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Climate Evolution of the Antarctic Peninsula Over the Last 1,000 Years: An Environmental Magnetism Analysis of Two High Resolution Sediment Cores

Brendan Reilly

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**ABSTRACT**

Two marine sediment cores from very different depositional environments, off the coast of western and northeastern Graham Land, Antarctic Peninsula (AP), record high resolution climatic records of the last 1,000 years. This study finds evidence in the sedimentary magnetic signature for a regional shift from warmer to colder climatic conditions around 1100-1400 AD. The first core, from middle Barilari Bay, western AP, displays a shift from seasonally open marine conditions to sub/proximal ice shelf ca. 1100 AD, with evidence for multiple grounding line advances in the magnetic mineral distributions during the first half of the last millennium. Prior to the glacial advance ca. 1100 AD, middle Barilari Bay was characterized by high primary productivity with pulses of ice rafted debris atypical of the fjord’s local geology. The second core, from Perseverance Drift, north of Joinville Island, northeastern AP, contains a change in the magnetic mineral assemblage ca. 1350 AD, interpreted as a reflection of higher-than-modern pore water sulfide concentration driven by decreased bioturbation and limited exchange between sediment pore water and ocean water. These events are interpreted as expressions of a regional Little Ice Age like event on the AP and indicate these study sites as prime locations for investigation of AP climate evolution over the last millennium leading to the abrupt climatic changes observed in recent history.
MONTCLAIR STATE UNIVERSITY

Climate evolution of the Antarctic Peninsula over the last 1,000 years:
An environmental magnetism analysis of two high resolution sediment cores

by

Brendan Reilly

A Master’s Thesis Submitted to the Faculty of
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CLIMATE EVOLUTION OF THE ANTARCTIC PENINSULA
OVER THE LAST 1,000 YEARS:
AN ENVIRONMENTAL MAGNETISM ANALYSIS OF
TWO HIGH RESOLUTION SEDIMENT CORES

A THESIS

Submitted in partial fulfillment of the requirements
for the degree of Master of Science

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May 2013
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INTRODUCTION

Observed Climate Change on the Antarctica Peninsula

The Antarctic Peninsula (AP) is a rapidly warming region, with average air temperatures rising 2.5 °C since the 1950s (Scambos et al., 2002; Figure 1). With the rise of remote sensing technologies in the past 50 years, scientists have observed seven of the twelve ice shelves on the AP retreat or completely disappear, totaling 28,117 km² of ice shelf loss (Cook and Vaughan, 2010). Ice shelves, the floating marine termini of the AP’s ice sheet, have a buttressing effect on their tributary glaciers, slowing glacial flow and stabilizing glacial grounding lines (De Angelis & Skvarca, 2003; Rignot et al., 2004). Removal of these ice shelves can cause rapid grounding line retreat, tributary glacial acceleration, reduced ice sheet mass, and transfer of freshwater glacial ice to the ocean, as clearly observed immediately following the disintegrations of the Larsen A and B ice shelves in 1995 and 2002, respectively (De Angelis & Skvarca, 2003; Rignot et al., 2004; Scambos et al., 2004; Hulbe et al., 2008). The implications for this, especially with regards to the presently stable Ross and Ronne-Filchner ice shelves, buttressing the West Antarctic Ice Sheet, could include global sea level rise due to increased discharge from the un-buttressed ice sheet, changes in floral and faunal distributions, and impacts on ocean circulation.

The abrupt environmental change on the AP and dramatic disintegration of the Larsen A and B ice shelves are unusual in the context of the Holocene (Bentley et al., 2009). This change is likely driven by anthropogenic forces and manifested, along with other changes, as a southern migration of the westerly winds (Bentley et al., 2009 and references therein).
Providing Historical Context for Observed Changes

The interdisciplinary LARISSA (LARsen Ice Shelf System, Antarctica) program includes glaciologists, biologists, geologists/geophysicists, and oceanographers and studies the former Larsen B ice shelf and surrounding northern AP area to better understand ice shelf systems from an earth systems science perspective. An important aspect of this study is to provide the historical context for modern changes through marine sediment cores and ice cores. These studies are used to better understand AP climate evolution, temporal/spatial ice sheet extents, and driving forces on climate since the last glacial maximum.

This study aims to contribute to our understanding of climate evolution in the last 1,000 years of the Holocene. Southern Hemisphere climate over the last 1,000 years is subject to great debate, particularly whether the Little Ice Age (LIA) was a global phenomenon or limited to the Northern Hemisphere. Some AP records find evidence for a cool period synchronous with the LIA, notably the Palmer Deep record (Domack et al., 2001; Shevenell et al., 2011), but this expression is not universally interpreted among AP records.

This study finds a shift in climatic conditions in the record of two high resolution marine sediment cores, from very different depositional environments and locations. Preliminary chronologies of these cores place the transition from warmer to cooler conditions 1100AD – 1400 AD. The primary goal of this study is to explore this shift in climate with the ultimate goal of determining the driving mechanisms of this change. In doing so, this study also investigates the use of environmental magnetism as a method to
understand sedimentary processes, provenance, and diagenesis in glacial marine sediments.

**Holocene Climate Evolution of the Antarctic Peninsula**

Combined records from marine sediment cores, terrestrial lake cores, ice cores, and glacial geomorphology have identified characteristics for several Holocene climatic intervals that are widespread, albeit manifested differently, on the AP. These are the warm early-Holocene climate optimum (~11-9.5 ka), the warm mid-Holocene climate optimum (~4.5-2.8 ka), and the cool Neoglacial (2.5-1.2 ka; Bentley et al, 2009). The Mediaeval Warm Period (MWP; ~1.2-0.6 ka) and LIA (0.7-0.15 ka), abrupt climatic events that are widely recognized in the Northern Hemisphere, are not well constrained by proxy data on the AP, and are identified as areas that require increased attention (Bentley et al., 2009). Further study of the MWP and LIA should provide valuable insight on the atmospheric and oceanic forcing on climate leading into the recent rapid regional warming. The timing of the LIA event is identified in the high resolution marine record from the Palmer Deep, on the Western AP, as occurring 700 – 150 BP (~1250-1800 AD; Domack et al., 2001; Shevenell et al., 2011).

Evidence from marine sediment cores recovered from beneath the former Larsen B suggests the Larsen B ice shelf was stable through Holocene climate fluctuations, making its destruction in 2002 unprecedented in the geologic record (Domack et al, 2005). This is opposed to the smaller, further north, former Prince Gustav ice shelf, which retreated to seasonally open marine conditions around the time of the mid-Holocene climatic optimum (~5 ka BP) and reestablished an ice shelf during the Neoglacial (~2 ka BP),
with some uncertainty in the $^{14}$C derived dates due to reworked carbon (Pudsey & Evans, 2001). Similarly, the Larsen A ice shelf shows a transition during the onset of the mid-Holocene climatic optimum (~6.3 ka) to a more diatom rich facies, suggesting instability or reduction in extent of the ice shelf, and reestablishment of a stable ice shelf in the late Holocene (~0.45 ka), with chronology constrained by relative paleomagnetic intensity (Brachfeld et al., 2003). Thus, the marine record suggests the Larsen ice shelf system has been susceptible to major Holocene climatic variations, with the Larsen B ice shelf located far enough south to mitigate the impacts of these variations until the recent rapid regional warming.

A number of mechanisms have been identified as potential driving forces on AP climate, including greenhouse gases, variation in solar insolation, upwelling of the warm circumpolar deep water (CDW), southern/northern migration of the mid-latitude derived westerly winds, El Nino Southern Oscillation frequency, sea ice extent, and others (Bentley et al., 2009). It is important to note that although connected, the Western and Eastern AP respond differently to these mechanisms. The warmer maritime climate of the Western AP is directly influenced by the westerly winds and upwelling of the CDW, while the colder, drier Eastern AP is subjected to persistent sea ice, cold air masses from the south, and foehn winds funneled through the continuous mountain spine of the AP (Bentley et al., 2009 and references therein).

Therefore, in order to understand the response of the Larsen ice shelf to recent rapid regional warming and the ice shelf system’s evolution through the Holocene, detailed marine records from both the western and eastern AP need to be considered, tracking both regional manifestations of climatic intervals and the mechanisms that drive them.
Environmental Magnetism in Marine Paleoclimatic Studies

The magnetic signatures of marine sediments are used in the paleoclimatic interpretation of sediment cores using techniques developed in the field of environmental magnetism. These magnetic signatures are largely determined by assemblages of ferrimagnetic minerals; such as magnetite (Fe\textsubscript{3}O\textsubscript{4}), greigite (Fe\textsubscript{3}S\textsubscript{4}), and maghemite (\(\gamma\)-Fe\textsubscript{2}O\textsubscript{3}); and antiferromagnetic minerals; such as hematite (\(\alpha\)-Fe\textsubscript{2}O\textsubscript{3}) and goethite (FeOOH). Iron is often replaced by titanium in magnetite, maghemite, and hematite, forming solid solution titanomagnetite (Fe\textsubscript{(3-x)}Ti\textsubscript{x}O\textsubscript{4}), titanomaghemite (\(\gamma\)-Fe\textsubscript{(2-x)}Ti\textsubscript{x}O\textsubscript{3}), and titanohematite (\(\alpha\)-Fe\textsubscript{(2-x)}Ti\textsubscript{x}O\textsubscript{3}), respectively, where \(x\) is between zero and one (Figure 2).

Verosub & Roberts (1995) categorize environmental magnetism studies into three categories; “geologic processes in sedimentary environments,” “origins of magnetic minerals in sedimentary environments,” and “transformations of magnetic minerals in sedimentary environments.”

The first category studies the physical sedimentary processes that influence the magnetic mineral assemblages. For example, magnetic susceptibility, a proxy heavily influenced by the concentration of magnetic minerals, is used in the study of turbidity currents, where magnetic minerals are concentrated in the coarse sand layers found at the base of turbidite deposits (Sagar & Hall, 1990), and in identifying marine productivity cycles in the absence of biogenic magnetite, where terrigenous sediments and the magnetic minerals they contain are diluted by biogenic sediments (Leventer et al., 1996).

The second category studies the characteristics and signatures of the detrital magnetic minerals to infer provenance of the sediment and properties of the sources material. For
example, domain state sensitive hysteresis parameter proxies are correlated with
titanomagnetite grain-size (Day et al., 1977), thus a change in provenance from a coarse­
grained titanomagnetite bearing gabbro to fine-grained titanomagnetite bearing basalt
will be reflected in a change in the down-core magnetic signature. Similarly, the
chemical composition and grain morphology of Fe-Ti oxides are highly correlated with
types of igneous source rocks (Grigsby, 1990), making reflected-light microscopy and x-
ray microanalysis of Fe-Ti oxides valuable tools in complementing environmental
magnetism provenance studies.

The third category looks at the alteration and dissolution of detrital magnetic minerals
and the authigenic magnetic minerals that form post-deposition. For example, one
ferrimagnetic mineral of importance is the iron-sulfide greigite, formed as a precursor to
the paramagnetic pyrite in anoxic, sulfate-reducing sediments (Figure 3). New studies
find greigite in the stable single-domain (from 17 up to 500 nm) and very-fine
superparamagnetic (less than 17 nm) states to be significantly more common than
previously thought, preserved in sediments when sulfide produced by bacterial anoxic
organic decomposition is limited by deposition of terrigenous sediment with plentiful
reactive iron or produced biogenically (Roberts et al., 2011 and references therein). As a
result, the presence of greigite can be an important factor in understanding the magnetic
signature of marine sediments and can complicate paleomagnetic intensity studies,
creating a post-depositional chemical remanent magnetization different from the detrital
remanent magnetization.
Environmental Magnetism Parameters and Tools

The following are environmental magnetism parameters and tools used to interpret marine sediment cores. This is not a comprehensive list; rather, it focuses on the techniques used in this study.

Low-Field Magnetic Susceptibility. Low-field magnetic susceptibility is a non-destructive measure of how a sample responds to a weak magnetic field and is reported as the sample’s induced magnetization (M) over the applied field strength (H) or M/H. The magnetic susceptibility is normalized by either sample mass (\(\chi\)) or volume (\(\kappa\)). In this study low-field mass-normalized susceptibility will be referred to as \(\chi_{lf}\) to differentiate it from high-field mass-normalized susceptibility (\(\chi_{hf}\)), calculated from the sample’s hysteresis loop. \(\chi_{lf}\) is mostly influenced by the concentration of ferromagnetic, ferrimagnetic, and canted antiferromagnetic particles in the sample.

Thermomagnetic Curves. Thermomagnetic curves, (\(\chi(t)\)), measure the \(\chi_{lf}\) as a function of changes in temperature. This study observes the \(\chi_{lf}\) as temperature increases from room temperature to 700 °C and then as the sample cools back to room temperature. It is also possible to observe the sample as it cools from room temperature to 77 °K.

Ferrimagnetic minerals have a unique order-disorder transition, above which the mineral becomes paramagnetic, known as the Curie temperature (\(T_c\)) that can be used to identify specific minerals. The Néel temperature (\(T_N\)) is a similar transition for antiferromagnetic minerals.

Hysteresis Loops. Hysteresis loops measure a sample’s M as a function of H, normalized by the sample’s mass. Measurements begin in a strong, sample-saturating H, decrease to zero, increase to an H equal to the initial field but in the opposite direction,
decreases to zero, and returns to the initial H. Diamagnetic materials have no hysteresis (i.e. their behavior is reversible) and create a line with a constant, negative slope. Paramagnetic materials also have no hysteresis and create a reversible line with a constant, positive slope. Ferromagnetic materials create a hysteresis loop, as ferromagnetic materials saturate in strong magnetic fields, retain a remanent magnetization after H is removed, but display a different M-H path upon exposure to the oppositely oriented magnetic field.

In order to correct for the diamagnetic and paramagnetic component of the sample, the slope of the line where the sample’s ferromagnetic component is saturated is calculated. This slope (M/H where H > H_{saturation}) is the high-field magnetic susceptibility (χ_{hf}) and represents only the diamagnetic and paramagnetic component of the magnetic susceptibility. The magnetization due to paramagnetic and diamagnetic minerals in calculated as χ_{hf} * H at each point along the hysteresis loop, and is subtracted from the measured M value along the entire hysteresis loop. The diamagnetic and paramagnetic corrected hysteresis loops reflect only the ferromagnetic component of the sample and the hysteresis parameters of the sample can be determined; the saturation magnetization (M_s), where M/H = 0; the remanent magnetization (M_r), where H = 0; and the bulk coercivity (H_c), where M = 0. χ_{hf} can also be used to calculate the ferromagnetic contribution to magnetic susceptibility (χ_{ferro}) by subtracting χ_{hf} from χ_{total}. Brachfeld (2006) discusses the limitation to using χ_{hf}, including that high-coercively minerals may not be fully saturated.

**DC Demagnetization of Remanence Curves.** The DC demagnetization of remanence curve is calculated by first measuring the isothermal remanent magnetization (IRM) after applying and removing a strong sample-saturating field. Then an incrementally
increasing back-field $H$ is applied until the sample's $M = 0$. The coercivity of remanence ($H_{cr}$) is thus the field strength required to force the $M_r$ of sample to zero.

**The S Ratio.** Magnetic minerals can be divided into low-coercivity minerals, like magnetite, titanomagnetites, and ferrimagnetic iron sulfides, and high-coercivity minerals, like hematite and goethite. Low-coercivity minerals saturate in $H$ less than 300 mT, while high-coercivity minerals may not saturate until $H$ is in excess of 1 T. Therefore, the S-ratio is the ratio of the sample’s isothermal remanent magnetization (IRM) in a 300 mT field divided by the Saturation IRM (SIRM) in a 1 T field (IRM$_{300mT}$/SIRM) and is a measure of low-coercivity (high values) to high-coercivity (low values) mineral concentration.

**The Day Plot and Theoretical Titanomagnetite Mixing Curves.** The Day Plot, introduced by Day et al. (1977), is an empirical tool used to visualize magnetic mineral grain size on an x-y scatterplot. Two ratios, $M_r/M_s$ (y-axis) and $H_{cr}/H_c$ (x-axis), are calculated and plotted. Single-domain (SD), pseudo-single-domain (PSD), and multi-domain (MD) fields were determined after measuring a range of synthetic titanomagnetite samples. SD titanomagnetites plot with $M_r/M_s > 0.5$ and $H_{cr}/H_c \approx 1 - 1.5$, MD titanomagnetites plot with $M_r/M_s < 0.05$ and $H_{cr}/H_c > 4$, and PSD titanomagnetites plot in between (Day et al., 1977).

