Geochemical Tracers of Holocene Environmental Change Along the East Antarctic Margin

Natalie Romanoff

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Geochemical tracers of Holocene environmental change along the East Antarctic Margin

by

Natalie Romanoff

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GEOCHEMICAL TRACERS OF HOLOCENE ENVIRONMENTAL CHANGE
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Montclair, NJ
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ABSTRACT

Marine sediment geochemistry targeting both organic and inorganic compounds can be used for the reconstruction of paleoenvironmental conditions. Part 1 of this study was a qualitative organic geochemical analysis implemented on sediment cores from the Antarctic Peninsula (AP) and East Antarctic Margin (EAM). Intervals of organic or diatomaceous rich sediment were analyzed by Pyrolysis-Gas Chromatography/Mass Spectroscopy (Py-GC/MS) with the goal of identifying soft-bodied algae responsible for elevated wt% carbon levels in horizons where diatoms are absent, and identifying the presence of methanogens in basins where cold seeps are likely to be present. The identification of biomarkers in Antarctic sediment was challenging due to low wt% carbon in the sediment and small samples sizes used in Py-GC/MS, however, one persistent diatom source biomarker was identified. Samples from the Perseverance Drift, northern AP, presented evidence of early diagenesis under anoxic conditions. Continuation of this work necessitates a change in sample collection protocols to minimize contact between the sediment and plastic sampling tools and storage containers.

Part 2 of this study examined the geochemistry of a complete Holocene record, retrieved from a sediment core in Nielsen Basin on the EAM. Major and trace element geochemistry of the Nielsen Basin diamict and open marine sediment matches the composition of local source rocks, indicating locally-derived material throughout the Holocene. Intervals of low Fe or low wt% carbon were observed, which likely limits the pyritization process and preserves ferromagnetic greigite. This is likely responsible for the strongly magnetic zones observed by Kacperowski, 2009. A sequence of paleoenvironmental intervals similar to those documented on the AP, were identified in JPC40, suggesting that Holocene environmental change observed on the AP were not isolated, but continent wide. However, the timing of the transitions between these intervals is not the same as observed on the AP. This may be a function of the challenges inherent in radiocarbon dating of acid insoluble organic matter, or to genuine time transgressive behavior of these climate events on the AP vs. the EAM.
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1. INTRODUCTION

Surrounded by the Southern Ocean and below ~60°S latitude, Antarctica is the southernmost continent. The cold air masses and strong winds traversing Antarctica propel the development of Circumpolar Deep Waters (Anderson, 1999). In other words, the world’s ocean circulation is steered by Antarctica’s atmospheric conditions (Berkman et al., 1998). The most significant Antarctic landform is the Transantarctic Mountains (TAM), one of the most impressive mountain range in the world. The TAM extends across the continent from the Weddell Sea to the Ross Sea for nearly 3500 km and is the physical boundary separating east and west Antarctica (Figure 1). The different geologic settings of these two regions affected the evolution of the overlying ice sheets. For example, East Antarctica consists of a “large stable continental craton” while west Antarctica developed by a “mosaic” of several groups of islands, therefore a significant difference in subglacial topography is observed (Anderson, 1999). This disparity produced the terrestrial East Antarctic Ice Sheet (EAIS), grounded above sea level, and the marine West Antarctic Ice Sheet (WAIS), grounded below sea level (Anderson, 1999).

Ninety-eight percent of Antarctica’s total area (~14.2 x 10^6 km^2) is covered by extensive ice sheets ranging in thickness from 1-4 km (Anderson, 1999). The WAIS covers an area of 1.97 x 10^6 km^2 and has been well studied. The EAIS, being less accessible and therefore not as well studied, is 9 times larger by volume than the WAIS (Anderson, 1999). It has been estimated that the complete collapse of the WAIS would raise global sea level by 5 m (Mercer, 1978). However, researches have estimated that if a complete collapse of the EAIS were to occur, sea level would rise by ~60 m (Mengel
and Leverman, 2014). There have been several recent ice shelf collapse events to warrant concern; one of the most significant was the ~12,500 km² collapse of Larsen B Ice Shelf (LIS-B) located on the Eastern Antarctic Peninsula (EAP) in 2002 (Domack et al., 2005a). Other recent major events included the collapse of Larsen-A Ice Shelf in 1995 and Wilkins Ice Shelf in 1998 (Rott et al., 1995; Scambos et al., 2002). Marine sediments record these events and reveal past drastic shifts in the climate. The presence or absence of diatoms, siliceous phytoplankton, in marine sediment indicate ice free or ice shelf covered waters, respectively (Domack et al., 2005a). However, some sedimentary records from former ice shelf embayments display elevated organic carbon content even in the absence of diatoms, which is unexpected and the source of this organic carbon is unknown (Roe and Domack, 2007; Domack et al., 2011).

