Mac.Robertson Land (MRL) and northern Prince Charles Mountains (NPCM) (data from Manton et al. 1992; Young et al. 1997; Zhao et al. 1997; Andronikov et al. 1998; Mikhalsky et al. 1999); 3) southern NPCM and central Prince Charles Mountains (data from Manton et al. 1992; Zhao et al. 1997; Andronikov et al. 1998; Mikhalsky et al. 1999); 4) the Southern Prince Charles Mountains and Mawson Escarpment (data from Mikhalsky et al. 2006, 2010; Boger et al. 2008); 5) the Grove Mountains and eastern flank of the Lambert Graben (data from the Hensen and Zhou, 1995; Liu et al 2006, 2007a, 2007b; Grew et al. 2012); 6) Princess Elizabeth Land (data from Black et al. 1991; Murphy et al. 2002); 7) Kerguelen Plateau (data plots off map); 8) Wilkes Land (data from Sheraton et al. 1990; Möller et al. 2002; Zhang et al. 2012). Offshore data from Brachfeld et al. (2007), Roy et al. (2007), Pierce et al. (2011), and this study.

(O'Brien et al. 2001, 2004). Ocean Drilling Site 1165 is located near the southern boundary of the eastward flowing Antarctic Circumpolar Current (ACC) (Orsi et al. 1995; Meijers et al. 2010) (Figure 6.3), although the main body of the ACC flows north of the Kerguelen Plateau (Figure 6.3), some 2000km to the north of Prydz Bay. Ocean Drilling Program Site 1165 is additionally influenced by westward flowing bottom currents (Orsi et al. 1999). Current speeds of the Antarctic Bottom Water (AABW) flowing over the Wild Drift today reach up to 5.6 cm s^{-1} (Meijers et al. 2010), with locally produced dense shelf waters flowing down the

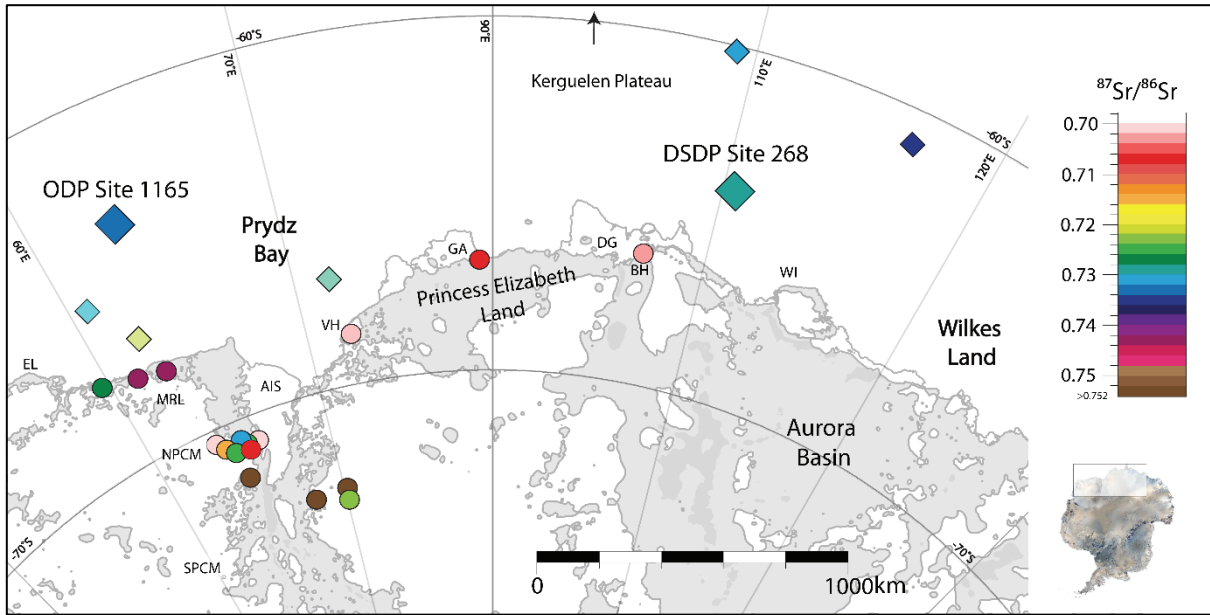


Figure 6.2. Onshore whole-rock (circles) and offshore marine sediment (diamond) strontium isotope map. Each onshore data point represents up to 15 individual whole-rock measurements. Data from Mac.Robertson Land are from Young et al. (1997). Data for the Northern Prince Charles Mountains are from Zhao et al. (1997), Andronikov et al. (1998) and Mikhalsky et al. (1999). Data for the Southern Prince Charles Mountains are from Boger et al. (2008) and Mikhalsky et al. (2010). Data for the Grove Mountains are from Liu et al. (2006, 2007a). Data for the Vestfold Hills are from Black et al. (1991). Data from the Gaussberg Volcanic Terrane are from Murphy et al. (2002). Data from the Bunger Hills from Sheraton et al. (1990). Offshore data from Hemming et al. (2007) and this study.

Wild Channel to the west of the Wild Drift from the MRL continental shelf at speeds of up to 50 cm s^{-1} (Ohshima et al. 2013) (Figure 6.3). Additionally the site is located in the vicinity of the westward flowing Antarctic coastal current, which carries icebergs in an anti-clockwise direction around the East Antarctic continent (Figure 6.3; see Chapter 5).

The top ~50mbsf of ODP Site 1165 contains a stratigraphic record of Pliocene and Pleistocene terrigenous and hemipelagic deposition (O'Brien et al. 2001; Passchier, 2011) (Figure 6.4). The lithostratigraphy of this interval consists of alternating green diatom-bearing silty clays and grey diatom-bearing clayey silts, diatom-rich clay and diatom-foraminifera ooze, with dispersed sand grains and dropstones (O'Brien et al. 2001; Passchier, 2011) (Figure 6.4). Sediments between 33 and 50 mbsf are relatively silt-rich (Grützner, 2003; Warnke et al. 2004; Passchier, 2011) with abundant smectite (Warnke et al. 2004; Junttila et al. 2005). They are additionally characterised by 2-5m fluctuations in terrigenous

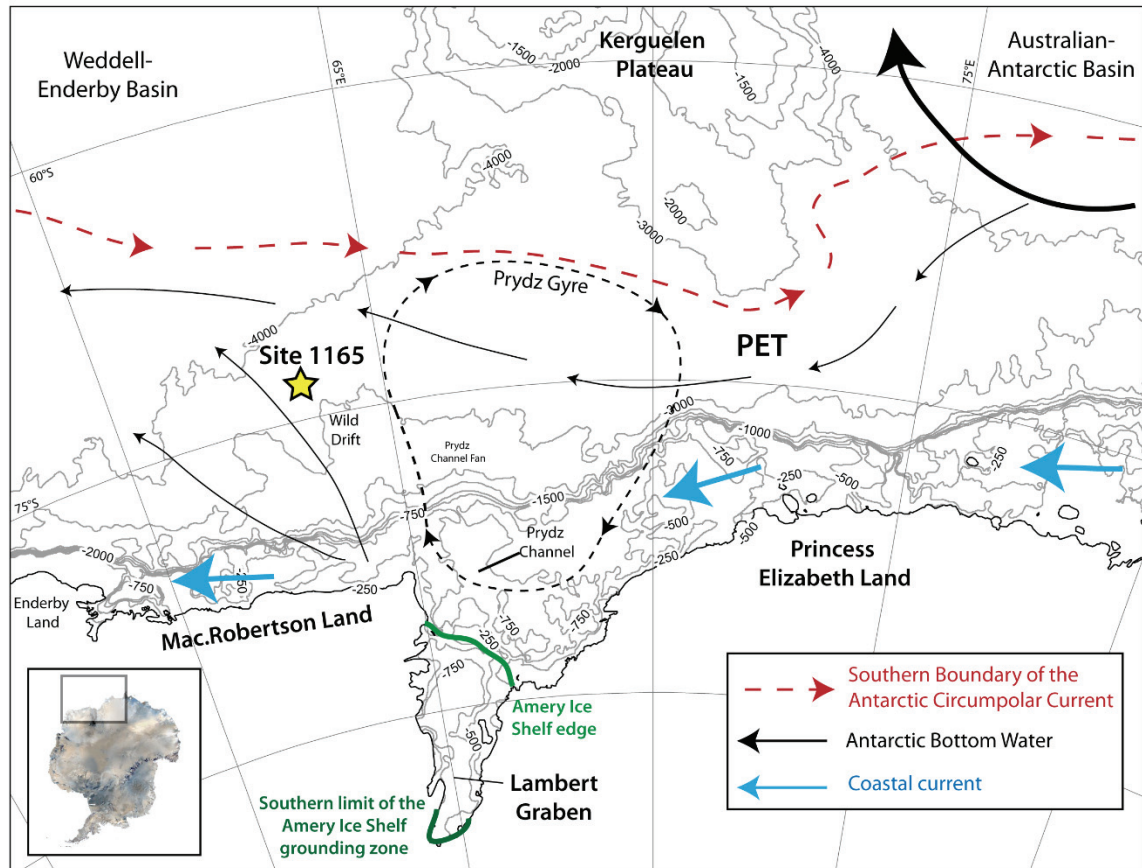


Figure 6.3. Map of study area showing seafloor bathymetry (Amante and Ealins, 2009) and major regional oceanographic features. Ocean current positions from Orsi et al. (1995, 1999), Heywood et al. (2008), Fukushima et al. (2010), Meijers et al. (2010), and Ohshima et al. (2013). Major flow of the ACC is located north of the Kerguelen Plateau (not shown), and the flow of ACC through the Princess Elizabeth Trough accounts for only ~5% of the total ACC transport through the Indian Sector of the Southern Ocean (Park et al. 2009). Blue arrows offshore represents transport direction of icebergs in the Antarctic coastal current (from the Antarctic Iceberg Tracking Database [1978–2012]; available at <http://www.scp.byu.edu/data/iceberg/database1.html>). Also shown is the position of the modern front of the Amery Ice Shelf, and the southern-most grounding line of the Lambert Glacier. PET: Princess Elizabeth Trough.

grain-size alternating between clay-rich/silt-poor and silt-rich/clay-poor units (Warnke et al. 2004; Passchier, 2011), and low sedimentation rates (Florindo et al. 2003) (Table 6.2). These sediments have been interpreted to represent suspension settling from meltwater plumes and delivery by bottom currents (Passchier, 2011). A significant change in sedimentation at ODP Site 1165 has been recognised at ~35 mbsf (O'Brien et al. 2001; Grützner, 2003; Warnke et

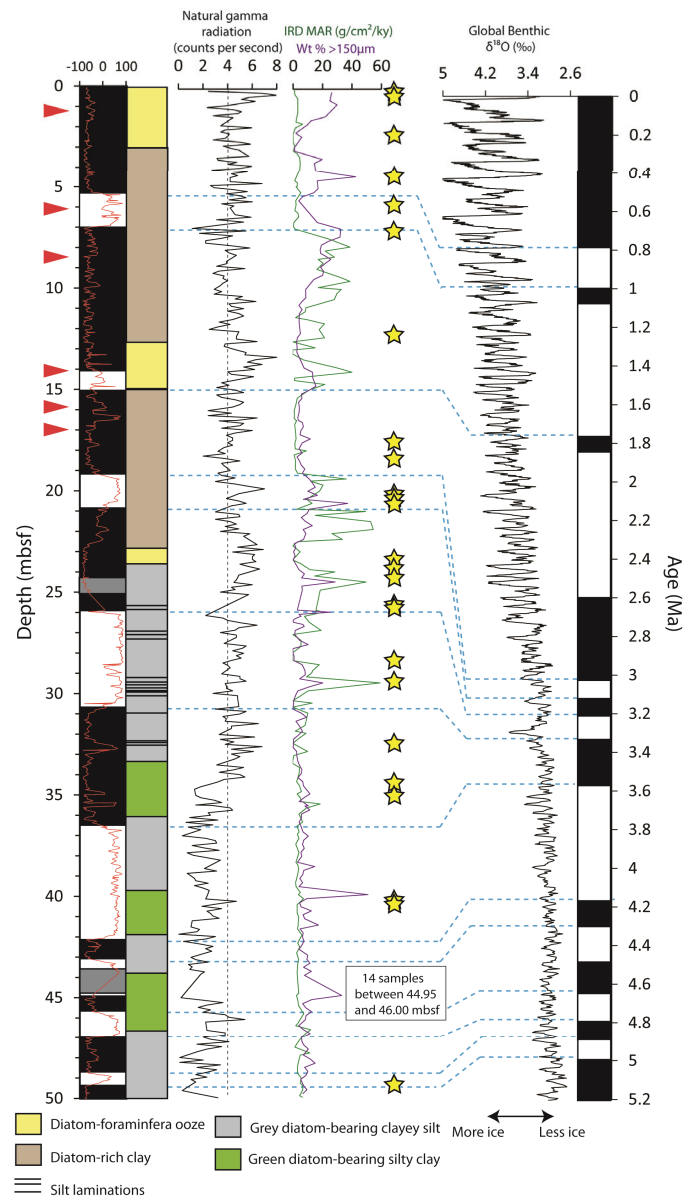


Figure 6.4. Downcore summary of Pliocene and Quaternary sediments from ODP Site 1165. From left to right: (i) depth in meters below sea floor; (ii) paleomagnetic chron boundaries (Florindo et al. 2003) with inclination data shown in red, and grey shading indicating areas with no data – red triangles denote the locations of hiatuses; (iii) lithostratigraphy (modified after O’Brien et al. 2001; Passchier, 2011); (iv) natural gamma radiation, as a proxy for clay mineral content (high values indicate more clay minerals that contain K, Th, and U, as they are the main source of naturally occurring gamma radiation); (v) grain size records: green represents ice rafted mass accumulation rates calculated for detrital fractions ($>125\mu\text{m}$) ($\text{IRD MAR} = \% >125\mu\text{m} \times \text{terrigenous fraction} \times \text{bulk density} \times \text{linear sedimentation rate}$; from Passchier [2011]), and purple represents the relative abundance of material $>150\mu\text{m}$ in size, from Warnke et al. (2004); (vi) yellow stars indicate the depths of samples analysed for Nd and Sr isotopes from this study; (vii) global benthic stable oxygen isotope stack (Lisiecki and Raymo, 2004); (viii) paleomagnetic chron boundaries from Gradstein et al. (2012).

Table 6.2. Age-depth tie points of ODP Site 1165 based on magnetostratigraphy (Florindo et al. 2003).

Depth (mbsf)	Age (ky)	Linear sedimentation rate (cm/kyr)
5.40	781	1.33
6.96	988	1.03
14.99	1778	0.34
19.23	3032	2.00
20.91	3116	5.55
25.96	3207	3.90
30.76	3330	2.14
36.46	3596	0.95
42.06	4187	1.01
43.19	4300	0.77
45.75	4631	0.72
46.96	4799	1.90
48.8	4896	0.32
49.12	4997	2.29
54.56	5235	1.04

al. 2004; Junttila et al. 2005) (Figure 6.4), where sedimentation rates double (Table 6.2), sediments become more clay-rich (Grützner, 2003; Warnke et al. 2004; Passchier, 2011) and dominated by illite, with an increase in kaolinite (Warnke et al. 2004; Junttila et al. 2005). Sediments between ~35 mbsf and 26 mbsf are characterised by several silt-rich layers, interpreted as originating from turbidity currents, and/or meltwater plumes and/or redistribution of shelf sediments by dense continental shelf bottom waters produced up-channel (Passchier, 2011). Additionally, at ~33 mbsf, a significant increase in the deposition of coarse grained detrital material occurs (Grützner, 2003; Warnke et al. 2004; Passchier, 2011), marked by a tenfold increase in ice rafted mass accumulation rates (IRD MAR) (Passchier, 2011) (Figure 6.4), representing an increase in iceberg related deposition at the site.

The age model for ODP Site 1165 is based on magnetostratigraphic datums (Figure 6.4) supported by biostratigraphy (O'Brien et al. 2001; Florindo et al. 2003; Warnke et al. 2004; Grützner et al. 2005; Villa et al. 2008; see Table 6.2 for age-depth tie-points). For the time interval of interest (from the coretop to 49.15 mbsf; 0 to ~4.99 Ma) I adapted the age model used by Grützner et al. (2005) and Passchier (2011), converted to the Gradstein et al. (2012) timescale. It is important to note that the intervals between ~15 and 17 mbsf (~1.8 to

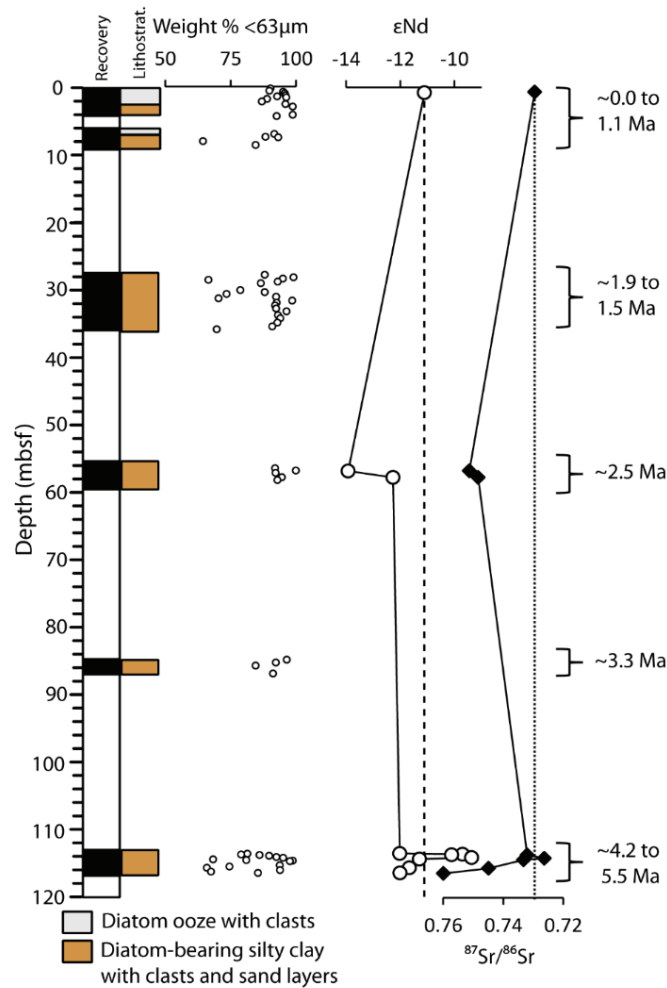


Figure 6.5. Downcore summary of Pliocene and Quaternary sediments from DSDP Site 268. From left to right: i) depth in meters below sea floor; ii) coring recovery, with black indicating recovery of sediments, and white indicating intervals of no recovery; iii) lithostratigraphy (modified after Hayes et al. 1973); iv) relative abundance of fine-grained sediments in percentage (Escutia, personal communication); v) ϵ_{Nd} values of $<63\mu m$ sediment fractions, black dashed line indicates coretop value; vi) $^{87}Sr/^{86}Sr$ ratios of $<63\mu m$ fractions, black dashed line indicates coretop value; vii) estimates ages of recovered sediments based on silicoflagellate biozones (Escutia, personal communication).

~3.0 Ma), and between ~5 and 10 mbsf potentially contains several hiatuses (Florindo et al. 2003; Villa et al. 2008).

In addition to ODP Site 1165, sediments from Deep Sea Drilling Program Site 268 ($63^{\circ}56'99''S$, $105^{\circ}09'34''E$) (Figure 6.1), located offshore of the Bunger Hills (Wilkes Land margin), were studied. This site was drilled in 3544m water depth, but due to poor recovery (~14%) only ~66m of Oligocene to Quaternary sediments were recovered from ~474m of penetration (Hayes et al. 1975) (Figure 6.5). Sediments above ~160m are composed of

diatom oozes, silty clays and clays with abundant sand and pebbles throughout (Hayes et al. 1975; Piper and Brisco, 1975), interpreted to represent hemipelagic and terrigenous turbidity related deposition with common iceberg rafting. The age model of DSDP Site 268 has been constrained by silicoflagellate assemblages (Escutia, personal communication), and suggests the following ages for sediments: i) 113.66 to 116.38 mbsf: ~4.2 to ~5.5 Ma, ii) 84.81 to 86.84 mbsf: ~ 3.3 Ma, and iii) 56.51 and 58.24 mbsf: ~ 2.5 Ma (Figure 6.5).

6.4 Sample Selection and Methods

Thirty-nine samples in total were selected for analysis of Nd and Sr isotopes from ODP Site 1165 (Figure 6.6; Table 6.3), consisting of 32 Pliocene samples (between 17.95 and 49.15 mbsf, ~2.65 to 4.99 Ma), six Pleistocene samples (0.80 to 12.59 mbsf, ~0.1 to 1.05 Ma) and a coretop sample (0.01 mbsf, Holocene age). Samples were selected from maxima and minima in grain size (Grützner et al. 2003; Warnke et al. 2004; Passchier et al. 2011), and from multiple lithologies, in order to capture the full range of potential sediment provenance endmembers at the site (Figure 6.6). Furthermore, 13 Pliocene samples were analysed between 45.50 to 46.00 mbsf, in order to provide a high resolution record of sediment provenance change in close proximity to a well-established age-depth tie point (the top of paleomagnetic chron boundary C3n.2n, 45.75 mbsf, 4.631 Ma). In order to investigate any potential grain size bias in the isotopic composition of detrital sediments, three samples (25.86 mbsf, 3.205 Ma; 40.40 mbsf, ~4.01 Ma; 45.90 mbsf, ~4.665 Ma) were selected for separation into clay (<4 μ m) and silt (4-63 μ m) sized fractions, and analysed for Nd and Sr isotopes (Table 6.3; Figure 6.7).

Additionally, 10 samples were selected for analysis of detrital Nd and Sr isotopic compositions at DSDP Site 268 (see Figure 6.1 for location): two Late Pliocene/Early Pleistocene samples (56.58 and 57.81 mbsf, ~2.5 Ma), seven Early Pliocene samples (113.53 to 116.39 mbsf, ~4.2 to 5.5 Ma), and one Holocene coretop sample (Figure 6.5; Table 6.4).

Bulk sediment samples were wet sieved into <63 μ m, 63-150 μ m and >150 μ m fractions. For three samples, the <63 μ m fractions were separated into clay (~<4 μ m) and silt (~4 to 63 μ m) sub-fractions by gravity settling in deionised water at room temperature (after U.S.G.S Open-File Report 01-041; <http://pubs.usgs.gov/of/2001/of01-041/html/docs/methods.html>) according to Stokes Law (Folk, 1954). Splits (~500mg) of homogenised sediment were sequentially leached to remove biogenic carbonate and

Table 6.3. Nd and Sr isotope values for ODP Site 1165 sediments (<63µm).

	Depth (mbsf)	~ Age (Ma)	⁸⁷ Sr/ ⁸⁶ Sr	± 2 S.E.	¹⁴³ Nd/ ¹⁴⁴ Nd	± 2 S.E.	εNd [†]	± 2 S.D. ⁺
1H 1W 1-3cm	0.01	0	0.732141	0.000010	0.511641	0.000018	-19.4	0.2
1H 1W 80-82cm	0.80	0.1	0.729198	0.000012	0.511859	0.000010	-16.1	0.4
reanalysis			0.729197	0.000010	0.511824	0.000018	-15.9	0.4
1H 2W 70-72cm	2.20	0.3	0.735443	0.000014	0.511767	0.000008	-17.0	0.3
1H 3W 140-142cm	4.40	0.6	0.735955	0.000008	0.511724	0.000010	-17.8	0.4
reanalysis			0.735934	0.000018	0.511737	0.000012	-17.6	0.4
1H 4W 110-112cm	5.60	0.8	0.737159	0.000010	0.511745	0.000010	-17.4	0.3
2H 2W 20-22cm	7.00	1.00	0.734728	0.000010	0.511777	0.000010	-16.8	0.1
2H 4W 129-131cm	12.59	1.05	0.736294	0.000014	0.511766	0.000020	-17.0	0.4
3H 2W 15-17cm	17.95	2.7	0.736654	0.000016	0.511660	0.000012	-19.4	0.5
3H 2W 45-47cm	18.25	2.8	0.732560	0.000016	0.511788	0.000018	-16.6	0.4
3H 3W 71-73cm	20.01	3	0.738296	0.000018	0.511840	0.000010	-17.6	0.3
3H 3W 109-111cm	20.39	3.09	0.735137	0.000008	0.511795	0.000018	-16.4	0.4
3H 3W 130-132cm	20.60	3.11	0.736836	0.000010	0.511737	0.000018	-17.6	0.4
3H 5W 110-112cm	23.40	3.16	0.732739	0.000008	0.511743	0.000012	-17.5	0.3
3H 6W 11-13cm	23.91	3.17	0.734988	0.000022	0.511975	0.000010	-15.0	0.3
3H 6W 70-73cm	24.50	3.19	0.741332	0.000016	0.511787	0.000010	-16.6	0.4
4H 1W 6-9cm	25.86	3.205	0.736648	0.000010	0.511594	0.000012	-20.4	0.3
4H 1W 15-17cm	25.95	3.207	0.735786	0.000016	0.511693	0.000008	-18.4	0.3
Reanalysis			0.735776	0.000008				
4H 2W 109-111cm	28.39	3.27	0.735678	0.000012	0.511695	0.000018	-18.4	0.3
4H 3W 70-72cm	29.50	3.3	0.743046	0.000034	0.511653	0.000012	-19.2	0.4
Duplicate			0.744692	0.000018	0.511594	0.000014	-20.4	0.2
4H 5W 90-92cm	32.70	3.42	0.735656	0.000010	0.511736	0.000018	-17.6	0.3
Reanalysis					0.511742	0.000008	-17.5	0.2
4H 6W 80-82cm	34.10	3.48	0.735187	0.000020	0.511885	8.000000	-14.7	0.3
Reanalysis			0.735204	0.000016				
4H 7W 20-22cm	35.00	3.53	0.739423	0.000026	0.511869	0.000010	-15.0	0.5
5H 4W 20-22cm	40.00	3.96	0.737007	0.000032	0.511882	0.000012	-14.8	0.4
Reanalysis					0.511859	0.000020	-15.2	0.4
5H 4W 60-62cm	40.40	4.01	0.739439	0.000012	0.511903	0.000008	-14.3	0.2
6H 1W 15-17cm	44.95	4.55	0.739700	0.000022	0.511728	0.000016	-17.8	0.5
Reanalysis					0.511748	0.000014	-17.4	0.6
6H 1W 70-72cm	45.50	4.6	0.742703	0.000024	0.511752	0.000014	-17.3	0.4
6H 1W 75-77cm	45.55	4.605	-	-	0.511970	0.000008	-13.0	0.2
6H 1W 80-82cm	45.6	4.61	-	-	0.511958	0.000001	-13.3	0.2
6H 1W 84-86cm	45.64	4.62	0.731405	0.000009	0.511881	0.000008	-14.8	0.5
6H 1W 90-92cm	45.7	4.63	0.729821	0.000032	0.511585	0.000008	-20.5	0.3
6H 1W 94-96cm	45.74	4.64	0.730189	0.000026	0.511911	0.000014	-14.2	0.5
Reanalysis			0.730187	0.000014				
6H 1W 95-97cm	45.75	4.645	-	-	0.512001	0.000005	-12.4	0.2
6H 1W 100-102cm	45.8	4.65	0.739490	0.000032	0.511804	0.000008	-16.3	0.3
6H 1W 104-106cm	45.84	4.655	0.731228	0.000008	0.511930	0.000012	-13.8	0.5
6H 1W 105-107cm	45.85	4.66	-	-	0.511999	0.000008	-12.5	0.2
6H 1W 110-112cm	45.9	4.665	0.728656	0.000012	0.511915	0.000010	-14.1	0.2

Reanalysis			0.728652	0.000012				
6H 1W 115-117cm	45.95	4.7	-	-	0.511978	0.000010	-12.9	0.2
6H 1W 120-122cm	46	4.75	0.737062	0.000001	0.511905	0.000018	-14.3	0.5
6H 3W 135-137cm	49.15	4.99	0.733045	0.000008	0.511872	0.000010	-14.9	0.2
5H 4W 60-62cm clay			0.74804	0.000052	0.512072	0.000018	-13.1	0.3
5H 4W 60-62cm silt			0.73761	0.000052	0.512041	0.000012	-13.7	0.3
4H 1W 6-9cm clay			0.736694	0.000006	0.511729	0.000014	-19.8	0.3
4H 1W 6-9cm silt			0.739314	0.000008	0.511714	0.000016	-20.1	0.3
6H 1W 110-112cm clay			0.737819	0.000026	0.512073	0.000012	-13.1	0.3
6H 1W 110-112cm silt			0.731516	0.000026	0.512024	0.000010	-14.0	0.3

[†] Calculated using a present day $^{143}\text{Nd}/^{144}\text{Nd}$ (CHUR) of 0.512638

[‡] External uncertainty (2 sigma standard deviation) is based on the standard reproducibility of the analytical session, or a propagated internal 2σ SE taking into account small beam signals (the larger of the two errors is reported).