Most environmental samples represent an assemblage of grain sizes and plot in the PSD range. This creates challenges in interpreting the data. For example, a mixture of SD-MD particles will plot in the PSD field even if no PSD grains are present (Dunlop, 2002a). Additionally, the Day Plot does not consider the contribution of very fine superparamagnetic (SP) grains, magnetostatic interaction of SD grains, and the non-
unique nature of each point (Heslop & Roberts, 2012 and references therein). Dunlop (2002ab) reassessed the Day Plot to better understand how mixtures of SD, PSD, MD, and SP grains plot, developing a series of theoretical mixing equations for $M_r/M_s$, $H_{cr}$, and $H_c$ based on synthetic titanomagnetite samples and applied to environmental samples. Using empirical data and observations collected from hysteresis loops, DC demagnetization curves, Curie temperatures, and the SEM-EDS, equation parameters can be determined and applied to Dunlop’s mixing equations in order to better understand the magnetic mineral assemblage present in the bulk sample measurements.

MATERIALS AND METHODS

Marine Sediment Core Samples

The marine sediment cores used in this study are part of a suite of cores collected during the NBP10-01 and NBP12-03 LARISSA cruises. Samples from these sediment cores were freeze-dried and packed into gelatin capsules.

The first section of this study focuses on cores collected from Barilari Bay, western AP (Figure 4). For all cores listed below, the thickness of the sample horizon is 1 cm. Samples from the NBP10-01 JPC126 core were taken every 20 cm from 1 to 161 cm and every 5 cm from 311–2146 cm. Additional samples were collected at 178 cm and 308 cm. To investigate sediments from inner Barilari Bay, select intervals were analyzed from sediment cores NBP10-01 KC54 and JPC125. Samples from NBP10-01 KC54 were taken every 1 cm. In depth analysis of diamict found in NBP10-01 KC54 focuses on 70-75 cm and 100-105 cm. Samples from NBP10-01 JPC125 were taken every 5 cm.
In depth analysis of turbidite sand found in NBP10-01 JPC125 focuses on 1780 cm – 1811 cm. Bulk samples from NBP10-01 JPC125, JPC126, and KC54 were also used.

The second section of this study focuses on a core from Perseverance Drift, a sediment drift located north of Joinville Island, northeast AP (Figure 30). Samples from NBP12-03 JKC36 were taken every 1 cm from 0 – 19 cm and every 2 cm from 20 – 518 cm.

χ₀f measurements of the gelatin capsules were made on an AGICO KLY-4 Kappabridge at an applied field of 300 A/m. The χ₀f presented here is the mean of three successive measurements.

χ(t) curves of bulk sediment were also measured on the Kappabridge in an argon atmosphere and an applied field of 300 A/m from intervals selected after observing the magnetic parameters of the entire core. In a few instances, curves were measured again without the argon atmosphere and are indicated in the text as such. The samples were heated from room temperature to 700°C and then cooled to 40°C. Order-disorder transitions were used to determine T_c and T_N. Samples with weak χ₀f had a more variable signal and a moving average was used to smooth the curves and identify features. Moving averages were calculated as the mean of the initial measurement and n measurements above and below. The moving averages are reported with an ma = (2n + 1).

Magnetic hysteresis parameters of the gelatin capsules were measured on a Princeton Measurements Corporation MicroMag 3900 Vibrating Sample Magnetometer (VSM), with a peak 1 T field. The raw hysteresis loops were mass-normalized and a diamagnetic/paramagnetic correction was calculated in the field between 700 mT and 1
T. Measurement averaging times were chosen based on the samples raw $M$ in a 1 T field, ranging from 100 ms to 1 s.

The VSM was also used to create a DC demagnetization of remanence curve, using an initial saturating field of 1 T and an increasing incremental back-field $H$ of -10mT. The $H_{cr}$ was determined from where $M = 0$ on the curve. The S-ratio was calculated on the VSM by first applying an initial saturating field of 1 T and then a back field $H$ of -300 mT.

For NBP12-03 JKC36, a log-likelihood SPSS 2-step cluster analysis of five parameters was used to compare core depth, $H_{cr}$, $H_c$, $M_r/M_s$, and the S-ratio, to categorize subtle differences in the magnetic parameters.

Bulk sediments from NBP10-01 KC54, JPC125 and JPC126 were sieved into three size fractions; 45 – 500μm, 500μm – 2mm and >2mm. The size fractions were dried in an oven at temperatures lower than 65°C. Sand- and gravel-sized lithic clasts from the 500μm – 2mm and >2mm fraction, where present, were prepared as grain mounts and thin sections. The thin sections were observed under a petrographic microscope to categorize the assemblage of lithologies present. Following this analysis, the thin sections were carbon coated for scanning electron microscopy.

Magnetic extracts were prepared from the 45 – 500μm fraction using a Franz magnetic separator at 20° in-field and 30° downslope angles and 0.4 amps. The magnetic extracts were then hand-picked under a binocular microscope for grains with metallic luster. The resulting grains were mounted in epoxy, polished, and carbon coated.

Heavy mineral extracts were prepared for select intervals from NBP10-01 JPC126 and NBP12-03 JKC36 from bulk freeze dried sediment, using sodium polytungstate with
a density of 2.88 g/cm$^3$. The heavy mineral extracts were mounted on carbon tape and carbon coated.

The thin sections, magnetic extracts, and heavy mineral extracts were analyzed using a Hitachi S-3400N scanning electron microscope (SEM) and Bruker X-flash energy dispersive spectrometer (EDS). For EDS analysis, a 15 keV accelerating voltage was used. Heavy mineral extracts were observed, imaged, and qualitatively analyzed using EDS. Quantitative EDS analysis was used on the polished epoxy-mounted magnetic extracts and thin sections, using the Bruker software standardless Phi-Ro-Z routine.

To establish solid solution grain chemistry of the 45-500 μm fraction magnetic extracts, point EDS analysis was performed on the homogenous, iron-rich regions of 50 unique Fe-Ti oxides grains. The chosen analyzed regions had to be large enough to minimize the impact of "contamination" due to x-rays contributed from adjacent titanium rich oxides, phosphates, and silicate minerals. Any spectra containing detectable contamination, such as Si or P peaks, were removed. For consistency, element selection was auto-selected by the Bruker software with a 1% weight concentration threshold. Although the existence of smaller element peaks and imperfection in the software is recognized, data presented here represents only elements present in a significant concentration (>1%) for reliable EDS analysis.

Analysis of the 2+ mm fraction thin sections used a two-step approach. First, EDS spectra were collected for a defined polygon to get a sense for whole grain chemistry. Then point EDS analysis was used on Fe-Ti oxides, iron sulfides, and some surrounding minerals to establish mineral chemistry. The 0.5-2 mm fraction was approached
similarly, but defining polygons for whole grain chemistry was limited to grains large enough to provide reliable data.

**Bedrock Samples**

Bedrock samples were loaned from the U.S. Polar Rock Repository (PRR) at the Byrd Polar Research Center, Ohio State University (sample details provided in Table 1 & Table 2). These samples were chosen based on proximity to core locations, availability of samples, and an attempt to represent regional lithologies. $\chi_f$ of the bulk rock samples were measured on the Kappabridge. Rock chips from the bulk sample were packed into gelatin capsules and immobilized with quartz Fiberfrax®. The $M_r$, $M_s$, $H_c$, $H_{cr}$, $\chi_{hf}$, and S-ratio were measured in the same manner as the sediment core samples using these gelatin capsules and the VSM. $\chi(t)$ was measured after grinding a portion of the rock sample to a fine powder. Small chips to be analyzed using the SEM-EDS were mounted in epoxy, polished, and carbon coated.

SEM-EDS analysis of the epoxy-mounted, polished rock chips were analyzed like the 2+ mm fraction thin sections from the sediment cores, with both polygon EDS analysis for general bulk chemistry and point analysis for mineral chemistry.

**STUDY AREA 1: BARILARI BAY**

**Regional Setting**

**Marine Survey Data**

Barilari Bay is a fjord located on the western AP, visited during the LARISSA NBP10-01 cruise (Figure 4). A suite of Holocene aged sediment cores was recovered
from Barilari Bay during this cruise (Domack, 2010). These include three jumbo piston cores and their associated trigger cores; JPC125 (JTC125), JPC126 (JTC126), and JPC127 (JTC127), from inner most to outermost bay, respectively; and four Kasten cores; KC54, KC42, JKC52, and JKC55, from inner most to outer most bay, respectively (Figure 5). Located on the western AP, the suite of cores has the potential to reflect the atmospheric and oceanographic influence of the Westerly Winds and the Antarctic Circumpolar Current.

The LARISSA ice-core site Beta, located on the Bruce Plateau, is located downwind 12 nautical miles to the southeast of Barilari Bay and provides the opportunity to correlate the atmospheric record of the ice core to the marine record from the Barilari Bay suite of sediment cores (Domack et al., 2012). The bay is also located at the same latitude and upwind of the former Larsen B ice shelf, building on the AP Holocene paleoclimatic context for the catastrophic break-up of the Larsen B ice shelf in 2002.

The bathymetry of Barilari Bay, charted by multibeam survey during NBP10-01, identifies a series of glacially carved basins and historic grounding lines. Figure 6 shows the profile along sediment core locations and shows that JPC126 was recovered from a separate basin than JPC125, KC42, and KC52 (Christ, 2011).

Historically, Barilari Bay was the southernmost drainage for ice into the Hugo Island Trough (Domack et al., 2010). Today, five named glaciers terminate in the bay—Otlet, Birley, Lawrie, Weir and Bilgeri glaciers. Offshore, to the west, is the Biscoe Islands Archipelago. This chain of islands includes Watkins Island, Lavoisier Island, Renaud Island, and the Pitt Islands, from south to north.
Correlation of NBP10-01 Barilari Bay sediment cores indicates a late Holocene glacial advance and formation of an ice shelf around the time of the LIA, with seasonally open marine conditions before and after this event (Elking et al., 2012; Figure 7). This ice shelf had collapsed prior to the first expedition to Barilari Bay, the French Antarctic Expedition 1903-1905, as seasonally open marine conditions were observed (Christ, 2011). Glacial fronts have remained relatively constant over observable history, with loss of small remainder ice shelves and the slight retreat of some calving fronts (Christ, 2011). This is in contrast to the observed retreat of most tidewater glaciers and ice shelves on the western AP over the past several decades (Cook et al., 2005).

Previous in-depth environmental magnetism study in Barilari Bay has focused on outer bay cores NBP10-01 JPC127 and JKC55, which contain a longer record of the Holocene (Natter, 2011). JKC55 holds a short record (62 cm) of a LIA event, similar in timing to the expression recognized in the Palmer Deep (Christ, 2011). This study focuses on the inner-middle bay, specifically NBP10-01 JPC126, to investigate a higher resolution record of only the past 1,000 years and uses JPC125 and KC54 to provide context of the local geologic setting of Barilari Bay.

**Bedrock Geology of the Barilari Bay Region**

The bedrock geology in and around Barilari Bay has not been extensively studied. Upper Jurassic volcanic rocks and the Upper Cretaceous-Lower Tertiary Andean Intrusive Suite rocks have been observed around the bay, as indicated in the AP geologic map (Aldie, 1969a/b; Figure 8). The bedrock geology in the bay itself is unknown; however, the general geology can be inferred based on the regional tectonic history.
Shallow marine sediments deposited during the late Paleozoic, mostly quartzose greywacke-shale sequences, were uplifted and metamorphosed to the greenschist and amphibolite facies, forming the Trinity Peninsula Series (Elliot, 1975 and references therein). These meta-sediments are unconformably overlain by Jurassic deposits, constraining the deformation to early Mesozoic (Elliot, 1975 and references therein). Upper Jurassic volcanic rocks likely form the core of the AP and are predominantly comprised of andesite and pyroclastics (Elliot, 1975 and references therein). Cretaceous intrusions, though not large enough to be considered batholiths, range from gabbro to alkali-granite and cross-cut the Trinity Peninsula Series, Jurassic strata, and Jurassic volcanics (Elliot, 1975 and references therein).

The geology of the Biscoe Islands, located directly west of Barilari Bay, is better studied. Outcrops are described as dominantly plutonic igneous rocks with Jurassic-Tertiary sedimentary, hypabyssal, and volcanic rocks at a few locations (Smellie et al., 1985). The plutonic rocks are mostly gabbros and diorites, likely members of the Andean Intrusive Suite and are observed cross-cutting the volcanic country rock throughout the island chain (Smellie et al., 1985). Notable exceptions include an observed volcanic neck that intrudes the plutonic bedrock on Pickwick Island, a member of the Pitt Islands, and the hypabyssal tonalitic Jinks Island Complex in the western Pitt Islands (Moyes, 1986).

Geologic terranes and metamorphic zones have been identified through use of magnetic anomaly geophysical surveys and field observations (Ferraccioli et al., 2006; Wendt et al., 2008). Barilari Bay sits on the boundary of two terranes, with the Mesozoic magmatic arc dominated Central Domain Western Zone to the west and the Trinity...
Peninsula Group Province Eastern Domain, representing the deformed Gondwanna continental margin, to the east (Ferraccioli et al., 2006).

The glacial drainage from the Eastern Domain terrane likely is dominated by greenstone to low amphibolite metasedimentary Trinity Peninsula Group, but also could include material from high amphibolite zone metasediments, orthogneisses, or igneous intrusions (Wendt et al., 2008; Wendt et al., 2012). However, bedrock samples from the Eastern Domain have the lowest mean magnetic susceptibility of any AP terrane, with the Trinity Peninsula series metasedimentary group among the weakest magnetic susceptibilities of any rock group on the AP (Wendt et al., 2012). Similarly, petrogenesis for Cretaceous and Jurassic intrusions in the Eastern Domain occurred when partial melts of crustal metasedimentary rocks created reducing conditions and formed dominantly ilmenite-series intrusions (Wendt et al., 2012). Therefore, source material from the Eastern Domain likely plays only a minor component in the environmental magnetism study of Barilari Bay sediments.

The Central Domain Western Zone, which includes the immediate vicinity around Barilari Bay and the Biscoe Islands, has the highest mean susceptibility values for measured rock samples of any AP terrane (Wendt et al., 2012). These high magnetic susceptibility rocks were formed when Cretaceous igneous intrusions were derived from partial mantle wedge melts, forming magnetite-series plutons under oxidizing conditions (Wendt et al., 2012). However, Jurassic intrusions in the Central Domain Western Zone are dominantly ilmenite-series, like those found in the Eastern Domain (Wendt et al., 2012). Therefore, source material from Cretaceous intrusions in the Central Domain
Western Zone is likely the greatest contributor to the detrital magnetic mineral assemblage found in Barilari Bay.

Results

Marine Sediment Core Samples

*NBP10-01 JPC126.* According to the core description, NBP10-01 JPC126 contains one interval affected by the coring process and two major depositional facies, which hereafter will be referred to as section 1, 2, and 3 (Figure 9). Section 1, 0 – 307 cm, contains water-rich sediment in which no sedimentary structures were preserved and for which there was zero recovery between 175-307 cm. Section 2, 307 – 1910 cm, is laminated silty mud, laminated silty clay, or homogenous silty mud with sections of graded turbidity sequences. This facies is interpreted as sub- or proximal ice shelf and sedimentation is largely controlled by glacial grounding line processes. Section 3, 1910 – 2146 cm, is a diatom-bearing pebbly sandy mud and is interpreted as a seasonally open marine facies.

*Low Field Magnetic Susceptibility.* $\chi_{lf}$ for NBP10-01 JPC126 is presented in Figure 10. The mean susceptibility for sections 1 and 2 are similar, $3.02 \times 10^{-6} \text{ m}^3/\text{kg}$ and $3.05 \times 10^{-6} \text{ m}^3/\text{kg}$, respectively, while section 3 is lower, $2.61 \times 10^{-6} \text{ m}^3/\text{kg}$.