An initial goal of this study was a qualitative analysis to determine the presence of biomarker fingerprints in Antarctic Peninsula (AP) and the East Antarctic Margin (EAM) sediment via pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Biomarkers are complex compounds that remain highly stable even during diagenesis. Therefore, they closely resemble their biological precursor (Wang and Stout, 2007; Killops and Killops, 2009). Identifying the source of biomarkers may reveal paleoenvironmental conditions and specific biomarkers that can be utilized as paleothermometry indicators. Researchers have successfully interpreted biomarker precursors in surface waters, meltwater ponds, and marine sediment throughout Antarctica (Harada et al., 1995; Sikes et al., 1997; Jungblut et al., 2009). A major source of organic matter in marine sediments is phytoplankton, or microalgae, and the Southern Ocean is highly productive. Therefore, utilizing the work by Volkman et al. (1998), we anticipated several different microalgal
biomarker signals such as fatty acids, long-chain alkenones, highly branched isoprenoid alkenes, sterols, and algaenans. All attempts to discern organic biomarkers and conclusively identify organic sources of Antarctic sediments in this study were ultimately unsuccessful. Due to the extremely low organic content (~0.2-1%) of the majority of samples, the organic geochemical signals were overwhelmed by prevailing plasticizer contamination or limited as a result of insufficient distribution, as described in the Results and Discussion.

Therefore, this study adopted a new approach to investigate an EAM Holocene record of environmental change. Domack et al. (2001) developed a paleoenvironment guide for the West Antarctic Peninsula (WAP) through an extensive study of the Holocene Palmer Deep site. In this report researchers highlighted five distinctive paleoenvironmental intervals, moving down core: (1) Neoglacial (0-3.5 ka); (2) Holocene Climate Optimum (3.5-9 ka); (3) Climatic Reversal (9-11 ka); (4) Deglaciation (11-13.2 ka); and (5) Last Glacial Maximum. These intervals have since been recognized in numerous AP sites. This thesis examines a similar high resolution Holocene Antarctic record from East Antarctica and evaluates the local vs. regional extent of these intervals. We use inorganic and organic geochemical proxies to complement a set of magnetic proxies reported by Kacperowski (2009). Magnetic proxies were used to search for intervals of intense melting in Nielsen Basin core NBP01-01 JPC40 in order to study the stability of the EAIS during the Holocene. Meltwater plumes would supply abundant terrigenous sediment to the ocean. Terrigenous sediment contains iron-bearing minerals. Therefore, Kacperowski (2009) looked for peaks in parameters such as magnetic susceptibility and induced remanences to identify terrigenous-rich horizons. Such peaks
were observed and originally interpreted as cyclical input of magnetite from terrigenous sediment (Kacperowski, 2009). However, a follow-up electron microscopy analysis of magnetic particles extracted from Nielsen Basin sediment revealed only iron sulfides, which are products of diagenesis (Brachfeld et al., 2011). This necessitated revisiting JPC40 with a new set of tools capable of differentiating terrigenous and diagenetic inputs.

The geochemical proxies utilized in this study are inductively coupled plasma-optical emission spectrometry (ICP-OES), and carbon-nitrogen-sulfur (CNS) analyses. The Southern Ocean is highly productive, though productivity and flux of organic carbon to the seafloor may have been restricted by ice shelves or sea ice in the past. Major element analysis in ICP-OES indicates the amount of terrigenous sediment, while total carbon content is an indicator of primary production. Sulfur content tracks the amount of diagenetic sulfides. Glacial deposits are the main source of terrigenous sediments on Antarctic shelf environments. Elements Fe, Al, and Ti are strictly terrigenous sources while Si occurs in both terrigenous and biogenic sources. Therefore, Si excesses due to biogenic inputs are determined by assessing the ratio Si/Al because Al sources are solely terrigenous. Additionally, evaluating the C/N and C/S ratios indicates the source of organic matter and degree of diagenesis. The availability of C and Fe is essential for diagenesis and these elements influence the pyritization process (Berner, 1970).
2. STUDY AREAS