Re-analysed values represent samples that were measured multiple times (same aliquot), while duplicate samples represent full procedural repeats (e.g. from digestion, through ion exchange chromatography, to mass spectrometry).

Table 6.4. Nd and Sr isotope data for DSDP Site 268 sediments (<63 μm).

Sample	Depth (mbsf)	~ Age (Ma)	$^{87}\text{Sr}/^{86}\text{Sr}$	± 2 S.E.	$^{143}\text{Nd}/^{144}\text{Nd}$	± 2 S.E.	ϵNd	± 2 S.D. [†]
1R 1W 81-82cm	0.81	0	0.729469	0.000034	0.512139	0.000007	-11.1	0.4
3R 1W 135-136cm	56.85	~2.5	0.751319	0.000010	0.511994	0.000005	-13.9	0.4
3R 2W 81-82cm	57.81	~2.5	0.748338	0.000012	0.512173	0.000005	-12.3	0.3
5R 1W 3-5cm	113.53	4.2-5.5			0.512186	0.000006	-12.0	0.3
5R 1W 15-16cm	113.65	4.2-5.5	0.731988	0.000006	0.512305	0.000005	-9.7	0.3
5R 1W 22-23cm	113.72	4.2-5.5			0.512190	0.000004	-10.1	0.4
5R 1W 65-66cm	114.15	4.2-5.5	0.726279	0.000008	0.512322	0.000006	-9.4	0.3
5R 1W 88-89cm	114.38	4.2-5.5	0.733185	0.000006	0.512129	0.000006	-11.3	0.4
5R 2W 64-65cm	115.64	4.2-5.5	0.744931	0.000012	0.512204	0.000005	-11.7	0.3
5R 2W 139-140cm	116.39	4.2-5.5	0.759982	0.000008	0.512161	0.000006	-12.0	0.3

[†] Calculated using a present day $^{143}\text{Nd}/^{144}\text{Nd}$ (CHUR) of 0.512638

[‡] External uncertainty (2 sigma standard deviation) is based on the standard reproducibility of the analytical session

authigenic ferromanganese oxides and hydroxides. Removal of CaCO_3 was achieved by leaching of dried sediments repeatedly with buffered acetic acid following the method of Biscaye et al. (1965). Ferromanganese oxides and oxyhydroxides were removed through repeated steps of leaching for 6-12 hours with a reductive solution, hydroxylamine hydrochloride (NH_2OH), following Rutberg et al. (2000). No removal of biogenic opal was carried out due to likely negligible effects of incorporated detrital Nd and seawater Sr compositions on isotopic values (see Chapter 2). A representative sub-sample of 50mg of

detrital sediment was dissolved by hotplate digestion using 2ml of 27M HF, 2ml of 15M of HNO₃ and 0.6ml of 20M HClO₄. A secondary digestion step using 2ml of 15M HNO₃ and 1ml of 27M HF was employed if any refractory minerals remained visible after this first step. Fluorides were removed in a subsequent step by fluxing samples in 6M HCl. In preparation for ion exchange chromatography, samples were converted to nitrate form. Target analytes (Nd and Sr) were selectively separated from the sample matrix by ion chromatography on three separate columns. The entire sample was first loaded on a Sr Spec column (*Sr-spec* resin: 100-120µm bead size, modified after Pin and Bassin [1992]). The matrix elute from this column was subsequently used to first separate Nd from the sample matrix (*TRU-Spec* resin: 100-120µm bead size, Pin and Zalduegui [1997]), and then from the other rare earth elements (*Ln-spec* resin: 50-100µm bead size, modified after Pin and Zalduegui [1997]).

Dried Nd cuts were taken up in ~1% HNO₃ in preparation for measurement of Nd isotopes on a Nu Instruments multi collector inductively coupled plasma mass spectrometer (MC-IPC-MS) in the MAGIC laboratories at Imperial College London, and results are shown in Table 6.3. Measurements were carried out in static mode. A ¹⁴⁶Nd/¹⁴⁴Nd ratio of 0.7219 was applied to correct for instrumental mass bias following the exponential law. Tests showed that interferences from ¹⁴⁴Sm are adequately corrected if the ¹⁴⁴Sm contribution is less than 0.1% of the ¹⁴⁴Nd signal. Samarium contributions of all samples were significantly below that level. Twelve analytical sessions over an 24 month period yielded the following ¹⁴³Nd/¹⁴⁴Nd JNdi ratios: 0.511970 ± 0.000018 (n=22); 0.511922 ± 0.000020 (n=20); 0.511926 ± 0.000018 (n=23); 0.511991 ± 0.000013 (n=19); 0.512007 ± 0.000012 (n=17); 0.511979 ± 0.000025 (n=18); 0.512022 ± 0.000012 (n=14); 0.512079 ± 0.000011 (n=16); 0.512153 ± 0.000018 (n=20); 0.512220 ± 0.000018 (n=18); 0.512279 ± 0.000015 (n=18); 0.512185 ± 0.000018 (n=22). All ¹⁴³Nd/¹⁴⁴Nd ratios in Table 6.3 are corrected to the recommended JNdi value of 0.512115 (Tanaka et al. 2000). Inter-batch measurements of processing monitor standard BCR-1 yielded ¹⁴³Nd/¹⁴⁴Nd ratios of 0.512651 ± 0.000034 (n=7), compared to the recommended value of 0.512646 ± 0.000016 (Weis et al. 2006). Total procedural blanks were consistently below 10pg Nd, less than 0.01% of the total approximate Nd concentration.

Strontium was loaded in 1µl of 6M HCl onto a degassed tungsten filament followed by 1µl of tantalum chloride. Measurements were performed in a single filament assembly on a Thermo Scientific Triton thermal ionisation mass spectrometer (TIMS) in the MAGIC laboratories at Imperial College London in static mode. The measured isotopic ratios were corrected for instrumental mass bias using the exponential law and a ratio of ⁸⁸Sr/⁸⁶Sr =

8.375. Interferences from ^{87}Rb were corrected for using a $^{87}\text{Rb}/^{85}\text{Rb}$ ratio of 0.3860. Samples were analysed over six analytical sessions. Measurements of NBS987 standards yielded average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.710256 ± 0.000012 (n=7), 0.710256 ± 0.000011 (n=15), 0.710256 ± 0.000010 (n=15), 0.710256 ± 0.000012 (n=18), 0.710260 ± 0.000016 (n=13), and 0.710266 ± 0.000015 (n=12). As these measured values are in good agreement with published NBS987 values (0.710252 ± 0.000013 ; n=88) (Weis et al. 2006), no correction has been applied to the sample results presented in Table 6.3. Repeated processing and analyses of procedural standard reference material BCR-1 yielded an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.705023 ± 0.000022 (2 SD) (n=8), in good agreement with the recommend value of 0.705018 ± 0.000013 (Weis et al. 2006). Procedural blanks were consistently below 40pg, less than 0.01% of the total approximate Sr concentration.

6.5 Results

Detrital fractions (<63 μm) from ODP Site 1165 sediments (Table 6.3) yielded ϵ_{Nd} values between -12.4 and -20.5 and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.729 and 0.743 (Figure 6.6). Comparison of Nd and Sr isotope results reveals no significant correlation ($r^2=0.1$). There is however a notable long term shift in downcore Nd isotopic compositions: between 3.48 and 4.99 Ma, sediments are characterized by an average ϵ_{Nd} value of -14.8, with 14 out of 19 samples yielding values between -12.4 and -15.0. This average value shifts after ~ 3.42 Ma, with less radiogenic Nd isotopic compositions becoming predominant: ϵ_{Nd} values between the Holocene coretop (-19.4) and ~ 3.42 Ma range from -15.9 to -20.4 (average of -17.6), with particularly low values between 3.205 Ma and 3.42 Ma (-17.6 to -20.4). An interesting observations is that the interval sampled at higher resolution, between 45.50 and 46.00 mbsf (~ 4.6 to ~ 4.75 Ma), captures the full range of ϵ_{Nd} values ($\epsilon_{\text{Nd}} = -12.4$ and -20.5). Two overall endmembers within this section are apparent, with ϵ_{Nd} values between -12.4 and -15.0, and -16.3 to -20.5.

In contrast to downcore Nd isotopic compositions, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios do not show the same systematic changes through time; sediments deposited between 3.48 and 4.99 Ma range from 0.729 to 0.743, with an average of 0.736, similar to the average of 0.735 derived for the sediments deposited between the Holocene and ~ 3.42 Ma. Neodymium and Sr isotopic compositions of sediments deposited between 3.48 and 4.99 Ma show a weak correlation ($R^2=0.4$), whereas those of sediments deposited between the Holocene and 3.42 Ma share no correlation ($R^2=0.1$) (Figure 6.6).

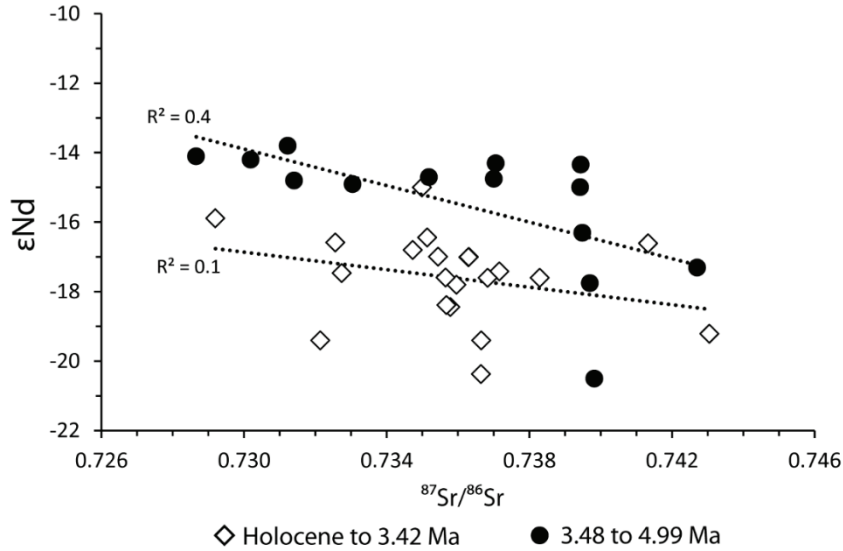


Figure 6.6. Plot of ϵ_{Nd} values and $^{87}Sr/^{86}Sr$ ratios for ODP Site 1156 sediments (error bars same size as data points or smaller), illustrating the correlation between sediments deposited between the Holocene and 3.42 Ma (white diamonds) and between 3.48 and 4.99 Ma (black circles).

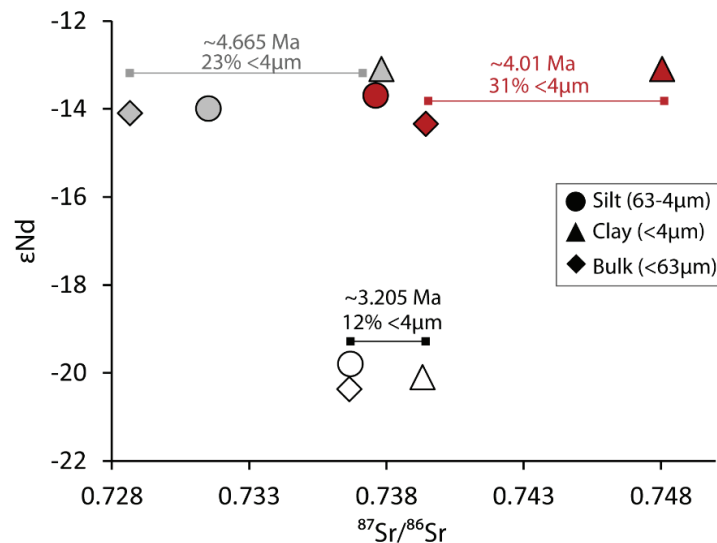


Figure 6.7. ϵ_{Nd} values and $^{87}Sr/^{86}Sr$ ratios for clay (<4 μm ; triangles), silt (4-63 μm ; circles) and bulk (<63 μm , diamonds) fractions for samples from ~3.205 Ma (black data points), ~4.01 Ma (red data points), ~4.665 Ma (grey data points). Error bars same size as data points or smaller. Clay fractions consistently show more radiogenic values than silt or bulk fractions, with $^{87}Sr/^{86}Sr$ values for the ~3.205 Ma sample showing an $^{87}Sr/^{86}Sr$ isotopic difference of 0.003 between the clay and bulk fractions, the ~4.01 Ma sample shows an $^{87}Sr/^{86}Sr$ isotopic difference of 0.009, and the ~4.665 Ma sample also showing an $^{87}Sr/^{86}Sr$ isotopic difference of 0.009. The silt fraction in the ~4.01 Ma sample is slightly less radiogenic than the bulk fraction, probably due to a mineralogical bias.

In the three samples separated into clay and silt fractions, clay fractions consistently display more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than corresponding silt fractions (Table 6.3, Figure 6.7). The clay and silt fractions of the sample deposited at 3.205 Ma comprised 12% and 88% of the total <63 μm sediment fraction respectively, and ϵ_{Nd} and $^{87}\text{Sr}/^{86}\text{Sr}$ results of -20.1 and 0.739, and -19.8 and 0.737, respectively, with the bulk sample (<63 μm) being characterized by an ϵ_{Nd} value of -20.4 and $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.737, indistinguishable from the silt sample.

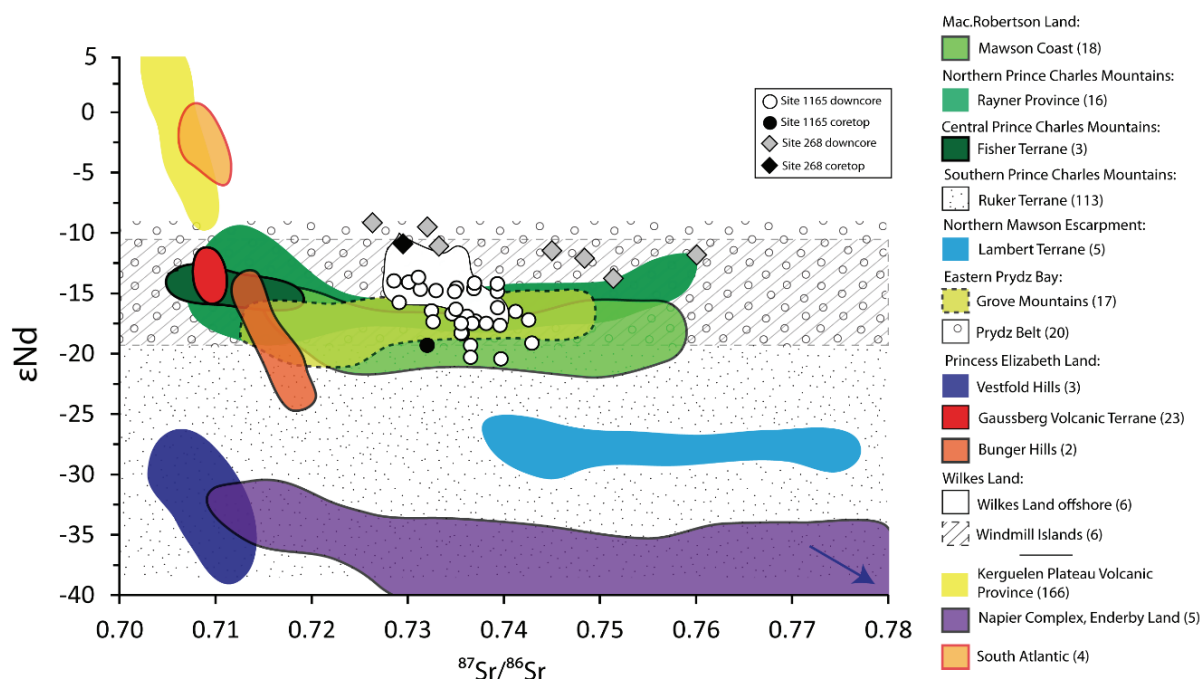
Separated clay and silt fractions from the ~4.01 Ma sample made up 31% and 69% of the <63 μm fraction respectively. The fractions yielded ϵ_{Nd} values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of -13.1 and 0.748 (clay), and -13.7 and 0.738 (silt), while the bulk sample was characterized by an ϵ_{Nd} value of -14.3 and an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.739. The clay and silt fractions of the <63 μm of the sample deposited at ~4.665 Ma (clay: 23%, silt: 77%) showed ϵ_{Nd} values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of -13.1 and 0.738, and -14 and 0.732 respectively, and bulk values of -14.1 and 0.728.

In comparison to ODP Site 1165 sediments, Nd isotopic compositions for samples from DSDP Site 268 are in general more radiogenic, and Sr isotope ratios are more variable. The Holocene coretop sample yielded a ϵ_{Nd} value of -11.1, and an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.729 (see Table 6.4 for DSDP Site 268 Sr and Nd isotope data). The remaining Pliocene samples produced ϵ_{Nd} values that range between -9.4 and -13.9 (n=9), and $^{87}\text{Sr}/^{86}\text{Sr}$ values between 0.726 and 0.759 (n=7). Late Pliocene/Early Pleistocene sediments produced ϵ_{Nd} and $^{87}\text{Sr}/^{86}\text{Sr}$ values between -12.3 and -13.9, and 0.751 and 0.748, respectively, whereas Early Pliocene sediments produced ϵ_{Nd} and $^{87}\text{Sr}/^{86}\text{Sr}$ values ranging between -9.4 and -12.3, and 0.731 and 0.759, respectively. In contrast to ODP Site 1165 detrital sediments, Nd and Sr isotope results at DSDP Site 268 show a strong negative correlation ($r^2 = -0.8$).

6.6 Discussion

6.6.1 Strontium isotopes in ODP Site 1165 sediments as a provenance indicator?

Comparison of measured Nd and Sr isotope compositions for Pliocene and Quaternary sediments from ODP Site 1165 with known isotopic compositions of potential source areas reveals good agreement between my data and numerous bedrock terranes throughout Prydz Bay and Wilkes Land (Figure 6.8). However, ϵ_{Nd} values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of sediments deposited between 3.38 and 4.99 Ma only share a very weak negative correlation ($R^2 = 0.4$; Figure 6.6), and isotopic compositions for sediments deposited between



the Holocene and 3.42 Ma show no significant correlation, suggesting a decoupling of Nd and Sr isotopes. Below I propose potential reasons for a departure of Sr isotopic compositions

Figure 6.8. Neodymium and strontium isotopic compositions of potential regional source areas (colored/shaded areas) overlain by results for marine sediments from ODP Site 1165 and DSDP Site 268 (error bars same size as data points or smaller). Numbers in brackets following source terranes indicate the number of samples used to define the terrane, and onshore data is reported for major lithologies only. Data for the Mawson exposures of the Rayner Province from Young et al. (1997). Data for the Rayner Province in the NPCM is from Andronikov et al. (1998), Manton et al. (1992), Zhao et al. (1997), and Mikhalsky et al. (1999). Data for the Ruker Terrane and the Lambert Terrane in the SPCM from Mikhalsky et al. (2006, 2010), and Boger et al. (2008). Data for the Grove Mountains is from Liu et al. (2006, 2007a). Data for the Prydz Belt is from Liu et al. (2007b), Hensen and Zhou (1995), and Grew et al. (2002). Data for the Vestfold Hills is from Black et al. (1991). Data from the Gaussberg Volcanic Terrane is from Murphy et al. (2002). Data from the Bunger Hills is from Sheraton et al. (1990). Data from the Windmill Islands from is Möller et al. (2002) and Zhang et al. (2012). Data for the Napier Complex in Enderby Land is from Black et al. (1987), Black and McColluch, (1987), and DePaolo et al. (1982). Data from the Kerguelen Plateau is from Barling et al. (1990, 1994), Davies et al. (1989), Clarke et al. (1983), Weis et al. (1989, 2001, 2002), Salters et al. (1992), Ingles et al. (2002), Neal et al. (2002), Frey et al. (2002) and Kieffer et al. (2002). Offshore data is from Brachfeld et al. (2007), Hemming et al. (2007), Roy et al. (2007), Pierce et al. (2011), Noble et al. (2012) and this study.

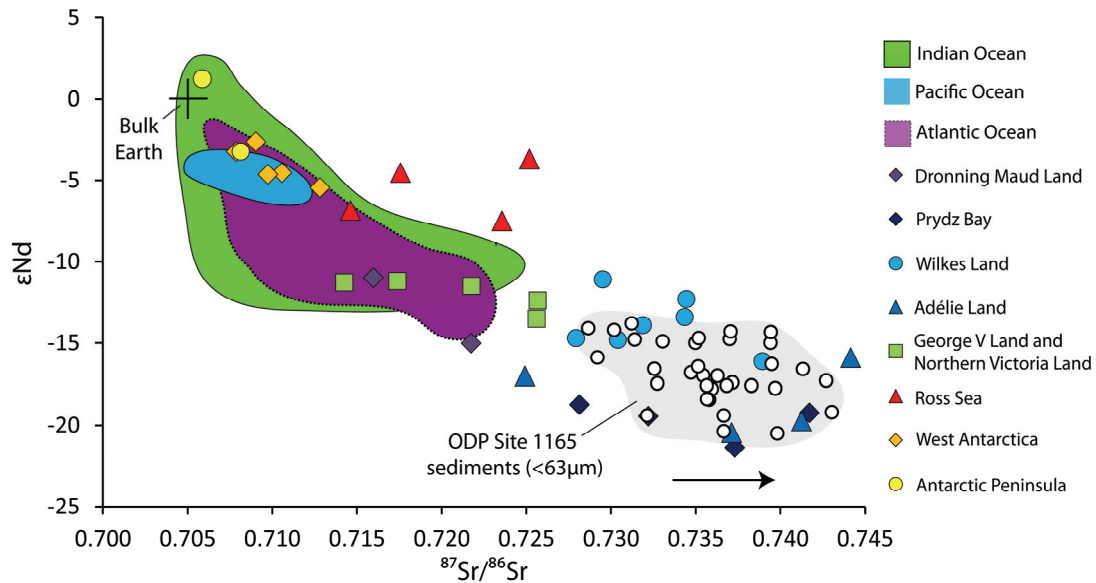


Figure 6.9. Global marine sediment signatures. Bulk Sr and Nd isotope signatures of modern marine sediments from the Atlantic, Indian and Pacific Oceans, consisting of unleached abyssal pelagic clays, terrigenous continental rise sediments and volcanoclastic sediments (coloured fields taken from Ben Othman et al. 1989; McLennan et al. 1990; Walter et al. 2000 and Ehlert et al. 2011), are shown along with Sr and Nd isotope signatures of leached fine-grained surface sediments from eight circum-Antarctic sectors (individual symbols; data from Farmer et al. 2006; Brachfeld et al. 2007; Hemming et al. 2007; Roy et al. 2007; van de Flierdt et al. 2007; Pierce et al. 2011; Chapter 2, Chapter 3), and measured Sr and Nd isotopic values of ODP Site 1165 sediments (white circles; this study; error bars same size as data points or smaller). Shown for reference is the bulk Earth isotopic composition (DePaolo and Wasserburg, 1976). Note that apart from the Ross Sea sector sediments, sediments sourced from younger terranes are characterized by a narrower range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, whereas sediments sourced from older terranes (e.g. Adélie Land, Prydz Bay) have wider ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, reflecting their more complex poly-metamorphic histories.

from expected provenance signatures based on Nd isotopes, and elaborate on possible environmental implications (regionally and globally) of this dataset.

Compilation of available bedrock compositions for Sr isotopes (Table 6.1 and Figure 6.2) demonstrates that the whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Archean, Proterozoic and Paleozoic terranes are characterized by a large degree of variability (e.g. the Lambert Terrane, Boger et al. 2008; the Grove Mountains, Liu et al. 2006, 2007a, Rayner Province NPCM, Mikhalsky et al. 1999; the Napier Complex, DePaolo et al. 1982) (Figure 6.8). These large ranges in Sr isotopic signatures (~ 0.705 to > 0.780) may be due to disturbance of the Rb-Sr systems during emplacement of Paleozoic intrusions and metamorphism. Rubidium (from Rb-rich

minerals) is often preferentially mobilized during crustal melting and major tectono-metamorphic processes (Dickin, 2005), often leading to more radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios within once open whole-rock systems. Conversely, the Sm-Nd system is usually unaffected by metamorphism (e.g. McCulloch and Wasserburg, 1978; DePaolo, 1980). Hence both radiogenic isotope systems can serve as provenance tracers, as has been shown for Pliocene sediments from IODP Site 1361 (Chapters 2 and 3). Younger bedrock terranes in George V Land and Northern Victoria Land have a simpler tectono-metamorphic history compared to Archean, Proterozoic and Paleozoic terranes in the Prydz Bay region, as reflected in the narrower ranges of reported whole-rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (see Chapters 2 and 3 for a detailed overview of the geological history of George V Land and Northern Victoria Land). The decoupling of whole-rock Sr and Nd isotopes in older bedrock terranes is illustrated by comparison of signatures of proximal fine-grained surface (Holocene) sediments deposited around Antarctica (Figure 6.9). Sediments derived from older terranes, such as the Adélie Craton in Wilkes Land, and the Rayner Province in Prydz Bay, have wider ranges of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios compared to younger terranes (Figure 6.9), reflecting potential resetting during poly-metamorphic histories.

Sedimentary sorting (i.e. a grain size effect) is an additional candidate to alter Sr isotopic composition in marine sediments. Compared to coarser-sized sediments, finer-grained detrital fractions are more enriched in Rb relative to Sr, as they contain clay minerals. Rubidium-rich minerals such as K-feldspar and micas tends to breakdown into clay minerals more readily than Sr-rich minerals such as plagioclase and pyroxenes (Biscaye and Dasch, 1971; Eisenhauer et al. 1999; Goldstein and Hemming, 2003; see Blum and Erel, 2003 and reference therein), resulting in increasingly radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in marine sediments with decreasing particle size (Blum and Erel, 2003). Conversely, the Nd isotopic composition of fine-grained sediments has been shown to largely reflect the bulk sediment composition (i.e. no major difference in Sm/Nd ratios in different rock forming minerals; Eisenhauer et al. 1999; Goldstein and Hemming, 2003). This effect can be observed in grain size separates for three samples (3.205 Ma, ~4.01 Ma, and ~ 4.665 Ma) from ODP Site 1165 (Figure 6.7). In all three samples, clay fractions are characterized by more radiogenic values than silt fractions or bulk (<63 μm) sediments (Figure 6.7). Notably, in two of the three samples there appears to be a relationship between the proportion of clay-sized material and how radiogenic clay fractions are relative to silt and bulk fractions, with lower amounts of clay corresponding to less radiogenic values (Figure 6.7). This suggests that size selective depositional processes could have played a role in shifting $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to more radiogenic values.