The $\chi_{lf}$ of section 2 is characterized by susceptibility highs and lows, with peaks correlating to sand layers located at the base of turbidity current sequences, and the lows correlating with homogenous silty mud near the top of turbidity current sequences. A trend line created for section 2 shows a down-core positive slope, controlled by increasing amplitude of susceptibility peaks.
The $\chi_r$ of section 3 is characterized by a negative down-core trend line with two susceptibility peaks at 2021 cm and 2061 cm.

**Thermomagnetic Curves.** Thermomagnetic curves of select intervals in NBP10-01 JPC126 were normalized and classified into 6 groups according to heating and cooling curve characteristics (Figure 11). The curves represent samples from each section of the core and unique lithologies within. In these, intervals were chosen to represent high and low values of $\chi_r$, the S-Ratio, and distinctive hysteresis parameters. Multiple samples were chosen from the larger turbidites to investigate the hydrodynamic sorting of various magnetic minerals during deposition.

Group 1 consists of a single measurement from section 1: 1-2 cm. The heating curve and cooling curve are typical for the majority of samples in this core. The largest order-disorder transition occurs around 580 °C, the $T_C$ characteristic of magnetite. This transition is retraced by the cooling curve. At temperatures above the $T_C$, the sample no longer has a ferromagnetic signal, indicating the absence of hematite. At temperatures below the $T_C$, the cooling curve is mostly greater than the heating curve. There is a bump on the heating curve that peaks around 320 °C, indicative of the presence of magnetic iron sulfides.

Group 2 consists of nine measurements from section 2: 321 – 322 cm, 616 – 617 cm, 876 – 877 cm, 1051 – 1052 cm, 1126 – 1127 cm, 1161 – 1162 cm, 1451 – 1452 cm, 1511 – 1512 cm, and 1711 – 1712 cm. The heating and cooling curves are almost identical to group 1, with a $T_C$ around 580 °C and cooling curves that are greater than the heating curve. The major difference is the heating curve bump peaks occur at about 250 °C, suggesting a different magnetic iron sulfide assemblage.
Group 3 consists of four measurements from section 2: 466 – 467 cm, 986 – 987 cm, 1621 – 1622 cm, and 1671 – 1672 cm. These thermomagnetic curves are almost identical to group 2, with a $T_C$ around 580 °C, a bump peaking around 250 °C, and cooling curves greater than the heating curves. The major difference is the $\chi_{hi}$ of the heating curves continues to decrease above 580 °C, indicating the presence of hematite.

Group 4 consists of two measurements from section 3: 2086 – 2087 cm and 2141 – 2142 cm. These heating curves are similar to group 2, with a $T_C$ around 580 °C, bump peaking around 250 °C, and no hematite signal; however, the drop in $\chi_{hi}$ following the 250 °C bump is greater than in group 2 or 3. The cooling curve for one of these two measurements, 2086 – 2087 cm, retraces the initial heating curve.

Group 5 consists of two measurements from section 3: 1926 – 1927 cm and 2101 – 2102 cm. These two thermomagnetic curves are different, but are grouped together because they both share a similar hematite signal at high temperatures. 1926 – 1927 cm has a slightly higher $T_C$ than those observed in groups 1 – 4, around 590 °C, but shares the 250 °C bump with groups 2 and 3. It also has a cooling curve that is greater than the heating curve. 2101 – 2102 cm has a similar 580 °C $T_C$ when compared with groups 1 – 4, has a 250 °C bump as described in group 4, and has a cooling curve that is less than the heating curve.

Group 6 contains thermomagnetic curves unlike any others in the core and consists of two measurements from section 3: 2021 – 2022 cm and 2066 – 2067 cm. 2021 – 2022 cm has a two-step decrease in $\chi_{hi}$, first a gradual decrease between about 225 °C and 430 °C and then a sharp decrease at about 575 °C. For this sample, the cooling curve is less than the heating curve. While, 2066 -2067 cm shares the slightly higher 590 °C $T_C$ with
1926 – 1927 cm, has a large bump at about 320 °C, has the characteristic hematite signal, and has a cooling curve greater than the initial heating curve.

**Hysteresis Loops, DC Demagnetization of Remanance Curves, and S-Ratios.** Pearson correlation coefficients (PCC) calculated for the three sections of NBP10-01 JPC126 comparing hysteresis loop parameters, $H_{cr}$, and the S-ratio to $\chi_f$ are presented in Table 3, mean values of the magnetic parameters for each section are presented in Table 4, and plots of magnetic proxies are presented in Figure 12. PCC values proved to be especially useful in the interpretation of this core, as the correlation between $\chi_f$ and other magnetic properties indicate a stark contrast in the depositional regimes.

Section 2 has a high PCC comparing the grain-size dependent ratios, $M_r/M_s$ and $H_{cr}/H_c$ (-0.84 and 0.86, respectively), to $\chi_f$. This is opposite to section 3, which has low PCC for these two parameters (-0.28 and 0.30, respectively). Therefore, large magnetic mineral grain size has a stronger correlation with high $\chi_f$ in section 2, than in section 3.

When plotted on a Day Plot, NBP10-01 JPC126 plots mostly in the PSD range (after Day et al., 1977; Figure 13). The mean values of each section indicate than on average, section 3 has the coarsest magnetic grain assemblage; however, individual measurements of samples from the base of turbidity sequences from section 2 are the coarsest bulk grain assemblages in the core. When compared to theoretical SD/MD mixing curves for magnetite, samples from JPC126 plot to the right, along a similar regression curve (after Dunlop, 2002).

PCC values between $M_s$ and $\chi_f$ are very high and positive throughout the core (0.99), as both are ferromagnetic mineral concentration dependent.
S-ratio and χIf PCC is low and negative (-0.29) throughout the core, suggesting the concentration of high-coercivity minerals have little correlation with either high or low χIf. However, the S-ratio trend line has a negative slope down core, indicating a decrease in the S-ratio and an increase in high coercivity mineral concentration down-core.

χIf has a strong negative PCC with χIf through section 2 (-0.84), suggesting lows in the χIf are the result of low ferromagnetic mineral concentration and high paramagnetic concentration. Meanwhile, there is a low negative PCC through section 3 (-0.28) and if the χIf peaks, at 2021 and 2061 cm, in section 3 are removed, there is a positive PCC (0.21). This suggests lows in the χIf through most of section 3 are related to low ferromagnetic mineral concentration, low paramagnetic concentration, and an implied higher diamagnetic concentration.

**NBP10-01 KC54.** Analysis of NBP10-01 KC54 focused on two intervals, 70 – 75 cm and 100 – 105 cm, comprised of diamict from inner Barilari Bay. Mean values for magnetic parameters of five samples from each interval are presented in Table 5, and likely represent the unsorted magnetic mineral assemblage local to inner Barilari Bay.

*Magnetic Parameters.* Mean Mr/Ms and Hcr/Hc (0.062 and 4.09, respectively) indicate these samples are coarser than the mean grain size for section 1, 2, or 3 in JPC126, and plot just outside of the PSD region on the Day plot (Figure 13). Mean S-ratio is slightly greater than one, indicating no significant concentration of high coercivity minerals.

Thermomagnetic curves for KC54 intervals, 70 -71 cm, 73 -74 cm, 100 – 101 cm, and 103 – 104 cm, have similar Tc to thermomagnetic curves in the majority of JPC126.
intervals (Groups 1-5), with almost no bump between 200 and 400 °C, cooling curves greater than the heating curves, and no hematite signal (Figure 14).

**NBP10-01 JPC125.** Analysis of NBP10-01 JPC125 focused on one interval, 1781 – 1805 cm, representing a sand turbidite-deposit. Mean values for magnetic parameters of five samples are presented in Table 5, and likely represent the sorted, coarser fraction, magnetic mineral assemblage local to inner Barilari Bay.

*Magnetic Parameters.* Mean $M_r/M_s$ and $H_{cr}/H_c$ (0.061 and 4.11, respectively) indicate these samples are coarser than the mean grain size for section 1, 2, or 3 in JPC126, and very similar to KC54, plotting just outside of the PSD box on the Day plot (Figure 13). Mean $H_c$ and $H_{cr}$ values for JPC125 (4.90 mT and 20.25 mT, respectively) are less than mean $H_c$ and $H_{cr}$ values for KC54 (7.16 mT and 29.34 mT, respectively), consistent with coarser titanomagnetites (Day et al, 1977). This suggests that although the mean grain size of the ferromagnetic mineral assemblage in KC54 and JPC125 are similar, the JPC125 samples are composed of a well-sorted, coarser assemblage. Mean S-ratio is slightly greater than one, indicating no significant concentration of high coercivity minerals.

Thermomagnetic curves from JPC125 intervals, 1790 cm and 1800 cm, have a $T_c$ identical to thermomagnetic curves from intervals in KC54 and the majority of JPC126, a slight bump peaking around 270 °C, cooling curves greater than the cooling curves, and a hematite signal (Figure 15).

**SEM-EDS and Petrographic Microscope Analysis.** To complement the environmental magnetic analysis, samples were analyzed using an SED-EDS and
petrographic microscope, looking at magnetic extracts, heavy mineral extracts, and grain-mount thin sections.

**Grain Mount Thin Sections.** Observations of grain mount thin sections, prepared from 0.5-2 mm and 2+ mm lithic fragments, under a petrographic microscope indicate that sedimentary and metasedimentary rocks are the dominant source material for the coarse fraction in Barilari Bay (Figure 16). Given the difficulty of determining metamorphic fabric in sand size grains and the inclusion of quartz grains with undulatory extinctions in very low grade or non-metamorphosed conglomerates, metasedimentary and sedimentary rocks are grouped together. It is likely they represent Paleozoic Trinity Peninsula Series and Jurassic strata, respectively. Nevertheless, comparison of relative lithic fragment abundance, grouped as sedimentary/metasedimentary, felsic plutonic, intermediate plutonic, mafic plutonic, and volcanic, are fairly consistent for the five samples, representing inner-middle bay diamict, a turbidity current sand deposit, and seasonally open marine facies.

The majority of lithic fragments greater than 2 mm from inner bay diamict indicate low-grade metamorphism, with the common presence of chlorite, and/or hydrothermal alteration. Certain metasedimentary grains are an exception and display distinct metamorphic fabric. These are interpreted as members of the Paleozoic Trinity Peninsula Series. These large clasts provided the opportunity to observe examples of the sub-ice bedrock geology local to Barilari Bay.

The sedimentary/metasedimentary lithologies in the 0.5 – 2 mm and 2+ mm diamict size fraction do not share consistent assemblages of Fe-Ti oxides and iron sulfides. Observed assemblages include only rutile, rutile/pyrite, rutile/ilmenite,
rutile/pyrrhotite/Fe-oxide, only ilmenite, pyrite/Fe-oxide, only Fe-oxide, or none of the above. In many cases these minerals are associated with chlorite or titanite and may reflect the degree of metamorphic alteration. Fe-oxides, when present, in all but one sedimentary lithology exist mostly on grain boundaries and appear to be formed by authigenic or metamorphic alteration (Figure 17). In these cases, the Fe-oxides do not appear as inclusions in sedimentary clasts and do not have a crystalline/detrital appearance.

One sedimentary lithology, a well-sorted quartz or subarkose siltstone, is different from the others with respect to Fe-oxides (Figure 18). Up to 40 μm detrital magnetite or titanomagnetite grains are abundant, with TiO₂ weight percent ranging from 0 to ~5%. The lithology is found in all middle-inner bay facies samples.

Volcanic grains in the 2+ mm diamict size fraction are rare. Two volcanic clasts of andesitic composition were observed, one from the 70-75cm interval and one from the 100-105cm interval. Both contain ilmenite as the only Fe-Ti oxide, with ~3-6.5% MnO.

Other volcanic grains are found in the 0.5 – 2 mm fraction samples. Of note are Fe-oxide bearing intermediate and mafic volcanic grains. The mafic Fe-oxide bearing volcanic grains are more common than the intermediate Fe-oxide bearing grains and contain abundant homogenous, composite, trellis, and exsolved type Fe-oxides. These volcanic types are present in all inner-middle bay facies and only contain Fe-oxides less than 40 μm in size.

Plutonic grains, for the most part, do contain large Fe-oxide crystals and are the only lithology observed to contain Fe-oxides greater than 45 μm. Felsic plutonic grains are the most common in the diamict samples, but intermediate and mafic compositions are also
found. Felsic plutonic rocks come in two varieties, one coarser-grained and one finer-grained. The finer grained variety displays more metamorphic alteration. The Fe-oxides contain little TiO$_2$, ranging from 0 – 3%, and are cracked along crystal planes. The coarser grained felsic plutonic grains display less metamorphic alteration. Fe-oxides with no TiO$_2$ are found in some, but not all of these coarser plutonic grains. Ilmenite is more common and mostly observed independent of the Fe-oxide, but in a couple cases as a composite-style grain.

Intermediate plutonic grains were rare, but when observed contained homogenous, trellis, or composite style Fe-oxide with ilmenite. The mafic plutonic rocks contained complex Fe-Ti oxides with composite, trellis, and exsolved structures and some low-grade metamorphic alteration. Observed TiO$_2$ weight percent ranged from 0 - ~10%. Pyroxene is often observed as inclusions within the Fe-oxides.

*Magnetic Extracts.* The magnetic extracts for Barilari Bay, prepared from the 45-500 μm lithic fragments, were observed using reflected light microscopy and SEM-EDS to establish the assemblages present in the dominant inner-middle bay facies. The intervals used were intervals that yielded sufficient magnetic extract during the separation. As a result, there is a bias. In the turbidity current dominated facies, the intervals represent sand layers at the bottom of turbidite sequences and not the homogenous fine-grained near the top. Similarly, in the seasonally open-marine facies, the interval used was one with significant ice rafted debris. The characterization was performed using two methods: EDS analysis of homogenous grain regions to define solid solution mineral chemistry and reflected light microscopy to define mineral morphologies.
EDS analysis of homogenous grain indicates a typical assemblage for inner-middle Barilari Bay with respect to solid solution Fe-oxide chemistry for all major facies (Figure 19). The majority of grains (44-64 %, depending on the facies) have EDS spectra that indicate pure Fe-oxide. TiO₂ + V₂O₃ weight percent, a proxy for identifying likely mafic plutonic source rocks (Grigsby, 1990), varies widely in the remaining grains, but has a similar distribution trend for all samples.

Grain morphologies were classified into five categories for each sample: homogenous, exsolved-types, composite-types, trellis-types, and others (Figure 20). The totals were plotted on a ternary diagram with homogenous, exsolved types, and composite/trellis-types as the three axes (Figure 21; after Grigsby, 1990). The result is a cluster, where all facies cluster around what is typical for Barilari Bay. Given the known local geology, the Fe-oxide solid solution chemistry and the morphologies, the magnetic extract samples are consistent with a mostly felsic plutonic source and mafic plutonic contribution.

Weathering and oxidation along grain cracks and edges was noticed on some grains while observing all grains under reflected light.

Heavy Mineral Extracts. Carbon tape mounted heavy mineral extracts allow for qualitative observation of Fe-Ti oxides and iron sulfides in JPC126. Four intervals were observed: three from the sub/proximal ice shelf facies (616-617cm, 1126-1127cm, 1431-1432cm) and one from the seasonally open marine facies (2101-2102cm).

Fe-Ti oxides are abundant and vary in grain size, morphology, and composition (Figure 22). Framboidal pyrite is observed in all intervals, indicating some degree of iron
dissolution and diagenesis in both facies. Iron sulfides that appear massive and weathered are identified as detrital and are also present.

**Polar Rock Repository Samples**

**The Northern Biscoe Islands.** Analysis of two PRR samples from Snodgrass Island, in the Pitt Islands (Figure 4), looked at a gabbro, PRR-06230, and a volcaniclastic rock, PRR-06231. Magnetic parameters are presented in Table 6.

Both samples have weak $\chi_f$. The $\chi_f$ of the volcaniclastic rock, $2.307 \times 10^{-7}$ m$^3$/kg, is similar to $\chi_f$ observed in volcanic rocks in the southern Biscoe Islands. The $\chi_f$ of the gabbro, $2.034 \times 10^{-7}$ m$^3$/kg, is significantly less than the $\chi_f$ of plutonic rocks to the south.