2.1 Antarctic Peninsula Region

The AP extends northward from the continent reaching the sub-polar latitudes, approximately 1000 km south of Cape Horn, South America. Due to its relatively lower latitude location compared with the main continent and its relatedly small size (5.22 x 10^5 km^2), the AP is predisposed to the influences of climatic change more than other coastal regions throughout Antarctica. Interestingly, the two sides of the peninsula comprise varying conditions due in part to the narrow mountain ridge that rises approximately 2500 m above sea level often referred to as “the spine of the Peninsula” (Domack et al., 2006. Winds reaching the eastern AP (EAP), originating in the Weddell Sea, are much colder than the milder Westerlies arriving at the western AP (WAP). Therefore, the climate on WAP is much warmer and wetter than EAP (Anderson, 1999). The climate disparity is presented by the scope of differing landforms such as extensive glacially-carved inlets on WAP vs. wide-ranging sea ice that envelops the EAP. Additionally, the stormier WAP weather adds precipitation to the bulk of the Antarctic Peninsula ice cap (APIC), which overlays the AP (Anderson, 1999).

Five different sites consisting of deep basins, troughs, or sediment drifts along the AP were analyzed in this study (Table 1; Figure 2). Three areas are located in the former Larsen Ice Shelf (LIS) A and B embayments on the EAP (Greenpeace Trough, NBP00-03 KC23; Hektori Basin, LMG05-02 KC5A; and Crane Glacier Trough, NBP06-03 KC5) as well as a fjord system on the Graham Land Coast, WAP (Barilari Bay, NBP10-01 JPC127). Another area studied was the northeastern region of the AP located in the
Larsen Channel between Joinville and d'Urville Islands (Perseverance Drift, NBP12-03 KC36).

2.2 East Antarctic Margin

On the East Antarctic Margin (EAM) between longitudes 60°E and 73°E stands Mac.Robertson Land, bordered by Kemp Land to the west and Princess Elizabeth Land to the east (Law, 1954) (Figures 1 and 3). Visible outcrops from the Fames and Prince Charles Mountains speckle the landscape and established glacial outlets extend into adjacent shelves (Clarke et al., 1989; Turner and Padley, 1991). Lambert Glacier/Amery Ice Shelf is the most prominent glacial outlet on the EAIS. Mackintosh et al., (2013) describe this system as one of the largest drainage basins on the entire continent (~16% of all drainage of EAIS). The ice flow for this system begins far inland and empties into Prydz Bay (Mackintosh et al. 2013). Significantly smaller glacier systems such as the Brunvoll, Strahan, Forbes, and Utstikkar Glaciers are located on Mac.Robertson Land, but currently do not extend onto the adjacent Mac.Robertson Shelf (Jezek, 2008; Foley et al., 2013).

Located west of Prydz Bay, the Mac.Robertson continental shelf (hereafter Mac.Robertson shelf) has an average width of 90 km and expands lengthwise for 400 km from longitude 60°E to 70°E (Leventer et al., 2006). Similar to other Antarctic continental shelf geomorphology, the Mac.Robertson shelf contains evidence of glacial erosion on the inner shelf. The shelf-slope break occurs at an average of 350 m water depth, and the banks of the mid- to outer shelf are <200 m deep (Harris and O’Brien, 1996; Mackintosh et al., 2013). Harris and O’Brien (1996) defined four geomorphic
zones associated with Mac.Robertson shelf: (1) high-relief ridge and valley topography with shallow banks and deep basins; (2) U-shaped depositional valleys and basins; (3) smooth shallow banks; and (4) iceberg gouged and current reworked surfaces (Figure 4). The shallow bank, Storegg Bank, is flat topped with evidence of ice-keel gouging seen elsewhere on the Antarctic coast and Alaska (O’Brien et al., 1994). The deep basins resemble fjord systems in that the morphology consists of steep sided, U-shaped troughs with flat floors (Harris and O’Brien, 1996). Curving east-west, Nielsen Basin and Burton Basin are the largest basins on Mac.Robertson shelf, while the smaller yet still significant Iceberg Alley is linear and trends north-south (O’Brien et al., 1994; Leventer et al., 2006).

Comprising of depths up to 1400 m and sides sloping at ~70°, Nielsen Basin, is the deepest and steepest of the three troughs (O’Brien et al., 1994; Harris and O’Brien, 1996). Located between 64°E and 66.5°E, Nielsen Basin (Figure 5), separates Storegg Bank into east and west sections (Harris and O’Brien, 1996; Mackintosh et al., 2013). Seismic studies have revealed seaward dipping normal faults in the basement rocks of Nielsen Basin, suggesting that the deepest parts of Nielsen Basin are remnants of a half-graben structure formed during a pre-rift extension along the continental margin (Stagg, 1985; Harris and O’Brien, 1996). Stagg (1985) indicates the original sediments that filled the half-graben were of Neocomian age or older, and have long since been eroded.