ODP Site 1165 is located on a sediment drift (Kuvaas and Leitchenkov, 1992; Kuvaas et al. 2004), formed as a result of deposition of fine-grained sediments by bottom currents (O'Brien et al. 2004). If preferential deposition of fine material played a role in bulk sediment Sr isotope composition through time, the long term variability of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in ODP Site 1165 sediments should co-vary with the amount of clay-sized material deposited. Warnke et al. (2004) and Passchier et al. (2011) identified a lower clay content in Early Pliocene sediments compared to later Pliocene and Pleistocene sediments, with a step increase in clay abundance after 3.42 Ma (Figure 6.4). While this step change is accompanied by a change in the average Nd isotopic composition of the sediments (see below), $^{87}\text{Sr}/^{86}\text{Sr}$ ratios remain largely unchanged, suggesting any grain-size effect on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ODP Site 1165 sediments is minor.

In summary, the poor correlation between Nd and Sr isotopic compositions of Pliocene ODP Site 1165 sediments is most likely due to the large degree of magmatic and metamorphic resetting of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in source bedrocks in the Prydz Bay area. The low number of available onshore wholerock $^{87}\text{Sr}/^{86}\text{Sr}$ data and their variability would make it difficult to distinguish between different sediment provenance sources. Hence, I will base any provenance discussions below on Nd isotopes alone.

6.6.2 Provenance of ODP Site 1165 sediments revealed by Nd isotopic compositions

Two groups of ϵ_{Nd} signatures have been identified in ODP Site 1165 sediments, the first with ϵ_{Nd} values between -12.4 and -15.0, and the second with ϵ_{Nd} values between -15.9 and -20.4. To constrain patterns of sediment supply to ODP Site 1165, below I compare these endmembers with known geochemical characteristics of numerous potential onland bedrock and marine sediment sources.

6.6.2.1 Sediment provenance from the Wilkes Land margin during the Early Pliocene?

The Wilkes Land margin is poorly exposed, but offshore values from regional marine sediment core tops range between -11.1 and -14.8 (Roy et al. 2007) (Figs. 6.1, 6.8 and 6.10). Core top and Pliocene sediments from DSDP Site 268 show similar Nd isotopic compositions (-9.4 to -13.9) (Figs. 6.5 and 6.8), suggesting that Wilkes Land may be a potential source for relatively radiogenic Nd isotope signatures at ODP Site 1165. Such an endmember seems to

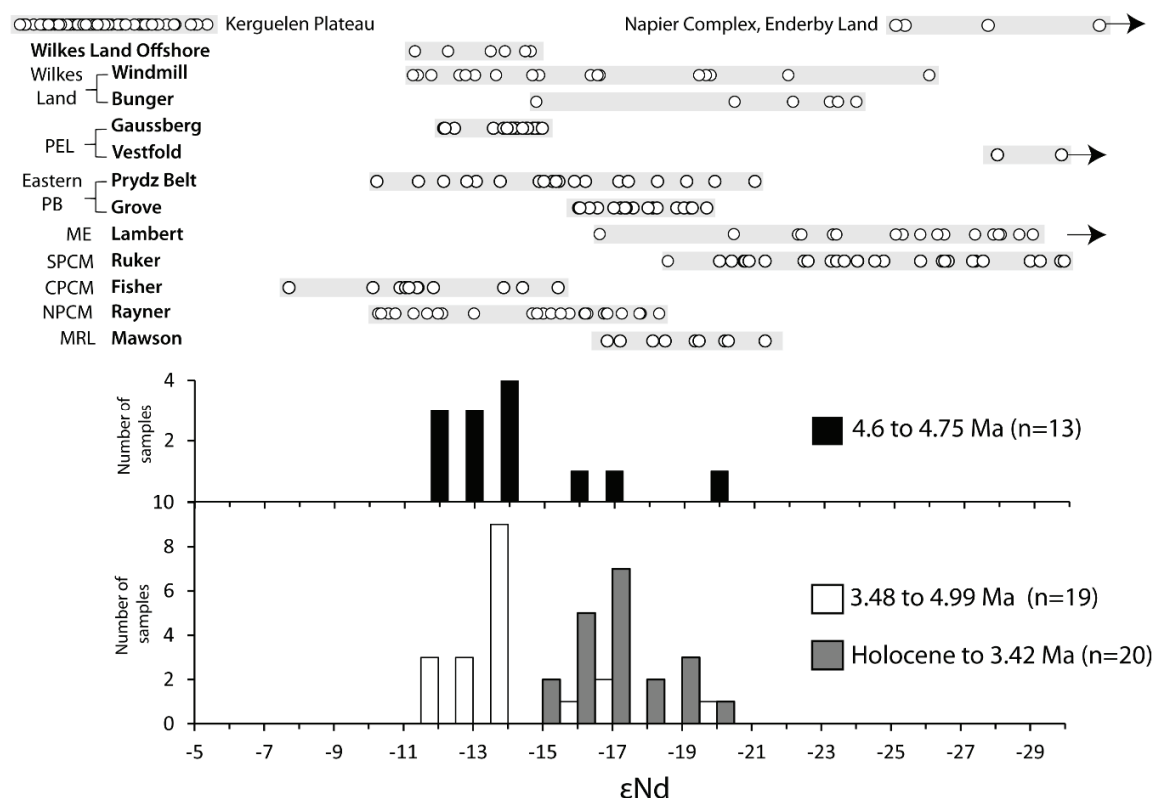


Figure 6.10. Comparison of the Nd isotopic signatures of potential source areas with values for time-separated ODP Site 1165 sediments. From top to bottom: i) ϵ_{Nd} ranges known bedrock terranes and provenance source areas (top plot), (see Figure 6.8 for references); ii) histogram illustrating distribution of ϵ_{Nd} values measured for ODP Site 1165 sediments deposited between ~ 4.6 and ~ 4.75 Ma (in black); iii) histogram illustrating distribution of ϵ_{Nd} values measured for ODP Site 1165 sediments deposited between the Holocene and 3.42 Ma (grey), and between ~ 3.48 and 4.99 Ma (in white). See text for further explanation on these two major time intervals. PEL: Princess Elizabeth Land; PB: Prydz Bay; ME: Mawson Escarpment; SPCM: Southern Prince Charles Mountains; CPCM: Central Prince Charles Mountains; NPCM: Northern Prince Charles Mountains, MRL: Mac.Robertson Land.

have been particularly important during the Early Pliocene (i.e. in sediments older than ~ 3.48 Ma).

Delivery of fine-grained detrital sediments from Wilkes Land to the Prydz Bay area during the Early Pliocene could have been achieved by ice rafting (e.g. Andrews, 2000), and/or transport by westward flowing bottom currents (e.g. Meijers et al. 2010). However, a strong argument against a significant role for ice rafting can be inferred from IRD provenance data presented in Chapter 5. Studies into provenance of Early Pliocene IRD reveal that not only were IRD mass accumulation rates at ODP Site 1165 low during the Early Pliocene (Passchier, 2011) (Figure 6.4), IRD was also dominantly sourced from the local Prydz Bay

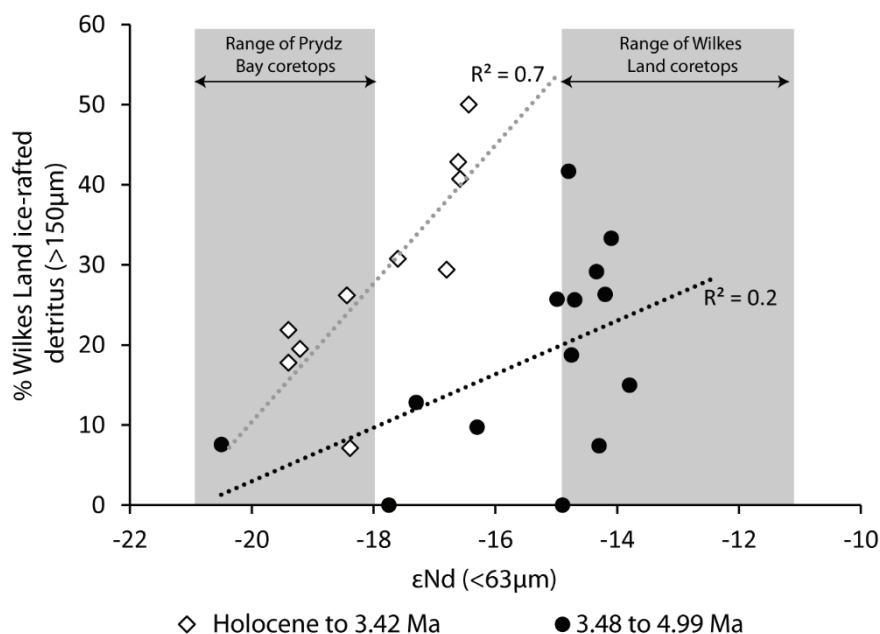


Figure 6.11. Relative abundance of Wilkes Land IRD (>150µm) (y-axis) versus ϵ_{Nd} values of fine-grained sediments (<63µm; error bars same size as data points or smaller) (x-axis) from the same samples, for sediments deposited before ~3.48 Ma, and after ~3.42 Ma. Linear regression lines are plotted for both time windows, with sediments deposited after ~3.42 Ma showing a strong positive correlation. The percentage of Wilkes Land IRD is relative to Prydz Bay IRD where together they equal 100% (i.e. not including any other IRD populations) (see Chapter 5).

region (Chapter 5). In fact, direct comparison between the amount of Wilkes Land IRD (relative to the amount of Prydz Bay IRD) and the ϵ_{Nd} composition of fine-grained sediments (<63µm) deposited before ~3.48 Ma reveals no correlation between the two, arguing against any significant component of iceberg-transported fine sediment from Wilkes Land (Figure 6.11, black circles). In contrast, during the Late Pliocene (i.e. sediments deposited after 3.42 Ma), Wilkes Land IRD increased in abundance at ODP Site 1165 (Chapter 5). A better correlation suggests that icebergs transported more fine-grained sediment from Wilkes Land to ODP Site 1165 (Figure 6.11; see below for a more detailed discussion into Late Pliocene marine provenance patterns at ODP Site 1165). However, from the lack of correlation prior to 3.48 Ma, I conclude that IRD sourced from the Wilkes Land margin did not significantly affect the provenance signatures of Early Pliocene fine-grained material at ODP Site 1165.

Alternatively, delivery of fine-grained detrital sediment from Wilkes Land to the Wild Drift in the Early Pliocene could have been by westward flowing bottom currents (Orsi et al. 1999; Meijers et al. 2010). Bottom currents can transport fine-grained material over long

distances as suspended load (e.g. Hillenbrand and Ehrmann, 2005), and today the presence of westward flowing AABW is well documented regionally (Orsi et al. 1999), as it travels westward towards Prydz Bay from sites of production in the Ross Sea (Orsi et al. 1999) and Adélie Land (Rintoul, 1998; Williams et al. 2008, 2010b) (Figure 6.3). Current speeds of the AABW as it travels towards the eastern flank of the Kerguelen Plateau reach up to 20 cm s^{-1} (Fukamachi et al. 2010), but most of this water is diverted northwards (Orsi et al. 1999; Fukamachi et al. 2010) by the sill of the Princess Elizabeth Trough, which separates the Kerguelen Plateau from the East Antarctic continent (~ 3750 meters water depth; Heywood et al. 1999) (Figure 6.3). However, AABW has also been observed to flow from east to west between 64.5°S and 66°S in the southern area of the Princess Elizabeth Trough into the Weddell-Enderby Basin (Heywood et al. 1999), with current speeds up to 12 cm s^{-1} (Meijers et al. 2010). The modern presence of easterly sourced AABW around ODP Site 1165 (Meijers et al. 2010) demonstrates the potential for similar patterns of ocean circulation during the Pliocene, but only very limited information on AABW formation areas and advection is available for this time (e.g. Josephs et al. 2002). Hence it is not possible to completely exclude a Wilkes Land supply of fine-grained detrital material to Prydz Bay during the Early Pliocene.

6.6.2.2 *Sediment provenance from Prydz Bay bedrock terranes during the Early Pliocene?*

More proximal areas that could supply sediments to ODP Site 1165 are located within the Prydz Bay region. Potential locations with lithologies with Nd isotopic compositions that match Early Pliocene ODP Site 1165 sediments (ϵ_{Nd} : -12.4 to -15.0) are provenance sectors 3 in Figure 6.1, corresponding to the south-eastern region of the NPCM and the Fisher Terrane of the CPCM (average ϵ_{Nd} : -13; Manton et al. 1992; Zhao et al. 1997; Andronikov et al. 1998; Mikhalsky et al. 1999, 2006), and provenance sector 5, corresponding to the Grove Mountains and the Prydz Belt of the eastern Lambert Graben (average ϵ_{Nd} : -14.5; Hensen and Zhou, 1995; Liu et al. 2006, 2007a, 2007b; Grew et al. 2012) (Figs. 6.1, 6.8 and 6.10).

Clay minerals in sedimentary successions can reflect sediment provenance (see Chapter 3), which has been interpreted as the primary control on the clay mineralogy of sediments in the Lambert Graben (Ehrmann et al. 2003). Clay mineral abundance data (Warnke et al. 2004; Junttila et al. 2005) reveal that ODP Site 1165 sediments deposited before $\sim 3.48 \text{ Ma}$, when more radiogenic Nd values are observed, are characterised by abundant smectite (Junttila et al. 2005). The most likely source for this smectite are Neogene

volcanic deposits located in the exposed western rift flank of the Lambert Graben (Mikhalsky et al. 2001), and sediments of the Pagodroma Group (Ehrmann et al. 2003; see below for detailed discussion of the Pagodroma Group). Outcrops of Eocene sediments on the Prydz Bay continental shelf may also be a source of smectite regionally, but clay assemblages in these Eocene sediments are dominated by kaolinite (Forsberg et al. 2008), which occurs in only minor abundances in Early Pliocene sediments at ODP Site 1165. An alternative source of smectite could also be the Kerguelen Plateau (Borchers et al. 2010) (Figure 6.3), but if Kerguelen-sourced detrital material (e.g. Coffin and Eldhom, 1992; Frey et al. 2000; Wallace et al. 2002) were a major source for smectite in ODP Site 1165 sediments, Nd isotope compositions of sediments would be expected to be more radiogenic than is observed (ϵ_{Nd} : -5.5 to + 5.0; Clarke et al. 1983; Barling et al. 1990, 1994; Davies et al. 1989; Weis et al. 1989, 2001, 2002; Salters et al. 1992; Ingles et al. 2002; Neal et al. 2002; Frey et al. 2002; Kieffer et al. 2002) (Figure 6.10). Conversely, a source of smectite from sites within the Lambert Graben agrees well with an interpretation of a source of detrital material from the southern NPCM, and the Prydz Belt of the eastern Lambert Graben, as suggested by Nd isotope values.

In summary, the western flank of the Lambert Graben (the Rayner and Fisher Terranes), and the eastern flank of the Lambert Graben (the Prydz Belt and Grove Mountains) is identified as the most likely source area for the Nd isotopic compositions in Early Pliocene ODP Site 1165 sediments, although a supply of fine-grained material from Wilkes Land cannot be excluded. However, an interpretation of a supply dominated by material from Prydz Bay is supported by clay mineral provenance work on ODP Site 1165 sediments, which hints to a provenance from the western flank of the Lambert Graben (Junttila et al. 2005).

6.6.2.3 The local Mawson Coast in MRL as a potential source for unradiogenic Nd isotope signatures in Late Pliocene ODP Site 1165 sediments

Exposures of the Rayner Province in MRL, the most proximal continental area to ODP Site 1165, are characterized by a range of ϵ_{Nd} values between -16.0 and -21.6 (average ϵ_{Nd} : -19.1; Young et al. 1997; Figs. 6.1, 6.8 and 6.10). These values match well with the range measured for the less radiogenic Nd isotope signatures observed in Pliocene and Pleistocene sediments at ODP Site 1165 (ϵ_{Nd} : -16.3 to -20.5) (Figure 6.10). Importantly, these signatures are also similar to those measured for Holocene core-top sediments offshore of

MRL, from sites located to the south and to the west of ODP Site 1165 (ϵ_{Nd} : -19.2 and -18.7; Roy et al. 2007) (Figure 6.1). In addition, the Holocene coretop sample from ODP Site 1165 yields a ϵ_{Nd} value of -19.4, in good agreement with all the other sites in its proximity (Figure 6.1). This convergence of provenance signatures in Holocene sediments, combined with their similarities to known isotopic characteristics of the Rayner Province in MRL, suggest this region may have been the main source of fine-grained detrital material for five samples analysed before ~ 3.48 Ma (with ϵ_{Nd} values between -16.3 and -20.5) and consistently after ~ 3.42 Ma (-15.0 to -20.5) at ODP Site 1165 (Figure 6.10).

One way to transport locally derived material from the MRL to ODP Site 1165 could be via bottom currents and/or turbidity currents. The study site was drilled from the Wild Drift, which is located to the east of the deeply incised Wild Channel (Figure 6.3). Oceanographic surveys suggest that the Wild Channel is today a major conduit of dense bottom waters formed on the MRL continental shelf (Figure 6.3) (Meijers et al. 2010; Ohshima et al. 2013), suggesting it may be a viable transport mechanism for fine-grained sediments eroded from the nearby MRL. A similar depositional process may have taken place during the later parts of the Pliocene and during the Pleistocene. For example, the presence of silt laminations in sediments deposited between ~ 3.2 and ~ 3.3 Ma with features characteristic of turbidites (Passchier, 2011) is potential evidence for the increased influence of turbidity currents carrying MRL derived material downslope at this time (Figure 6.4). I conclude that the good agreement between Holocene marine sediments at ODP Site 1165 and other regional core top results, with Late Pliocene and Pleistocene sediments at ODP Site 1165, as well as published Nd isotopic characteristics of exposed bedrock in MRL, can be taken as strong evidence for the increased presence of locally derived continental shelf material during these times.

6.6.2.4 Exclusion of other potential sources for ODP Site 1165 Plio-Pleistocene sediments

Alternative potential bedrock sources for unradiogenic Nd isotopic signatures in ODP Site 1165 (ϵ_{Nd} : -16.3 to -20.5) are Prydz Bay provenance sector 4 (the Ruker Terrane of the SPCM, and Lambert Terrane of the Mawson Escarpment; ϵ_{Nd} : -18.8 to -38.8, average ϵ_{Nd} : -29; Mikhalsky et al. 2006, 2007, 2010; Boger et al. 2008; Figure 6.1), the western region of sector 6 of Princess Elizabeth Land (the Vestfold Hills; ϵ_{Nd} : -27.4 to -38.7, average ϵ_{Nd} : -32; Black et al. 1991), or sector 1 (the Napier Complex of Enderby Land; ϵ_{Nd} : -25.0 to -47.0, average ϵ_{Nd} : -40; DePaolo et al. 1982; Black et al. 1987; Black and McColluch, 1987) (Figs.

6.1, 6.8 and 6.10). I render all of these areas unlikely to have contributed significantly to Pliocene and Pleistocene sediment provenance signatures based on the fact that, apart from some small overlap with the Ruker Terrane (ϵ_{Nd} : -18.8 to -38.8), even the most unradiogenic Nd isotopic values measured for ODP Site 1165 sediments (ϵ_{Nd} : -20.5) do not approach any of these extreme signatures (Figure 6.10).

Bedrock associated with the Gaussberg Volcanic Terrane (Figs 6.1, 6.8 and 6.10) is characterized by ϵ_{Nd} values between -12.1 and -14.9 (Murphy et al. 2002), a range that matches well with more radiogenic Nd isotope signatures in ODP Site 1165 sediments (ϵ_{Nd} : -12.4 to -14.8). However, limited age constraints appear to suggest that this primarily Quaternary-aged terrane is too young to have been a source of detrital material for sediments before ~3.48 Ma at ODP Site 1165 (see Chapter 5, Geological Overview; Murphy et al. 2002).

Another potential source of fine-grained detrital material for ODP Site 1165 is the eastward flowing ACC, if the location of its southern boundary, which today is located close to the latitude of ODP Site 1165 (Orsi et al. 1995; Meijers et al. 2010), has shifted southward in the past (Figure 6.3). A southward shift of the polar fronts of the ACC has been suggested to have taken place during warmer than present climates (e.g. Barron, 1996; Toggweiler et al. 2006; Brierley et al. 2009; Kemp et al. 2010), but three lines of evidence argue against significant supply of sediments from the west during the Pliocene. Firstly, Nd and Sr isotopic data for bulk sediments from ODP Sites 1094 and 1093 in the South Atlantic Southern Ocean sector of the ACC, more than 3000 km to the west of Prydz Bay show Holocene ϵ_{Nd} values between 0.4 and -5.2 (Noble et al. 2012), signatures that are too radiogenic to explain the Nd isotopic provenance of ODP Site 1165 sediments. Secondly, my own IRD provenance data (Chapter 5) suggest that even during the warm Early Pliocene, some IRD from Wilkes Land was delivered to ODP Site 1165, suggesting similar ocean circulation patterns to today (see Figure 5.2, Chapter 5). Thirdly, the majority of the flow of the ACC is located to the north of the Kerguelen Plateau approximately 2000km north of Prydz Bay (Park et al. 2009), so even if the southern boundary of the ACC shifted south over ODP Site 1165, it is likely that only minor transport of western sourced detrital material would take place.

I conclude that bedrock in the MRL area and detrital material eroded from the nearby continental shelf of the Mawson Coast, was probably the source for unradiogenic Nd isotope provenance signatures in Late Pliocene and Pleistocene (<3.42 Ma) ODP Site 1165 sediments, pointing to increased delivery of locally derived material via dense shelf waters and turbidites during these times. The Neoproterozoic Rayner and Fisher Terranes of the

south-easterly region of the NPCM in the western region of Prydz Bay, and the Prydz Belt in the eastern region, appear to be a potential source for more radiogenic Nd isotope provenance signatures for ODP Site 1165 sediments deposited before ~3.48 Ma.

6.7. Paleoenvironmental context and significance of variable provenance signatures in ODP Site 1165 sediments

Two patterns of provenance variability are apparent in Pliocene and Pleistocene sediments from ODP Site 1165: i) fluctuations in Nd isotopes covering the full range of Pliocene values (ϵ_{Nd} : -12.4 to -20.5) over a 50cm interval of core between ~4.6 and ~4.75 Ma ($n = 13$; Figs. 6.10 and 6.12), and (ii) a long term shift in average Nd isotopic compositions, from more radiogenic signatures, sourced from the flanks of the Lambert Graben, before ~3.48 Ma, to more unradiogenic signatures, supplied from the local Mawson Coast, after ~3.42 Ma (Figure 6.10). Below I will discuss each of these provenance patterns in terms of their depositional environments and paleoclimatic implications.

6.7.1. Evidence for obliquity-modulated provenance changes in Early Pliocene sediments at ODP Site 1165

The high resolution sampling interval between ~4.6 and ~4.75 Ma was chosen for detailed study as it includes the paleomagnetic chron boundary between C3n.2r (4.631 Ma to 4.799 Ma) and C3n.2n (4.300 to 4.631 Ma). The sample at 45.75 mbsf (ϵ_{Nd} : -12.4) can therefore be precisely dated to 4.631 Ma (Figure 6.12), placing it into the interglacial interval of Marine Isotope Stage (MIS) N9 (Lisiecki and Raymo, 2005) (Figure 6.12). Using linear sedimentation rates of 0.72 cm/kyr and 0.77cm/kyr up to the next older and next younger age tie points at 46.96 mbsf (4.799 Ma) and 43.19 mbsf (4.300 Ma) (see Table 6.2), which are assumed to be valid due to no significant changes in lithology during this interval, the Nd isotope provenance record reveals an oscillating pattern of variability between more radiogenic and less radiogenic values, that closely mirrors the global benthic oxygen isotopes stack. For example, on either neighboring side of the C3n.2r chron boundary at 45.74 mbsf, ϵ_{Nd} values between -12.4 and -14.8 appear to correspond to interglacial intervals MIS N7 and MIS NS1, and ϵ_{Nd} values between -15.0 and -20.5 correspond to the glacial intervals MIS N8 and MIS N10 (Figure 6.12). The sampling resolution for this interval is suborbital (~11,500

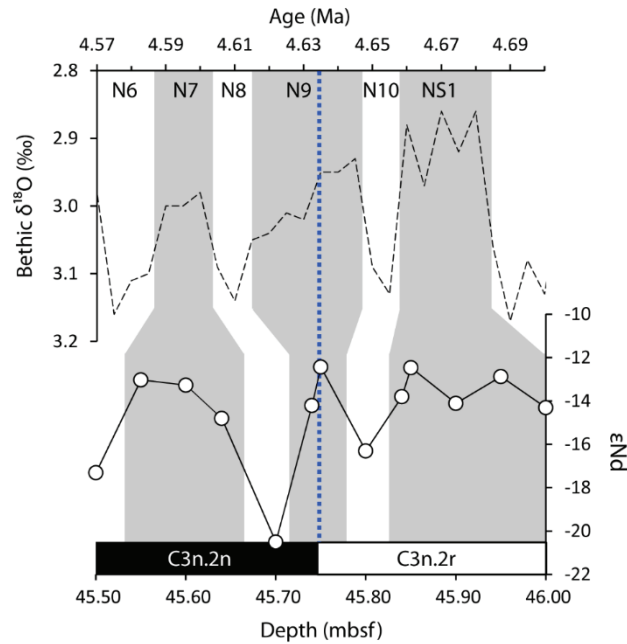


Figure 6.12. Interval between ~4.6 Ma and ~4.75 Ma sampled at ~10,000 year resolution (ODP Site 1165; 13 samples in total). From top to bottom: i) depth in meters below sea floor; ii) paleomagnetic chron boundary at 4.631 Ma (blue line, Florindo et al. 2003); iii) ϵ_{Nd} values for ODP Site 1165 sediments; iv) benthic oxygen isotope stack (Lisicki and Raymo, 2005), with marine isotope stages labelled; v) age in million years. Grey vertical bands represent inferred interglacial intervals, which match more radiogenic Nd isotopic compositions.

years), and hence sufficiently high enough to detect orbital-paced shifts in sediment provenance. This interpretation agrees well with spectral analysis carried out on the mass accumulation rates of terrigenous material for ODP Site 1165 sediments deposited between 4.8 and 5.2 Ma, which also show an enhanced pronounced obliquity-paced signal (Grützner et al. 2005). Building on this observation, I interpret that Early Pliocene interglacial sediments were sourced from the flanks of the Lambert Graben (more radiogenic Nd isotopic signal), and that Early Pliocene glacial sediments originated predominantly from the local Mawson Coast (more unradiogenic Nd isotopic signal).

6.7.2. Retreat of the EAIS driven by climatic warmth before ~3.48 Ma

Invoking a supply of fine-grained sediments to ODP Site 1165 before ~3.48 Ma from bedrock terranes located on the flanks of the Lambert Graben requires their erosion and transport of eroded material offshore. One way to achieve this is by retreat of the Lambert Glacier and Amery Ice Shelf to a location in the vicinity of the Fisher Terrane (see Figure 5.1

for location), more than 450km south of the current edge of the Amery Ice Shelf front. Most sediments melt out from ice shelves to form sub-ice shelf deposits where the base is in contact with the ocean in front of its grounding line (Alley et al., 1989) or are deposited in close proximity to its calving front (Domack and Harris, 1998), whereas marine terminating glaciers are more effective at injecting large quantities of sediment into the marine water column (O'Cofaigh and Dowdeswell, 2001). In addition, removal of buttressing ice shelves has been shown to result in increased velocity in flow speed of glaciers upstream (De Angelis and Skvarca, 2003; Rignot et al. 2004; Dupont and Alley, 2005; Jacobs et al. 2011). Surging of glaciers as a result of this decoupling may increase subglacial erosion rates (Smith et al. 2012). Hence, a scenario of Pliocene ice sheet retreat to explain provenance signatures at ODP Site 1165 requires that tributary glaciers that today flow from topographic highlands in the NPCM and to the east of Prydz Bay into the Amery Ice Shelf, acted as fjordal-type glaciers with their calving fronts situated on the flanks of the Lambert Graben. These glaciers could have then eroded bedrock in these regions, with detrital material being subsequently transported offshore.