Hysteresis loops also indicate a low concentration of ferromagnetic minerals. The ferromagnetic minerals that are present plot in the PSD field on the day plot and have S-ratios that suggest no significant concentration of high-coercively minerals (Figure 23). Thermomagnetic curves for these two samples are very similar and suggest magnetite as the dominant ferromagnetic mineral, with finer grained magnetite in the volcaniclastic sample (Figure 24).

Potential small Fe-oxide, about 0.5-1 μm, were observed as inclusions in titanite (CaTiSiO$_5$) in the volcaniclastic sample during SEM-EDS analysis (Figure 25). However, due to the small crystal size, smaller than the electron beam interaction volume, contaminants from the titanite are present in the EDS spectrum, making a definitive analysis of the Fe-oxide impossible. Still, the presence of small, rare magnetite crystals in the volcaniclastic sample are consistent with hysteresis and thermomagnetic
curves. Ilmenite and rutile are abundant in the gabbro sample, intergrown with titanite, but no iron-rich oxides were observed.

**The Southern Biscoe Islands.** Samples of five PRR samples from islands near Watkins Island (grouped from hereon as simply Watkins Island) and Belding Island can be grouped into two categories. The first are the plutonic rocks and include a gabbro (PRR-06041) and tonalite (PRR-06046) from Watkins Island and a gabbro (PRR-16387) from Belding Island (Figure 4). The second group contains volcanic/sedimentary rocks and includes a volcaniclastic (PRR-06049) and a volcaniclastic chert (PRR-06052) from Watkins Island. Magnetic parameters of these samples are presented in Table 7.

The plutonic samples from the Southern Biscoe Islands have the strongest $\chi_{df}$ of the Biscoe Islands bedrock samples, with $\chi_{df}$ ranging from $1.16 \times 10^{-5}$ m$^3$/kg to $3.59 \times 10^{-5}$ m$^3$/kg. The volcanic bedrock samples have weak $\chi_{df}$ similar to the northern Biscoe Island samples.

The hysteresis parameters for the plutonic bedrock samples indicate coarse, MD ferromagnetic minerals with an S-ratio that suggests no significant concentration of high-coercivity minerals (Figure 23). Thermomagnetic curves have large order-disorder transitions; with the gabbro samples initial $T_C$, $\sim$565 °C, slightly lower than the tonalite sample $\sim$575 °C. The Belding Island gabbro sample has a second $T_C$ around 585 °C (Figure 26).

Large 100+ $\mu$m Fe-Ti oxides were observed during SEM-EDS analysis of the Southern Biscoe Island plutonic bedrock. The tonalite sample contained homogenous, pure magnetite, associated with apatite, with no observed titanium rich oxides. Both gabbro samples contained composite-type or exsolved magnetite and ilmenite. The
majority of EDS spectra indicate pure magnetite, with some indicating low concentrations of titanium. Some of these titanium peaks may be related to sub-micron exsolution texture; however, EDS spectra from clearly homogenous regions indicate some solid solution titanomagnetite. EDS spectra for all measured ilmenites contained about 2-3 weight percent manganese. Iron sulfides were also present in the Belding Island and Watkins Island gabbro, where EDS spectra is consistent with paramagnetic pyrite in both samples and chalcopyrite at Belding Island.

The hysteresis parameters for the volcanic/sedimentary bedrock samples indicate low concentration of PSD ferromagnetic minerals and S-ratios indicate little concentration of high coercivity minerals. Thermomagnetic curves indicate magnetite as the dominant mineralogy; although, some of the magnetite signal observed is likely due to the alteration of another mineral while heating (Figure 27).

No evidence for magnetite was found while observing these volcanic samples during SEM-EDS analysis. The only Fe-Ti oxide found is tentatively identified as elongated <7 μm 50-50 solid solution ilmenite-pyrophanite ((Fe, Mn)TiO₃) and exists in both the chert and volcanioclastic.

**Barilari Bay Discussion**

This study of the Barilari Bay area furthers our understanding of the distinct depositional facies represented in NBP10-01 JPC126 and investigates the sub-ice geology of the glacial drainage area. Four radiocarbon dates, calibrated using CALIB 6.0 software and the MARINE09 database (Reimer et al., 2009) with a preliminary ΔR value of 860 (Berkman & Forman, 1996; Gordon & Harkness, 1992), indicate that JPC126
contains a ~1,000 year record, with the transition between the sandy, pebbly mud and homogeneous silty mud occurring at a minimum of 850 yr BP or around 1100 AD (Eugene Domack, Hamilton College, unpublished data; Figure 28). However, depleted $^{14}$C in the ocean around Antarctica, makes identifying an appropriate reservoir age difficult and this date must be treated with some uncertainty (Gordon & Harkness, 1992). Other limitations of the age model include no account for the variation in sedimentation rate within section 2 between the grounding line driven rhythmic laminations and the larger turbidite deposits and no account for change in sedimentation rate between the sub/proximal ice shelf and seasonally open marine facies. Using this age model, the most recent sediment (0-1 cm) is dated at ~1660 AD. It is likely that a significant portion of the recent sediment was lost due to coring disturbance; however, this date is likely erroneously old and again does not consider the possibility of slower sedimentation following glacial retreat.

The environmental magnetic record of JPC126 indicates different depositional regimes during the sub/proximal ice shelf facies (section 2) and the seasonally open marine facies (section 3). $\chi_f$ and $\chi_{hf}$ values show a negative correlation in the concentration of paramagnetic minerals and ferromagnetic minerals in the sub/proximal ice shelf facies. Hysteresis parameters suggest that coarser grained magnetic minerals are concentrated at the susceptibility peaks. These observations are consistent with hydrodynamic sorting of minerals and interpreted as deposition dominated by glacial grounding line processes, where movement of the grounding line due to diurnal/fortnightly tidal periods, storm events, and/or grounding line advance/retreat.
trigger sudden deposition events. These events are manifested as the mm-scale rhythmic laminations and larger graded turbidites.

The presence of an ice shelf during this period is supported by consistently uniform thermomagnetic curves, indicating little variation in magnetic mineralogy. These curves match the inner bay KC54 diamict and JPC125 turbidity current sand, supporting this mineralogy as local to Barilari Bay. The presence or absence of the hematite signal at temperatures greater than 600 °C is likely a weathering product and does not likely reflect the sediment provenance. Oxidation rims around magnetite grains, observed on the 45-500 μm magnetic extracts using reflected light microscopy, suggest the weathering occurred following erosion of the bedrock; however, it is uncertain if these rims are related to a transport or post-depositional process. These oxidation rims were not observed on magnetite in the 0.5-2 mm lithic fragments.

Other proxies also support the presence of an ice shelf during this period, including low TOC, low TN, and low IRD (Elking et al., 2012). Interestingly, diatoms are present and relatively abundant through section 2, although not as abundant as in section 3 (Amy Leventer, Colgate University, unpublished data). This suggests that the JPC126 core site is located near the ice shelf edge and diatoms are advected under the ice shelf from nearby open water (Amy Leventer, personal communication).

The seasonally open marine facies, section 3, is represented in the environmental magnetic record as dilution of ferromagnetic and paramagnetic minerals, and thus a positive correlation between $\chi_{\text{ir}}$ and $\chi_{\text{hr}}$, by a diamagnetic component, interpreted as biogenic sedimentation. Also, hysteresis parameters indicate the average magnetic mineralogy is coarser in section 3 than section 2, reflecting the increased contribution of
IRD (Elking et al., 2012). The change in hysteresis parameters is consistent with a change from sorted grounding-line dominated sedimentation to steady melt water plumes, variable IRD, and increased primary productivity. Higher TOC and TN concentrations are observed in this interval (Elking et al., 2012) and total diatom counts are five times greater or more than section two (Amy Leventer, Colgate University, unpublished data).

Thermomagnetic curves are largely similar in section 3 as those found in section 2, again suggesting the magnetic mineralogy is dominated by what is typical for Barilari Bay. However there are some notable differences in section 3, especially at the 2021-2022 cm and 2066-2067 cm $\chi_f$ peaks. These peaks, based on their thermomagnetic curves, are interpreted as containing a terrigenous component from a source atypical of Barilari Bay. This suggests that although the vast majority of the IRD is likely sourced to glaciers terminating in the bay, some IRD may have been delivered from an external source. Alternatively, the atypical mineralogy could indicate a supraglacial IRD component derived from bedrock further inland. Attempts to source this variation in provenance through studying lithic fragments from inner-middle bay facies proved inconclusive, as the coarse fraction of JPC126 seasonally open marine sediments appeared to have lithological and Fe-Ti oxide assemblages characteristic of Barilari Bay.

The down core decreasing S-ratio trend is likely related to diagenetic enrichment of high-coercivity magnetic minerals. Framboidal pyrite is observed though the core indicating sulfate reducing diagenesis of iron; however, pyrite, in itself, does not indicate magnetite dissolution (Canfield & Berner, 1986). Reductive diagenesis and magnetite dissolution seem to have a minimal impact on the environmental magnetic record, with
only small expressions in thermomagnetic curves and perhaps a contribution to the coarser magnetic mineral grain size in section 3.

This expression of glacial advance to sub/proximal ice shelf conditions around 1100 AD is interpreted as a significant climatic change in the last 1,000 years. The conclusion of the seasonally open marine conditions preceding this transition corresponds to the end of the MWP. It is interesting to note that the $\chi_f$ increases and diatom counts decrease towards this transition, suggesting a gradual decrease in primary productivity. However, even though the timing of the end of the MWP is consistent with northern hemisphere records, it is difficult to call this the MWP without the context of older sediment.

If 1100 AD is also interpreted as the onset of the LIA, it would indicate an earlier LIA in Barilari Bay than the high resolution record of the western AP Palmer Deep, beginning ca 1250 AD (Domack et al., 2001; Shevenell et al., 2011), or the onset recognized in the northern hemisphere. This could be associated with the difficulties surrounding radiocarbon dating on the AP. However, if we assume that the higher $\chi_f$ peaks and larger turbidite sequences are associated with large glacial grounding line advances rather than tidal or storm related movements, there is evidence for a second grounding line advance preceding 1430 AD and following 1250 AD (Figure 10; Figure 29). $\chi_f$ amplitudes increase near the base of section 2, where the ~1100 AD grounding line advance that alters the depositional regime is interpreted. Similar, but smaller turbidite peaks are present between 800 and 1000 cm, suggesting the possibility of a smaller grounding line advance between 1300 and 1400 AD. This is supported by low diatom counts in the core between 700 and 1000 cm, possibly indicating a larger ice-shelf and further distance between the JPC126 core location and open water.
The sub-ice geology within the Barilari Bay drainage area is dominated by Trinity Peninsula Series and Mesozoic (~Jurassic) sedimentary strata, consistent with the Eastern Domain deformed Gondawana margin terrane. However, these units do not contribute significant magnetic minerals to the marine sediments found in JPC126. The central domain western zone accreted Cretaceous magmatic arc intrusions, and the large PSD-MD Fe-oxides they contain, are the primary influence on the environmental magnetic record. Within Barilari Bay, felsic intrusive bedrock is more common than mafic intrusive bedrock. This is consistent with geochemical observation from the outer bay NBP10-01 JPC125, which also found core sediments to contain a provenance record from a felsic source (Natter, 2011).

Major variation in provenance in NBP10-01 JPC126 is only suggested at two intervals in the seasonally open marine facies, 2021-2022 cm and 2066-2067 cm, by thermomagnetic curves and spikes in the $\chi_r$. The cause of this variation was not observed during petrographic or SEM-EDS observation. Nevertheless, this could suggest pulses of IRD external to Barilari Bay. However, the source of the IRD or the mechanism for delivery (i.e. the westerly winds, the northern flowing Antarctic circumpolar current, the southern flowing Antarctic Peninsula Coastal Current, etc.) is unknown. Alternatively, the variation could reflect supraglacial debris derived from further upstream.
STUDY AREA 2: PERSERVERANCE DRIFT

Regional Setting

*Marine Survey Data*

Perseverance Drift is the unofficial name for a sediment drift located north of Joinville Island, northeast AP, visited for the first time on cruise LMG04-04 to investigate if sediment drifts form when tidal/geostrophic currents slow at channel openings on the Antarctic shelf (Domack, 2004; Figure 30; Figure 31). The sediment drift is located in the Larsen Channel Trough at the eastern opening of the Larsen Channel, between Joinville and d'Urville Islands (Domack, 2004). A kasten core, LMG04-04 KC3, was recovered from the drift in 2004. A second kasten core, LMG04-04 KC16, was also recovered from this same general region (Perez et al., 2005, 2007), but following new seismic profiling is now known to be from a sedimentary basin separate from the drift (Vernet, 2012).

Perseverance Drift was revisited during the LARISSA NBP12-03 cruise, when a more extensive, although incomplete, multi-beam and seismic survey was conducted, revealing a complex bottom with sediment accumulated to at least 90 m in thickness (Vernet, 2012; Figure 32). A jumbo kasten core, NBP12-03 JKC36, and a 24+ m jumbo piston core, JPC36, were recovered at this time.

The cores collected from Perseverance Drift have the potential to be important in high-resolution Holocene paleoclimatic interpretation of the AP, as they represent rapidly accumulating sediments and have abundant carbonate shells for establishing a geochronology (Vernet, 2012). Perseverance Drift also lies in the path of cold Weddell Sea water that flows westward around the tip of the AP and into the Bransfield Straight,
offering the ability to compare the timing of variations in this current during the late Holocene to other regional records.

Additionally, NBP12-03 JKC36 and JPC36 were found to contain the authigenic mineral ikaite (CaCO$_3$$\cdot$6H$_2$O), which is only found on the northeast tip of the AP even though similar organic-rich biosiliceous sediments are common in AP bays and fjords (Domack et al., 2007; Lu et al., 2012; Vernet, 2012). Ikaite is only stable at cold temperatures and its formation may be associated with the presence of cold Weddell Sea water. The formation of ikaite is closely related to pore water geochemistry and elevated levels of dissolved inorganic carbon (Lu et al., 2012). The detailed pore water geochemistry of these cores provides context for the study of the magnetic mineral assemblages and sulfide driven iron diagenesis and provides the unique opportunity to investigate paleo-pore water conditions.

**Bedrock Geology of the Joinville Island Area**

Joinville Island lays in the deformed Gondwana margin Eastern Domain terrane and is a continuation of the geology found on the northeast tip of the AP (Figure 33; Elliot, 1967; Ferraccioli et al., 2006). The bedrock succession is typical for the AP and includes Paleozoic (~Carboniferous) metasedimentary Trinity Peninsula Series, Lower-Middle Jurassic Conglomerate Beds, Upper Jurassic Nordenskjöld Formation, Upper Jurassic Volcanics, Cretaceous-Tertiary Andean Intrusive Suite, and minor Tertiary intrusions (Elliot, 1967; Farquharson, 1983). Some volcanic outcrops visible on the southern coast are believed to be more recent and related to the Miocene James Ross Island Volcanic Group (Elliot, 1967). Bedrock geology for the nearby d’Urville Island, located north of
the Larsen Channel, has not been studied. Small offshore islands, the Wideopen Islands and Etna Island to the north and the Danger Islands to the southeast, are composed of Cretaceous mafic Andean Intrusive Suite plutons (Elliot, 1967; Hamer & Hyden, 1984; Grunow, 1993).

The Trinity Peninsula Series metasedimentary rocks are the dominant bedrock on Joinville Island and the Lower-Middle Jurassic Strata are mostly shallow water conglomerates composed of Trinity Peninsula Series clasts (Elliot, 1967). Similar metasedimentary rocks from the Eastern Domain were found to have some of the lowest magnetic susceptibilities on the AP (Wendt et al., 2012). Hematization of the Trinity Peninsula Series is observed in a few locations (Elliot, 1967). Attempts to use sedimentary rocks from Joinville Island for paleomagnetic studies proved to be unsuccessful, as they contained multicomponent and inconsistent magnetizations (Grunow, 1993).

The Upper Jurassic volcanic rocks are andesitic to rhyolitic in composition (Elliot, 1967). On the north coast of Joinville Island at King Point, dykes are observed with plagioclase phenocrysts and Fe-oxides in the matrix, although these have not been dated (Elliot, 1967). The sedimentary Nordenskjöld formation is also dated to the Upper Jurassic and likely continued to the early Cretaceous (Farquharson, 1983). Deposition of these radiolarian rich mud-stones occurred in a calm anoxic basin and features frequent ash/tuff deposits (Farquharson, 1983).