Harris and O’Brien (1996) described a zero net sedimentation on Mac.Robertson Shelf. This suggests erosion and sediment production are in balance. Additionally, the authors invented the phrase “scalped shelf” based on the absence of organic growth and presence of ample substrate on Mac.Robertson shelf. Data from current meters on the
upper slope of Mac.Robertson shelf revealed the strongest currents (maximum velocity, 1.96 m/s) of any region on the Antarctic shelf (Harris and O’Brien, 1998). This same survey also recorded weaker currents on the mid- and inner shelf (~0.3 m/s). Fine-grained particles are unable to settle and deposit in the strong currents of the outer shelf. However, the coarser-grained sands and gravel are capable of amassing in the higher velocity outer shelf (Harris and O’Brien, 1998). The deposition of fine particulates is restricted to the inner shelf (Figure 6), and this is responsible for the thick biosiliceous ooze deposits that fill Nielsen Basin (Leventer et al., 2006).
3. METHODS

3.1 Field Methods

In February of 2001, the Research Vessel Ice Breaker Nathaniel B. Palmer (NBP01-01) conducted a marine geologic and geophysical investigation of the East Antarctic Margin (EAM). The cruise explored the region from Wilkes Land to Edward VIII Gulf, approximately 150°E to 50°E. The researchers inspected the Palmer’s CHIRP sonar sub-bottom profiling and swath Multibeam mapping instruments as well as previous cruise surveys to determine and identify appropriate core locations (Leventer et al., 2006). The methods of sample retrieval at a core site were dependent on the assessed expanse and depth of sediment.

A jumbo piston core (NBP01-01 JPC40) was deployed at 750 m water depth at Nielson Basin, Mac.Robertson Shelf and retrieved 24 m of sediment. This core was stored in a refrigeration unit on the Palmer, then shipped to the Antarctic Marine Geology Research Facility (AMGRF) at Florida State University. At AMGRF the core was carefully sliced lengthwise into sample and archive halves. Photographs were taken and a detailed core description was recorded. Samples for magnetic and geochemical analysis were collected every 2.5 cm down core (Kacperowski, 2009).

3.2 Major and Trace Element Analysis

Bulk sediment samples with a 20-cm spacing down core were prepared for ICP-OES analysis by utilizing the flux fusion technique. A mass of 0.1000 g (±0.0005 g) for each sample was carefully mixed with 0.4000 g (±0.0020 g) of lithium metaborate (LiBO₂) flux. A blank sample was also prepared for each batch by following the flux fusion procedure. The thoroughly mixed sample-flux and the flux blank were transferred
to graphite crucibles and placed in a furnace at 1050°C. In addition to graphite’s ability to withstand high temperatures, graphite minimally affected the sample element composition in the fusion process. After 30 min the crucibles were removed from the furnace, where the sample-flux mixture was fused into a molten bead. The molten bead was carefully dropped into a Teflon beaker containing 50 ml of 7% nitric acid (HNO₃) solution. Once the molten bead contacted the acid solution it shattered, which enabled the sample to dissolve in the solution. The beaker was placed on a magnetic stir plate to accelerate the dissolution of the shattered bead and homogenize the solution. Then the solution was filtered into 60 ml Nalgene bottles using Whatman 540 filter paper. This filtered solution was too concentrated (500x dilution factor) for the instrument threshold. Therefore, it was diluted by pipetting a 6.5 ml aliquot of the 7% filtered sample solution (500x dilution factor) into 50 ml of 2% HNO₃ solution. This new diluted solution was placed in a 60 ml Nalgene bottle and stored in a standard refrigerator.

The 2% sample solutions (4000x dilution factor) were analyzed on a Jobin Yvon inductively-coupled plasma optical emission spectrometer (ICP-OES) for major and trace elements including Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P, Ba, Cr, Ni, Sc, Sr, V, Y, and Zr. Each sample was analyzed three times and the raw data was mass-, blank-, and drift-corrected. The blank correction adjusted the sample values for any possible element contribution from the LiBO₂ flux, graphite crucibles, or nitric acid. To continually monitor and correct for instrument operating conditions a drift solution was analyzed after every four samples. This solution was prepared by spiking previously analyzed 4000x solutions with known single element standards. To convert corrected photon counts to weight percent (wt%) oxide (majors) and ppm (trace), rock standards from the
U.S. Geological Survey were analyzed. In total, 12 rock standards with known elemental compositions were prepared in the previously outlined procedure and analyzed with the samples. The intensity (photon counts) vs. known concentration data were plotted to determine a calibration line for each element. The equation derived from the calibration line was used to convert counts into element concentration.