An interpretation of Pliocene retreat of the AIS-LG into the Lambert Graben is supported by the presence of the Pagodroma Group (Hambrey and McKelvey, 2000; Whitehead and McKelvey, 2001; McKelvey et al. 2001; Whitehead et al. 2004) located in the NPCM (McKelvey et al. 2001; Whitehead et al. 2004), the CPCM, and the SPCM (Whitehead and McKelvey, 2002) (see Figure 5.1 for locations). These marine sediments were deposited up to 450 km south of the current position of the edge of the Amery Ice Shelf, in a fjordal-type setting during glacial retreat, and were subsequently uplifted, eroded and redeposited during glacial advance, so that today they occupy the above sea-level flanks of the Lambert Graben (Barker et al. 1998). Marine diatom fossils, both reworked and in situ, provide limited biostratigraphic ages for the Pliocene deposits of the Pagodroma Group, which range from 3.6 to 5.8 Ma (Whitehead et al 2004), in good agreement with my data from ODP Site 1165.

Additional evidence for Pliocene retreat of the EAIS in the vicinity of Prydz Bay comes from fossil-rich marine sediments in the Larsemann Hills (Quilty et al, 1990; McMinn and Harwood, 1995) and in the Vestfold Hills in Princess Elizabeth Land (e.g. Harwood et al. 2000). The Sørsdal Formation in the Vestfold Hills (Figure 6.1) (Quilty, 1991, 1992; Adamson and Pickard, 1993; Harwood et al. 2000; Whitehead et al. 2001; Fordyce et al 2002) is a sandy diatomite and diatomaceous sand unit, interpreted to have been deposited in a coastal marine embayment on the East Antarctic continental margin, in <25m water depth

(Harwood et al. 2000). The presence of aeolian delivered material implies that during its deposition, the ice-sheet margin was at least 50 km inland of its current position (Adamson and Pickard, 1993). Tentative diatom biostratigraphy suggests these sediments were deposited between 4.1 and 4.5 Ma (Harwood et al. 2000).

Ocean temperature most likely played an important factor in Pliocene ice shelf and ice sheet retreat (Chapters 2 and 5). Ambient warm deep water masses upwelling onto continental shelves likely drive retreat of ice shelves and marine-terminating glaciers in West Antarctica today by basal melting, where their grounding lines are in contact with ocean waters (Rignot and Jacobs, 2002; Jenkins et al. 2010; Pritchard et al. 2012). This observation has important implications for the sensitivity of the Lambert Glacier-Amery Ice Shelf to ocean warming, as it is currently grounded ~0.6 km below sea level at the southern edge of the Lambert Graben (Fricker et al. 2000) (Figure 6.3). Evidence for warmer-than-present ocean waters during the Early Pliocene (see Chapter 5) have been inferred from silicoflagellate assemblages in ODP Site 1165 sediments (Whitehead and Bohaty, 2003; Escutia et al. 2009), which imply periods of either extreme or prolonged summer sea surface temperatures between 4.55 and 4.8 Ma (~4°C above modern), 4.3 to 4.4 Ma (~4°C above modern), ~3.7 Ma (>5.6°C above modern), ~3.6 Ma (2.5 to 4°C above modern) and ~3.5 Ma (~2.5°C above modern) (Whitehead and Bohaty, 2003; Escutia et al. 2009). Extant diatom assemblages within the Sørsdal Formation also indicate that summer sea surface temperatures during its deposition (~4.1 to 4.5 Ma) were between ~1.6 and 3°C warmer than today (Whitehead et al. 2001), reflecting slightly cooler temperatures than the more continentally distal ODP Site 1165. Paleothermometry estimates from TEX₈₆^L measurements of sediments in the Ross Sea, West Antarctica, reveal seasonally warm upper ocean temperatures of up to 5°C higher than today before ~3.3 Ma (McKay et al. 2012a) (Figure 6.13). Additional evidence for regionally warm temperatures comes from significantly low amounts of sea ice as indicated by marine diatom assemblages in the Sørsdal Formation, between 3.1 and 4.9 Ma (Whitehead et al. 2005). Diatom assemblages in ODP Site 1165 sediments, and in nearby continental shelf sediments, suggest winter sea ice levels were ~22% of the maximum winter extent today (Whitehead et al. 2005). Warm sea surface temperatures during the Early Pliocene have also been invoked to explain the low flux and limited amount of distally-sourced IRD at ODP Site 1165 (Passchier, 2011; Chapter 5).

Based on observational data collected over the last 50 years, current estimates for the threshold of ice shelf instability in the Antarctic Peninsula are between -9°C and -5°C (Cook et al. 2005), suggesting Early Pliocene temperature estimates for ocean waters in the vicinity

of Prydz Bay ($>5.6^{\circ}\text{C}$; Escutia et al. 2009) may have been sufficiently high to drive collapse of the LG-AIS up to its southern grounding line (Figure 6.3). In fact, a scenario of regional ice sheet retreat within the Lambert Graben during the Early Pliocene is compatible with retreat of the EAIS into the low-lying Wilkes Subglacial Basin (Chapter 2), inferred from sediment provenance signatures in IODP Site U1361 to have taken place during interglacials and extended intervals throughout the Pliocene, and into the Pleistocene (Chapters 2 and 3). Interestingly, collapse of the Ross Ice Shelf, as indicated by the deposition of diatomites at AND-1B (Naish et al. 2009), also occurred at various intervals throughout the Early Pliocene, at ~ 4.87 Ma, ~ 4.8 Ma, 4.75 Ma, 4.6 Ma, ~ 4.4 Ma, and between ~ 3.4 to 3.6 Ma, but not during the Late Pliocene (McKay et al. 2012a).

In conclusion, an interpretation of increased supply of detrital material delivered to ODP Site 1165 from the flanks of the Lambert Graben during retreat of the Lambert Glacier, during Early Pliocene interglacials and for most sediments deposited before ~ 3.48 Ma, is supported by analysis of regional onshore sedimentary deposits, regional and circum-Antarctic SST reconstructions, and circum-Antarctic evidence for significant ice retreat/ice shelf collapse. Together, these records imply that multiple regions of the EAIS were sensitive to warmer-than-present temperatures during the Early Pliocene.

6.7.3 Evidence for ice sheet growth after 3.42 Ma

After ~ 3.42 Ma, and during glacial intervals between ~ 4.6 and ~ 4.75 Ma, sediment provenance signatures at ODP Site 1165 become dominated by locally derived material sourced from the nearby MRL and continental shelf along the Mawson Coast, a pattern that appears to have been maintained throughout the Late Pliocene and Quaternary (Figure 6.10). Contemporaneous with this change in provenance signature is a significant increase in sedimentation rates and an increase in the amount of clay-sized detrital material deposited at ODP Site 1165 (Warnke et al. 2004; Passchier, 2011) (Figure 6.4).

Clay mineral provenance after ~ 3.42 Ma reveals sediments are dominated by illite, which in the Southern Ocean is typically derived from physical erosion of extensively chemically weathered crystalline rocks in glacial environments (Ehrmann et al. 2003). Analyses of the clay mineralogy of Holocene shelf sediments regionally reveal that illite dominates assemblages in the Prydz Bay area (Hambrey, 1991; Forsberg et al. 2008; Borchers et al. 2010). One possible scenario to explain the change in sediment provenance, the overall increase sedimentation rates, and increased delivery of clay sized-material to ODP

Site 1165 is erosion of gneisses and granites of the locally abundant Rayner Province (Young and Black, 1991; Boger et al. 2000; Carson et al. 2000; Kelly et al. 2002). Subsequent deposition of this detrital material as fine-grained sediments on the continental shelf, and re-deposition of these shelf sediments downslope by an advancing EAIS grounding line to the continental shelf edge would result in an increase in turbidity related deposition. Silt laminations in Late Pliocene sediments (3.42 to ~3.2 Ma) at ODP Site 1165 (Passchier, 2011) hint at the increased proximity of the ice sheet edge to the site during this time (Figure 6.4).

An interpretation of ice sheet advance regionally after ~3.48 Ma is supported by seismic data from the Prydz Bay area (O'Brien et al. 2007; Volpi et al. 2009), which reveal an unconformity between Eocene and Late Pliocene shelf sediments (O'Brien et al. 2004; Volpi et al. 2009), interpreted to represent a glacial erosional surface associated with ice sheet advance. Additionally, initiation of excavation of the Prydz Channel (Figure 6.3) into shelf sediments took place at a similar time (O'Brien et al. 2004, 2007), associated with growth of the Lambert Glacier several hundreds of kilometres north of its current grounding line position. Hence, multiple lines of evidence suggest that during the Late Pliocene, the Lambert Glacier, and also possibly the EAIS margin along MRL, advanced northwards, resulting in the increased delivery of detrital material with provenance signatures characteristic of shelf sediments and bedrock in MRL to ODP Site 1165.

Growth of the EAIS during the Late Pliocene was related to cooling temperatures regionally and globally (Figure 6.13). Evidence for cooler sea surface temperatures relative to the Early Pliocene are inferred from silicoflagellate and diatom assemblages from ODP Site 1165 (<2.5 °C; Whitehead and Bohaty, 2003; Escutia et al. 2009) and from sediments recovered near the Kerguelen Plateau (Bohaty and Harwood, 2000). In addition, sediments in ODP Site 1165 record a ten-fold increase in the deposition of IRD at ~3.3 Ma (Warnke et al. 2004; Passchier et al. 2011) (Figs. 6.4 and 6.13). The increase in ice-rafting recorded regionally is also contemporaneous with major advance of the grounding line of the West Antarctic Ice Sheet in the western Ross Sea (Naish et al. 2009; McKay et al. 2012a). While an increase in iceberg production may have been in part a product of increased ice volume regionally, IRD provenance patterns at ODP Site 1165 reveal that between ~3.207 and ~2.5 Ma, an increase in icebergs sourced from the distal Wilkes Land margin took place (Chapter 5). Iceberg trajectory modelling suggests that this increase was largely due to declining sea surface temperatures (Chapter 5), whereby cooler temperatures permitted icebergs to travel longer distances before melting.

The dramatic increase in IRD deposition at ODP Site 1165 after ~3.3 Ma (Figure 6.13) may have had an impact on fine-grained sediment provenance patterns. Comparison of the provenance of ice-rafted detritus and fine-grained sediments deposited at ODP Site 1165 after 3.42 Ma, when Nd isotopic signatures become less radiogenic, may offer some insights into whether IRD supplied to the site contained a fine-grained component. Calculated correlation coefficients between the provenance of IRD and fine-grained sediments reveal that fine-grained sediments deposited before 3.48 Ma, which have signatures that overlap with a fine-grained Wilkes Land endmember, share no correlation with the amount of Wilkes Land IRD deposited. However, sediments deposited after 3.42 Ma display a notable positive correlation ($R^2=0.7$) (Figure 6.11), where fine-grained sediment signatures trend towards the Wilkes Land ϵ_{Nd} endmember (-11.1 to -14.8) when more Wilkes Land IRD is deposited at the site (Figure 6.11). Importantly, ϵ_{Nd} values for fine-grained sediments never overlap with the ϵ_{Nd} values of Wilkes Land endmember even though Wilkes Land material may still compose a significant component of bulk sediment. Additionally, the disparity between the timing of the increased delivery of local MRL material at ODP Site 1165, as evident in fine-grained sediment provenance (~3.42 Ma), and the timing of the increase in Wilkes Land IRD identified at the site (after 3.3 Ma; Chapter 5) suggests that fine-grained Wilkes Land IRD delivery may only have been important after 3.3 Ma.

6.8 The role of the Pliocene EAIS in global climate change

Results presented in this chapter, along with onshore (e.g. Whitehead and McKelvey, 2001; McKelvey et al. 2001; Whitehead et al. 2004) and marine records (Chapter 2) from East Antarctica, suggest that the East Antarctic ice sheet may have been retreated in marginal, low-lying regions during the Early Pliocene. Today, upwelling of the relatively warm deep water mass, the Circumpolar Deep Water (CDW), has been observed along the West Antarctic margin (Rignot and Jacobs, 2002; Jenkins et al. 2010; Pritchard et al. 2012) and as a modified water mass in Prydz Bay (Yabuki et al. 2006). The upwelling of CDW is ultimately linked to the southern-most position of the Southern Hemisphere midlatitude westerlies (Toggweiler and Samuels, 1993). Modelling of deep ocean circulation on glacial-interglacial timescales (Toggweiler et al. 2006), and during the Pliocene (Zhang et al. 2013) suggest that during times of atmospheric warmth, the position of Southern Hemisphere westerlies shift poleward, hence potentially causing increased upwelling of CDW-type water masses onto the Antarctic shelf (e.g. Hillenbrand and Ehrmann, 2005), which in turn could

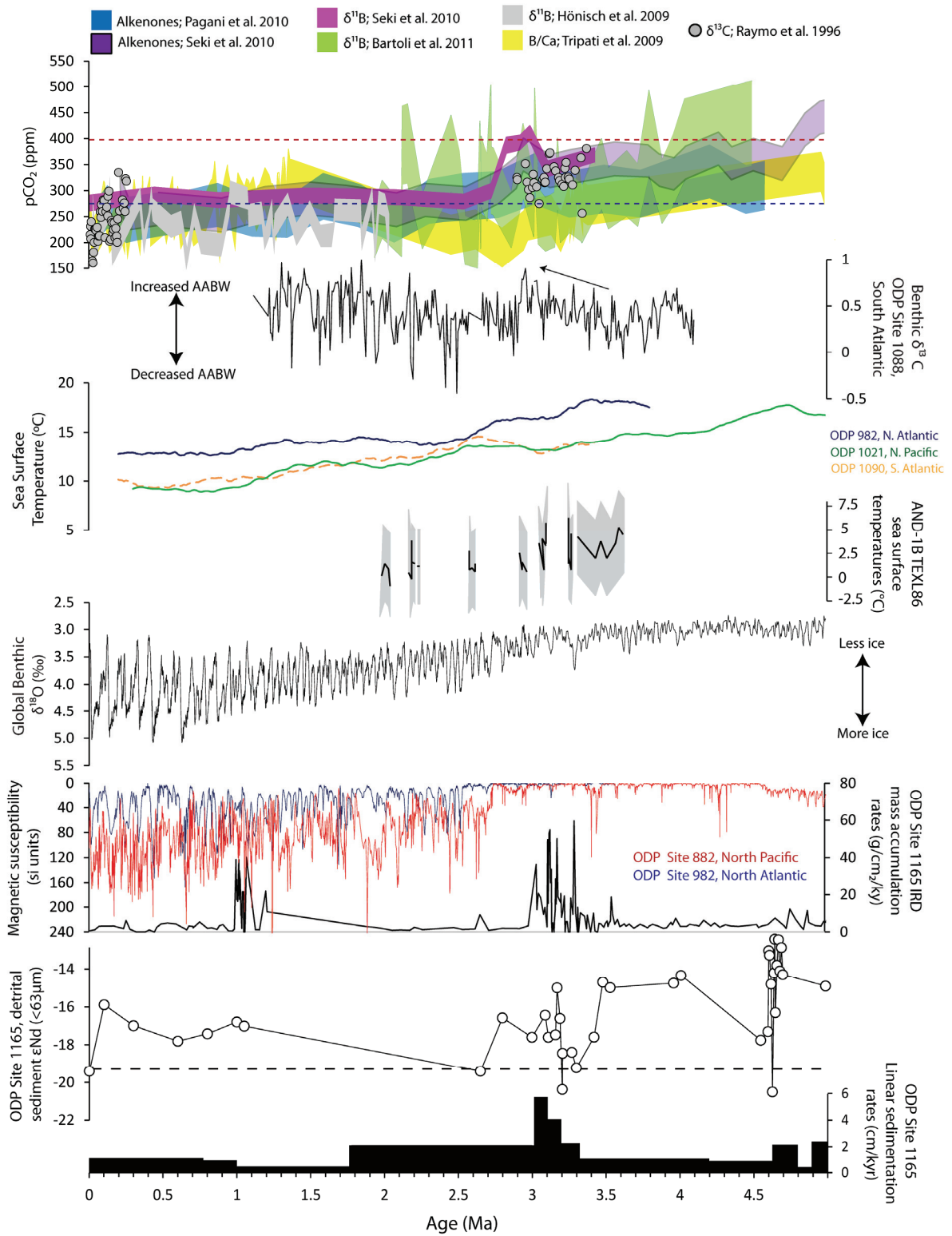


Figure 6.13 (Previous page). Synthesis of Antarctic and global paleoclimatic records over the last five million years. From bottom to top: i) linear sedimentation rates of ODP Site 1165 sediments (Table 6.2); ii) fine-grained detrital ϵ_{Nd} provenance record from ODP Site 1165 (this study); iii) IRD mass accumulation rate record of sediments $>125\mu m$ in size at ODP Site 1165 (from Passchier, 2011), illustrating the increase in ice-rafted deposition in the Late Pliocene in the Southern Hemisphere; iv) magnetic susceptibility records from the North Atlantic (blue, ODP Site 982) (from Lawrence et al. 2009) and from the North Pacific (red, ODP Site 882) (Haug et al. 2005), illustrating the increase in ice-rafted deposition in the Late Pliocene in the Northern Hemisphere high latitudes; v) global benthic stable oxygen isotope stack as a proxy for ice volume and temperature (Lisiecki and Raymo, 2005); vi) paleothermometry estimates of upper ocean temperatures in the Ross Sea, West Antarctica, from TEX^L_{86} data based on organic membrane lipids in marine sediments (McKay et al. 2012a) – grey shading represents calibration envelope; vii) paleothermometry estimates of sea surface temperatures (from $U^{K'}_{37}$ alkenones) from the North Atlantic (top blue line: ODP Site 982; Lawrence et al. 2009), the North Pacific (middle yellow line: ODP Site 1021; LaRiviere et al. 2012), and the South Atlantic (bottom green line: ODP Site 1090; Martinez-Garcia et al. 2010), sites selected to illustrate high latitude Early Pliocene warmth and declining sea surface temperatures during the Late Pliocene - note matching scale bars between these records and Ross Sea data paleothermometry data below; viii) Benthic carbon isotope record from ODP Site 1088, to illustrate changing inputs of AABW into the South Atlantic (Hodell and Venz-Curtis, 2006); iv) Global atmospheric CO_2 reconstructions based on alkenones (Pagani et al. 2010; Seki et al. 2010), boron isotopes (Hönisch et al. 2009; Seki et al. 2010; Bartoli et al. 2011), boron/calcium ratios (Tripathi et al. 2009), and carbon isotopes (Raymo et al. 1996) - red line: current atmospheric CO_2 concentration, blue line: preindustrial atmospheric CO_2 concentration.

drive marginal ice sheet retreat during the Early Pliocene. However, the presence of CDW upwelling onto the continental shelf in Prydz Bay today (Yabuki et al. 2006) suggests that only a minor shift in the position of westerlies would be required. In fact, fine-grained sediment provenance patterns at ODP Site 1165 show no evidence for delivery of western sources of detrital material by the ACC to the site. This would be expected to happen if westerlies were situated closer to the continental margin than today. This observation suggests that if increased upwelling of a CDW-type water mass was responsible for marginal ice sheet retreat, significant flow of the ACC must have remained north of ODP Site 1165, similar to today, where the majority of the flow is constrained by the bathymetry of the Kerguelen Plateau (Park et al. 2009).

As inferred from data presented in this study, the East Antarctic ice sheet expanded in the Prydz Bay area as early as ~ 3.42 Ma. The presence of a glacial unconformity at ~ 3.4 Ma AND-1B and a change from deposition of diatomite (indicative of open water conditions) to diamictite indicates that advance of the Ross Ice Shelf over the Ross Sea took place at the same time (Naish et al., 2009; McKay et al. 2012a). Major growth of the Ross Ice Shelf and a significant increase in IRD deposition at ~ 3.3 Ma (Passchier et al. 2011) correspond to the M2 glacial (Figure 6.13), one of the largest positive $\delta^{18}\text{O}$ excursions during the Pliocene (Lisiecki and Raymo, 2005).

The timing of inferred advance of the East Antarctic ice sheet in Prydz Bay at ~ 3.42 Ma, and of growth of the West Antarctic ice sheet in the Ross Sea after this time (Naish et al. 2009; Pollard and DeConto, 2009; McKay et al. 2012a), may offer some insights into the role of high latitude ice expansion on global climate change. For example, McKay et al. (2012a) propose that growth of Antarctica's ice sheets and regional cooling in the Ross Sea in the Late Pliocene shifted Southern Hemisphere westerlies to a more northerly position relative to the Early Pliocene, helping to reduce production of North Atlantic Deep Water and increase Northern Hemispheric cooling, by reducing the flow of surface waters into the Atlantic Ocean, similar to Pleistocene glacial intervals (Bard and Rickaby, 2009). Increased export of Southern Ocean waters, is evidenced by decreasing benthic $\delta^{13}\text{C}$ values in the western equatorial Atlantic at Marine Isotope Stages MG2 and M4 (~ 3.4 Ma) (Billups et al. 1997). It seems possible that ice sheet advance in Prydz Bay at ~ 3.42 Ma may have been contemporaneous with increased production of Antarctic bottom water (Figure 6.13; Hodell and Venz-Curtis, 2006), possibly as a result of increased sea ice production in the Southern Ocean. Increased sea ice in Prydz Bay and the Ross Sea during the Late Pliocene has been identified from diatom assemblages in marine sediments (Whitehead et al. 2005; McKay et al. 2012a). Foraminifera assemblages in South Atlantic sediments deposited after this time are furthermore characterised by increases in the abundance of *Nuttalides umbonifera*, a benthic species that is today associated with AABW (Hodell et al. 1985). In addition, analysis of bottom current related sediment erosional surfaces in the western Atlantic Sector of the Southern Ocean reveal evidence for major intensification of AABW production during the Late Pliocene (Maldonado et al. 2003). This evidence together hints that growth of the EAIS and increased bottom water production at this time may have contributed to driving further global cooling, consequently leading to major expansion of Northern Hemisphere ice sheets (Figure 6.13; Haug et al. 2005; Lawrence et al. 2009) in the Late Pliocene and Early Pleistocene.

6.9 Conclusion

Analysis of the provenance signature of fine-grained ($<63\mu\text{m}$) detrital sediments deposited offshore of Prydz Bay, East Antarctica, during the Pliocene and Pleistocene, reveals evidence for significant variability in sediment delivery on multiple timescales. Comparison of Nd isotopic compositions with potential regional bedrock lithologies reveals that sediments at ODP Site 1165 were derived from two predominant areas in the Prydz Bay region: the local Mawson coast and the flanks of the Lambert Graben, although Wilkes Land may also have supplied fine-grained detrital material to the site. While a Lambert Graben supply seems to dominate sedimentary supply before ~ 3.48 Ma, the Mawson endmember is more prevalent after ~ 3.42 Ma. Both endmembers are, however, found during a high resolution interval in the Early Pliocene, where a clear linkage can be established that Mac.Robertson Land sediments are delivered to ODP Site 1165 during glacials, and sediments from the Lambert Graben during interglacials.

The overall provenance pattern of ODP Site U1361 sediments can be interpreted to reflect retreat of the Amery Ice Shelf-Lambert Glacier several hundreds of kilometres south of its current position during the Early Pliocene, possibly in response to upwelling of warm deep ocean water masses in response to southward shifted westerlies. In contrast, a change in provenance signatures at ~ 3.42 Ma reveal an increase in supply of nearby continental shelf sediments, likely deposited by an advancing ice margin and/or dense shelf bottom waters. It seems that regional growth of the EAIS in the Prydz Bay area was contemporaneous with ice growth in West Antarctica and declining sea surface temperatures around Antarctica, and linked to increased production and export of Antarctic Bottom Water, suggesting it playing an important role in driving late Pleistocene global cooling and onset of ice growth in the Northern Hemisphere.

CHAPTER 7

Concluding Remarks: Thesis Findings and Outlook

6.1 Major Findings and Future Research Directions

The principal aim of this thesis was to improve understanding of the behaviour of the East Antarctic ice sheet during the Pliocene Epoch. Below I summarise how this aim has been achieved, by discussing the major findings of my research and their wider implications, along with potential future research directions, within the framework of the five main objectives presented in Chapter 1.

Objective 1: Improve constraints on the behaviour of the East Antarctic ice sheet in the Wilkes Subglacial Basin during the Early Pliocene

As presented in Chapter 2, by studying the neodymium and strontium isotopic provenance of fine-grained sediments in IODP Site U1361, Wilkes Land, I have identified evidence for significant ice sheet retreat events extending several hundreds of kilometres into the Wilkes Subglacial Basin during interglacials, and during prolonged warm intervals in the Early Pliocene. These findings are significant, as they are the first from a proximal marine sediment record to show that the East Antarctic ice sheet was sensitive to climatic warmth in this particular low-lying region, and provide a new and important target for ice sheet modelling.

An unanswered but important question that has arisen from this study is: how quickly did past ice sheet retreat events take place? A future strategy to address this uncertainty is to resample IODP Site U1361 sediments at several of the transitions from cooler to warmer climatic intervals at high resolution, in order to capture the rate of change. Additionally, a prerequisite for assigning a timeframe for retreat events is development of an orbitally tuned age model for Early Pliocene sediments. Finally, erosion and transport mechanisms of Ferrar Large Igneous Province bedrock from within the Wilkes Subglacial Basin remain elusive at this point. It may be desirable to combine erosion rates of Ferrar Large Igneous Province bedrock from ice sheet models (e.g. Jamieson et al. 2010) and maps of sediment thickness based on seismic data (e.g. in preparation by colleagues in Granada) to derive a better understanding of Cenozoic erosion rates.

Objective 2: Investigate the limitations associated with glaciomarine sediment provenance studies by comparing different provenance tools

In Chapter 3, I presented a unique perspective on the benefits and problems associated with utilising different glaciomarine sediment provenance tools when studying sediments deposited offshore of the glaciated Antarctic continent. By comparing provenance information derived from argon ages of ice-rafted hornblende grains, visual petrographic characterisation of ice-rafted grains, and neodymium and strontium isotopes and clay mineralogy on fine-grained sediments from IODP Site U1361, I identified that mineralogical bias of source rocks can cause a significant disparity between fine-grained provenance tools and ice-rafted hornblende argon ages. Additionally, my investigation confirmed that radiogenic isotopes can provide improved constraints on the provenance of clay minerals. These findings show the importance of a multi-proxy approach when studying the provenance of detrital sediments derived from continental bedrock sources obscured by ice, and highlight how different tools can provide complimentary insights into source rock characteristics, glacial erosional and depositional processes.

In the particular case of Pliocene sediments derived from IODP Site 1361, preliminary investigations by colleagues into the potassium-argon concentrations of fine-grained components suggest they would make a valuable tool to test the Ferrar Large Igneous Province origin of the sediments. Alternatively, similar analyses could be carried out on ice-rafted clasts of basalt deposited offshore that may have been sourced from Ferrar Large Igneous Province bedrock from within the Wilkes Subglacial Basin.