Outcrops of dioritic-gabbroic Andean Intrusive Suite are visible on the southern coast of Joinville Island, near and on the Mount Alexander peninsula, and on the Wideopen Islands, Etna Island, and the Danger Islands (Elliot, 1967; Hamer & Hyden, 1984;
Grunow, 1993). Field observation suggests that these outcrops are part of a larger layered mafic intrusion and it is believed that Andean Intrusive Suite, although not exposed, intrudes much of the Trinity Peninsula Series through southern Joinville Island (Elliot, 1967). A gabbro sample from Etna Island is described to contain titanium rich Fe-oxides (Elliot, 1967). Other samples from the area reveal small Fe-oxide inclusions in plagioclase crystals (Elliot, 1967). Study of the Danger Island pluton suggests hydrothermal alteration and, while Fe-oxides are still present, skeletal ilmenite is observed (Hamer & Hyden, 1984). Geochemical analysis of the Danger Island pluton indicates derivation from subcontinental mantle with probable volatiles from the ocean floor (Hamer & Hyden, 1984). Samples from the Wideopen Islands, the Danger Islands, and Mount Alexander contain magnetic mineral assemblages that have successfully been used in paleomagnetic studies (Watts et al., 1984; Grunow et al., 1993). These observations suggest that these mafic Andean Intrusive Suite plutons likely play the largest role in local sedimentary detrital magnetic mineral assemblages in the Joinville Island area.

Results

Marine Sediment Core Samples

**NBP12-03 JKC36.** NBP12-03 JKC36, a 5.18 m kasten core, is a dark, organic-rich, sediment core that smells strongly of hydrogen sulfide. The core degassed significantly after recovery, with the gas assumed to be methane based on later analysis of pore fluids. The core was described onboard ship (by collaborator Dr. Amy Leventer, Colgate University) immediately after recovery. The sediment is described as diatomaceous mud
containing mm-scale laminations, streaks, and patches of dark, organic material from 0 - 350 cm. The interval from 196 - 203 cm is described as a lighter grayish olive diatomaceous mud with laminae and 205 cm is described as a moderate olive brown silty mud with sharp contacts. The core becomes increasingly mottled with evidence for bioturbation below 350 cm, although laminae are still observed at some intervals. Calcareous shells are found throughout the core and are most abundant below 350 cm. Four authigenic ikaite crystals were found at 303-305 cm, 463-465 cm, 479-481 cm, and 505 cm. Large, visible foraminifera were observed in the cutter nose at depths below 518 cm.

Interpreted zones for JKC36 are based on preliminary pore water geochemistry (courtesy of Dr. Mike McCormick, Hamilton College, unpublished data), \( \chi_{lf} \) measurements, and SPSS 2-step cluster analysis of five parameters; core depth, \( H_c \), \( H_r \), \( M_r/M_s \), and the S-ratio (Figure 34; Figure 35). It is important to note that sulfate (\( SO_4^{2-} \)) concentration in the pore water geochemistry is not yet available and error for methane (\( CH_4 \)), sulfide (\( S^{2-} \)), and dissolved ferrous iron (\( Fe^{2+} \)) have not yet been calculated. Therefore, the zones described here may be modified when analysis of pore water geochemistry is complete. The zones are: zone 1 from 0-32 cm, zone 2a from 34-86 cm, zone 2b from 88-130 cm, zone 3a from 132-328 cm, and zone 3b from 330-518 cm.

Low-field Magnetic Susceptibility. The most notable \( \chi_{lf} \) feature is a sharp decline in values from 0 – 40 cm, with a 0-1 cm value of 1.04 x 10\(^{-6}\) m\(^3\)/kg and a 40-41 cm value of 4.18 x 10\(^{-7}\) m\(^3\)/kg. This is followed by lower values of variable \( \chi_{lf} \) from 40 – 320 cm with a mean value of 4.07 x 10\(^{-7}\) m\(^3\)/kg. 320 – 518 cm is marked by slightly higher \( \chi_{lf} \) values and continued variation with a mean value of 4.98 x 10\(^{-7}\) m\(^3\)/kg.
Hysteresis Loops, DC Demagnetization of Remanence Curves, and S-Ratios. The sharp decline in $\gamma_f$ in from 0–32 cm (zone 1) is accompanied by 'coarsening' of the grain size dependent parameters, $M_r/M_s$ and $H_c/H_{cr}$, interpreted as down core removal of finer detrital titanomagnetite and potentially the addition of an authigenic SP component (Figure 36). $\chi_{hf}$ also rapidly decreases through this section, indicating decreasing concentrations of iron-bearing paramagnetic minerals.

$H_{cr}$ remains relatively consistent from 34 cm through 130 cm. This is opposed to $H_c$ which has low values from 34-86 cm (Zone 2a) and high values from 88-130 cm (Zone 2b). This drives the $H_{cr}/H_c$ ratio up from 34-86 cm and is likely caused by the presence of an SP component from 34-86 cm and a minimal or absent SP component from 88-130 cm.

$H_{cr}/H_c$ values indicate variable concentration of SP grains through 132-518 cm (section 3). Distinct horizons, with $M_r$, $H_{cr}$, and $H_c$ values peaking at 206-207 cm and 442-443 cm, indicate high concentrations of SD grains. It is likely that an authigenic SD component is present elsewhere throughout 132-518 cm (section 3) in low, variable concentration.

132-328 cm (Zone 3a) grain size parameters, in the context of SP-independent $H_{cr}$, indicate a detrital titanomagnetite component similar to 32-130 cm (Zone 2). From 330-518 cm (Zone 3b), $H_{cr}$ and $M_r/M_s$ values are lower, indicating a 'coarser' assemblage of non-SP grains.

The Day Plot is difficult to interpret for this core due to effects of SP grains on both $M_r/M_s$ and $H_{cr}/H_c$ ratios (Figure 37). Bulk $M_r/M_s$ are diluted by the non-remanence bearing SP fraction, where
Bulk $H_c$ values are also diluted while $H_{cr}$ values are unaffected by the SP component, driving the $H_{cr}/H_c$ ratio up. Bulk $H_c$ is calculated as:

$$H_c(\text{Bulk}) = H_c(\text{SD+PSD+MD}) \times \frac{\%_{(SD+PSD+MD)} \times \chi_{(SD+PSD+MD)}}{\chi_{(SD+PSD+MD)} + (\%_{(SP)} \times \chi_{(SP)})}$$

or

$$H_c(\text{Bulk}) = H_c(\text{SD+PSD+MD}) \times \left(1 - \frac{\%_{(SP)}}{\%_{(SD+PSD+MD)}} \frac{M_r/M_s}{(SD+PSD+MD)}\right)$$

Bulk $H_{cr}$ is calculated as:

$$H_{cr}(\text{Bulk}) = H_{cr}(\text{SD/PSD/MD})$$

The subscript SD+PSD+MD represents only the non SP, remanence-bearing fraction. As a result of these properties, a companion plot, $M_r/M_s$ vs. $H_{cr}$, is presented to better visualize grain size distribution of the non-SP component (Figure 38).

**Thermomagnetic Curves.** Thermomagnetic curves of selected intervals from JKC36 are variable due to their weak $\chi_f$ signal. In addition, a cyclic artifact is introduced by Mallory Hall's electrical power supply and is present in the curves. As a result, a moving average ($ma = 7$) was used to smooth all curves and remove the artifact.

The thermomagnetic curves for JKC36 are complex. They likely reflect multiple order-disorder transitions, unblocking of fine grained magnetic minerals, the destruction of some magnetic minerals (e.g. maghemite inverting to hematite), and/or the creation of others during the heating process (e.g. iron sulfides oxidizing to magnetite).

To track overall creation or destruction of magnetic minerals while measuring the thermomagnetic curves, the $\chi_f$ at 100 °C for the heating curve was subtracted from the same temperature on the cooling curve. These values were plotted down core (Figure...
Intervals measured from 0-31 cm have cooling curves less than their heating curves, indicating destruction of magnetic minerals. This interval correlates with the sharp decline in $\chi_f$ and the 'coarsening' of the hysteresis parameters. Measurements made at and down core of 40-41 cm all have cooling curves greater than their heating curves, indicating the creation of magnetic minerals.

Next, to identify intervals of significant change (ISC), the first derivative was calculated and plotted for each normalized heating curve. Local minima and local maxima were recorded and four ISCs were determined by where inflection point clusters exist. ISC1 is an interval with a positive derivative and represents the 220-280 °C. ISC2, ISC3, and ISC4 are intervals with negative derivatives and represent 350-375 °C, 435-490 °C, and 560-585 °C, respectively. The average derivatives were calculated for each one of these intervals and are plotted down core to track the relative contribution to $\chi_f$ gains or losses at each heating interval (Figure 40).

To take a closer look at destruction and creation of magnetic minerals and the intervals of significant change, select intervals were measured a second time without an argon atmosphere to study how the samples respond to heating in an oxygen-rich atmosphere (Figure 41). Heating curves are strikingly similar, indicating no difference in magnetic mineral creation or destruction in the initial heating. On the other hand, cooling curves are consistently greater without the argon atmosphere, suggesting greater magnetic mineral creation at high temperatures. Also, a new feature in the cooling curve only previously present on the 100-101 cm is introduced, suggesting the creation of pyrrhotite in the oxygen-rich atmosphere.
These observations suggest the presence of magnetite, possible maghemite in or out of solid solution with magnetite, and iron-sulfide. Magnetite, with a $T_c \sim 580 \, ^\circ$C and tracked by ISC4, is present in highest concentrations at 0-1 cm and declines in concentration quickly between 0 and 41 cm. It is important to note that throughout the core ISC4 could be influenced by alteration magnetite produced from iron-bearing minerals and conversion of maghemite to hematite.

Maghemite is identified by the cooling curves that are less than the heating curves from 0 – 41cm with and without an argon atmosphere. This occurs as a result of the instability of maghemite at high temperatures where maghemite converts to stable hematite (Gehring et al, 2009). This process contributes to the steady decline in $\chi_{df}$ at temperatures above 400 °C, tracked by ISC3 and ISC4. The $T_c$ of maghemite, believed to be at or in excess of $\sim 615 \, ^\circ$C, is not observed at any interval due to this destruction (Gehring et al, 2009).

Unblocking temperatures of finer-grained magnetite minerals, either maghemite, magnetite, or magnetic iron sulfide, tracked by ISC1, indicate lower rates of change down core. ISC1 decreases from 10 to 41cm indicating decreasing concentration in finer-grained magnetic minerals through this interval. Measurements from 50 – 250 cm are higher and more variable than the consistently lower ISC1 values from 300 – 500 cm, indicating less influence of finer-grained magnetic minerals in the 300 – 500 cm interval. The temperature, above 200 °C, at which the peak $\chi_{df}$ occurs is tracked through the core and indicates a shift to higher temperatures down core (Figure 42). This is interpreted as a shift of these peaks being influenced by unblocking or fine-grained detrital magnetite/maghemite assemblage to the authigenic iron-sulfide assemblage.
The gap between ISC3 and ISC4 are likely due to the creation of magnetite from iron sulfide at temperatures ~500 °C (Tudryn & Tucholka, 2004). As the concentration of iron sulfides increases and the concentration of the detrital assemblage, more magnetite is created from the iron sulfide than maghemite converted to hematite. This is manifest in the cooling curves becoming increasingly greater than the heating curves through the top 41 cm of the core. The high temperature $\chi_{hf}$ behavior of the magnetic iron sulfide greigite is consistent with thermomagnetic curve observations with and without the argon atmosphere (Roberts, 1995; Roberts et al., 2011; Tudryn & Tucholka, 2004). However, these curves alone are not diagnostic of greigite.

**SEM-EDS Observation of Heavy Mineral Extracts.** Heavy mineral extracts for four intervals, 0-1 cm, 148-149 cm, 206-207 cm, and 450-451 cm, were prepared and mounted on carbon tape for qualitative SEM-EDS analysis.

Detrital Fe-oxide grains are common in the 0-1 cm heavy mineral extract and almost completely absent in the other three intervals (Figure 43). When rare detrital Fe-Ti oxides are present in the 148-149 cm, 206-207 cm, and 450-451 cm, they indicate significant iron dissolution and have a pitted morphology. In the 148-149 cm interval, dissolution of detrital Fe-Ti oxides is observed with replacement by authigenic iron sulfide (Figure 44).

Iron sulfides are present in both detrital massive and authigenic framboidal form in every interval (Figure 45). An unidentified iron sulfide is observed in two instances in the 148-149 cm, appearing authigenic and growing as platy crystals (Figure 45a). It is possible these are authigenic antiferromagnetic pyrrhotite due to their apparent hexagonal crystal structure, but quantitative chemical EDS analysis is not possible for this
unpolished sample. Presence of framboidal iron sulfide in the 0-1 cm interval suggests anoxic conditions at the sediment-water interface. Authigenic iron sulfide is more abundant in the 148-149 cm, 206-207 cm, and 450-451 cm samples.

In the 206-207 cm interval, ~1 μm octahedral iron sulfide crystals were observed next to a broken iron-sulfide framboid and are interpreted as authigenic ferrimagnetic single-domain greigite (Figure 46). This interval corresponds with observed \( H_c \) and \( M_r \) peaks, consistent with elevated concentrations of ferrimagnetic single-domain crystals.

**LMG04-04 Smith-McIntyre Grab Samples.** The \( \chi_r \) of surface sediments collected with a Smith-McIntyre Grab (SMG) were plotted and the values were interpolated to establish a sense of the magnetic susceptibility gradient for surface sediments in the Larsen Channel, Larsen Trough, and Perseverance Drift (Figure 30). The results indicate highest \( \chi_r \) values at the Larsen Channel with values decreasing towards the northeast. The lowest values exist north of Ambush Bay. It is worth noting that this was created using only 11 samples and could be significantly improved with more grab samples.

**Polar Rock Repository Samples**

**Joinville Island and Patella Island Sedimentary and Volcanics.** The majority of PRR samples from Joinville Island are identified by the PRR as ~Jurassic Nordenskjöld formation or coeval volcanics, with timing established by field relationships. The sandstone sample from Patella Island is grouped with these Joinville Island rocks, due to its proximity and similarity. The diorite sample from the Mount Alexander peninsula is discussed separately as it is unique compared with the other Joinville Island samples.
In general, these sedimentary and volcanic samples have weak magnetic susceptibilities, with hysteresis loops and thermomagnetic curves that suggest the magnetic signals are dominated by paramagnetic minerals. In most cases, the $\chi_{hf}$ representing only the diamagnetic and paramagnetic susceptibility, constitutes the majority of the $\chi_f$ signal.

SEM-EDS analyses of the sedimentary samples show abundant pyrite, iron-rich clay minerals, and rutile. One sample, PRR-20553, a shale from Ambush Bay, contains an authigenic Fe-oxide/phosphate precipitate. This sample has a relatively strong $\chi_{lf}$, $1.36 \times 10^{-7}$ m$^3$/kg, when compared with other sedimentary or volcanic samples from Joinville Island and a low S-Ratio, 0.75, supporting the presence of a hematite alteration product (Table 9). Fe-oxides are not observed elsewhere in these samples.

The andesite sample from King Point is different from the other samples in this category, in that it has a strong $\chi_{lf}$, $2.22 \times 10^{-6}$ m$^3$/kg for the region (Table 9). Present as blocks that crop out in the Nordenskjöld formation, this andesite is consistent with the Upper Jurassic volcanic group. Hysteresis parameters indicate a finer PSD grain size and the S-ratio and the thermomagnetic curve indicate (titano)magnetite as the dominant mineralogy (Figure 47). Rutile, pyrite, and an altered ilmenite were observed during SEM-EDS observation. It is likely the altered ilmenite has exsolved in to rutile and Fe-rich oxide zones, but this exsolution structure is smaller than the interaction volume of the electron beam.