3.3 Total Carbon-Nitrogen-Sulfur wt% Analysis

Selected bulk sediment samples were taken every 5-20 cm from core JPC40 for total carbon, nitrogen and sulfur wt% measurements using an Elementar Vario EL CHNS elemental analyzer. A prewash procedure was developed for this project in order to remove sulfate salts from the pore water. Roughly 150 mg of sample was placed in a 15 ml centrifuge tube and filled with “nanopure water” (water that has been filtered such that it has an electrical resistivity of 18 MΩ-cm). The slurry filled tubes were sonicated for 10 min then centrifuged for 5 min at 1500 rpm. The water was discarded and the wash procedure was repeated. After the second wash was complete and the water discarded, the tubes were placed in a standard freezer for a minimum of 4 hrs, then freeze dried overnight. A sample mass of 25 mg (± 1.0 mg) of the freeze dried sediment was measured in a tin boat and the mass recorded after the boat was tightly folded into a compressed cube. This folding technique carefully removes ambient air that is trapped within the boat. The initial calibration procedure for the instrument entailed replicating four sample boats with 5 mg (± 1.0 mg) of sulfanilic acid standard (C₆H₇NO₃S). For quality control purposes each sample was run in duplicate or triplicate. Diluted standards and blanks were inserted every 10 boats to ensure instrument accuracy. Additionally, to
reduce any possible ambient air contamination, (which mainly affects N) the blanks from each run were averaged and subtracted from samples and diluted standards during data analysis, analogous to the ICP-OES blank correction. The diluted standard was determined during this study to simulate expected CNS levels in Antarctic sediment (Leventer et al., 1996; Domack et al., 2003). Silica powder (SiO₂) from Fisher Scientific was utilized as the blank sample, while the diluted standard was prepared by homogenizing a 1:39 ratio of sulfanilic acid standard (0.025 g) to SiO₂ (0.975 g). This ratio of standard to silica yields values of 1.04, 0.2, and 0.46 wt% for C, N, and S, respectively.

3.4 Organic geochemistry analysis by Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS)

This study largely followed the Py-GC/MS method detailed in Micić et al., 2013. Py-GC/MS was performed using a CDS 2000 pyroprobe, coupled to a Thermo Finnigan Focus DSQ GC/MS equipped with a 15 m Restek Rtx-5MS column (0.25 mm i.d., film thickness 0.1 μm) (Micić et al., 2013). The GC oven temperature was programmed from 50°C to 300°C (at 5°C min-1), with an initial hold of 5 minutes at 50°C and a final hold of 30 minutes at 300°C (Micić et al., 2103). Pyrolysis was performed for 20 seconds at 610°C. The MS was operated in full scan mode (50-500 Da, 0.92 scans sec-1). Measured aliquots (up to several mg) of dry, homogenized sediment were pyrolyzed directly, without derivatization.
4. RESULTS

4.1 Antarctic Peninsula Region

4.1.1 Lithology

In total six stations were considered, five on the Antarctic Peninsula (AP) and one on the East Antarctic Margin (EAM) (Table 1; Figures 1, 2, and 3). The AP core locations include sites along both the eastern and western peninsula. The cores from the EAP were collected from the former Larsen Ice Shelf (LIS) A and B embayments: NBP00-03 KC23 (LIS-A), LMG05-02 KC5A (LIS-B), and NBP06-03 KC5 (LIS-B). The other two cores are from the northeastern region of the AP located in the Larsen Channel between Joinville and d'Urville Islands (NBP12-03 KC36), and in Barilari Bay on the WAP (NBP10-01 JPC127).

Core NBP00-03 KC23 from LIS-A contains three distinctive lithologic units (Brachfeld et al., 2003) (Figure 7). The first unit (0-130 cm) consists of silty-clay with scattered sand and gravel, and three distinct diatom laminae. The second unit (130-150 cm) displays an increase in grain size beginning as a finely laminated silty-clay at 130 cm and coarsening to sand and gravel facies at 133 cm. In the third unit (150-230 cm) the sediment shifts to a structureless clay-rich diamict. The LIS-B core, LMG05-02 KC5A, exhibits a distinctive laminated pattern of silty-clay to fine grained sand (0-60 cm) with angular pebbles between 50-60 cm. Below 60 cm, the sediment settles to a stratified sandy mud (60-95 cm) and then homogenous mud (95-225 cm) with the occasional sand clots at 145, 200, and 210 cm. The second LIS-B core, NBP06-03 KC5, consists primarily of laminated silty-clay (0-57 cm) stratigraphically above the grounding line (57-60 cm) and a diamict bottom (60-75 cm) (Figure 7).
Core NBP10-01 JPC127 from Barilari Bay, WAP, consists of mottled to bioturbated diatomaceous mud. The core alternates between structureless and laminated intervals from the core top down to 868 cm, (Figure 7). Core NBP12-03 KC36 from the northeastern AP, Perseverance Drift, primarily contained laminated, dark organic-rich, diatomaceous mud (0-350 cm). Below 350 cm the laminated silty-clay is still discernable though with greater bioturbation.