Objective 3: Search for evidence for dynamic ice sheet behaviour during the warmth of super-interglacial Marine Isotope Stage 31

Chapter 4 presented new information on the provenance patterns of sediments deposited offshore of the Wilkes Subglacial Basin during the Pleistocene super-interglacial Marine Isotope Stage 31 (~1 million years ago) and nearby interglacial intervals, periods that are characterised by similar climatic conditions as those of times during the Pliocene. Analyses of argon ages of ice-rafted hornblende grains in IODP Site U1359 reveal evidence for an increase in West Antarctic IRD during interglacials, potentially hinting at dynamic behaviour of the West Antarctic ice sheet during these times. Results of analyses of neodymium and strontium isotopes of fine grained sediments suggest that the East Antarctic ice sheet within the Wilkes Subglacial Basin was stable during interglacials. These findings are significant, as substantiation of dynamic West Antarctic ice sheet behaviour during MIS 31 is required, and very little constraints currently exist on the behaviour of the East Antarctic

ice sheet during this time. However, some uncertainties remain about the exact location of MIS 31 within IODP Site U1359, and further analyses of the provenance of sediments in interglacial sediments adjacent to those already analysed will be the focus of future work. Additionally, and in order to place results within an orbital framework, selected samples from neighbouring glacial intervals will also be analysed for their neodymium and strontium isotopic composition.

Objective 4: Improve constraints on the Pliocene behaviour of the East Antarctic ice sheet in the Aurora Subglacial Basin and assess the effect of sea surface temperature on distally sourced IRD records

In Chapter 5, I presented a relatively high resolution study into the argon ages of ice-rafted hornblende grains from Pliocene sediments at ODP Site 1165, located in Prydz Bay. Provenance results reveal a significant increase in the amount of distally sourced IRD supplied from the Wilkes Land margin, over 1500 km to the east, around 3.3 million years ago, a pattern that coincides with major growth of the East Antarctic ice sheet and regionally cooling climatic conditions. By integrating my results with sensitivity tests of iceberg melting in an iceberg trajectory model, I show that this increase in distal IRD can be largely explained by cooling regional sea surface temperatures. This is a very important finding, as it suggests that iceberg melting rates play a first order control on far-travelled IRD in the Southern Ocean. However, orbitally-modulated variability of IRD provenance patterns, superimposed on the temperature-controlled overall pattern outlined above, suggests that iceberg flux plays an additional role during interglacial destabilisation events of the East Antarctic ice sheet within the Aurora Subglacial Basin. These results are the first to indicate orbitally dynamic behaviour of the East Antarctic ice sheet within the Aurora Subglacial Basin during the Pliocene. To further substantiate orbital-scale changes in IRD delivery, orbital tuning of the age model of ODP Site 1165 is needed along with increased sampling resolution, and this will be the target of future work.

Objective 5: Constrain the behaviour of the Pliocene EAIS in the Prydz Bay region and evaluate its role in global Pliocene climate change

Results in Chapter 6 were based on the Sr and Nd isotopic compositions of fine-grained sediments at ODP Site 1165, located offshore of the Lambert Glacier-Amery Ice

Shelf. These records span the whole Pliocene, and suggest that the Lambert Glacier was likely retreated several hundreds of kilometres inland of its current position during the Early Pliocene, in good agreement with existing records in the area and further afield (Chapters 2 and 5). Conversely, Late Pliocene sediment provenance indicates an increase in the supply of material derived from the proximal continental shelf, hinting at the increased proximity of the ice sheet margin to the study site, and major ice sheet growth taking place around 3.4 Ma, during a time of declining global temperatures.

Constraints presented in this chapter suggest the growth of the East Antarctic ice sheet in the Prydz Bay region was contemporaneous with advance of the West Antarctic ice sheet. Comparison to global records hints to an important role of increased Antarctic bottom water supply to the Atlantic, potentially contributing to driving global cooling in the Late Pliocene and Early Pleistocene.

6.3 Concluding Remarks

The results presented in this thesis highlight new and significant insights into the behaviour of the East Antarctic ice sheet during climatic warmth of the geological past, and suggest that low-lying areas of the ice sheet may be particularly sensitive to destabilisation. These findings have profound implications for the response of the East Antarctic ice sheet to future warming, as they show that in a climate scenario with similar $p\text{CO}_2$ concentrations and global temperatures a few degrees warmer than today, low-lying areas of the East Antarctic ice sheet behaved dynamically and almost certainly contributed to global eustatic sea level rise.

In addition, my thesis has provided further insights into the use of provenance tools to constrain past ice stability, and particularly into the role of sea surface temperatures on IRD provenance patterns. My data show that IRD records derived from locations distal to places of inferred ice instability can be significantly influenced by ocean temperatures and hence iceberg melting rates, with implications for similar records in both the Southern Ocean and the Northern Hemisphere high latitudes.

To conclude, the research presented in this thesis demonstrates the strengths associated with utilising radiogenic isotopes to study past marine sediment provenance patterns around circum-Antarctica. These tools have here provided unprecedented insights into the subglacial geology of the East Antarctic continent, and have allowed for significant

advancements in the understanding of the behaviour of Earth's largest continental ice sheet during past climatic change.

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APPENDIX 1

Published Manuscript

Dynamic behaviour of the East Antarctic ice sheet during Pliocene warmth

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Warm intervals within the Pliocene epoch (5.33–2.58 million years ago) were characterized by global temperatures comparable to those predicted for the end of this century¹ and atmospheric CO₂ concentrations similar to today^{2–4}. Estimates for global sea level highstands during these times⁵ imply possible retreat of the East Antarctic ice sheet, but ice-proximal evidence from the Antarctic margin is scarce. Here we present new data from Pliocene marine sediments recovered offshore of Adélie Land, East Antarctica, that reveal dynamic behaviour of the East Antarctic ice sheet in the vicinity of the low-lying Wilkes Subglacial Basin during times of past climatic warmth. Sedimentary sequences deposited between 5.3 and 3.3 million years ago indicate increases in Southern Ocean surface water productivity, associated with elevated circum-Antarctic temperatures. The geochemical provenance of detrital material deposited during these warm intervals suggests active erosion of continental bedrock from within the Wilkes Subglacial Basin, an area today buried beneath the East Antarctic ice sheet. We interpret this erosion to be associated with retreat of the ice sheet margin several hundreds of kilometres inland and conclude that the East Antarctic ice sheet was sensitive to climatic warmth during the Pliocene.

Recent satellite observations reveal that the Greenland and West Antarctic ice sheets are losing mass in response to climatic warming⁶. Basal melting of ice shelves by warmer ocean temperatures is proposed as one of the key mechanisms facilitating mass loss of the marine-based West Antarctic ice sheet⁷. Although thinning of ice shelves and acceleration of glaciers has been described

for some areas of the East Antarctic margin⁷, the mass balance of the predominantly land-based East Antarctic ice sheet is less clear⁸. Its vulnerability to warmer-than-present temperatures may be particularly significant in low-lying regions, such as the Wilkes Subglacial Basin (Fig. 1).

This hypothesis can be tested by studying intervals from geological records deposited under similar environmental conditions to those predicted for the near future. Warm intervals within the Pliocene epoch are such analogues, with mean annual global temperatures between 2 and 3 °C higher than today¹ and atmospheric CO₂ concentrations between 350 and 450 ppm, 25–60% higher than pre-industrial values^{2–4}. Estimates for eustatic sea level highstands during these times, reconstructed from benthic foraminiferal oxygen isotopes⁵ and palaeoshoreline reconstructions⁹, are variable but indicate 22 ± 10 m of sea level rise, although estimates derived from palaeoshoreline reconstructions may need corrections for glacio-isostatic adjustments¹⁰. Complete melting of Greenland and West Antarctica's ice sheets could account for around 12 m (ref. 11) of eustatic sea level rise, indicating that most estimates for Pliocene sea level require a contribution from the East Antarctic ice sheet. Although ice sheet modelling suggests that low-lying areas of the East Antarctic continent may be candidates for Pliocene ice sheet loss^{12,13}, direct evidence from ice-proximal records on locations of ice margin retreat are limited^{14–16}.

To improve our understanding of the response of the East Antarctica ice sheet to past warm climates, Integrated Ocean Drilling Program Site U1361 (64° 24' 5" S 143° 53' 1" E; 3,465 m water depth) was drilled during Expedition 318 into a submarine

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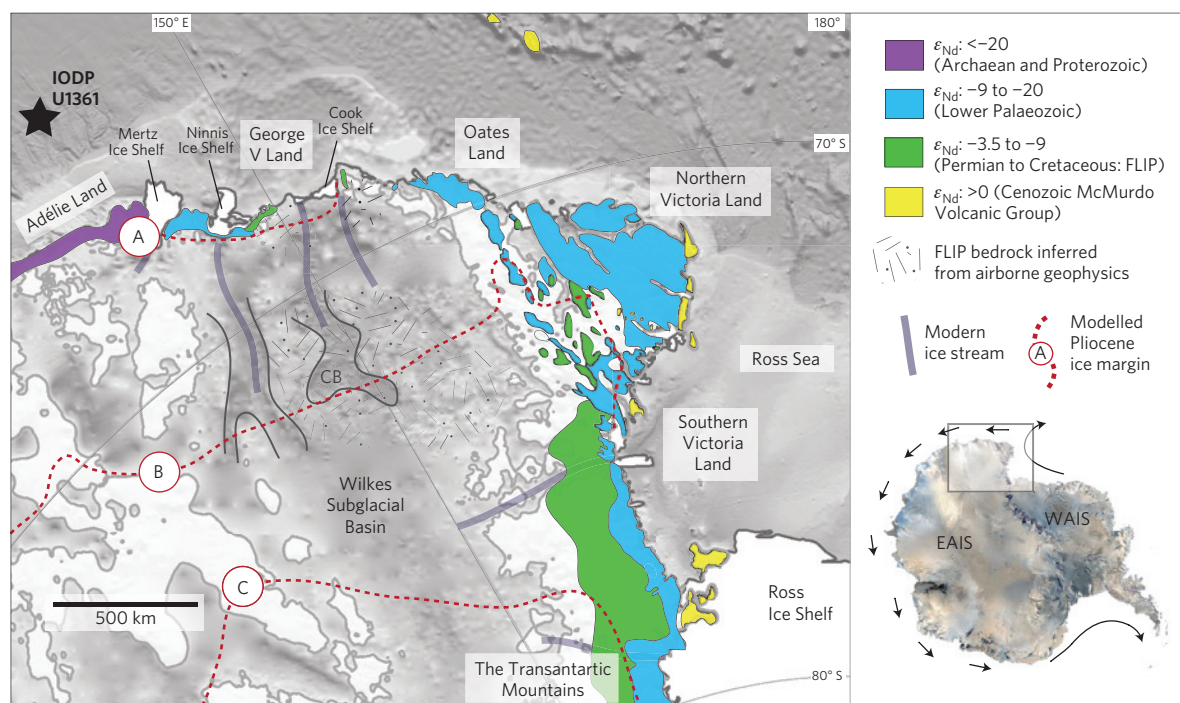


Figure 1 | Regional map of study area, including geology of outcrops and inferred subglacial geology. Coloured shading represents the simplified geographical extent of four geological terranes differentiated according to their neodymium isotopic characteristics (expressed as ϵ_{Nd} ; see Supplementary Section S1 for detailed geological context). Areas above sea level are shown in pale grey with grey outlines, and ice shelves are shown in white²⁴. Outline of the Central Basin (CB) denotes its location within the Wilkes Subglacial Basin²³. Red lines denote the spatial extent of modelled maximum East Antarctic ice sheet retreat for the Pliocene: Line A, 3 m (ref. 28), line B, 10 m (ref. 12), line C, 16 m (ref. 13). The inset map illustrates the westward-flowing Antarctic coastal current (arrows). EAIS, East Antarctic ice sheet; WAIS, West Antarctic ice sheet.

levee bank, 310 km offshore of the Adélie Land margin, East Antarctica (Fig. 1). Approximately 75 m of continuous Pliocene marine sediments, within the resolution of available biostratigraphic and magnetostratigraphic data¹⁷, were recovered. Available physical property¹⁸, sedimentology¹⁸, and palaeomagnetic and micropalaeontology data¹⁷ are here combined with new opal (%) data, bulk geochemistry data, and radiogenic isotope data from analyses of detrital sediments.

The Pliocene study section at IODP Site U1361 spans an interval between 5.3 and 3.3 Myr ago and contains a sedimentary sequence alternating between eight diatom-rich silty clay layers, and eight diatom-poor clay layers with silt laminations (Fig. 2). Diatom-rich sediments have higher diatom valve and bulk-sediment biogenic opal concentrations, and distinctively lower signals in natural gamma radiation (Fig. 2), indicating lower clay content. The diatom-rich units are also characterized by higher Ba/Al ratios (Fig. 2), pointing to multiple extended periods of increased biological productivity related to less sea ice, and warmer spring and summer sea surface temperatures. This inference is supported by diatom and silicoflagellate assemblage and TEX₈₆ palaeothermometry data from marine and land-based records from the Antarctic Peninsula margin¹⁹, the Kerguelen Plateau²⁰, Prydz Bay^{15,16,19,21} and the Ross Sea²². These reconstructions identify elevated mean annual Pliocene sea surface temperatures^{15,19–21}, spring and summer sea surface temperatures between 2 and 6 °C above modern levels^{19,22}, and prolonged warm intervals spanning up to 200,000 years in duration, superimposed on a baseline of warmer-than-present temperatures.

To constrain the effects of prolonged warming on the dynamics of the East Antarctic ice sheet, we produced a Pliocene record of continental erosion patterns based on detrital marine sediment provenance (<63 μm grain-size fraction) from IODP Site U1361. We used the radiogenic isotope compositions of neodymium

(¹⁴³Nd/¹⁴⁴Nd, expressed as ϵ_{Nd} , which describes the deviation of measured ¹⁴³Nd/¹⁴⁴Nd ratios from the Chondritic Uniform Reservoir in parts per 10,000) and strontium (⁸⁷Sr/⁸⁶Sr), both of which vary in continental rocks on the basis of the age and lithology of geological terranes. In IODP Site U1361 sediments, both ratios show significant variations throughout the studied Pliocene interval, with ϵ_{Nd} values ranging from −5.9 to −14.7 and Sr isotopic compositions from 0.712 to 0.738 (Fig. 2). Notably, both ratios co-vary in a distinct pattern that parallels lithological units, physical properties and bulk sediment geochemistry (Fig. 2), with a more radiogenic Nd isotopic composition and a less radiogenic Sr isotopic composition characteristic of sediments deposited during periods of Pliocene warmth (ϵ_{Nd} : −5.9 to −9.5; ⁸⁷Sr/⁸⁶Sr: 0.712–0.719; Figs 2–3).

East Antarctic continental geological terranes in the vicinity of IODP Site U1361 encompass a diverse range of lithologies and ages: Archaean to Proterozoic basement along the adjacent Adélie Land coast; Lower Palaeozoic bedrock in the vicinity of the nearby Ninnis and Mertz glaciers, along the Oates Land coast, in Northern and Southern Victoria Land, and in the Transantarctic Mountains; Jurassic to Cretaceous volcanic rocks (the Ferrar Large Igneous Province (FLIP) and associated sedimentary rocks of the Beacon Supergroup) along the George V Land coast, in Northern and Southern Victoria Land, and in the Transantarctic Mountains; and Cenozoic volcanics of the McMurdo Volcanic Group. Each of these terranes can be characterized in Nd–Sr isotope space (Fig. 3). The provenance signatures of the two Pliocene sedimentary types at IODP Site U1361 (that is, diatom-rich and diatom-poor) can be best explained by a mixture of FLIP bedrock (ϵ_{Nd} : −3.5 to −6.9; ⁸⁷Sr/⁸⁶Sr: 0.709–0.719), and lower Palaeozoic bedrock (ϵ_{Nd} : −11.2 to −19.8; ⁸⁷Sr/⁸⁶Sr: 0.714–0.753; Fig. 1) (Fig. 3; see Supplementary Section S1 for further details on local geology and potential endmembers).

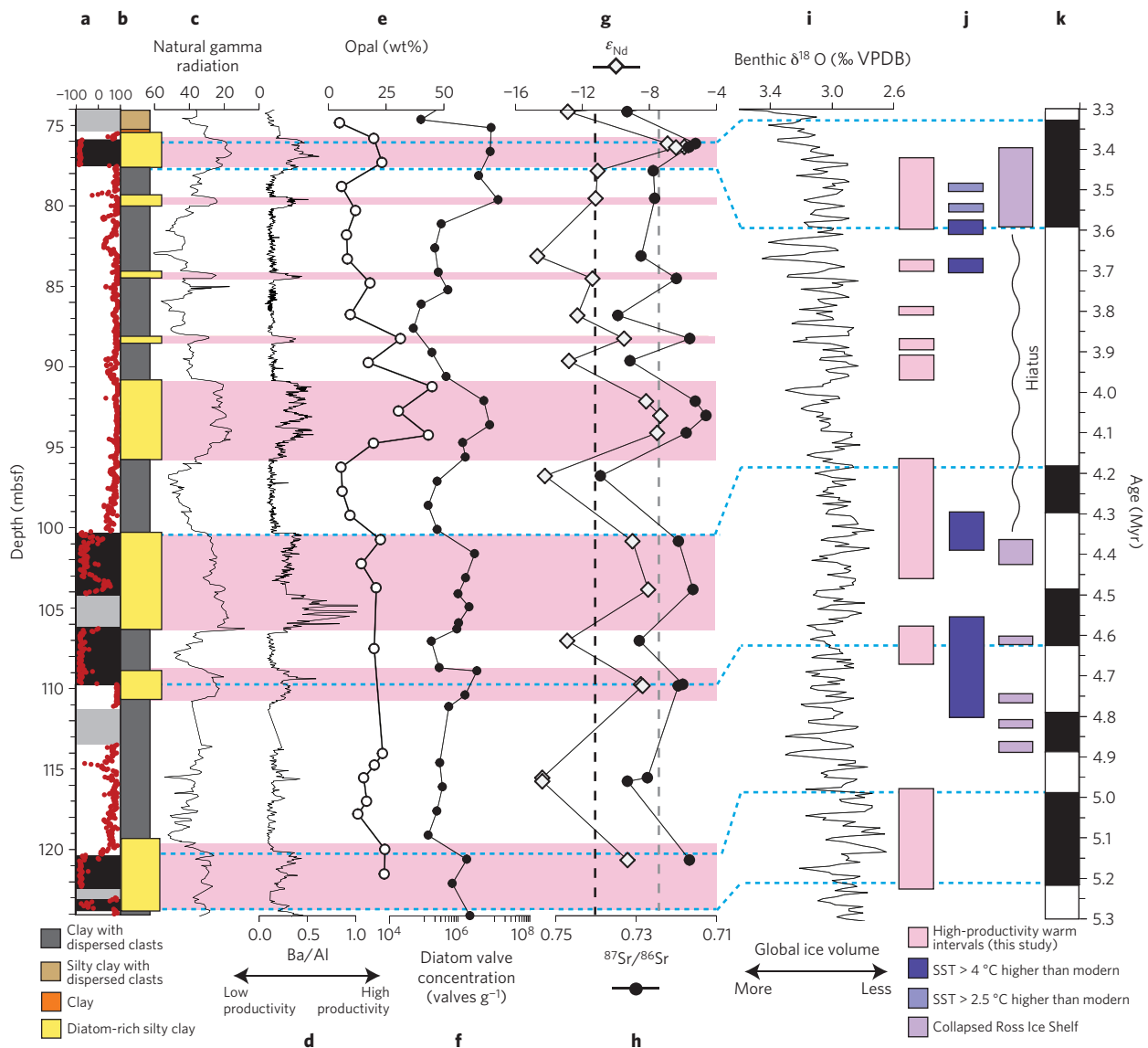


Figure 2 | Pliocene records from IODP Site U1361 in comparison to other circum-Antarctic and global records. **a**, Palaeomagnetic chron boundaries based on inclination measurements¹⁷ (red data points); grey shading indicates intervals with no data. **b**, Lithostratigraphy¹⁸. **c–h**, Expedition 318 shipboard record of natural gamma radiation, and new records of Ba/Al, opal wt%, diatom valve concentrations, and Nd and Sr isotopic compositions; pink shading, high-productivity intervals based on natural gamma radiation; vertical black stippled lines, Holocene Nd and Sr isotopic compositions (core-tops). **i**, Global benthic oxygen isotope stack (LR04; ref. 29). **j**, Circum-Antarctic indicators for warm temperatures; pink, Pliocene high-productivity intervals at IODP Site U1361; dark blue, diatom and silicoflagellate assemblages from the Kerguelen Plateau²⁰ and Prydz Bay¹⁹; light blue, silicoflagellate assemblages from Prydz Bay²¹; lilac, diatomite deposits from ANDRILL cores in the Ross Sea²⁵. **k**, Palaeomagnetic timescale³⁰.

Diatom-poor sediments have a provenance signature that matches lower Palaeozoic bedrock, most likely sourced from granitic bedrock in the hinterland of the nearby Ninnis Glacier (Fig. 1). In contrast, the provenance fingerprint of sediments deposited during warm Pliocene intervals (diatom-rich units) reveals that they are predominantly composed of FLIP material. This FLIP provenance fingerprint is not found in Holocene deposits at IODP Site U1361 or in sediments in its vicinity, and seems to be unique to diatom-rich Pliocene marine sediments over the past 5.3 Myr (Fig. 3 and Supplementary Section S1).

We suggest that the most likely source of eroded FLIP material is the Wilkes Subglacial Basin, which requires Pliocene retreat of the East Antarctic ice sheet. Aeromagnetic data collected over the Wilkes Subglacial Basin between ~70°S and 74°S (ref. 23) reveal anomalies that resemble exposed FLIP bedrock in Southern Victoria Land, indicating the presence of abundant

intrusive sills, as well as two large approximately 2-kilometre-deep graben-like sub-basins²³ (Fig. 1). Recent subglacial topographic data compilations²⁴ furthermore demonstrate that these sub-basins are directly connected to the Southern Ocean below sea level, and aerogeophysical data suggest that the Central Basin contains unconsolidated sediments inferred to be FLIP in origin²³ (Fig. 1).

We propose that enhanced erosion of FLIP material in the Central Basin was achieved by multiple retreats of the ice margin. Ice sheet modelling and modern observations suggest that sub-surface melting at the ice edge in response to warm ocean temperatures drives retreat in areas where grounding lines lie below sea level⁷, such as the mouth of the Wilkes Subglacial Basin²⁴ (Supplementary Section S1). Warm Pliocene ocean waters would have facilitated retreat into the Central Basin, contemporaneous with ice shelf collapse and ice margin retreat in other circum-Antarctic locations, such as in the Prydz Bay area^{15,16} and the Ross Sea²⁵.

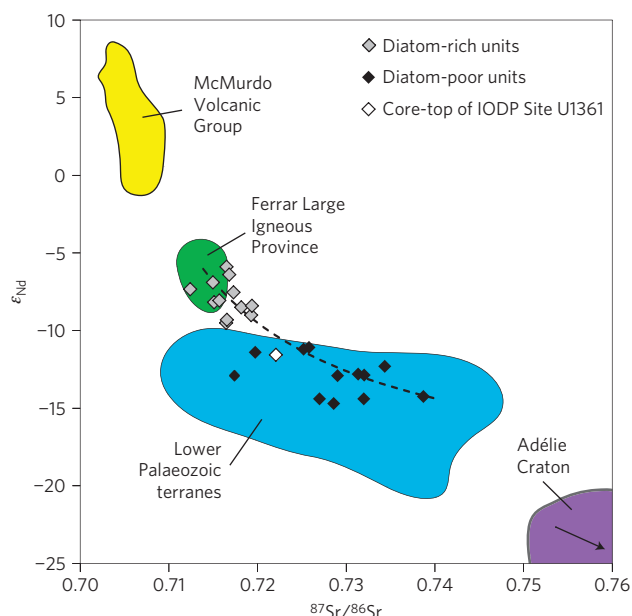


Figure 3 | Neodymium and strontium isotopic composition of Pliocene detrital sediments from IODP Site U1361 and East Antarctic geological terranes proximal to the study area. Fields for the isotopic composition of various terranes are based on literature values (see Supplementary Section S1). Data corresponding to the Adélie Land Craton primarily plot outside the neodymium and strontium isotopic space shown (ϵ_{Nd} : -20 to -28 ; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.750 – 0.780).

Zones of maximum glacial erosion are typically associated with the margins of an ice sheet^{26,27}, suggesting that the retreated Pliocene ice margin was situated on FLIP bedrock within the Central Basin. Existing ice sheet models imply that between ~ 3 m (ref. 28; line A, Fig. 1) and ~ 16 m (ref. 13; line C, Fig. 1) of Pliocene glacio-eustatic sea level rise could be derived from retreat of the East Antarctic ice sheet. The smallest estimate (3 m) is unlikely to accurately represent the response of the ice margin to the warmest range of Pliocene climate conditions²⁸, and larger estimates (10–16 m; refs 12,13) are probably influenced by initial ice sheet configurations used within climate modelling frameworks. Our new data, as well as maximum modelled erosion for the northern part of the Wilkes Subglacial Basin²⁷ are in agreement with retreat of the ice margin several hundred kilometres inland. Such retreat could have contributed between 3 and 10 m of global sea level rise from the East Antarctic ice sheet, providing a new and crucial target for future ice sheet modelling. Irrespective of the extent of ice retreat, our data document a dynamic response of the East Antarctic ice sheet to varying Pliocene climatic conditions, revealing that low-lying areas of Antarctica's ice sheets are vulnerable to change under warmer-than-modern conditions, with important implications for the future behaviour and sensitivity of the East Antarctic ice sheet.

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Author contributions

C.P.C., T.v.d.F., T.W. and S.R.H. designed the research; C.P.C. carried out the neodymium and strontium isotope analyses; M.I. and M.K. performed the diatom counts, interpreted in discussion with S.M.B. and C.R.R.; F.J.J.-E., J.J.G. and C.E. were responsible for XRF bulk geochemistry analyses; R.M.M., M.O.P. and S.P. carried out sedimentological analyses; A.L.G., F.J.J.-E. and C.E. collected clay mineralogy data;

B-K.K. analysed opal contents; L.T. and S.S. were responsible for magnetic analyses. All authors contributed to the interpretation of the data. C.P.C. and T.v.d.F. wrote the paper with input from all authors.

Additional information

Supplementary information is available in the [online version of the paper](#). Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to C.P.C.

Competing financial interests

The authors declare no competing financial interests.

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APPENDIX 2

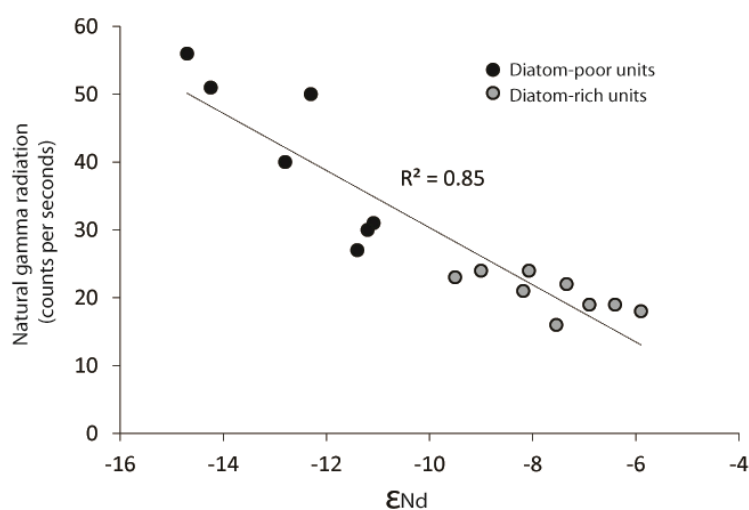
Supplementary Information for Chapter 2 and Published Manuscript

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1. Fine-grained Sediment Provenance

Pliocene sediments from IODP (Integrated Ocean Drilling Program) Site U1361 are composed of alternating lithostratigraphic units, defined according to their diatom content, which is delineated from smear slides (Escutia et al. 2011). For consistency, this classification is similar to that used for ANDRILL cores (Krissek et al. 2007), with sediments composed of 25 to 50% diatoms classified as ‘diatom-rich’. In contrast to ANDRILL classification, however, here sediments with less than 25% diatoms are classified as ‘diatom-poor’. Measurements of neodymium (Nd) and strontium (Sr) isotopic compositions in $<63\mu\text{m}$ fractions of both diatom-rich and diatom-poor Pliocene detrital sediments from IODP Site U1361 were carried out in order to constrain their provenance signatures and hence continental source regions. Results reveal two distinct isotopic signatures for diatom-rich and diatom-poor sediments respectively, which co-vary with changes in physical properties and bulk geochemistry (Figure A1, Figure 2.2 in Chapter 2). The first signature is characterised by ϵ_{Nd} values of -5.9 to -9.5 and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.712 to 0.719, and the second by ϵ_{Nd} values of -11.0 to -14.7 and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.719 to 0.738 (Table A1).