For all samples in this category, thermomagnetic cooling curves are much greater than their heating curves due to the alteration of iron-bearing minerals, like clays and iron sulfides, to magnetite with heating.
**Mount Alexander Pluton.** The diorite sample from the Mount Alexander Peninsula is not likely a direct source of sediment for Perseverance Drift, but this or associated plutons probably intrude other parts of the Trinity Peninsula Series on Joinville Island (Elliot, 1967). Although definitive timing of this intrusion is not established, the diorite and associated gabbro bedrock on the Mount Alexander Peninsula are believed to be ~90 Ma and considered to be late Cretaceous Andean Intrusive Suite (Grunow, 1993). The relatively low magnetic susceptibility value, at $2.40 \times 10^{-7} \text{ m}^3/\text{kg}$, indicate reducing conditions for the parental magma and associate this intrusion with other Eastern Domain Cretaceous ilmenite-series plutons formed when magmatic intrusions interacted with partial melts from the metasedimentary-dominated crust (Wendt et al., 2012; Table 9).

SEM-EDS analysis shows abundant ilmenite and an iron sulfide with EDS spectra consistent with pyrrhotite. In some cases, the pyrrhotite displays partial alteration to an Fe-oxide (Figure 48). Infrequent ~2 µm Fe-oxide inclusions in plagioclase crystals are also observed; however, definitive EDS analysis is limited by the beam interaction volume and “contamination” from the plagioclase host.

The thermomagnetic curve reveals a distinct drop in $\chi_f$ at ~330 °C in the heating curve and a cooling curve significantly greater than the heating curve, supporting the presence of ferrimagnetic pyrrhotite. There is a second heating curve order-disorder transition indicative of magnetite, although it is difficult to determine how much magnetite is created due to the alteration of pyrrhotite and other iron-bearing minerals versus how much was originally present. At temperatures greater than 600 °C, there is a continued decline in $\chi_f$, suggesting the presence of hematite, likely present due to the subaerial weathering of iron-bearing minerals.
On the Day Plot, the diorite sample plots on the finer end of the PSD range, supporting the contribution of a fine-grained magnetite component, such as SD or fine PSD inclusions in plagioclase crystals (Figure 47). The S-ratio is 0.82, supporting the presence of a high-coercivity mineral, like hematite.

**Wideopen Island and Heroína Islands.** The gabbro samples from the Wideopen Islands and Heroína Island (Danger Islands) have distinctly different magnetic properties (Table 10). The Danger Islands gabbroic pluton is dated at 89 ±11 Ma and the Wideopen Islands pluton is also believed to be ~90 Ma, placing these plutons as members of the Cretaceous Andean Intrusive Suite (Hamer & Hyden, 1984; Grunow, 1993). Both samples have very strong $\chi_0$ for the region, with $5.70 \times 10^{-6} \, m^3/kg$ for the Wideopen Islands sample and $1.74 \times 10^{-6} \, m^3/kg$ for the Heroína Island sample. However, these susceptibilities are not strong enough to be grouped with the magnetite-series plutons of the Central Domain Western Zone, suggesting petrogenesis similar to the weaker-$\chi_0$ Mount Alexander pluton (after Wendt et al, 2012).

Both samples plot in the PSD region on the Day Plot, with the Heroína Island sample plotting in the upper left, suggesting a finer grain size assemblage, and the Wideopen Islands sample plotting in the lower right, suggesting a coarser grain size assemblage (Figure 47). S-ratios are at or close to one, indicating no significant concentration of high-coercivity minerals.

Unlike the Mt. Alexander Diorite, pyrrhotite is not observed in either of these samples. However, large titanium rich Fe-oxides are abundant. Both samples have Fe-Ti oxides that show signs of hydrothermal alteration, also observed during Hamer & Hyden’s petrological study of the Danger Island pluton (1984).
The Wideopen Islands gabbro contains large Fe-Ti oxides with dendritic alteration from hydrothermal fluids (Figure 49). Solid solution TiO₂ weight percent, ~25%, is high for these Fe-Ti oxides.

The Heroina Island gabbro contains large Fe-Ti oxides, although with a very different morphology than those found in the Wideopen Island Gabbro. The structure contains large ilmenite laminae and iron rich zones with high, ~20%, TiO₂, in solid solution (Figure 50). Iron appears to be removed from hydrothermal fluids along grain cracks, leaving rutile where ilmenite existed and calcite in empty spaces. Ilmenite is abundant elsewhere in the sample and the most common Fe-Ti oxide observed.

SEM-EDS observation of the Heroina Island gabbro did not positively identify a fine-grained magnetic component that would explain the hysteresis properties of this sample. However, if true SD magnetite was present as inclusions, it would be below the SEM-EDS resolution.

The thermomagnetic curves for both of these samples are inconclusive, due to a large degree of alteration of both the magnetic minerals and other iron bearing minerals with heating. The increase in \( \chi_f \) below 200 °C, especially in the Heroina Island gabbro, could be explained by the presence and alteration of ferrihydrite in these highly weathered samples.

**Perseverance Drift Discussion**

An SPSS two-step cluster analysis was conducted using core depth, \( H_c \), \( H_{cr} \), \( M_r/M_s \), and the S-Ratio as parameters. \( H_c \) and \( H_{cr} \) were treated separately as each parameter responds differently to the contribution of an SP component. \( H_c \) values, measured in the
presence of an applied field, are strongly affected by SP concentration, which reduces $H_c$, where $H_{cr}$ is a remanence-based parameter, measured in a zero applied field, and is not affected by SP grains (Dunlop, 2002a). Four unique clusters were identified and mean magnetic parameter values for each cluster are summarized in Table 8 (box and whisker plots of the clusters are presented in Figure 35). Cluster 1 has values typical of a detrital titanomagnetite dominated assemblage. Cluster 2 has values that reflect the detrital component in cluster 1 with an additional SP component. Cluster 3 has values that indicate contribution of a fine SD component. Cluster 4 has values that indicate a coarser detrital component than cluster 1 and an additional SP component. These assemblages were used to mark magnetic mineral assemblage changes in the context of pore water geochemistry determined zones 1, 2 and 3. Zone 2a is dominated by cluster 2, while zone 2b is dominated by cluster 1. Zone 3a is dominated by cluster 2, while zone 3b is dominated by cluster 4.

The environmental magnetic signature of NBP12-03 JKC36 is governed by intense sulfate reduction, a rapid sedimentation rate, dissolution of iron-bearing minerals, and authigenic paramagnetic/ferrimagnetic iron sulfide formation. Therefore, it is important to consider these factors first in order to interpret this core and, ultimately, associated cores' paleoclimatic expressions. Additionally, magnetite dissolution and digenesis is a direct reflection of pore water chemistry, specifically sulfide concentrations, and observed characteristics of magnetite, such as pyrite replacement or degree of dissolution, can serve as a better proxy for paleo-pore water conditions than sedimentary pyrite alone (Canfield & Berner, 1986).
Two radiocarbon dates are available from the nearby ~2.5 m LMG04-04 KC3 (Eugene Domack, Hamilton College, unpublished data), and are used to establish an approximate 0.5 cm/yr sedimentation rate for the area and, using this rate, a rough age model for JKC36 (Figure 28). Once dated, abundant calcareous shell fragments recovered from JKC36 will provide a robust chronology. At that point, the age model used in this study should be discarded.

Zone 1 of JKC36, 0 – 32 cm, represents a sharp decline in $\chi_{fr}$ associated with a 6.5x increase in sulfide concentration. Sulfide is produced during bacterially driven sulfate reduction reactions and migrates up core to react with soluble, reactive ferrous iron. In JKC36, sulfide concentrations exceed dissolved ferrous iron concentrations within the top 10 cm, indicating the crystalline iron dissolution of detrital minerals begins very close to the sediment water interface and within the first 20 years of deposition. Thermomagnetic curves indicate decreasing relative concentrations of magnetite down core through zone 1. This is also reflected in the $\chi_{fr}$ decline, indicating the dissolution of detrital iron-oxides, and 'coarsening' of the hysteresis parameters, indicating the removal of finer-grained detrital magnetite. It is likely that the formation of SP ferrimagnetic iron sulfides also contributes to the apparent 'coarsening' of the hysteresis parameters.

Zone 2 of JKC36, 34 – 130 cm, is dominated by sulfidic pore water chemistry and $\chi_{fr}$ values indicate that the significant magnetite dissolution observed in zone 1 has ceased. Sulfide concentration peaks in this interval due to upwelling of methane from deeper in the core, supplying abundant organic carbon to drive sulfide producing bacterial reactions, and also due to the limited reactive iron. $H_c$ values are fairly consistent through zone 2, while $H_c$ values are lower in zone 2a versus 2b. This can be explained by
the presence of SP ferrimagnetic iron sulfides in 2a that form as intermediates to pyrite in sulfate reducing sediments. By zone 2b, these SP ferrimagnetic iron sulfides have reacted with pore water sulfide and become stable paramagnetic pyrite. Limited reactive iron limits the production of new intermediary SP grains.

Zone 3, 132 – 518 cm, has methane dominated pore water geochemistry, marking a decline in sulfide concentration and an initial rise in dissolved ferrous iron. Limited sulfide allows for the creation and preservation of authigenic ferrimagnetic iron sulfides, like greigite, as the formation of pyrite is incomplete. For the majority of zone 3, these iron sulfides mostly exist as SP grains in variable concentration. Two horizons are identified where SD greigite is present in significant concentration (Figure 36). It is possible that SD greigite are present elsewhere in zone 3, in lesser concentration.

Magnetite dissolution is a function of sulfide concentration, magnetite grain size, and magnetite concentration (Canfield & Berner, 1986). The relationship between these three can be explained by the following equation:

\[
\frac{dC_{mag}}{dt} = kC_s^{0.5}C_{mag}A_{mag}
\]

where \(C_{mag}\) is the concentration of magnetite, \(t\) is time, \(k\) is the rate constant, \(C_s\) is the concentration of sulfide, and \(A_{mag}\) is specific surface area of the magnetite present (Canfield & Berner, 1986). To establishing the paleo-sulfide concentrations in JKC36, we first must calculate the rate constant. To do so, we make two assumptions for the source material. First, that the detrital concentration of Fe-oxides are constant with time. Second, that the grain size of detrital Fe-oxides are constant with time.

The concentration of magnetite is calculated by dividing the \(M_s\) of the bulk sediment by the \(M_s\) of pure magnetite (90 Am²/kg). This is imperfect because this assumes that the
Ms signal only represents magnetite. Thermomagnetic curves and hysteresis observations also indicate the presence of magnetic iron sulfides and maghemite. However, for simplicity, the concentration of magnetite at time zero is calculated at 0-1 cm, while the concentration of magnetite following dissolution is an average of the modern sulfidic zone, following the magnetite dissolution front (40-130 cm). The specific surface area of the magnetite present is given a value of 1, following our assumption that the original detrital grain size does not change over time. The modern concentration of sulfide is also given a value of 1.

After calculating k, the rate constant, the down core magnetite concentrations are calculated and smoothed with an 80 year moving average to account for the ~80 years it takes to dissolve detrital magnetite at this core location and to smooth decadal variation unrelated to pore water geochemistry. The equation is solved for Cₛ and values represent relative paleo-sulfide concentrations (where 1 is the equivalent of the modern value).

These calculations show two-fold fluctuations in paleo-sulfide concentration, with a distinct period of higher than modern sulfide concentration from ca 1350 – 1820 AD and lower sulfide concentration before ca 1350 AD (Figure 51). Given the core description, one of the driving factors for this variation in pore water sulfide is bioturbation. Canfield & Berner showed that given all other things equal, bioturbation can account for a 50% reduction in sulfide concentration due to increased exchange of pore water with sea water below the sea floor (1986). Therefore, since χₘ largely represents the concentration of ferrimagnetic minerals, 80+ year variations could reflect intensity of bioturbation.

Similarly, pyrite coated detrital Fe-Ti oxides are only observed in the 148-149 cm heavy mineral extract, which indicated pyrite replacement and is another indicator for
very high sulfide concentrations (Canfield & Berner, 1986; Figure 44; Figure 45c). These types of grains were not observed in the 450-451 cm heavy mineral extract, consistent with lower concentrations of sulfide.

Hysteresis parameters indicate a coarser detrital assemblage in zone 3b than in zone 3a, corresponding with the higher susceptibility, and calculated lower sulfide concentrations. It is possible that pyrite replacement of magnetite in zone 3a preserved finer grained magnetite (after Canfield & Berner, 1986). Where, although zone 3b experienced less overall magnetite dissolution, the lack of pyrite replacement means that no finer grained magnetite was preserved.

This hypothesis of paleo-sulfide variations needs to be tested by further study of JKC36, especially investigation of the variation in depositional conditions over time. Similarly, the change in $\chi_{lf}$ and magnetic grain-size parameters could also be explained by strong bottom currents winnowing finer grained material in zone 3b more than in zone 3a. Down core sediment grain size data will ultimately help with this problem.

However, if we consider the role of variation in sulfide concentrations as the driving force in centennial variation of magnetic parameters, the transition from low to high sulfide concentration is interpreted either as related to a force or response to a climatic shift within the last 1,000 years. This potential expression of the LIA, manifested as decreased bioturbation from benthic productivity, ca 1350 – 1820 AD, suggests decreased levels of dissolved oxygen and nutrients in bottom water. However, it is impossible to say at this time if this is related to variation in primary productivity, upwelling of cold nutrient-rich Weddell Sea Deep Water, or another factor.
Another aspect of this core worth further investigation are the elevated concentrations of authigenic SD greigite at 206-207 cm and 442-443 cm. The SD greigite horizon at 206-207 cm indicates a significant amount of greigite forming relatively quickly following deposition (within ~400 years). Also, at this 206-207 cm interval, a layer of moderate olive brown silty mud with sharp contacts, versus the black to olive mud in the rest of the core. This suggests that whatever causes this change in physical characteristic is related to the formation of elevated SD greigite concentrations. If this is an oxidation layer, is there a relationship between non-soluble ferric iron and greigite, in that higher concentrations of ferric iron reduce to ferrous iron later, increasing dissolved ferrous iron concentration in the menthanic zone? Or in this layer the product of an animal burrow, driving sulfide concentration down due to increasing mixing with ocean water and again increasing concentrations of preserved ferrous iron in the menthanic zone?

The source material for sediment in JKC36 also requires further investigation. Dissolution and alteration of the majority of detrital Fe-oxides limits this provenance study. However, it seems apparent that the sedimentary strata and the majority of volcanic rocks studied on Joinville Island play a minimal role in the magnetic signatures of Perseverance Drift sediments. The magnetic susceptibility gradient interpolated from SMG surface samples indicates higher $\chi_f$ values towards the Larsen Channel, which could suggest a major source for the magnetic minerals found in Perseverance Drift originate in sediment transported from the west through the Larsen Channel (Figure 30). It is also worth further investigation of the role of characteristic Fe-Ti oxides in the mafic plutons found at the Wideopen, Etna, and Danger Islands as potential indicators of
sediment transported by other means from the north or east, such as by the Weddell Sea/Bransfield Straight Surface Water.

**INTEGRATED ANTARCTIC PENINSULA DISCUSSION**

Presented in this study are the analyses of two very different high resolution marine sediment cores that reflect a response to change in climatic conditions around the AP during the first half of the last 1,000 years. One core, from a fjord on the Western AP, NBP10-01 JPC126 from Barilari Bay, indicates a change in depositional regime due to grounding line advance around 1100 AD and likely again between 1300 and 1400 AD, shifting from a seasonally open marine to sub/proximal ice shelf conditions. The second core, from an organic rich sediment drift off the northeastern AP, NBP12-03 JKC36 from Perseverance Drift, indicates a change in the magnetic mineral assemblage around 1350 AD likely due to increased pore water sulfide concentrations indicative of decreased bioturbation.

These observations are significant, as the presence of a LIA event in the southern hemisphere and its relationship with the northern hemisphere LIA is subject to great debate and is poorly studied (Bentley et al., 2009). Abrupt climate changes and the driving mechanisms behind them in the last millennium are important to provide context for the rapid changes observed in recent history on the AP and around the world. Although this analysis does not answer all these questions, it affirms the need to continue study of these expressions, both at the Barilari Bay and Perseverance Drift study locations and in other high resolution sediment cores from the AP.
Driving forces on climate change along the western AP, like the Barilari Bay study site, are influenced by southern/northern migrations in the westerly winds, which deliver warmer air from mid-latitudes, and upwelling of warm circumpolar deep water on to the continental shelf. A southern migration of the westerly winds is cited as one of mechanisms of the recent warming and has likely played a role in previous warming periods (Bentley et al., 2009). NBP10-01 JPC126 offers an expression of the response (i.e. glacial advance) and timing of the climatic shift; however, this analysis finds little in clues for the driving mechanisms. However, the two pulses of ice rafted debris with magnetic mineral assemblages atypical of the local fjord geology, as identified through thermomagnetic curves, may offer clues to the ocean or atmospheric patterns in the warm pre-1100 AD period after determining their source.