4.1.2 Chronology

Previous geological studies have reconstructed the chronology of past climate events on the AP by dating key stratigraphic intervals in marine sediment cores. To summarize, the transition from Last Glacial Maximum (LGM) to the Holocene interval is observed by an abrupt change in the sediment facies: till and gravelly mud overlain by silty-clay or diatomaceous mud in sub-ice shelf open marine settings, respectively (Domack et al., 2001, 2005a; Brachfeld et al., 2003). All AP cores in this study that recovered the LGM display this stratigraphic trend.

The middle Holocene interval of KC23 contains three diatomaceous ooze laminae that were dated via geomagnetic paleointensity dating, and the ages ranged between 3.8-1.4 ± 0.5 ka (Brachfeld et al., 2003). The other Larsen core, LMG05-02 KC5A (LIS-B), demonstrates sub-ice shelf conditions during the entire Holocene (Domack el al., 2005a). Open marine conditions were only established after 2002 when the LIS-B ice shelf collapsed (Scambos et al., 2003; Domack et al., 2005a). A detailed chronology is unavailable for the LIS-B cores as result of insufficient biogenic calcite for $^{14}$C dating,
but the available sparse dates put deglaciation at approximately 11.0 ka (Domack et al., 2005a).

Surveys across the eastern end of the Larsen Channel on the northern AP revealed a complex sediment drift, which has been named the Perseverance Drift. NBP12-03 KC36 is likely a high-resolution Holocene record (Domack et al., 2004; Reilly, 2013; Darley, 2014). Pb-210 data from the top of KC36 (E. Domack, personal communication) and available ages from a kasten core collected in 2004 (Darley, 2014) both suggest sedimentation rates of 0.8 to 0.9 mm/yr, which suggests that all of KC36 spans the last 600-700 years.

Barilari Bay’s fjord-like conditions also produce a high sediment accumulation rate. NBP10-01 JPC127 represents sedimentation from the Mid- to Late Holocene, though the basal age is unknown (Natter, 2011). A radiocarbon age model for the shorter companion kasten core KC55 (Christ et al., 2014) can be used to extrapolate an age for JPC127, which is approximately 6177 yr BP at its base.

4.1.3 Organic Geochemistry: Pyrolysis-Gas Chromatography/Mass Spectrometer Analysis

Antarctic marine sediments are notoriously low in organic carbon content (Domack et al., 2003). Therefore, several cores were analyzed during this study in order to determine a promising study region. The five AP region cores (Table 1) held different aims and objectives in this study. The original goal was a qualitative analysis to determine the presence of biomarker fingerprints in the sediment. Two overall factors were involved in choosing the depth at which to analyze: diatom abundance and carbon
percentages. Selected sample depths (0, 25, 35, 65, and 75 cm) in NBP00-03 KC23 from the LIS-A region were within the observable diatom ooze horizons, and 185 cm depth had the highest examined TOC value (1.36%) for the core (Brachfeld et al., 2003). The samples for LMG05-02 KC5A from the LIS-B region (75, 80, 85, 90, and 95 cm) were chosen based on “high” total carbon results (0.2-0.3%) compared to < 0.2% for the other depths (Domack et al., 2005a). Interestingly, this interval of “high” carbon values precedes the diatom abundance peaks.

NBP10-01 JPC127, located at the mouth of Barilari Bay, was significantly more diatom-rich than the Larsen embayment cores. JPC127 samples at 465 cm and 695 cm are from diatom ooze horizons. Reported total carbon wt% hovered around 1% (Natter, 2011). Data for NBP12-03 KC36 was limited at the time of initial inspection. Therefore, KC36 sample depths (88, 298, and 504 cm) were selected for organic geochemical analysis based uniquely on the core description. Two of the samples, 88 cm and 298 cm, are located within the observable diatomaceous ooze horizons, while 504 cm is between the sediment layers where ikaite (CaCO₃·6H₂O) crystals were discovered (Reilly, 2013). Likewise, samples from NBP06-03 KC5 (0, 25, 57, 60, 70 cm) were chosen based on visual changes in the sediment core. These samples ranged from laminated, light olive-gray, silty-clay to medium dark-grey, clay-rich diamicton and included an interesting orange-brown layer in between (unpublished core description by the NBP12-03 shipboard scientific party).