Appendix Figure 1. Neodymium isotopic composition of fine-grained detrital material versus natural gamma radiation in the same samples. Black and grey circles denote the two main lithological units identified in Pliocene sediments at IODP Site U1361 respectively. Higher natural gamma radiation values are associated with higher clay content, as minerals that contain K, Th, and U, such as clay minerals, are the principal source of naturally occurring gamma radiation. Diatom-rich units contain less clay minerals, yielding lower values in gamma radiation.

1.1 Onland geology

In order to constrain possible onland sources for detrital marine sediments offshore of East Antarctica, published Nd and Sr isotope compositions of different bedrock types in the vicinity of IODP Site U1361 have been compiled (Figs. A2 and A3). This compilation is summarised in Appendix Table 2. From this, I determine that four isotopically distinct geological terranes comprise regional bedrock: (1) Archean and Proterozoic basement exposures in Adélie Land, most proximal to IODP Site U1361; (2) Lower Paleozoic metasediments and granitoids outcropping in the vicinity of the proximal Ninnis Glacier, at the Oates Land coast, in Southern and Northern Victoria Land, and in the Transantarctic Mountains; (3) Upper Paleozoic and Mesozoic sediments and volcanic rocks along the George V Land coast and the Transantarctic Mountains; and (4) Cenozoic volcanics from the McMurdo Volcanic Group. The following is a brief outline of the locations of each of the terranes relevant to this study, their geological nature, and Nd and Sr isotopic compositions.

The coastal sector of Adélie Land west of the Mertz Glacier contains exposures of high-grade metamorphic Archean and Proterozoic metasedimentary and metaigneous rocks (Peucat et al. 1999; Menot et al. 2005; Goodge and Fanning, 2010). These rocks form part of the Adélie Craton, which constitutes part of the oldest Archean basement in Antarctica and is the conjugate margin of the Gawler Craton in Australia (Boger, 2011). Bedrock in Adélie Land is characterised by ϵ_{Nd} values between -20 and -29, and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.750 to 0.780 (Borg and DePaolo, 1994; Goodge and Fanning, 2010), and can therefore be excluded as an end-member for Pliocene IODP Site U1361 sediments (not included in Appendix Table 2).

Bedrock exposed between the Mertz and Ninnis Glaciers in George V Land, in Oates Land (153°E to 160°E) and the north-west region of Northern Victoria Land are composed of Lower Paleozoic-aged metasediments and intrusive igneous rocks. Situated between the Mertz Glacier and the Ninnis Glacier are Lower Paleozoic granitic outcrops (Adams, 2004; Di Vincenzo et al. 2007; Goodge, 2007; Goodge and Fanning, 2010) – no Nd and Sr isotope data are available for these exposures, but zircon U-Pb ages and hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ ages of these outcrops date at ~500 Ma (Goodge and Fanning, 2010; Di Vincenzo et al. 2007). Similarly, the Cambrian to Ordovician Wilson Terrane, a polymetamorphic sequence composed of metasediments of granulitic and amphibolitic facies (Turner et al. 1993; Schussler et al. 1999; Henjes-Kunst and Schussler, 2003) and its associated Granite Harbour Intrusives (Borg et al. 1987; Goodge et al. 2002; Rocchi et al. 2004) exposed in Oates Land

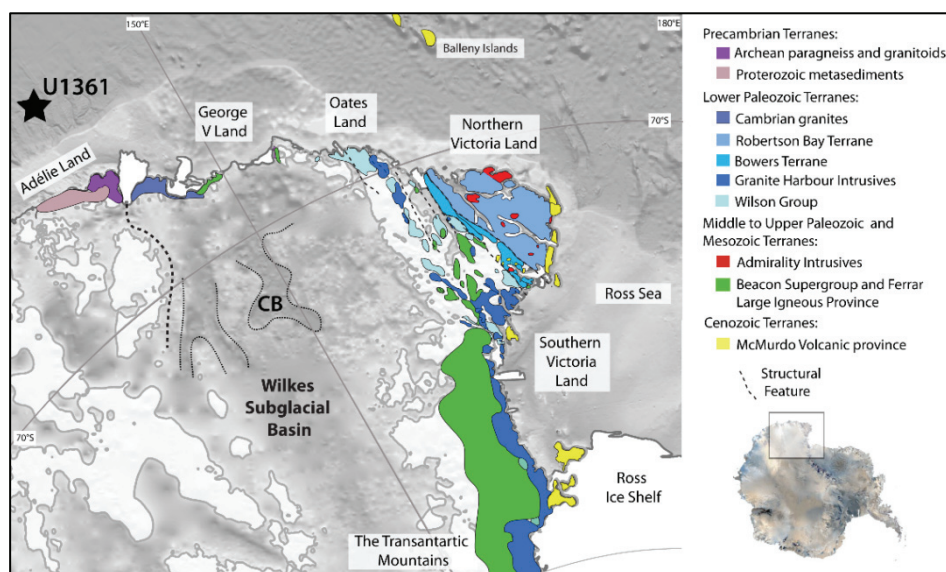
and Northern Victoria Land, have zircon U-Pb ages between 400 and 500 Ma (Schussler et al. 1999). Exposures of these terranes in the north-west region of Northern Victoria and along Oates Land have average ϵ_{Nd} values of -14.4 and average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ~ 0.738 (refs. Borg and DePaolo, 1994; Borg et al. 1987; Dallai et al. 2003). It is likely that contemporaneous Lower Paleozoic granitoids exposed in the hinterland of the Ninnis Glacier have similar Nd and Sr isotopic signatures. Accreted onto the eastern margin of the Wilson Terrane in Northern Victoria Land are Paleozoic-aged metasediments and granites of the Robertson Bay Terrane (Henjes-Kunst and Schussler, 2003), Bowers Terrane (Borg et al. 1987) and the geographically limited Admiralty Intrusives.

Adjacent to Lower Paleozoic granitoids in George V Land, and further to the east in the vicinity of the Cook Ice Shelf (Figure A2), the Permian to Cretaceous Beacon Supergroup is exposed and intruded by sills of dolerite of the Jurassic to Cretaceous continental flood basalt formation, the Ferrar Large Igneous Province (FLIP) (Goodge and Fanning, 2010; Elliot and Flemming, 2008). Major lithologies of the FLIP regionally are dolerite, flood basalts, tuffs and pyroclastics (Elliot and Fleming, 2008). No Nd and Sr data are available for the Beacon Supergroup, but detrital zircons are dominated by U-Pb ages of between 430 Ma and 620 Ma (Goodge and Fanning, 2010), suggesting a genetic link to regionally abundant Lower Paleozoic terranes. The FLIP is characterised by average ϵ_{Nd} values of -5.4 and average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ~ 0.713 (see Appendix Table 2).

The Cenozoic McMurdo Volcanic Group (LeMasurier and Thompson, 1990; Tessensohn and Worner, 1991) forms an important geological feature along the western margin of the Ross Sea region (Figure A2). The Balleny Islands lie in the southern sector of the Southern Ocean approximately 300 km directly north of Northern Victoria Land, and are thought to be related to the McMurdo Volcanic Group. The McMurdo Volcanic Group is characterised by average ϵ_{Nd} values of +5.3 and average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of ~ 0.704 (see Appendix Table 2).

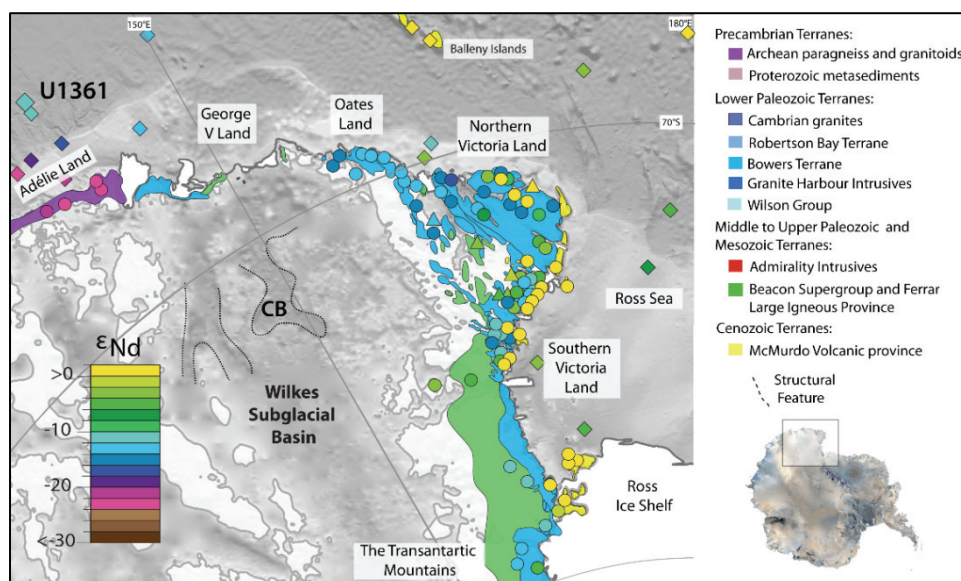
1.2 Provenance end-members for Pliocene IODP Site U1361 sediments

The Nd and Sr isotopic compositions of Pliocene detrital sediments are best explained by mixtures of two distinct continental source areas (Figure A4). The first proposed end-member is likely sourced from Lower Paleozoic granitic terranes. The most unradiogenic Nd



Appendix Figure S2. Simplified geological map of exposed bedrock around East Antarctica in proximity to the study area. Different colours highlight different aged source terranes in this area of East Antarctica, with outcrop limits and identification of individual units modified from Bushnell and Craddock, 1970). Subglacial topography (BEDMAP 2; Fretwell et al. 2013) is shown in grey shadings, with continental regions above sea level shaded white, and below sea level shaded darker grey. Similarly, lighter grey shading in the ocean depicts the continental shelf, and darker shading marks areas of deeper bathymetry. Black stippled lines mark structural features, including the Mertz Shear Zone around 140° (Ferraccioli et al. 2009) and a number of features in Northern Victoria Land (Flottmann et al. 1993). CB: Central Basin.

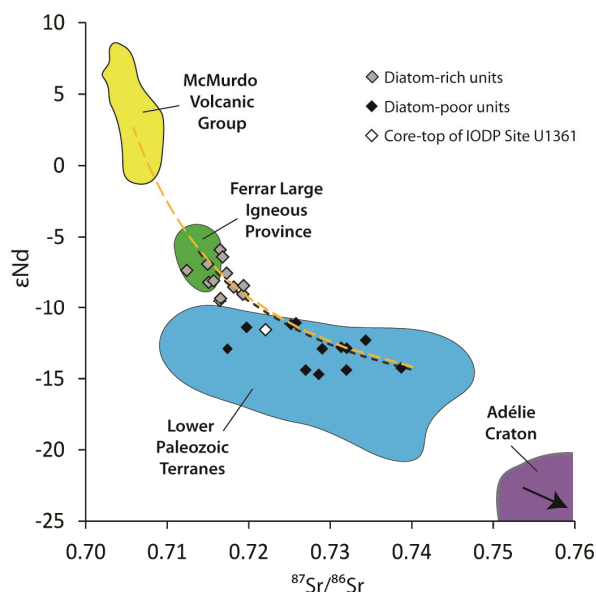
isotopic signatures and the most radiogenic Sr isotopic signatures in IODP Site U1361 sediments match very well the reported signatures from terranes in north-west Northern Victoria Land and Oates Land (Figs. A3 and A4; average ϵ_{Nd} : -14.4, average $^{87}\text{Sr}/^{86}\text{Sr}$: 0.738 (Henjes-Kunst and Schussler, 2003; Rocchi et al. 1998). While such a source for Pliocene detritus at IODP Site U1361 is feasible, I propose a supply of Lower Paleozoic material derived from drainage of the Ninnis Glacier (Goodge and Fanning, 2010; Di Vincenzo et al. 2007) more likely, as it is proximal to the study site. Modern sediment pathways indicate local transport of material sourced from bedrock near the Ninnis Glacier and the surrounding shelf offshore via turbidity currents (Presti et al. 2011). Holocene shelf sediments and offshore sediments in the vicinity of IODP Site U1361 (Goodge and Fanning, 2010; Pierce et al. 2011; this study), are composed of detrital material with Nd isotopic compositions between -11 and -14.5 (Figure A5). This signature matches Lower Paleozoic outcrops (Figure A4).



Supplementary Figure S3. Regional neodymium isotopic composition map of bedrock and marine sediments. Geological map of the study area showing published Nd isotopic compositions of bedrock on land (circles), onland moraine sediments ($<5\mu\text{m}$, triangles) and detrital marine core-top sediments ($<63\mu\text{m}$; diamonds). Colours of neodymium isotope data points correlate to the scale bar. Each data point represents up to 32 individual reported values. A list of references for outcrop values is provided in Appendix Table 2. Moraine data are taken from Delmonte et al. (2010). Marine data are taken from Farmer et al. (2006); Roy et al. (2007); van de Flierdt et al. (2007); Pierce et al. (2011) and this study. CB: Central Basin.

Given the Lower Paleozoic age of the rocks exposed in the hinterland of the Ninnis Glacier (Di Vincenzo et al. 2007; Goodge and Fanning, 2010) and their granitic lithology (Goodge and Fanning, 2010), I consider them the most likely end-member for the mixing model (Figure A4), with values for mixing model calculations taken from the similarly aged outcrops in north-west Northern Victoria Land and Oates Land.

The second proposed end-member contributing to Pliocene marine sediments at IODP Site U1361 is the FLIP (ϵ_{Nd} : -3.5 to -6.9; $^{87}\text{Sr}/^{86}\text{Sr}$: 0.712 to 0.719) (see Appendix Table 2). When calculating mixing curves between a FLIP end-member ($\epsilon_{\text{Nd}} = -5.4$, $[\text{Nd}] = 19\text{ppm}$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.713$, $[\text{Sr}] = 138\text{ ppm}$; Figure A4) and a Lower Paleozoic end-member ($\epsilon_{\text{Nd}} = -14.4$, $[\text{Nd}] = 39\text{ ppm}$, $^{87}\text{Sr}/^{86}\text{Sr}$: 0.740, $[\text{Sr}] = 120\text{ ppm}$; Figure A4), all measured Sr and Nd isotope values from Pliocene sediments can be modelled. In detail, mixing calculations suggest that diatom-rich Pliocene sediments are dominated by 95 to 75% of FLIP derived material, with the balance delivered from the Lower Paleozoic terranes discussed above.



Appendix Figure 4. Pliocene neodymium and strontium radiogenic isotopic compositions of sediments from IODP Site U1361 in context of proximal East Antarctic source rock signatures. White diamond represents the Late Pleistocene core-top sample of IODP Site U1361, and coloured areas represent different regional bedrock terranes. The yellow stippled line denotes a mixing calculation between Lower Paleozoic terranes and the McMurdo Volcanic Group. The black stippled line denotes a mixing calculation between Lower Paleozoic terranes and the FLIP, the preferred combination to explain measured values from IODP Site U1361 (see also Figure 2.3 in Chapter 2). Apart from Lower Paleozoic terranes, isotopic values used for end-member calculations are based on weighted means for each lithological group reported in Appendix Table 2, and average elemental concentration data from published literature, and are as follows: FLIP - ϵ_{Nd} : -5.4, [Nd] 19ppm, $^{87}\text{Sr}/^{86}\text{Sr}$: 0.713, [Sr] 138ppm; McMurdo Volcanic Group - ϵ_{Nd} : 5.3, [Nd] 73ppm, $^{87}\text{Sr}/^{86}\text{Sr}$: 0.704, [Sr] 754ppm. Isotopic values for Lower Paleozoic terranes represent average values for the Wilson Terrane and the Granite Harbour Intrusives exposed in north-west Northern Victoria Land, and Oates Land (ϵ_{Nd} : -14.4, [Nd] 39ppm, $^{87}\text{Sr}/^{86}\text{Sr}$: 0.740, [Sr] 120ppm), the approximate range of which is shown by the blue area.

Diatom-poor sediments, in contrast, have signatures dominated (up to 95%) by Lower Paleozoic material, with much smaller contributions from the FLIP. The absolute proportions of the two end-members are, however, affected by the choice of values used to calculate mixing lines between them (Figure A4). In the following I will elaborate on the FLIP end-member, by discussing potential geographical sources, as well as alternative end-member choices.

Appendix Table 1. Strontium and neodymium isotopic compositions of detrital marine sediments from IODP Site U1361.

Sample name	Depth (mbsf)	$^{87}\text{Sr}/^{86}\text{Sr}$	2σ SE	$^{143}\text{Nd}/^{144}\text{Nd}$	2σ SE	$\epsilon_{\text{Nd}}^{\dagger}$	2σ SD ⁺
IODP Expedition 318, Site U1361							
1H 1W 3-5cm	0.03	0.721744	± 0.000018	0.512046	± 0.000010	-11.5	± 0.3
8H 6W 57-59cm	74.09	0.732150	± 0.000019	0.511979	± 0.000010	-12.9	± 0.3
9H 1W 57-59cm	76.07	0.715075	± 0.000008	0.512283	± 0.000010	-6.9	± 0.3
9H 1W 77-79cm	76.27	0.716604	± 0.000010	0.512284	± 0.000018	-6.9	± 0.5
Duplicate		0.716460	± 0.000014	0.512341	± 0.000010	-5.9	± 0.3
9H 1W 81-82cm*	76.31	0.716901	± 0.000008	0.512261	± 0.000016	-7.4	± 0.7
9H 2W 77-79cm	77.77	0.725630	± 0.000016	0.512070	± 0.000018	-11.1	± 0.2
re-analysis		0.725570	± 0.000014	-	-	-	-
9H 3W 97-99cm	79.47	0.725313	± 0.000012	0.512064	± 0.000010	-11.2	± 0.3
9H 6W 5-7cm	83.05	0.728710	± 0.000018	0.511882	± 0.000006	-14.7	± 0.3
9H 6W 145-147cm	84.45	0.719850	± 0.000008	0.512052	± 0.000006	-11.4	± 0.3
10H 2W 25-27cm	86.75	0.734461	± 0.000006	0.512008	± 0.000014	-12.3	± 0.3
10H 3W 17-19cm	88.17	0.716557	± 0.000014	0.512150	± 0.000012	-9.5	± 0.3
Duplicate		0.715515	± 0.000016	-	-	-	-
10H 4W 5-7cm	89.55	0.731468	± 0.000010	0.511981	± 0.000010	-12.8	± 0.3
10H 5W 107-109cm	92.07	0.715194	± 0.000012	0.512218	± 0.000010	-8.2	± 0.2
10H 6W 35-37cm	92.95	0.712514	± 0.000014	0.512262	± 0.000008	-7.3	± 0.3
10H 7W 3-5cm	94.03	0.717386	± 0.000014	0.512252	± 0.000010	-7.5	± 0.4
re-analysis		0.717370	± 0.000016	-	-	-	-
11H 2W 70-72cm	96.70	0.738815	± 0.000008	0.511908	± 0.000008	-14.2	± 0.3
11H 5W 25-27cm	100.75	0.719381	± 0.000010	0.512175	± 0.000008	-9.0	± 0.4
11H 7W 26-28cm	103.76	0.715787	± 0.000010	0.512224	± 0.000020	-8.1	± 0.2
12H 4W 63-65cm	106.94	0.729142	± 0.000001	0.511975	± 0.000008	-12.9	± 0.3
12H 6W 40-41cm*	109.65	0.718272	± 0.000014	0.512202	± 0.000010	-8.5	± 0.4
12H 6W 49-51cm	109.74	0.719470	± 0.000004	0.512206	± 0.000012	-8.4	± 0.4
13H 2W 44-46cm	115.45	0.727110	± 0.000012	0.511890	± 0.000018	-14.5	± 0.2
13H 2W 62-63cm*	115.67	0.732095	± 0.000006	0.511899	± 0.000018	-14.4	± 0.2
13H 5W 110-112cm	120.55	0.716649	± 0.000010	0.512161	± 0.000008	-9.3	± 0.3
<hr/>							
10H 6W 35-37cm, >150µm, handpicked							
ash fragments	92.95	0.703414	± 0.000012	0.512991	± 0.000004	6.9	± 0.3
10H 7W 3-5cm, <63µm, magnetic							
fraction	89.55	0.716689	± 0.000012	0.512220	± 0.000006	-8.1	± 0.3
10H 7W 3-5cm, <63µm, residual							
fraction	89.55	0.716764	± 0.000030	0.512218	± 0.000005	-8.2	± 0.3

Appendix Table 1 continued.

Additional regional core top results:										
IODP Expedition 318, Site U1359										
1H CC 1-3cm	0.01	0.717393	±	0.000008	0.512066	±	0.000004	-11.2	±	0.3
IODP Expedition 318, Site U1360										
1R 1W 0-8cm	0.01	0.744233	±	0.000016	0.511810	±	0.000005	-16.2	±	0.3
IODP Expedition 318, Site U1358										
1R 1W 18-22cm	0.18	0.741152	±	0.000014	0.511630	±	0.000006	-19.7	±	0.3
DSDP Expedition 28, Site 269										
1R 2W 11-12cm	1.16	0.725571	±	0.000012	0.511948	±	0.000006	-13.5	±	0.3

† Calculated using a present day $^{143}\text{Nd}/^{144}\text{Nd}$ (CHUR) of 0.512638 (Jacobsen and Wasserburg, 1980)

† External uncertainty (2 sigma standard deviation) is based on the standard reproducibility of the analytical session

*Bulk samples were analysed, all others <63µm

Re-analysed values represent samples that were measured multiple times (same aliquot), while duplicate samples represent full procedural repeats (e.g. from digestion, through ion exchange chromatography, to mass spectrometry).

Appendix Table 2. Present day whole rock neodymium and strontium isotopic compositions of key continental bedrock lithologies in the vicinity of IODP Site U1361.

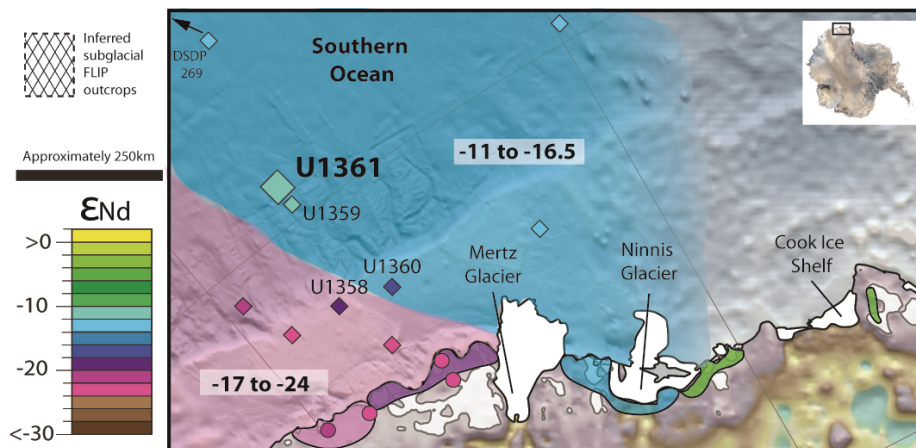
Source Bedrock	ϵ_{Nd}	Weighted Mean*	[Nd] (ppm)	Weighted Mean*	$^{87}\text{Sr}/^{86}\text{Sr}$	Weighted Mean*	[Sr] (ppm)	Weighted Mean*
FLIP (ref: 1-18)	-3.5 to -6.9 (n=39)	-5.4	8 to 35 (n=82)	19	0.709 to 0.719 (n=358)	0.713	75 to 220 (n=272)	138
Wilson Terrane (NVL) (ref: 19-25)	-11.2 to -19.8 (n=107)	-12.9	14 to 70 (n=48)	39	0.714 to 0.753 (n=131)	0.728	90 to 330 (n=36)	188
Granite Harbour Intrusives (ref: 19, 26-28)	-9.7 to -16.6 (n=30)	-12.4	38 to 85 (n=8)	64	0.712 to 0.744 (n=39)	0.723	135-331 (n=12)	237
McMurdo Volcanic Group (ref: 29-53)	-0.1 to +8.4 (n=134)	+5.3	32 to 192 (n=214)	73	0.703 to 0.7134 (n=161)	0.7045	4 to 1770 (n=585)	754

* Weighted means were calculated for individual analyses, by establishing the average value of the population frequency of values, in order to remove bias from outliers.

References 1: Antonini et al. (1999); 2: Compston et al. (1968); 3: Elliot et al. (1995); 4: Elliot et al. (1999); 5: Faure et al. (1972); 6: Faure et al. (1974); 7: Faure et al. (1982); 8: Fleming et al. (1992); 9: Fleming et al. (1995); 10: Hornig-Kjarsgaard (1993); 11: Mensing and Faure (1996); 12: Mensing et al. (1984); 13: Molzahn et al. (1996); 14: Siders and Elliot (1985); 15: Wilhelm and Worner (1996); 16: Demarchi et al. (2001); 17: Thompson et al. (1983); 18: Brotzu et al. (1988); 19: Armienti et al. (1990); 20: Cox et al. (2000); 21: Henjes-Kunst and Schussler (2001); 22: Rocchi et al. (2004); 23: Schussler et al. (1999); 24: Talarico et al. (1995); 25: Turner et al. (ref. 1993); 26: Borg et al. (1987); 27: Borg and DePaola (1994); 28: Dallai et al. (2003); 29: Cooper et al. (2011); 30: Ben Othman and Menzies (1990); 31: Hart (1988); 32: Berlin and Henderson (1969); 33: Shen-Su and Hanson (1976); 34: Goldich et al. (1975); 35: Green et al. (1992); 36: Kyle et al. (1992); 37: Gamble and Kyle (1987); 38: Rocholl et al. (1995); 39: Kyle et al. (1981); 40: Sims and Hart (2006); 41: Hornig and Worner et al. (2003); 42: Muller et al. (1997); 43: Armienti et al. (2003); 44: Armienti and Vita-scaillet (2003); 45: Worner et al. (1989); 46: Cooper et al. (2007); 47: Sims et al. (2008); 48: Kelly et al. (2008); 49: Rocchi et al. (2002); 50: Nardini et al. (2009); 51: Caldwell and Kyle (1994); 52: Perinelli et al. (2011); 53: Oppenheimer et al. (2011).

1.3 Potential geographical sources of the Ferrar Large Igneous Province

Although coarse-grained shelf sediments and clasts along Adélie Land and George V Land proximal to IODP Site U1361 have been described as being composed of significant proportions of FLIP dolerite (Domack et al. 1980), the fine-grained core top provenance mapping approach as presented in Figure A5 shows no indication of local FLIP material (Pierce et al. 2011; this study). Fine-grained shelf sediments appear to be characterised by similar detrital isotope signatures as those of the bulk rock compositions exposed on the adjacent continent (i.e. Lower Paleozoic bedrock in the hinterland of the Mertz and Ninnis Glaciers, and Archaean to Proterozoic bedrock to the west of the Mertz glacier; Figure A2). This good correlation between the radiogenic isotopic compositions of onshore outcrops and modern offshore marine sediments is a relationship identified in many areas around Antarctica (Farmer et al. 2006; Hemming et al. 2007; Roy et al. 2007; van de Flierdt et al. 2007; Pierce et al. 2011), and excludes the local shelf as a viable source for FLIP bedrock.