The northeastern AP is also likely influenced by changes in the westerly winds, but rather than reflecting warm circumpolar deep water, this location likely reflects the role of upwelling cold Weddell sea bottom water, southern migration of sub-polar water, and/or the Weddell Sea/Bransfield Straight surface water. This study’s interpretation of the environmental magnetic signature of NBP12-03 JKC36 indicates variation in pore water sulfide concentrations due to changes in benthic productivity, likely related to bottom water conditions, during the last 1,000 years. It is difficult to determine if this is a mechanism (e.g. the introduction or retreat of a nutrient rich/poor water mass) or a response of the colder conditions recorded on the western AP, but further analysis of core properties will help with this problem.

The timing of these transitions are different than the onset of the LIA identified in the Palmer Deep (~1250 AD). This could be the result of limitations in the age models used
and the uncertainty in radiocarbon dating around the AP, as discussed earlier. It could also be the result of each study site manifesting the LIA through different expressions, in that first glacial grounding lines advanced (as recorded in Barilari Bay), then regional records are influenced by cooler temperatures (as recorded in the Palmer Deep), and finally the regional cooling alters ocean circulation resulting in a change in bottom water conditions around the northeastern AP (as recorded in Perseverance Drift). Alternatively, these differences in timing could be explained by a northward migration of the warm westerly winds or circumpolar deep water, impacting Barilari Bay (65.9° Latitude) by 1100 AD, the Palmer Deep (64.9° Latitude) by 1250 AD, and Perseverance Drift (63.2° Latitude) by 1350 AD.

CONCLUSIONS

This study finds expressions of a significant climatic shift from warmer to colder conditions around the northern AP between 1100 and 1350 AD. These are manifested in the environmental magnetic signature of two high resolution sediment cores from geographically different locations and very different depositional settings, supporting the controversial case for a LIA like event on the AP occurring fairly synchronously with the well document LIA event in the northern hemisphere. However, this study is not able to determine the driving mechanisms of this event. However, the interpretations made here indicate:

- Evidence for grounding line advance ca. 1100 AD in Barilari Bay, western AP, in the change of magnetic mineral distribution indicating a change in the depositional regime.
• Grounding line instability in Barilari Bay, interpreted as a second major advance ca. 1300 – 1400 AD, potentially indicating the onset of the furthest ice extent.

• Pulses of ice rafted debris in middle Barilari Bay atypical of the fjord’s local geology during the highly productive, seasonally open marine conditions prior to ca. 1100 AD.

• A change in bottom water conditions in Perseverance Drift ca. 1350 AD, reflected in a change in the magnetic mineral assemblage due to the degree of magnetite dissolution from pore water sulfide. Decreased bioturbation from ca. 1350 to 1800 AD limited exchange of pore water with ocean water, elevating sulfide concentrations significantly.

Additionally, this study finds environmental magnetic techniques as powerful tools in interpreting the terrigenous component in Antarctic glacial marine systems. Magnetic mineral distributions in grounding line driven depositional environments, like NBP10-01 JPC126, offer a method to study grounding line behavior. Magnetic mineral assemblages in high accumulation, organic-rich sediments offer insight into paleo-pore water conditions. Further study of these proxies will allow for even greater insight into the paleoclimate of the Antarctic Peninsula.
AKNOWLEDGEMENTS

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<td>PRR-06041</td>
<td>Watkins Island, Biscoe Islands</td>
<td>Gabbro</td>
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<td>Medium grained diorite-gabbro. Small island 8 km SW of Watkins Is.</td>
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<td>PRR-06046</td>
<td>Watkins Island, Biscoe Islands</td>
<td>Tonalite</td>
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<td>Black and white fine grained tonalite. Small island SW of Watkins Is. and ~1 km NNE of PRR-06041.</td>
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<td>PRR-06230</td>
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<td>Black, fine-medium grained gabbro.</td>
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<td>PRR-16387</td>
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Table 2. Joinville Island area Polar Rock Repository samples (adapted from PRR database at http://bprc.osu.edu/rr/).

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<td>PRR-16328</td>
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<td>Diorite</td>
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<td>Sandstone includes thin shaley horizons.</td>
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<td>Nordenskjold Formation. Clast in conglomerate.</td>
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<tr>
<td>PRR-20549</td>
<td>Wideopen Islands</td>
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<td>Strongly jointed gabbro which weathers readily. Composition: plagioclase-pyroxene-opaques.</td>
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Table 3. NBP10-01 JPC126 Pearson correlation coefficients, compared with $\chi_{lf}$.

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<th>Section 1</th>
<th>Section 2</th>
<th>Section 3</th>
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<tr>
<td>$M_r$</td>
<td>0.1745</td>
<td>0.6565</td>
<td>0.8189</td>
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<tr>
<td>$M_s$</td>
<td>0.9908</td>
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<td>0.9886</td>
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<tr>
<td>$M_r/M_s$</td>
<td>-0.9409</td>
<td>-0.8352</td>
<td>-0.2778</td>
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<td>$H_c$</td>
<td>-0.9344</td>
<td>-0.8265</td>
<td>-0.1456</td>
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<tr>
<td>$H_{cr}$</td>
<td>-0.8564</td>
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<td>$H_{cr}/H_c$</td>
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<td>$X_{hf}$</td>
<td>-0.9409</td>
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<td>S-ratio</td>
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<td>-0.4858</td>
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<td>-0.2911</td>
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Table 4. NBP10-01 JPC126 mean values of magnetic parameters.

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<th>Whole Core</th>
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<td>$X_{hf}$ (m$^3$/kg)</td>
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<td>3.04E-06</td>
<td>2.61E-06</td>
<td>2.99E-06</td>
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<td>$M_r$ (Am$^2$/kg)</td>
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<td>0.0383</td>
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<td>$M_s$ (Am$^2$/kg)</td>
<td>0.3613</td>
<td>0.1810</td>
<td>0.3042</td>
<td>0.3546</td>
</tr>
<tr>
<td>$M_r/M_s$</td>
<td>0.103</td>
<td>0.110</td>
<td>0.101</td>
<td>0.109</td>
</tr>
<tr>
<td>$H_c$ (mT)</td>
<td>11.39</td>
<td>12.21</td>
<td>11.05</td>
<td>12.04</td>
</tr>
<tr>
<td>$H_{cr}$ (mT)</td>
<td>37.87</td>
<td>37.94</td>
<td>36.27</td>
<td>37.73</td>
</tr>
<tr>
<td>$H_{cr}/H_c$</td>
<td>3.34</td>
<td>3.16</td>
<td>3.30</td>
<td>3.19</td>
</tr>
<tr>
<td>$X_{hf}$ (m$^3$/kg)</td>
<td>1.29E-07</td>
<td>1.38E-07</td>
<td>1.27E-07</td>
<td>1.37E-07</td>
</tr>
<tr>
<td>S-ratio</td>
<td>0.965</td>
<td>0.963</td>
<td>0.942</td>
<td>0.961</td>
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Table 5. NBP10-01 KC54 (diamict samples) and JPC125 (turbidite sand samples) mean values of magnetic parameters.

<table>
<thead>
<tr>
<th></th>
<th>NBP10-01 KC54</th>
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<th>NBP10-01 JPC125</th>
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<tr>
<td></td>
<td>70 – 75 cm</td>
<td>100 – 105 cm</td>
<td>Both Sections</td>
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<tr>
<td>$X_m$ (m³/kg)</td>
<td>2.94E-06</td>
<td>2.84E-06</td>
<td>2.90E-06</td>
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<tr>
<td>$M_r$ (Am²/kg)</td>
<td>0.0203</td>
<td>0.0203</td>
<td>0.0203</td>
</tr>
<tr>
<td>$M_s$ (Am²/kg)</td>
<td>0.3260</td>
<td>0.3251</td>
<td>0.3255</td>
</tr>
<tr>
<td>$M_r/M_s$</td>
<td>0.062</td>
<td>0.063</td>
<td>0.062</td>
</tr>
<tr>
<td>$H_c$ (mT)</td>
<td>7.05</td>
<td>7.27</td>
<td>7.16</td>
</tr>
<tr>
<td>$H_{cr}$ (mT)</td>
<td>28.80</td>
<td>29.87</td>
<td>29.34</td>
</tr>
<tr>
<td>$H_{cr}/H_c$</td>
<td>4.09</td>
<td>4.11</td>
<td>4.10</td>
</tr>
<tr>
<td>$X_{hf}$ (m³/kg)</td>
<td>6.54E-08</td>
<td>6.39E-08</td>
<td>6.49E-08</td>
</tr>
<tr>
<td>S-ratio</td>
<td>1.01</td>
<td>1.01</td>
<td>1.01</td>
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Table 6. Magnetic parameters for Polar Rock Repository samples from the Northern Biscoe Islands.

<table>
<thead>
<tr>
<th></th>
<th>PRR-06230 Gabbro</th>
<th>PRR-06231 Volcaniclastic</th>
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<tbody>
<tr>
<td>$X_{hf}$ (m$^3$/kg)</td>
<td>2.03E-07</td>
<td>2.31E-07</td>
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<tr>
<td>$M_r$ (Am$^3$/kg)</td>
<td>0.00014</td>
<td>0.00061</td>
</tr>
<tr>
<td>$M_s$ (Am$^3$/kg)</td>
<td>0.0037</td>
<td>0.0070</td>
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<tr>
<td>$M_r/M_s$</td>
<td>0.085</td>
<td>0.108</td>
</tr>
<tr>
<td>$H_c$ (mT)</td>
<td>12.01</td>
<td>10.51</td>
</tr>
<tr>
<td>$H_{cr}$ (mT)</td>
<td>26.39</td>
<td>34.72</td>
</tr>
<tr>
<td>$H_{cr}/H_c$</td>
<td>2.20</td>
<td>3.30</td>
</tr>
<tr>
<td>$X_{hf}$ (m$^3$/kg)</td>
<td>2.02E-07</td>
<td>2.03e-07</td>
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<tr>
<td>S-ratio</td>
<td>1.11</td>
<td>1.00</td>
</tr>
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</table>
Table 7. Magnetic parameters for Polar Rock Repository samples from the southern Biscoe Islands.

<table>
<thead>
<tr>
<th></th>
<th>Plutonic Bedrock</th>
<th>Volcanic Bedrock</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PRR-06041 Gabbro</td>
<td>PRR-06046 Tonalite</td>
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<tr>
<td>$X_{hf}$ (m$^3$/kg)</td>
<td>3.59E-05</td>
<td>1.16E-05</td>
</tr>
<tr>
<td>$M_r$ (Am$^3$/kg)</td>
<td>0.0130</td>
<td>0.0041</td>
</tr>
<tr>
<td>$M_s$ (Am$^3$/kg)</td>
<td>1.2770</td>
<td>1.0170</td>
</tr>
<tr>
<td>$M_r/M_s$</td>
<td>0.009</td>
<td>0.003</td>
</tr>
<tr>
<td>$H_c$ (mT)</td>
<td>1.38</td>
<td>0.60</td>
</tr>
<tr>
<td>$H_{cr}$ (mT)</td>
<td>17.50</td>
<td>14.18</td>
</tr>
<tr>
<td>$H_{cr}/H_c$</td>
<td>12.66</td>
<td>23.77</td>
</tr>
<tr>
<td>$X_{hf}$ (m$^3$/kg)</td>
<td>9.84E-08</td>
<td>5.04E-08</td>
</tr>
<tr>
<td>$S$-ratio</td>
<td>1.05</td>
<td>1.11</td>
</tr>
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</table>
Table 8. Mean NBP12-03 JKC36 magnetic parameters values for SPSS two-step cluster analysis groups. Cluster parameters were core depth, $H_c$, $H_{cr}$, $M_r/M_s$, and the S-Ratio. Box and whisker plots of $H_c$, $H_{cr}$, $M_r/M_s$, and the S-Ratio is presented in Figure 35.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cluster 1 (n=56)</th>
<th>Cluster 2 (n=122)</th>
<th>Cluster 3 (n=5)</th>
<th>Cluster 4 (n=87)</th>
<th>Whole Core (n=270)</th>
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</thead>
<tbody>
<tr>
<td>$X_{hf}$ (m³/kg)</td>
<td>6.19E-07</td>
<td>4.07E-07</td>
<td>3.74E-07</td>
<td>5.07E-07</td>
<td>4.82E-07</td>
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<tr>
<td>$M_r$ (Am²/kg)</td>
<td>0.0040</td>
<td>0.0022</td>
<td>0.0039</td>
<td>0.0026</td>
<td>0.0028</td>
</tr>
<tr>
<td>$M_s$ (Am²/kg)</td>
<td>0.0445</td>
<td>0.0255</td>
<td>0.0247</td>
<td>0.0340</td>
<td>0.0322</td>
</tr>
<tr>
<td>$M_r/M_s$</td>
<td>0.0891</td>
<td>0.0884</td>
<td>0.1487</td>
<td>0.0768</td>
<td>0.0859</td>
</tr>
<tr>
<td>$H_c$ (mT)</td>
<td>7.03</td>
<td>6.59</td>
<td>11.70</td>
<td>5.99</td>
<td>6.58</td>
</tr>
<tr>
<td>$H_{cr}$ (mT)</td>
<td>30.32</td>
<td>33.07</td>
<td>58.04</td>
<td>29.72</td>
<td>31.88</td>
</tr>
<tr>
<td>$H_{cr}/H_c$</td>
<td>4.34</td>
<td>5.02</td>
<td>5.22</td>
<td>4.97</td>
<td>4.87</td>
</tr>
<tr>
<td>$X_{hf}$ (m³/kg)</td>
<td>6.42E-08</td>
<td>6.08E-08</td>
<td>6.26E-08</td>
<td>6.12E-08</td>
<td>6.17E-08</td>
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<tr>
<td>S-ratio</td>
<td>0.97</td>
<td>0.96</td>
<td>0.91</td>
<td>0.97</td>
<td>0.96</td>
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Table 9. Magnetic properties for Joinville Island Polar Rock Repository samples. Only samples with $\chi_f$ greater than $10^{-7}$ m$^3$/kg are included. The $H_c$ for sample PRR-20633 was below the VSM detection limit.

<table>
<thead>
<tr>
<th></th>
<th>PRR-16328 Mt. Alexander Diorite</th>
<th>PRR-20553 Ambush Bay Shale</th>
<th>PRR-20570 King Point Andesite</th>
<th>PRR-20578 King Point Shale</th>
<th>PRR-20633 Fitzroy Point Clast</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi_f$ (m$^3$/kg)</td>
<td>2.40E-07</td>
<td>1.36E-07</td>
<td>2.22E-06</td>
<td>1.08E-07</td>
<td>1.29E-07</td>
</tr>
<tr>
<td>$M_r$ (Am$^2$/kg)</td>
<td>0.00058</td>
<td>0.00007</td>
<td>0.00069</td>
<td>0.00017</td>
<td>0.00010</td>
</tr>
<tr>
<td>$M_s$ (Am$^2$/kg)</td>
<td>0.0028</td>
<td>0.0011</td>
<td>0.0036</td>
<td>0.0031</td>
<td>0.0012</td>
</tr>
<tr>
<td>$M_r/M_s$</td>
<td>0.2053</td>
<td>0.0632</td>
<td>0.1909</td>
<td>0.0844</td>
<td>0.0832</td>
</tr>
<tr>
<td>$H_c$ (mT)</td>
<td>18.20</td>
<td>12.75</td>
<td>14.96</td>
<td>9.94</td>
<td>-</td>
</tr>
<tr>
<td>$H_{cr}$ (mT)</td>
<td>38.77</td>
<td>23.70</td>
<td>34.64</td>
<td>23.90</td>
<td>32.58</td>
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<tr>
<td>$H_{cr}/H_c$</td>
<td>2.13</td>
<td>1.86</td>
<td>2.32</td>
<td>2.41</td>
<td>-</td>
</tr>
<tr>
<td>$X_{hf}$ (m$^3$/kg)</td>
<td>4.09E-08</td>
<td>1.52E-07</td>
<td>1.51E-07</td>
<td>1.05E-07</td>
<td>1.15E-07</td>
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<tr>
<td>S-ratio</td>
<td>0.82</td>
<td>0.75</td>
<td>0.99</td>
<td>1.11</td>
<td>0.93</td>
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Table 10. Magnetic properties for Polar Rock Repository samples from the Wideopen Islands and Heroina Island (Danger Islands), located near Joinville Island.