Larsen A: NBP00-03 KC23
In the upper depths of KC23 (0-80 cm) there are three diatomaceous ooze laminae within green colored silty-clay (Brachfeld et al., 2003). One source of the green color is pigments from diatoms. The presence of soft-bodied algae is also possible, but it has not been explored. Therefore, Py-GC/MS was utilized to determine the organic source found in the silty-clay. However, this method was not sensitive enough due to the lean organic content, approximately 0.4% TOC (Brachfeld et al., 2003). One distinctive peak was detected near 13.9 min for depths: 0, 25, 35, 65, and 75 cm (Figure 8ab). The base peak for this compound was m/z 161, a methylindoledione isomer (C₉H₇NO₂) (Figure 8ab). The phthalate abundance was inconsistent down core with the greatest relative abundance observed at 35 cm and 75 cm. Additionally, 185 cm was analyzed to compare the upper core with the lower core. This lower part of the core has a relatively high TOC (>1%) compared to the rest of the core due to the presence of black shale in the sediment (Brachfeld et al., 2003). In addition to the m/z 161 peak, 75 and 185 cm has identifiable even number normal alkane (n-alkane) peaks, but the signal is weak (Figure 9). This even number n-alkane dominance is also seen in the other depths, but the signal was not distinct.

**Larsen B: LMG05-02 KC5A**

Diatom-bearing mud is present in KC5A between 35 and 75 cm, but an increase in the carbon content is observed stratigraphically below the diatom peaks starting at 95 cm (Leventer et al., 2012). The GC/MS is an effective tool in determining carbon sources in marine sediments, and was attempted in this study to identify the carbon source that emerges before the appearance of diatoms. Py-GC/MS analyses were conducted every
5 cm between 75 cm and 95 cm. The signal results for 75 cm are too low to distinguish any peaks, but even number carbons of \( n \)-alkanes, particularly \( n-C_{12}, n-C_{14}, n-C_{16}, \) and \( n-C_{18} \) were detected in the other depths (Figure 10). The abundance of the even numbered carbons varied down core.

**NBP06-03 KC5**

An investigation of the LIS-B seafloor after the 2002 collapse of the Larsen B ice shelf revealed a benthic chemosynthetic community underneath the former ice shelf (Domack et al., 2005b). Core NBP06-03 KC5 collected marine sediments within the basin housing the "cold seep" (the inferred origin of the chemosynthetic community) and adjacent to a region in which a video survey imaged rings of giant clams and a possible bacterial mat (Domack et al., 2005b). An investigation for possible biomarkers was attempted in this study in order to determine the type of primary producers in this community. This sediment core is 75 cm in length and is separated into three lithological units: Unit 1 sub-ice shelf (0-57 cm), Unit 2 deglacial (57-60 cm), and Unit 3 glacial (60-75 cm) (Roe and Domack, 2007). Depths 0 cm and 25 cm in Unit 1, 57 cm in Unit 2, and in Unit 3 60 cm and 70 cm were analyzed. The results are limited due to the low organic content (< 0.7% TOC) (Roe and Domack, 2007). Most notable was the presence of low level naphthalenes in depths 0 cm, 60 cm and 70 cm (Figure 11). Co-eluting with the naphthalenes are indene, indole, and unidentified compounds comprising of hydroxyl or carboxyl groups attached to one or more benzene rings. Again, even number carbon dominance is observed in the characteristic ion for \( n \)-alkanes and \( n \)-alkenes. However, in KC5 an increasing trend of peak distribution is discerned down core (Figure 12ab). The
core top (0 cm) had a carbon distribution that differed from the previous cores and the other depths analyzed for KC5 in that \( n-C_{16} \) was distinctly larger than \( n-C_{14} \). The prominent methylindoledione peak around 13.9 min recognized in NBP00-03 KC23 is also present in Unit 1 of this core (Figure 13ab).

**Barilari Bay, western AP: NBP10-01 JPC127**

Core JPC127 alternates between structureless and laminated diatomaceous mud and is considerably more diatom-rich than the Larsen embayment cores. This study intended to examine the diverse biomarkers from the abundant diatom remnants in JPC127. Throughout the core the TOC values are low (below 1%) and the Py-GC/MS method available was not able to accurately detect biomarkers with such lean organic carbon levels. However, there were detectable amounts, though at very low levels, of \( n \)-alkanes, naphthalenes, indenes, indoles, pyrrolidines, alkynitriles, and methylated benzene compounds (Figure 14). Additionally, the prominent methylindoledione peak discerned in NBP00-03 KC23 and Unit 1 of NBP06-03 KC5 likewise is detected in JPC127 (Figure 14). A small peak at 18.3 min retention time reveals another phthalate signal, \( m/z \) 149. No apparent trends are seen in the Py-GC/MS data for JPC127.