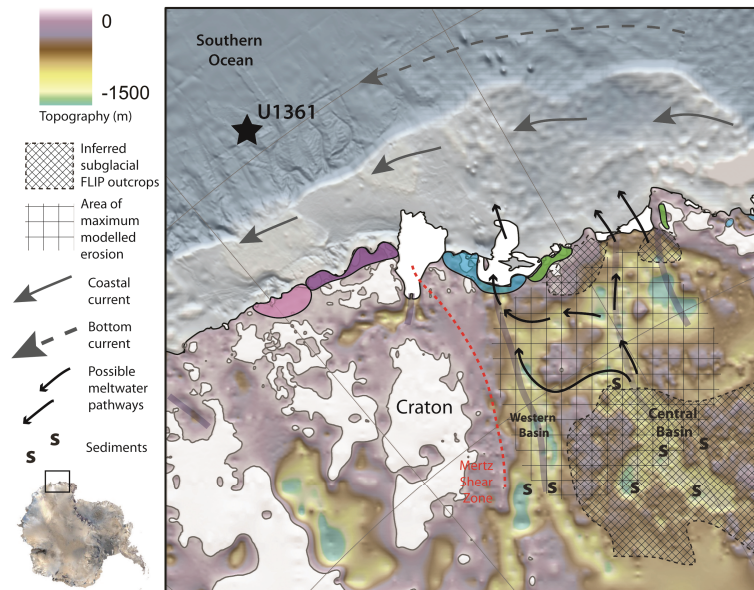


Appendix Figure 5. Close-up map of study area illustrating neodymium isotope provenance sectors delineated from core-top sediments within the vicinity of IODP Site U1361. Topography from BEDMAP (Fretwell et al. 2013). See Figure A2 for geology. Number ranges in the Southern Ocean represent ϵ_{Nd} values for core top sediments, denoting an Lower Paleozoic terrane (blue shading), and an Adélie Craton terrane (Archean-Proterozoic) (pink shading). It is important to note that while shelf sediments off of Adélie Land are characterised by material supplied by erosion of old cratonic material from the Adélie Craton to the west of the Mertz Glacier, none of this material appears to reach IODP Site U1361, an observation confirmed by a core-top measurement on the neighbouring IODP Site U1359 drilled during Expedition 318. Sources for Nd isotope data: Roy et al. (2007), Pierce et al. (2011), this study (Table 1).

Outcrops of the FLIP regionally are observed in two locations: the first is in the Transantarctic Mountains and adjacent Victoria Land, and the second along George V Land, particularly in the vicinity of the Cook ice shelf (Figure A2) and further to the west in coastal highlands ~100 km east of the Ninnis Glacier. While I cannot fully exclude a Ross Sea source for fine-grained FLIP material, I consider it an unlikely mechanism to explain the dominant FLIP signature observed in Early Pliocene sediments. This is because if fine-grained FLIP material was sourced from the Ross Sea area (e.g. by icebergs or ocean currents), it would be expected to see a corresponding increase in fine-grained volcanic material associated with the Cenozoic McMurdo Volcanic Group, which dominates western Ross Sea shelf sediment compositions (Farmer et al. 2006). As discussed below, the McMurdo Volcanic Group has a distinct geochemical composition, and fine-grained sediments from IODP Site U1361 do not appear to carry that signature, demonstrating a lack of evidence for fine-grained material travelling from the Ross Sea to the study site during the Pliocene.

Exposures of FLIP bedrock closer to IODP Site U1361 along the George V Land coast are limited to small outcrops (Figs. A5 and A6). However, aeromagnetic data collected along this region of the coast reveal subglacial spatial frequency anomalies that resemble signatures of known FLIP exposures, interpreted to indicate outcrops of FLIP basalts (Damaske et al. 2003). Despite topographically constrained ice stream drainage upstream of the Cook Ice Shelf over these outcrops, there is no evidence for FLIP material in offshore sediments near to IODP Site U1361 (Goodge and Fanning, 2010; Roy et al. 2007; Pierce et al. 2011). This suggests that if modern erosion of this FLIP bedrock is taking place, evidence for it must be confined to the local shelf offshore of the Cook Ice Shelf, such as observed for the erosion of the Adélie Craton to the west (Figure A5). These observations make it difficult to infer that a simple increase in erosional capacity of Pliocene ice streams could have supplied a FLIP end-member from this point source at the mouth of the Wilkes Subglacial Basin to IODP Site U1361 in quantities that would regionally overprint other sediment sources.

Therefore I propose that Pliocene provenance patterns, and particularly the occurrence of relatively pure FLIP end-member compositions during warm Pliocene intervals, were related to erosion of a larger area of FLIP than exposed today, potentially partnered with increased erosion of a more easily erodible area of FLIP material. Geophysical surveys of the Wilkes Subglacial Basin to date have covered the coastal areas in the vicinity of the Ninnis Glacier and the Cook ice shelf (Damaske et al. 2003), the inland area between 70°S and 74°S



Appendix Figure 6. Close-up map of study area illustrating possible erosional pathways out of the Wilkes Subglacial Basin based on subglacial topography from BEDMAP 2 (Fretwell et al. 2013). Sedimentary deposits and inferred subglacial FLIP outcrops within the Wilkes Subglacial Basin are taken from airborne geophysical work (Damaske et al. 2003; Studinger et al. 2004; Ferraccioli et al. 2009), as is the inferred location of the Mertz Shear zone (Ferraccioli et al. 2009), which separates the cratonic highland in the west from the western basin of the Wilkes Subglacial Basin to the east. Area of maximum modelled erosion is taken from the work of Jamieson et al. (2010). See Figure A2 for geological terrains (purple, blue, and dark green colours). Inferred subglacial outcrops are taken from Damaske et al. (2003).

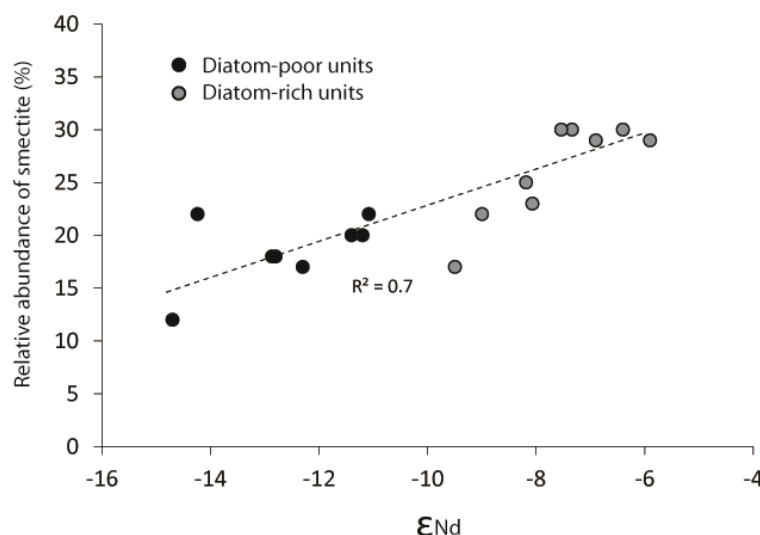
(Ferraccioli et al. 2009), and the inland area between $\sim 74.3^{\circ}\text{S}$ and $\sim 77.3^{\circ}\text{S}$ including the western flank of the Transantarctic Mountains (Studinger et al. 2004). From this work it is clear that the eastern margin of the Wilkes Subglacial Basin in Southern Victoria Land, 400 to 500 km inland from the most westerly bedrock exposure, is characterised by distinctive mesa topography, similar to that of exposed Beacon Supergroup and FLIP successions in the Transantarctic Mountains and Southern Victoria Land (Studinger et al. 2004; Ferraccioli et al. 2009). Sills of FLIP intrusives and basalts have also been inferred within the Wilkes Subglacial Basin (Ferraccioli et al. 2009) (see Chapter 2), along with several kilometres of unconsolidated sedimentary infill with FLIP signatures within the Central Basin, making this a likely source for erosion upon ice retreat and/or a warmer thermal ice regime. In contrast, the thick sedimentary infill of the second sub-basin, the Western Basin (Ferraccioli et al. 2009), will most likely have a significant sediment component derived from the Adélie

Craton (Di Vincenzo et al. 2007; Goodge and Fanning, 2010) which is expressed as a highland running along the western margin of the Wilkes Subglacial Basin. In fact, geophysical surveys suggest there is little FLIP derived material within the Western Basin (Ferraccioli et al. 2009), which is drained by the ice stream associated with the Ninnis Glacier. I therefore propose that the Central Basin is the most likely source for erosion of unconsolidated FLIP lithologies during the Pliocene, eroded by multiple retreats of the ice margin.

A lack of geophysical data in the region connecting the coastal areas at the mouth of the Wilkes Subglacial Basin with the Central Basin inhibits a precise estimate on how far the ice margin may have retreated inland. It is important to note, however, that sub-glacial topography dictates the routing of eroded material from the continent to the ocean (Figure A6). One possible route would be northwards out of the Central Basin through low-lying topographic conduits where the Cook Ice Shelf sits today, and also towards low lying areas in the hinterland of the Ninnis Glacier, which would then serve as a drainage point into the Southern Ocean (Figure A6).

1.4 Further supporting evidence for a Ferrar Large Igneous Province source

In order to further investigate sediment composition and provenance, clay mineral compositions were measured by x-ray diffraction. Diatom-rich sediments often show an increase in the relative abundance of smectite (Figure A7), which in turn shows a positive correlation with Nd isotopes in the fine detrital fraction of sediments (linear regression coefficient $R^2 = 0.7$; Figure A7). Smectites identified in Pliocene-Pleistocene channel levee sediments from the Adélie Land margin (Damiani et al. 2006) are Al-Fe-rich and detrital in origin, likely derived from basic volcanic rocks (Ehrmann et al. 1992). Authigenic smectites have been identified in Ross Sea sediments alongside similar detrital smectites (Setti et al. 2000), and are likely derived from submarine weathering of volcanic material of the McMurdo Volcanic Group (Damiani et al. 2006; Setti et al. 2000). I suggest that the predominance of detrital smectite in Adélie Land margin sediments implies that little or no authigenic smectite derived from weathering of the McMurdo Volcanic Group reached the Adélie Land margin during this time. A more likely source for detrital smectite in IODP Site U1361 is the FLIP (Claridge and Campbell, 1989).



Appendix Figure 7. Neodymium isotopic composition of fine-grained detrital material versus abundance of smectite in the same samples.

Analyses of the magnetic properties of sediments were carried out to further investigate lithological and provenance properties (Sugisaki and Tauxe, in preparation). Pliocene sediments have patterns related to higher amounts of hematite and/or magnetite in diatom-rich sediments providing additional evidence for a different sediment provenance. These magnetic minerals are possibly sourced from the FLIP and the Beacon Supergroup (Sagnotti et al. 1998).

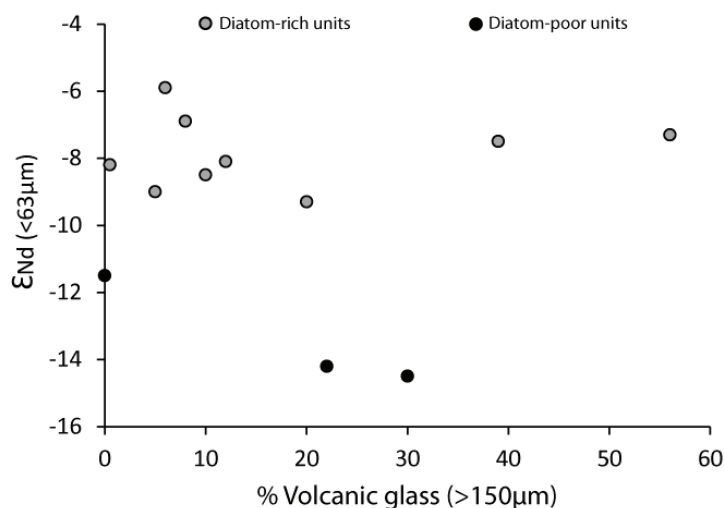
1.5 The McMurdo Volcanic Group as a potential end-member?

The Cenozoic McMurdo Volcanic Group (e.g. LeMasurier and Thompson, 1990; Tessensohn and Worner, 1991) forms an important geological feature along the western margin of the Ross Sea region (Figure A2). Abundant volcanic glass and mineral grains characterised by distinct petrological, geochemical and thermochronological signatures representative of the McMurdo Volcanic Group have been identified in marine sediments in the Ross Sea (Shane and Froggatt, 1992; Farmer et al. 2006; Roy et al. 2007; Huang et al. 1973, 1975, Kyle and Seward, 1984; Pompilio et al. 2007). Additionally, volcanic glass and phenocrysts have been identified in layers within continental ice in Northern Victoria Land and the Transantarctic Mountains (Perchiazzi et al. 1999; Smellie et al. 2011).

The McMurdo Volcanic Group is characterised by very radiogenic Nd and unradiogenic Sr isotopic compositions (Appendix Table 2), and hence would constitute a well-fitting mixing model end-member (instead of the FLIP) for Pliocene sediments from IODP

Site U1361 (Figure A4). In detail, diatom-rich sediments deposited during warm intervals in the Pliocene can be modelled by a mixture of between 15 and 35% McMurdo Volcanic Group material, with <85% Lower Paleozoic-aged material (Figure A4, see caption for exact end-member choice). Neodymium and Sr isotope analyses on handpicked glass grains, >150µm in diameter, from Pliocene IODP Site U1361 reveal a composition identical to that reported for the McMurdo Volcanic Group (Appendix Table 1). These results indicate that part of the coarse fraction of the Pliocene IODP Site U1361 sediments is sourced from the McMurdo Group Province. Such grains are however too large to have been transported by wind or bottom currents, pointing to either ice rafting, or proximal explosive volcanic activity. The latter could be argued due to the proximity of the volcanic Balleny Islands (e.g. Green, 1992), approximately 1000 km to the east of IODP Site U1361 (Figure A2). There is no data available on the Pliocene eruptive history of these volcanic islands, but it is unlikely that their eruptive periods would match the exact timing and reoccurrence of Early Pliocene warm events. This is supported by qualitative microscopic studies of the coarse fractions (>150µm) of sediments from IODP Site U1361 used in this study. While volcanic glass can make up significant proportions of some of these samples, I do not find that they are more abundant during warm intervals. In fact, no clear correlation emerges between lithostratigraphic and geochemical sediment units and the abundance of volcanic glass (Figure A8).

In addition, multiple lines of evidence argue against a major component of McMurdo Volcanic Group fine-grained material being delivered from the Ross Sea to IODP Site U1361: (i) none of the samples have ϵ_{Nd} values more positive than -5.9, and as such their isotopic compositions can all be explained without invoking the McMurdo Volcanic Group as an end-member. If the McMurdo Volcanic Group were the end-member, some proportion of the samples may be expected to fall closer to this end-member along the mixing line, but this is not observed. (ii) I tested the effect of volcanic glass on fine-grained sediment (<63µm) composition, by removing all magnetic minerals and volcanic glass from a sample composed of 39% volcanic glass in the >150µm fraction using a hand magnet. Comparison of glass-free and bulk sediment samples (Appendix Table 1) reveals identical Nd and Sr isotopic compositions. (iii) As discussed above (sub-section iv), geochemical analyses of clay minerals from Pliocene Adélie Land sediments show no evidence for authigenic smectite (Setti et al. 2000) which comprises marine sediments in the Ross Sea and is a product of weathering of the McMurdo Volcanic Group.



Appendix Figure 8. Detrital Nd isotopic composition of fine-grained sediments and the abundance of volcanic glass in coarse-grained fractions relative to other lithic grains. Volcanic glass abundance was derived by counting the number of grains in a 4cm³ area of randomly distributed grains under a microscope and extrapolating this number for the rest of the sample. No correlation can be observed.

In conclusion, multiple lines of evidence lead us to conclude that volcanic material sourced from the McMurdo Volcanic Group is unlikely to contribute significantly to the Nd and Sr isotopic composition of Pliocene fine-grained detrital sediments at IODP Site U1361.

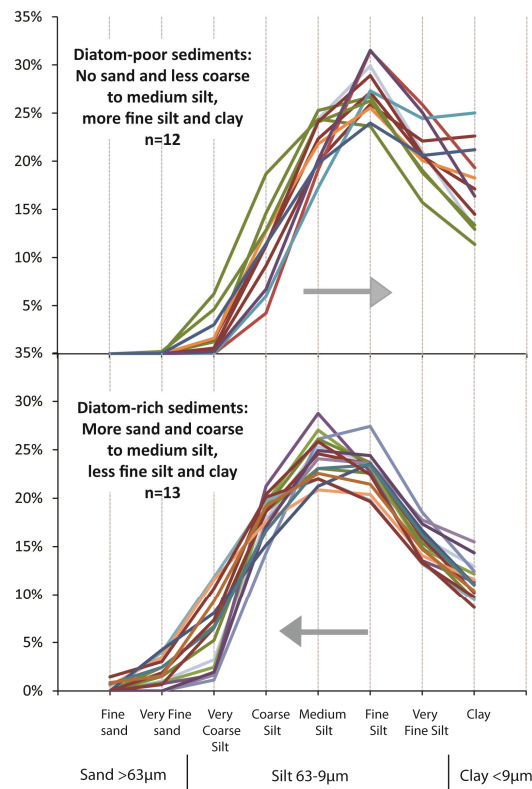
1.6 Potential contribution of biogenic opal to detrital neodymium and strontium isotopic composition

Biogenic opal is the dominant sedimentary component in diatom-rich sediments from IODP Site U1361, deposited during warm Pliocene intervals (Escutia et al. 2011). Direct measurements of opal contents on IODP Site U1361 Early Pliocene sediments indicate up to 40% opal by weight. As biogenic silica was not removed from bulk sediments prior to analysis of the ‘detrital’ fraction (see Section 3), the question is warranted whether biogenic opal could compromise the terrigenous radiogenic isotope signal. Neodymium and Sr concentrations in biogenic opal are reported as 1-4ppb and <3ppm, respectively (Grousset et al. 1998; Bayon et al. 2002). Typical upper continental crust concentrations of Nd and Sr are 25ppm and 350ppm, respectively (Taylor and McLennan, 1991). Strontium in diatom tests is likely authigenic in nature (Andersen et al. 2011) and may therefore carry a Pliocene seawater signature (⁸⁷Sr/⁸⁶Sr of ~0.709 [Hodell et al. 1991]). Using above outlined values for biogenic opal and typical upper continental crust in conjunction with the isotopic compositions derived

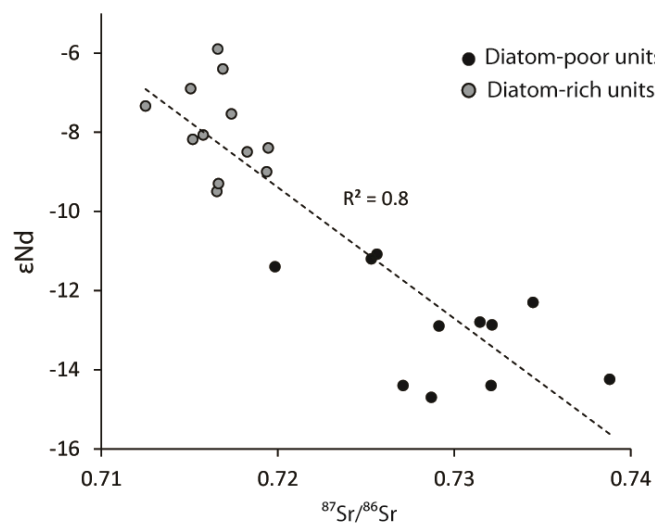
for Pliocene IODP Site U1361 sediments, mixing calculations demonstrate that it is unlikely that even high amounts of opal would have a significant effect on the detrital strontium isotopic composition at IODP Site U1361. Unlike Sr, Nd in biogenic opal is most likely not authigenic in nature, but rather sourced from clay-sized sediment particles incorporated into diatom frustules. This is supported by positive correlations of Nd and aluminium in cleaned diatoms (Andersen et al. 2011), and would imply an isotopic composition of Nd similar to the detrital sediment fraction in IODP Site U1361 sediments (i.e. continental bedrock signatures). Therefore, I consider it unlikely that Nd contribution from biogenic opal will significantly affect measured detrital values.

1.7 Potential grain size effect on the Sr isotope signal

Fine-grained sediments in open ocean environments are typically deposited by ocean currents, turbidity currents, or by wind, depositional mechanisms that can lead to preferential grain-size selection (e.g. Diekmann and Kuhn, 1999). Diatom-rich sediments in IODP Site U1361 are characterised by a slightly coarser grain-size compared to diatom-poor sediments (Figure A9), which, along with provenance-related grain-size variability, could indicate some post-depositional winnowing of fine-grained sediment components during warmer intervals. Finer grained sediment components, such as clay minerals tend to be enriched in composition of fine-grained sediments has been shown to remain unchanged by size selective sorting processes (e.g. Goldstein and Hemming, 2003; Eisenhauer et al 1999). Therefore, good correlation of Sr and Nd isotopes argues against any major grain-size control on the Sr isotope signal (Figure A10). I conclude that observed changes in Nd and Sr isotopes can be interpreted as terrigenous provenance signals, in turn supporting variations in erosional patterns on Antarctica during the Pliocene.



Appendix Figure 9. Grain-size data comparisons for diatom-poor and diatom-rich sediments from IODP Site U1361. ‘n’ represents the number of samples analysed for grain-size distributions from diatom-poor sediments (top plot) and diatom-rich sediments (bottom plot) from the Pliocene interval from IODP Site U1361. Each individual sample is shown as a different coloured line. Sediments were leached prior to analysis to remove organics by using 30% H₂O₂ and biogenic opal using 2M NaOH. The grain size frequency distribution for the <150µm fraction was subsequently analysed with a LS 13 320 Laser Diffraction Particle Size Analyser.



Appendix Figure 10. Neodymium versus strontium isotope correlation for Pliocene sediments analysed from IODP Site U1361

2. Additional insights into Pliocene retreat of the East Antarctic Ice Sheet, and new diatom assemblage data

2.1 Land-based stratigraphic and paleontological records of Pliocene retreat of the East Antarctic Ice Sheet

Interpretation of Pliocene East Antarctic ice sheet margin retreat in the vicinity of the Wilkes Subglacial Basin is supported by evidence that implies Pliocene East Antarctic ice margin retreat in the Prydz Bay area. The Sørsdal Formation in the Vestfold Hills of Prydz Bay (Adamson and Pickard, 1993; Pickard et al. 1998; Quilty, 1991, 1992; Harwood et al. 2000; Whitehead et al. 2001) is composed of marine sediments (sandy diatomites and diatomaceous sand) that were deposited in a coastal marine embayment on the East Antarctic continental margin, in <25m water depth (Harwood et al. 2000). Diatom biostratigraphy suggests these sediments accumulated between 4.1 and 4.5 Ma (Harwood et al. 2000), with extant diatom assemblages indicating summer sea surface temperatures (SSST) between ~1.6 and 3°C warmer than today (Whitehead et al. 2001) a conclusion supported by the presence of numerous cetacean fossils from species that today inhabit regions with no sea ice and SSTs between 4 and 5°C (Fordyce et al. 2002). The presence of considerable aeolian delivered material in the sediments of the Sørsdal Formation implies that during deposition, the ice-sheet margin was at least 50 km inland of its current position (Adamson and Pickard, 1993).

Pliocene deposits of the Pagodroma Group (Whitehead and McKelvey, 2001; McKelvey et al. 2001; Whitehead et al. 2004; Hambrey and McKelvey, 2000) in inland Prydz Bay are composed of fjordal marine sediments deposited by marine terminating glaciers ~250 km south of the current front of the Amery Ice Shelf (Hambrey and McKelvey, 2000). These sediments were deposited in the Lambert Graben when the Amery Ice Shelf front had retreated sufficiently far south, and were subsequently uplifted so that today they occupy the above sea-level flanks of the Lambert Graben.

In addition to this evidence for ice shelf and ice sheet retreat in the Prydz Bay area, alternations between diamictons and open-water facies in the Ross Sea during the Pliocene have been interpreted as evidence for an oscillating Ross Ice Shelf (Naish et al. 2009). Also, investigations into the provenance of ice-rafted detritus offshore of East Antarctica suggest that Pliocene intervals at 3.5 Ma and 4.6 Ma saw significant increases in iceberg production into the Southern Ocean from along the Wilkes Land and potentially even the Adélie Land margin (Williams et al. 2010). In summary, several studies suggest that the East Antarctic Ice

Sheet and Ross Ice Shelf were dynamic during the Pliocene, in support of my interpretation of ice sheet retreat in the Wilkes Subglacial Basin.

2.2 *Diatom Assemblages*

In order to substantiate Pliocene changes in water column productivity inferred from physical property, bulk geochemistry and opal (%) measurements, and to reconstruct paleoenvironmental conditions, quantitative diatom counts were carried out on 38 samples from IODP Site U1361 between 124 and 74.5 mbsf (~5.3 to 3.3 Ma). Diatom-rich sediments are characterised by higher total diatom abundances (up to ~12 million valves/gram) than diatom-poor sediments (<~800,000 valves/gram). This potentially indicates that diatom-rich sediments represent intervals of comparatively higher productivity, although confirmation of this would require calculation of accumulation rates, which the current age model for IODP Site U1361 does not permit (Figure 2, Chapter 2, and Appendix Table 3). The total number of valves counted per sample ranges between 48 and 315 (average: 120 per slide); although I acknowledge that counts within diatom-poor intervals in particular are too low to permit for good statistical confidence (Zielinski and Gersonde, 1997) these numbers are sufficient to document the most common taxa and their relative proportions. Around 30 individual species were recognised in Pliocene sediments from IODP Site U1361 (Appendix Table 3), but I here focus only on extant species that have well defined environmental tolerances.

While most extant diatom species with an affinity for sea ice have first appearance datums that are younger than the interval investigated here, those which evolved before or during the Pliocene (e.g. *Stellarima microtrias*, *Fragilariopsis vanhuerckii*, *F. curta*, *F. sublinearis*, *Eucampia antarctica*; Zielinski and Gersonde, 1997; Armand et al. 2005) are absent or occur at low abundance throughout the interval of focus (Escutia et al. 2011), suggesting minimal Pliocene sea ice cover at IODP Site U1361. Today, in contrast, IODP Site U1361 lies within the maximum winter sea ice zone, which is reflected by the abundance of sea-ice-affiliated diatom species in proximal modern marine sedimentary assemblages (Leventer et al. 1992; Armand et al. 2005).

Several extant ‘open ocean’ diatom species (Crosta et al. 2005) are present at IODP Site U1361 and encompass a range of different ecologies, from ice-tolerant, cold open ocean species, to warmer open ocean species. Here, this group includes *Rhizosolenia* spp., *Shionodiscus oestrupii* (transferred from the genus *Thalassiosira*; Alverson et al. 2006), *Thalassionema nitzschioides*, *Thalassiothrix antarctica*, and *Azpeitia* spp. The diatom genus

Rhizosolenia encompasses a wide range of species that are endemic to Southern Ocean waters (Crosta et al. 2005), and *Rhizosolenia antennata* f. *semispina* is the most abundant *Rhizosolenia* species in the Pliocene section of IODP Site U1361 (Escutia et al. 2011). The modern biogeography of *R. antennata* f. *semispina* indicates a preference for cool open ocean conditions (Froneman et al. 1995), with maximum abundances below 1.5°C (Crosta et al. 2005). The diatom *Thalassionema nitzschioides* has not been differentiated on a variety level, and is hence reported as *T. nitzschioides* s.l. However, as noted by previous studies (e.g. Zielinski and Gersonde, 1997; Crosta et al. 2005), the majority of *T. nitzschioides* s.l. support a warm affinity of the group. The diatom species *Thalassiothrix antarctica* occurs throughout the Early Pliocene section in IODP Site U1361, but decreases in abundance upcore. As *Thalassiothrix antarctica* and *Thalassiothrix longissima* can be difficult to distinguish from each other in fragmented assemblages, they are often regarded together as a group, *Thalassiothrix* spp. (Crosta et al. 2005). This group is cosmopolitan in the Southern Ocean but is associated with high productivity conditions such as upwelling or increased meltwater, and although it is ice tolerant (Froneman et al. 1995), it occurs in maximum abundances between 2 and 20°C (Zielinski and Gersonde, 1997; Crosta et al. 2005; Kemp et al. 2010; Winter et al. 2010).