<table>
<thead>
<tr>
<th></th>
<th>PRR-20549 Wideopen Is. Gabbro</th>
<th>PRR-20604 Heroina Is. Gabbro</th>
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</thead>
<tbody>
<tr>
<td>$X_{nf}$ (m³/kg)</td>
<td>5.70E-06</td>
<td>1.74E-06</td>
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<tr>
<td>$M_r$ (Am²/kg)</td>
<td>0.035</td>
<td>0.226</td>
</tr>
<tr>
<td>$M_s$ (Am²/kg)</td>
<td>0.507</td>
<td>0.585</td>
</tr>
<tr>
<td>$M_r/M_s$</td>
<td>0.0648</td>
<td>0.3821</td>
</tr>
<tr>
<td>$H_c$ (mT)</td>
<td>2.60</td>
<td>47.96</td>
</tr>
<tr>
<td>$H_{cr}$ (mT)</td>
<td>6.86</td>
<td>79.41</td>
</tr>
<tr>
<td>$H_{cr}/H_c$</td>
<td>2.63</td>
<td>1.66</td>
</tr>
<tr>
<td>$X_{hf}$ (m³/kg)</td>
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<td>1.58E-07</td>
</tr>
<tr>
<td>S-ratio</td>
<td>1.04</td>
<td>0.99</td>
</tr>
</tbody>
</table>
Figure 1. The Antarctic Peninsula with the Barilari Bay and Joinville Island study areas identified. General ocean currents are identified for reference (after Bentley et al., 2009).
Figure 2. Ternary diagram displaying iron and titanium oxide end members and solid solution lines (Butler, 1992).
Figure 3. Conceptual model illustrating the formation of pyrite and one of its precursors, greigite, in anoxic, sulfate-reducing sediment (Rowan & Roberts, 2006).
Figure 4. A map of the Barilari Bay study area, including NBP10-01 marine sediment core locations and approximate location of the Biscoe Islands Polar Rock Repository samples. Contour lines indicate 500 m elevation. The blue area surrounding Barilari Bay indicate the drainage area for glaciers terminating in the bay, with the five major glaciers-Otlet, Birley, Lawrie, Weir, and Bilgeri-indicated (elevation contours and drainage delineation determined from Antarctic Peninsula digital elevation model, Cook et al., 2012). The gray dashed line indicates the approximate terrane boundary between the Central Zone Western Domain and the Eastern Zone (after Ferraccioli et al., 2006). The approximate location of Circumpolar Deep Water is included for reference (after Bentley et al., 2009).
Figure 5. Barilari Bay bathymetry and core locations.
Figure 6. Bathymetric profile of Barilari Bay, from inner fjord (right) to outer fjord (left), intersecting each core location from NBP10-01 (Christ, 2011).
Figure 7. Time-distance diagram of Barilari Bay displaying late Holocene glacial advance (Elking et al., 2012).
Figure 8. Portions of the geologic map for the Antarctic Peninsula, featuring Barilari Bay and the Biscoe Islands (adapted from Adie, 1969).
Figure 9. NBP10-01 JPC126 physical properties (Elking et al., 2012) and defined sections (this study).
Figure 10. NBP10-01 JPC126 magnetic susceptibility with positive trend line in section 2 and negative trend line in section 3. $\chi(t)$ measurement locations are marked with groups as defined in Figure 11.
Figure 11. NBP10-01 JPC126 thermomagnetic curves categorized into six groups. All values are normalized by the initial $\chi_f$ measurement. Heating curves are presented with dark lines, while companion cooling curves are presented with lightly colored lines.
Figure 12. NBP10-01 JPC126 magnetic proxies, including low-field susceptibility ($\chi_0$), $M_r/M_s$, the S-Ratio, and high-field susceptibility ($\chi_{hf}$). Markings on the x-axis indicate $\chi(t)$ locations (see Figure 10 and Figure 11 for details). Core log included with section 2 composed of rhythmic lamination and graded turbidites and section 3 composed of pebbly and sandy diatomaceous mud.
Figure 13. NBP10-01 JPC126 Day Plot with $M_r/M_s$ versus $H_{cr}/H_c$, and pseudo-single domain (PSD) and multi-domain (MD) fields marked after Day et al., 1977. Mean values of intervals measured in KC54 and JPC125 are included. Theoretical single-domain (SD) and MD mixing curves for magnetite plotted with percent MD (Dunlop, 2002). Mean values for $M_r/M_s$ and $H_{cr}/H_c$ for JPC126 sections and the entire core are also presented.
Figure 14. NBP10-01 KC54 thermomagnetic curves. Cooling curves are included as lighter colors.
Figure 15. NBP10-01 JPC125 thermomagnetic curves. Cooling curves are included as lighter colors.
Figure 16. Relative abundance of lithic fragments represented in the 0.5-2 mm size fraction in inner-middle Barilari Bay. Sedimentary and metasedimentary rocks are categorized together, but likely represent contribution from both Paleozoic Trinity Peninsula Series and Mesozoic strata. The percentages represent only the relative contribution towards the sum of lithic fragments. Mud clumps, quartz, feldspars, and other single minerals are not included here.
Figure 17. Element mapping of iron oxides found in metasedimentary diamict samples from inner Barilari Bay. Iron oxides appear to have formed as the result of authigenic or metamorphic alteration.
Figure 18. Well-sorted quartz/subarkose siltstone lithologies present in all inner-middle Barilari Bay facies samples. Iron oxides up to 40 μm are abundant and range in composition from pure magnetite to ~5% weight TiO₂. A good example of this lithology from JPC126 2066-2070cm is represented with (a) an element map, (b) plain-polarized light micrograph, and (c) cross-polarized light micrograph.
Figure 19. Iron oxide solid solution chemistry for inner-middle Barilari Bay facies. Greens indicate diamict samples, blue indicates inner-bay turbidity current sand deposits, oranges indicate middle-bay sand turbidity current sand deposits, and red indicates seasonally open marine facies. Chemistry determined from EDS analysis of magnetic extracts from the 45-500 µm lithic fraction.
Figure 20. Major grain morphology categories for inner-middle Barilari Bay (Ap = Apatite; Mg = Magnetite; Ti = Titanium rich oxide). All images are from NBP10-01 KC54 70-75cm.
Figure 21. Ternary diagram representing the iron oxide morphologies present in inner-middle Barilari Bay with typical felsic and mafic pluton ranges included (diagram and ranges after Grigsby, 1990).
Figure 22. Heavy mineral extracts from NBP10-01 JPC126. (a, b) Overview of heavy mineral extract from 616-617cm (a) and 1126-1127cm (b). (c) Large frambooidal pyrite from 616-617cm. (d-f) Various Fe-Ti oxide morphologies from 616-617cm (d-e) and 1431-1432cm (f). Elemental mapping colors: Red = Fe, Blue = Ti, Green = Si, and Yellow = S.
Figure 23. Day plot of Biscoe Island Polar Rock Repository samples with single domain (SD), pseudo-single domain (PSD), and multi domain (MD) regions indicated (after Day et al., 1977). Theoretical SD-MD mixing line for magnetite after Dunlop, 2002a. Both axis are log scales.
Figure 24. Thermomagnetic curves from the two Polar Rock Repository samples from the northern Biscoe Islands. Both sample are from Snodgrass Island in the Pitt Islands. Cooling curves are included as lighter colors. A moving average was used due to the weak $\chi_{df}$ of the samples to better represent the data.
Figure 25. Backscatter electron images of representative Fe-Ti oxides found in Polar Rock Repository samples (minerals: Ap = Apatite, Ch = Chalcopyrite, Il = Ilmenite, Mg = Magnetite, Rt = Rutile, Ti = Titanite).
Figure 26. Thermomagnetic curves of plutonic Polar Rock Repository samples from the southern Biscoe Islands. Cooling curves are included as lighter colors. Normalized $\chi(t)$ between 525 and 625 °C is included to emphasize slight variation in $T_C$. 
Figure 27. Thermomagnetic curves of volcanic Polar Rock Repository samples from the southern Bisceoe Islands. Cooling curves are included as lighter colors. A moving average was used due to the weak $\chi_f$ of the samples to better represent the data.
Figure 28. Age models for NBP10-01 JPC126 and NBP12-03 JKC36. The NBP10-01 JPC126 age model should be interpreted with caution due to complications with \(^{14}\text{C}\) dating on the Antarctic Peninsula, inconsistent sedimentation rates due to turbidity currents, and absence of modern sediment (\(^{14}\text{C}\) data courtesy of Eugene Domack, Hamilton College, unpublished data). The NBP12-03 JKC36 age model is developed from the sedimentation rate from LMG04-04 KC3 (~0.5 cm/yr), based on two \(^{14}\text{C}\) dates (Eugene Domack, Hamilton College, unpublished data).
Figure 29. NBP10-01 JPC126 magnetic susceptibility, IRD counts, diatom abundance, and total organic carbon plotted against this study's age model (Elking et al., 2012; Amy Leventer, Colgate University, unpublished data). These parameters indicate a transition from warmer to colder climatic conditions within the last 1,000 years, potentially expressions of the mediaeval warm period (MWP) and little ice age (LIA).
Figure 30. A map of the Joinville Island study area, including NBP12-03 and LMG04-04 marine sediment core locations and approximate Polar Rock Repository sample locations. Magnetic susceptibility of grab samples from LMG04-04 are interpolated and show a gradient of higher values towards the Larsen Channel. The Weddell Sea/Bransfield Strait surface water current is included for reference (after Bentley et al., 2009).
Figure 31. Joinville Island and d'Urville Island with sample sites from LMG04-04 (KC = Kasten core; G = grab samples). Sub bottom profile of the sediment drift is included as an insert (Domack, 2004).
Figure 32. Multibeam bathymetry of Perseverance Drift with core locations from NBP12-03 (Vernet, 2012).
Figure 33. Geologic map of the Joinville Island area (from Adie, 1969a).
Figure 34. NBP12-03 JKC36 magnetic susceptibility and preliminary pore water geochemistry (preliminary pore water geochemistry courtesy of Dr. Mike McCormick, Hamilton College, unpublished data). Zones 1, 2a, 2b, 3a, 3b were determined from pore water geochemistry and an SPSS two-step cluster analysis, using core depth, $H_c$, $H_{cr}$, $M_r/M_s$, and the S-ratio as parameters.
Figure 35. Box and whisker plots for four of the five parameters in the 2-Step cluster analysis of NBP12-03 JKC36. A box and whisker plot of core depth is not included. Boxes represent the 2nd and 3rd quartiles, whiskers represent the range, full width black line represents the median, and the grey dash represents the mean. Clusters are identified in Figure 34.
Figure 36. Down core magnetic proxies for NBP12-03 JKC36 with identified 'authigenic SD greigite horizons' identified by very high concentration of an SD component. $H_{cr}$ values are presented on a reversed log scale.
Intervals from 0-130 cm (Zones 1, 2a, and 2b), from the inferred sulfidic section of the core. Lower panel: Intervals from 132-518 cm (Zones 3a and 3b), from the methanic section of the core. ‘PSD’ and ‘MD’ zones are indicated, although values are heavily influenced by an SP component.

Figure 37. Day Plots for NBP12-03 JKC36 (after Day et al., 1977). Upper panel: Intervals from 0-130 cm (Zones 1, 2a, and 2b), from the inferred sulfidic section of the core. Lower panel: Intervals from 132-518 cm (Zones 3a and 3b), from the methanic section of the core. ‘PSD’ and ‘MD’ zones are indicated, although values are heavily influenced by an SP component.
Figure 38. NBP12-03 JKC36 $M_r/M_s$ vs. $H_{cr}$, which is independent of SP contribution. This companion plot to the Day Plot (Figure 37) uses a reversed log $H_{cr}$ axis. Upper panel: Intervals from 0-130cm (Zones 1, 2a, and 2b), from the inferred sulfidic section of the core. Lower panel: Intervals from 132-518cm (Zones 3a and 3b), from the methanic section of the core.
Figure 39. The difference between the heating and cooling curves in NBP12-03 JKC36 normalized thermomagnetic curves at 100 °C. Samples measured from 0-31 cm indicate magnetic mineral are destroyed while measuring the thermomagnetic curves, with cooling curves less than the heating curves. This corresponds with the sharp decline in $\chi_{fr}$ and the ‘coarsening’ of the hysteresis parameters. Measurements at and down core of 40-41 cm all have cooling curves that are greater than their heating curves.
Figure 40. Mean derivatives of thermomagnetic heating curve intervals of significant change (ISC). ISC1 represents increases in $\chi_f$ over 220-280 °C, while ISC2-4 represent decreases in $\chi_f$. The sharp increase in ISC4 correlates with the sharp decrease in $\chi_f$ from 0-41 cm, indicating the decrease in $\chi_f$ is related to a decrease in magnetite concentration.
Figure 41. NBP12-03 JKC36 thermomagnetic curves measured in an argon atmosphere (solid line) and without an argon atmosphere (dashed line).
Figure 42. Temperature above 200 °C at which the $\chi_{f}$ is greatest. These points were determined from thermomagnetic curves measured in an argon atmosphere.
Figure 43. Element maps for regions of the heavy mineral extracts prepared for NBP12-03 JKC36. Detrital Fe-oxide is only abundant in the 0-1 cm interval. Samples from the rest of the core have abundant iron sulfides.
Figure 44. Elemental maps displaying dissolution of Fe-Ti oxides and replacement by iron sulfide observed in a heavy mineral extract from NBP12-03 JKC36 148-149cm.
Figure 45. Secondary electron photomicrographs of authigenic iron sulfides found in heavy mineral extracts for NBP12-03 JKC36. Iron sulfides were confirmed through acquisition of qualitative EDS spectra.
Figure 46. SEM-EDS observation of ~1 μm octahedral iron sulfide crystals, interpreted as authigenic ferrimagnetic greigite (Fe₃S₄), in heavy mineral extract from NBP12-03 JKC36 206-207cm. This interval corresponds with $H_{cr}$ and $M_r$ peaks in the down core magnetic parameters, indicative of increased concentration of single-domain minerals. EDS spectrum from the unpolished sample included for qualitative purposes.
Figure 47. Day plot for Joinville Island area igneous/volcaniclastic sample (after Day et al., 1977). Single-domain (SD), pseudo-single-domain (PSD), and multi-domain (MD) regions (after Day et al., 1977) and the theoretical SD-MD mixing line for magnetite (after Dunlop, 2002a) are included for reference. Percentages refer to the theoretical fraction of single-domain magnetite present.
Figure 48. Element map and thermomagnetic heating curve for the Mount Alexander Peninsula diorite. The magnetic mineral displayed in the element map is an altered pyrrhotite, supported by the 330 °C curie temperature in the thermomagnetic heating curve and 600+ °C hematite signal. Unaltered pyrrhotite is also present in this sample.
Figure 49. Element maps and thermomagnetic curves for the Wideopen Islands gabbro sample. Thermomagnetic curves were measured twice, first with an argon atmosphere (solid lines) and then without an argon atmosphere (dashed lines).
Figure 50. Element map and thermomagnetic curves for the Heroina Island (Danger Islands) gabbro sample.
Figure 51. Calculated paleo-sulfide concentration in NBP12-03 JKC36 given the hypothesis that the driving force for centennial changes in the magnetite concentration is related to changes in pore water sulfide concentrations. If this is the case, the little ice age (LIA) was a period of higher-than-modern sulfide concentration, associated with less benthic productivity/bioturbation, and the mediaeval warm period (MWP) was a period of lower-than-modern sulfide concentration, associated with greater benthic productivity/bioturbation.