Support for an interpretation that ocean temperatures at IODP Site U1361 were warmer-than-present during the Pliocene is provided by the occurrence of the sub-Antarctic diatom genus *Azpeitia*. This genus includes several species, and although I report *Azpeitia* spp. as a group pending further taxonomic investigation, this genus is presently found at highest abundances north of the Polar Front (Romero et al. 2005). In addition, the diatom *Shionodiscus oestrupii*, which has been linked to warm open ocean conditions in the modern Southern Ocean (Abelmann et al. 1990; Romero et al. 2005; Alverson et al. 2006) and North Atlantic (Jiang et al. 2001) and to warmer-than-present Pliocene conditions in the Ross Sea (Winter et al. 2010; McKay et al. 2012; Riesselman and Dunbar, 2013) and Prydz Bay (Whitehead et al. 2001), is present at IODP Site U1361, providing further evidence of climatic warmth.

In summary, several extant diatom species with well-constrained modern ecological preferences indicate a high productivity environment with minimal summer/spring sea ice, and warmer-than-present ocean temperatures at IODP Site U1361 throughout the Pliocene. Superimposed upon a baseline of warmer-than-present temperatures are intervals of high primary productivity recorded by the presence of diatom-rich sediments. The significant differences between Pliocene and modern diatom assemblages at Site U1361 demonstrate

major differences in environmental conditions, most likely associated with warmer sea surface temperatures.

Appendix Table 3. Diatom species counts.

Depth (mbsf)	Total valve counted	Total <i>Chaetoceros</i> resting spores	Number of fields observed	dry weight of sample used (mg)	Diatom Valve Concentration (DVC; valves/g)	<i>Chaetoceros</i> resting spores concentration (#/g)	Ch/(Ch+all diatoms)	<i>Actinocyclus ingens</i>	<i>Azpeitia nodulifera</i> s.l.	<i>Azpeitia</i> sp.	<i>Coscinodiscus marginatus</i>	<i>Cocconeis costata</i>	<i>Cocconeis</i> sp.	<i>Dactyliosolen antarcticus</i>	<i>Denticulopsis delicata</i>	<i>Denticulopsis simonsenii</i> s.l.	<i>Eucampia antarctica</i>	<i>Fragilariopsis barronii</i>
74.51	43.5	8	709	50.2	80711.36	14843.47	0.16							2		1		
75.03	216.0	33	35	50.4	8086312.23	1235408.81	0.13	1						11			2	46
76.50	229.0	54	40	50.0	7561375.80	1783031.85	0.19							16		1	1	5
78.00	227.0	29	85	49.8	3541383.22	452423.41	0.11							21		1	1	29
79.50	315.0	22	33	50.1	12582131.63	878752.05	0.07							25				67
81.00	100.0	46	433	50.2	303811.16	139753.13	0.32	2						6		15	1	5
82.50	100.5	16	665	49.9	200004.24	31841.47	0.14	3			1			2		28		1
84.00	100.0	9	519	50.4	252462.83	22721.65	0.08							6			1	15
85.10	103.0	20	288	50.2	470474.79	91354.33	0.16	3						2	1	51	2	
86.00	43.5	5	705	50.2	81169.29	9329.80	0.10	2					1	4		9		
87.50	26.5	11	708	50.1	49336.71	20479.39	0.29							1	1	4		2
89.00	88.5	22	702	50.3	165513.53	41144.61	0.20	3	1		1			1	1	1		5
90.50	101.0	7	320	50.1	416034.17	28834.05	0.06	8			2			8		23		1
92.00	226.0	18	60	50.3	4945207.73	393866.10	0.07				1			22	1			45
93.50	248.5	13	45	50.2	7264496.16	380034.00	0.05				2			31			4	16
94.60	100.5	45	106	50.5	1239835.75	555150.34	0.31		1		3			11		2	2	4
95.50	117.5	13	105	50.0	1477998.18	163523.20	0.10				4			15		4		11
97.00	101.0	19	570	50.5	231713.04	43589.58	0.16	5						3		28	1	
98.50	63.5	20	647	50.1	129368.06	40745.84	0.24	3					1	1		21		
100.00	122.0	16	692	50.3	231462.74	30355.77	0.12	2			2			3		2		
101.50	113.5	21	55	50.2	2714718.43	502282.70	0.16		2		6			17		1	2	2
103.00	108.5	12	95	50.1	1505441.01	166500.39	0.10		2	12				13				1
104.00	120.0	15	171	50.4	919496.19	114937.02	0.11	1	3	8	2			19			1	
104.80	108.5	9	76	50.3	1874318.95	155473.46	0.08		9	4				8		2		
105.80	100.5	13	138	50.2	958028.86	123924.13	0.11		4	2				1	1	2		
106.18	101.0	15	157	50.3	844596.10	125435.06	0.13	2	3	1				8		2		
106.93	84.0	41	690	50.5	159196.73	77703.17	0.33		2					3		17		
108.59	103.0	11	512	50.1	265170.30	28319.16	0.10	3	6	2	3			6	1		1	
108.78	107.5	11	45	50.4	3130118.29	320291.17	0.09		1	1				11	1		1	
110.28	103.5	10	94	50.5	1439847.36	139115.69	0.09		7	1	1			12			1	
111.00	101.0	16	267	50.4	495649.77	78518.78	0.14	1	5					2		4	1	
114.50	113.5	44	546	49.9	275104.70	106648.52	0.28	1	1		1			4	3	12	4	
116.00	100.0	28	399	50.3	329044.36	92132.42	0.22				1				3	1	1	
117.50	100.0	16	576	50.1	228841.68	36614.67	0.14							1	2	2		
119.00	68.0	22	688	50.7	128738.32	41650.63	0.24							1			1	
120.50	100.0	16	81	50.1	1627318.61	260370.98	0.14							3				
122.00	101.0	52	215	50.0	620452.08	319440.68	0.34				3			1		4		
124.00	167.5	34	110	50.2	2003151.26	406609.81	0.17				1	1				4	4	

Appendix Table 3 continued.

<i>Fragilariopsis interfrigidaria</i>	<i>Fragilariopsis praeinterfrigidaria</i>	<i>Rhizosolenia</i> spp.	<i>Rhizosolenia costata</i>	<i>Rouxia</i> spp.	<i>Shionodiscus oestrupii</i>	<i>Stellarima microtrias</i>	<i>Stephanopyxis</i> spp.	<i>Thalassionema nitzschioides</i> s.l.	<i>Thalassiosira complicata</i>	<i>Thalassiosira inura</i>	<i>Thalassiosira inure</i> (central hyaline area)	<i>Thalassiosira oliverana</i>	<i>Thalassiosira oliverana</i> var.C	<i>Thalassiosira striata</i>	<i>Thalassiosira torokina</i>	<i>Thalassiothrix antarctica</i>	<i>Thalassiothrix frauenfeldii</i>	<i>Triceratium polymorphus</i>	unidentified
		11		6	1		2	1	1	3	1	1				2			12
2	1	4		94	8			1	3	18	7	1		1	1	3			13
12	8	1		44	33		8	9	1	24	2	4			1	7			52
22	7	5		42	2		4	4	4	2	25	2		1		7	1		48
2	3	1		75	6		2	3	7	64	29	1		2		5			23
	1	8		12	6		4	9	3	4	14					2			9
	2	19		3	7	2	11	3	6	2	1					3			7
	4	5		9	6		3	1	11	9	12			3		5			10
	1	23		1	3		4	4	1							2		1	5
		2		1	3		2	1	2	3	4	1		2		1			6
				2	2		3	4	2	1	2					2			1
	2	5		8	10		9	9	1	4	4					3			21
	2	7		3	6		4	9	3	7	3			1		4			11
3	13	9		4	9		2	17	1	13	14			5	1	9			58
2	1	4		12	5		9	4	7	28	1	4		2	1	4			112
1	2	1		14	7		3	12	2	9	1	1		1		6			18
	3	3		6	10		5	22	3	4	4	1		1		8	2		12
		14		1	5	1	4	19	2	3	4					4	2		6
		16					9	7								2			4
	7				16	1	6	57	1	5	2					3	1		15
	6	1	3	8			5	16	5	2	9			1		7	2		19
	6		5	3			6	23	5	2	1					5			25
	8		1	9				20	4	5	8	2				10	2		20
	7			6	1			8	1	11	26	1				15			10
	11		1	7				9	2	7	23				2	15	1		13
	8		2	8				13	4	1	24	3				12	1		12
	25		2	3	1	3		7	1	1	2					4			13
	9		1	3	2	5		6	1	5	9	1	5		1	1			33
	1		2	11				8	6	18	13			2		8	1		19
	9		3	5				5	2	1	11			1		3			41
	16		4	5			1	10	5	3	3		1		1	13			25
	23				4	3		8	6	5	1	1	1		1	16	1		16
	25		1		2	4		8	8	3	4	2			1	10			28
	19			2	3			2	2	1				1	1	12	2		51
	14		2	1	3	1	1	1	4	1	1		1		5	10	2		21
	16			4			2	14	9	6	18		4		1	15			9
	31					1	1	5	1	4	15				1	6	1		28
	24		4	1	2	15		6		29	25		2		1	9	1		39

3 Methodologies

3.2 Neodymium and strontium isotopes

A total of 24 sediment samples were selected for processing from IODP Site U1361. Of these, three samples were analysed for bulk Nd and Sr isotopes, while the remaining samples were wet sieved into $<63\mu\text{m}$, $63\text{--}150\mu\text{m}$ and $>150\mu\text{m}$ fractions. Additionally, four core-top sediment samples from nearby drill sites were analysed. Splits ($\sim 500\text{mg}$) of homogenised $<63\mu\text{m}$ sediment were sequentially leached to remove biogenic carbonate and authigenic ferromanganese oxides and hydroxides. Removal of CaCO_3 was achieved by leaching of dried sediments repeatedly with buffered acetic acid following the method of Biscaye (1965). Ferromanganese oxides and oxyhydroxides were removed through repeated steps of leaching for 6–12 hours with a reductive solution, hydroxylamine hydrochloride (NH_2OH), following Rutberg et al. (2000). No removal of biogenic opal was carried out (see Section 1, sub-section vi). A representative sub-sample of 50mg of detrital sediment was dissolved by hotplate digestion using 2ml of 27M HF, 2ml of 15M HNO_3 and 0.6ml of 20M HClO_4 . A secondary digestion step using 2ml of 15M HNO_3 and 1ml of 27M HF was employed if any particles remained visible after the first step. Fluorides were removed in a subsequent step by fluxing samples in 6M HCl. In preparation for ion exchange chromatography, samples were then converted to nitrate form.

Target analytes (Nd and Sr) were selectively separated from the sample matrix by ion chromatography on three separate columns using Eichrom Sr Spec, TRU Spec, and Ln Spec resins (*Sr-spec* resin: $100\text{--}120\mu\text{m}$ bead size, modified after Pin et al. [1992]; TRU-Spec resin: $100\text{--}120\mu\text{m}$ bead size, Pin et al. [1997]; Ln-spec resin: $50\text{--}100\mu\text{m}$ bead size, modified after Pin et al. [1997]).

Dried Nd cuts were taken up in $\sim 1\%$ HNO_3 in preparation for measurement of Nd isotopes on a Nu Instruments multi collector inductively coupled plasma mass spectrometer (MC-IPC-MS) in the MAGIC laboratories at Imperial College London. Measurements were carried out in static mode. A $^{146}\text{Nd}/^{144}\text{Nd}$ ratio of 0.7219 was applied to correct for instrumental mass bias following the exponential law. Tests showed that interferences from ^{144}Sm are adequately corrected if the ^{144}Sm contribution is less than 0.1% of the ^{144}Nd signal. Samarium contributions of all samples were significantly below that level. Average $^{143}\text{Nd}/^{144}\text{Nd}$ JNdi values for ten analytical sessions over a sixteen month period were: 0.511979 ± 0.000028 ($n=55$); 0.512079 ± 0.000011 ($n=22$); 0.512138 ± 0.000020 ($n=40$);

0.512161 $\pm$ 0.000015 (n=30); 0.512153 $\pm$ 0.000012 (n=23); 0.512110 $\pm$ 0.000017 (n=33); 0.512093 $\pm$ 0.000014 (n=28); 0.512279 $\pm$ 0.000015 (n=18); 0.512254 $\pm$ 0.000015 (n=5); 0.512220 $\pm$ 0.000018 (n=18) (2 σ SD). All reported $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in Appendix Table 1 are corrected to the recommended JNdi value of 0.512115 (Tanaka et al. 2000). Inter-batch measurements of processing monitor standard BCR-1 yielded a $^{143}\text{Nd}/^{144}\text{Nd}$ of 0.512650 $\pm$ 0.000021 (n=4), compared to the recommended value of 0.512646 $\pm$ 0.000016 (Weis et al. 2006). Total procedural blanks were consistently below 10pg Nd. While re-analysis of samples always yielded the same values within error, total procedural duplicates of sediments reveal a larger uncertainty, probably due to sample heterogeneity (Appendix Table 1).

Strontium was loaded in 1 μl of 6M HCl onto degassed tungsten filaments followed by 1 μl of tantalum chloride. Measurements were performed in static mode in a single filament assembly on a Thermo Scientific Triton thermal ionisation mass spectrometer (TIMS) in the MAGIC laboratories at Imperial College London. The measured isotopic ratios were corrected for instrumental mass bias using the exponential law and a ratio of $^{88}\text{Sr}/^{86}\text{Sr}$ = 8.375. Interferences from ^{87}Rb were corrected for using a $^{87}\text{Rb}/^{85}\text{Rb}$ ratio of 0.3860. Samples were analysed over the course of a thirteen month period in five sessions. Repeated analyses of NBS987 standards over this period (n = 71) yielded $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.710260 $\pm$ 0.000015 (2 σ SD). As the measured value is in agreement with published values for NBS987 (0.710252 $\pm$ 0.000013; n=88) (Weis et al. 2006), no correction has been applied to sample results in Appendix Table 1. Repeated processing and analyses of procedural standard reference material BCR-1 yielded an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.705025 $\pm$ 0.000018 (2 σ SD) (n=10). Procedural blanks were consistently less than 300pg, and usually less than 30pg. While re-analysis of samples usually reproduced values within the fourth decimal place, total procedural duplicates of sediments reveal a larger uncertainty in the third decimal place, probably due to sample heterogeneity (Appendix Table 1).

3.3 *Diatom assemblages*

Diatom slides of 38 Pliocene samples from IODP Site U1361 were prepared following the quantitative technique of Koizumi and Tanimura (1985) by colleague Masao Iwai. In brief, bulk sediment samples were placed in an oven at 60°C for 24 hours. Approximately 50 mg of dry sediment sample was subsequently subsampled, weighed, and then treated with hydrogen peroxide solution (15% H_2O_2 in a 15ml centrifuge tube) to remove organic matter. After decanting the solution, the settled residue was re-suspended in

15ml of deionised water and 0.01M sodium hexametaphosphate in order to obtain better dispersion of clay minerals. Samples were allowed to settle for a minimum of two hours, after which suspended clays were decanted, and water was added back to the sediment residue. A 1ml subsample was taken from the shaken suspension using a micropipette with a disposable plastic tip, and strewn evenly onto an 18x18 mm cover slip. The cover slip was oven dried at <40°C then permanently mounted on a glass slide with Pleulax (refractive index = 1.78). Random field traverses of the microscope slide were made under a Normarskii differential interference contrast microscope at x630 magnification. The counting method of Schrader and Gersonde (1978) was utilised for all diatom specimens

3.4 Age model

The age model for IODP Site U1361 is based on paleomagnetic inclination measurements and diatom and radiolarian datums (Tauxe et al. 2012). Detailed methodologies have been published by Escutia et al. (2001) and Tauxe et al. (2012). The six tie points provided in Appendix Table 4 have been used to derive the ages reported throughout the paper.

Appendix Table 4. Age-depth tie points taken from Tauxe et al. (2012).

Chron	Age (Ma)	Depth (mbsf)
C2An.3n	3.33	74.52
C2An.3n	3.596	77.48
C3n.1n	4.187	99.99
C3n.2n	4.631	109.68
C3n.4n	4.997	120.32
C3n.4n	5.235	123.67

3.5 X-ray fluorescence geochemistry

To better understand lithological changes observed in sediments from IODP Site U1361, non-destructive bulk geochemical analyses were carried out by X-ray Fluorescence (XRF) core scanning by colleagues at the University of Granada, Spain. The scanning was performed with a step of 5 cm between 124 and 74 m composite depth (mcd) on the archive-half of sediment cores at the IODP core repository in College Station, Texas, USA. The used Avaatech XRF Core Scanner allows continuous analysis of elements ranging from Aluminum

(Al, atomic number 13) through to Uranium (U, atomic number 92) (Richter et al. 2006). The basic unit of the XRF core scanner measurements is total counts or counts per second (cps), which is proportional to the real chemical concentration of the measured element (Tjallingii et al. 2007; Paytan and Griffith, 2007) For this study the Ba/Al ratio was selected in order to identify productivity changes. Results on other elements obtained by the scans will be published separately.

It has been suggested that the amount of the trace element barium (Ba) in marine sediments can serve as a proxy for biological paleoproductivity (Tjallingii et al. 2007). Measured Ba counts have been normalized to Al in order to minimize the effects of physical properties and close-sum dilution effects. This normalization assumes that Al concentrations in sediments are contributed by alumino-silicates (Paytan and Griffith, 2007). Previous studies demonstrate Ba/Al increases are linked to high productive interglacial conditions in Antarctic environments. Obtained Ba/Al ratios shows cyclic variations, probably in response to changing climatic conditions on orbital and millennial time scales. Despite different resolutions, Nd and Sr isotopes variations are coincident with Ba/Al enrichments, interpreted as contemporaneous with variations in productivity and detrital sediment provenance.

3.6 Bulk and clay mineralogy

For clay mineral identifications carried out by colleagues at the University of Granada, the carbonate fraction was removed from 79 samples using acetic acid. The reaction was initiated at a very low acid concentration (0.1M), and the concentration was increased to 1M, depending on the carbonate content of each sample. Clay was deflocculated by successive washing with demineralised water after carbonate removal. The <2- μ m fraction was separated by centrifugation at 9000 rpm for 1.3 min. The clay fraction was smeared onto glass slides for XRD. Separation of the clay fraction and preparation of samples for XRD analyses were performed following the international recommendations compiled by Kirsch (1991) including glycolation and heat treatment (550°C) in representative samples.

Samples were examined using a Panalytical X-Pert Pro diffractometer with Cu K α radiation (45 kV, 40 mA), Ni filter, RTMS X'Celerator detector, 4°-69.9928° scan range, 0.0084° step size, 10.150s counting time, for a total of 7898 points and 11 min/sample. Data processing was performed using the X Powder[®] program in order to obtain the qualitative and quantitative mineral composition (Martin-Ramos, 2004). X Powder incorporates a powerful tool that allows precise quantitative studies and that takes full advantage of the information

contained in the database records. The analysis can be conducted on an isolated specimen or groups of up to 50 samples simultaneously. The weighting is achieved with the standard method RIR (Normalized RIR Method), described by Chung (1974).

The quantitative analysis was carried out by the least squares method of adjustment between each experimental diffractogram and the best weighted combination of reference patterns of a database specially created for this purpose from monophasic samples (standards) obtained in the same experimental conditions as the analysed samples (Martin-Ramos et al. 2012). Calculation and background correction were performed with the aid of a grade 8 polynomial function, at the bottom of the diffractogram. All database intensities were scaled at 1000.

During the quantitative analysis of each sample (**s**), theoretical mathematical fractions of each component (**k**) in the diffractogram were calculated. At the same time other instrumental parameters, such as the linear **2θ** offset of experimental patterns and random mismatches for individual reflections (**r**) in each database pattern (**k**) are fitted. The intensities of individual reflections of database patterns were not adjusted. The weighing schema (**w**) for experimental data (**I_i**) was $w_i^2 = 1 / I$. The quality of the fit is controlled by the agreement factor R:

$$R = \frac{\sum_r w_r (I_o - I_c)_r}{\sum_r w_r I_{o_r}}$$

(**I_o** observed intensities, **I_c** calculated intensities)

The fractions were converted to absolute values using scale factors normalized from the diffractogram of a standard sample with known composition using several methods: normative chemical analysis, SEM point counts and pure substances additions. Unit was taken as reference to quartz (**Q**) due to its high crystallochemical stability and because it appears in all analyzed samples.

The scale factors (**RIR_k**) were obtained by the expression:

$$RIR_k = (\% \text{ Xtal }_k / \% \text{ Xtal }_Q) \cdot (\text{Weight}(mg)_Q / \text{Weight}(mg)_k)$$

where **Xtal¹** concerns fractions obtained with **RIR_k** initial values = 1; and **Weight** (mg) corresponds to each component (**k** or **Q**) in the standard sample. RIR is calculated as the ratio

between the intensities of the major diffraction peak of the mineral phases and the major diffraction peak of a reference phase (normally corundum) on 50-50 binary samples. The **RIR** scaling factor used here includes the total of the reflections of each component in multiple samples, where the absorption coefficients of each component, the total sample, and other factors such as crystallinity and orientation vary over short intervals. Also, all scale values are referred to an internal compound (**Q**), thus allowing a statistical treatment of the diffraction data. The percentage values obtained were corrected for absorption following Chung (1974).

3.7 Biogenic opal concentrations

Colleague Boo-Kuen Khim from Pusan National Univeristy, Korea, analysed the biogenic silica content on 30 sediment samples selected at discrete intervals from 121.55 mbsf to 73.84 mbsf at IODP Site U1361 using a wet alkaline extraction method modified from DeMaster (1981). Approximately 10 mg of samples was transferred into a 50-ml polypropylene tube. About 30 ml of a 1N NaOH solution was added to the tubes, which were then closed and placed in a drying oven at 85°C for five hours. The tubes were vigorously shaken to re-suspend the solids at every hour, before 0.1 ml solution was transferred into a 10 ml vial containing 2 ml 0.1N HCl. Dissolved silica was measured using a molybdate blue spectrophotometric method. The relative uncertainty on the biogenic silica content in sediment samples was less than 1%. The opal content was calculated by multiplying biogenic silica content by 2.4 (Mortlock and Froelich, 1989), and results are presented in Appendix Table 5.

Appendix Table 5. Biogenic opal content.

Depth (mbsf)	Opal (%)
73.84	15.8
74.81	4.9
75.78	19.7
77.28	23.2
78.78	5.7
80.28	11.8
81.78	7.9
83.28	8.3
84.78	18.0
86.74	9.5
88.24	31.3
89.74	17.3
91.24	45.1
92.74	30.5
94.24	43.4
94.74	19.6
96.24	5.5
97.74	6.1
99.24	9.4
100.74	22.6
102.24	14.3
103.74	20.7
107.53	19.8
114.05	23.6
114.77	20.0
115.57	15.3
117.02	16.5
117.81	12.8
120.01	24.5
121.55	24.2

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APPENDIX 3

Supplementary Data Tables

Table 1. Petrography of ice-rafted mineral grains and lithologies of clasts from IODP Site U1359 sediments (>150µm)

Sample I.D.	Depth (mbsf)	Quartz (%)	Feldspar (%)	Pyroxene (%)	Garnet (%)	Magnetite (%)	Hornblende (%)	Muscovite (%)	Clast characteristics
1359 4H 3W 35-37cm	22.95	89.2	6	0.7	1				Schist, granite, vesicular ash, quartzite,
1359 4H 4W 125-127cm	25.35	82.5	11	0.6	1.3		1		Schist, vesicular ash, siltstone, quartzite
1359 4H 5W 35-37cm	25.95	71	11	1			3		Siltstone
1359 4H 5W 115-117cm	26.75	93	3	0.4		0.4			Siltstone
1359 4H 6W 5-7cm	27.15	85	9	2		1	1	1	Vesicular grains, siltstone

Table 2. Strontium isotope results for Miocene samples from ODP Site 1165 (<63µm).

	Depth (mbsf)	⁸⁷ Sr/ ⁸⁶ Sr	± 2σ S.E.
10H 2W 35-37cm	84.7	0.739053	0.000016
36X 7W 20-22cm	309	0.730724	0.000016
48X 3W 75-77cm	418.7	0.736935	0.000022
10R 3W 120-122cm	753.7	0.739589	0.000024
11R 2W 45-47cm	761.5	0.736103	0.000016
11R 3W 115-117cm	763.3	0.739966	0.000024

Strontium was loaded in 1µl of 6M HCl onto a degassed tungsten filament followed by 1µl of tantalum chloride. Measurements were performed in a single filament assembly on a Thermo Scientific Triton thermal ionisation mass spectrometer (TIMS) in the MAGIC laboratories at Imperial College London in static mode. The measured isotopic ratios were corrected for instrumental mass bias using the exponential law and a ratio of ⁸⁸Sr/⁸⁶Sr = 8.375. Interferences from ⁸⁷Rb were corrected for using a ⁸⁷Rb/⁸⁵Rb ratio of 0.3860. Analyses of NBS987 standards yielded average ⁸⁷Sr/⁸⁶Sr ratio of 0.7102501 ± 0.000014 (n=16). As these measured values are in agreement with published values for NBS987 (0.710252 ± 0.000013; n=88) (Weis et al. 2006), no correction has been applied to sample results. Repeated processing and analyses of our procedural standard reference material BCR-1 yielded an ⁸⁷Sr/⁸⁶Sr ratio of 0.7050255 ± 0.000017 (2σ SD) (n=3), in good agreement with the recommend value of 0.705018 ± 0.000013 (Weis et al. 2006).

Table 3. Strontium isotopes of numerous coretop samples from the East Antarctica margin (<63 μ m).

Core	Depth (cmbsf)	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\sigma$ S.E.
ELT37-09	25	0.730705	0.000014
ELT37-13	34	0.744546	0.000014
DF80-20	164	0.720250	0.000014
DF80-34	805	0.710444	0.000010
DF79-47	576	0.732310	0.000016
ELT37-16	34	0.730767	0.000020
ELT49-30	43	0.734272	0.000016

Strontium was loaded in 1 μ l of 6M HCl onto a degassed tungsten filament followed by 1 μ l of tantalum chloride. Measurements were performed in a single filament assembly on a Thermo Scientific Triton thermal ionisation mass spectrometer (TIMS) in the MAGIC laboratories at Imperial College London in static mode. The measured isotopic ratios were corrected for instrumental mass bias using the exponential law and a ratio of $^{88}\text{Sr}/^{86}\text{Sr} = 8.375$. Interferences from ^{87}Rb were corrected for using a $^{87}\text{Rb}/^{85}\text{Rb}$ ratio of 0.3860. Analyses of NBS987 standards yielded average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710256 ± 0.000010 (n=15). As these measured values are in agreement with published values for NBS987 (0.710252 ± 0.000013 ; n=88) (Weis et al. 2006), no correction has been applied to sample results. Repeated processing and analyses of our procedural standard reference material BCR-1 yielded an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.705014 ± 0.000014 (2 σ SD), in good agreement with the recommend value of 0.705018 ± 0.000013 (Weis et al. 2006).