**Perseverance Drift, northern AP: NBP12-03 KC36**

Core KC36 contains laminated, dark organic-rich, diatomaceous mud (0-350 cm) and the core emitted a strong hydrogen sulfide odor (Reilly, 2013). The goal of organic Py-GC/MS analysis was to ascertain the biomarkers present, especially biomarkers from bacterial sulfate reduction processes. Again, the Py-GC/MS method was not sensitive
enough to produce a more detailed array of peaks, but KC36 contained the most
remarkable results of all the Antarctic cores analyzed. First, the analyzed depths (88, 298,
and 504 cm) prominently displayed a sulfur peak, defined as cyclic octaatomic or S₈
(Figure 15a). Second, thiophenes (aromatic sulfur compounds) were detected after the S₈
peak at 28.1, 28.5, 29.0 min retention time for all depths analyzed, with the greatest
abundance at 29.0 min (Figure 15b). The thiophenes in KC36 are deemed C₂₀ isoprenoid
thiophenes, meaning the aromatic sulfur compound contains a branched aliphatic chain.
Again no discernable trends are observed for the thiophenes down core. Additionally, the
even number carbon dominance for n-alkanes and n-alkenes was less distinctive than in
previous cores because they are lost with in the other larger signals (Figure 16).

We observe alkylnaphthalenes co-eluted with nitrogen compounds in KC36. This
coclution was observed in the LIS-B and WAP cores, however in KC36 the
naphthalenes are more distinct. Noticeable nitrogen compound signals, such as indoles,
benzonitriles, alkylnitriles, and indole-diones, are observed throughout KC36. The m/z
161 methylindoledione peak seen in the other cores at 13.9 min, is less pronounced in
KC36. This was determined due to the distinctive m/z 147 isomer peak observed after the
m/z 161 indole-dione peak for all three analyzed depths. Phthalate contamination is
apparent in KC36 with a m/z 149 phthalate peak emerging at 18.3 min retention time.
Again no distinctive trends are seen in the signals down core.

4.2 East Antarctic Margin, Nielsen Basin

4.2.1 Lithology
The uppermost portion (0-148 cm) of core NBP01-01 JPC40 contains a coring-induced disturbance where the water content was high. Between 148 and 1803 cm the core consists of silty-clay biosiliceous ooze and mud (hereafter referred to as siliceous mud ooze or “SMO”) (Figure 17). Laminations are horizontal in this interval, indicating that the coring-induced disturbance is confined to the uppermost 148 cm. The SMO contains two homogenous zones (509-547 and 1630-1650 cm), but primarily this segment alternates between laminated and bioturbated sections. At 1803-2108 cm the silty-clay sediment coarsens to a medium-fine grained sandy SMO. The alternating pattern of laminated and bioturbated sections continued, with one homogenous zone at 1956-2097 cm. A 47 cm thick varved section was observed at 2108-2155 cm (Leventer et al., 2006). These annually paired rhythmic laminations or couplets are inversely graded with the coarser summer and fall deposits overlaying the fine spring diatom bloom deposit (Stickley et al., 2005; Leventer et al., 2006). Below the varved sediment there is strong evidence of bioturbation between 2155 and 2170 cm. The sediment core displays an abrupt shift to a sand-free homogenous silty-clay at 2170-2220 cm. Again an abrupt change is seen at 2220 cm depth where the clay shifts to laminated sand that is rich in granules until 2360 cm. Lastly, the bottom of JPC40 (2360-2393 cm) consists of a medium to thinly bedded diamict unit representing the Last Glacial Maximum (LGM), indicating a complete record of the Holocene at this location (Figure 17).

4.2.2 Chronology

Preservation of datable biogenic calcite material such as calcareous foraminifera is rare around Antarctica due to a shallow carbonate compensation depth (CCD)
The bulk organic fraction in Antarctic diatomaceous rich muds and ooze are utilized in radiocarbon dating when calcite is absent (Domack et al., 1989; Andrews et al., 1999). Radiocarbon dates generated from the zero-age sediment water interface in Antarctic sediment cores are unusually old (Gordon and Harkness, 1992; Andrews et al., 1999). Therefore, corrections for the carbon reservoir and reworked carbon effects must be derived. In addition, anthropogenic processes since the industrial revolution have also affected radiocarbon ages.

The most dominant influence on the Antarctic reservoir age is the upwelling of Circumpolar Deep Water (Domack et al., 1989; Berkman et al., 1998). This old deep water mass, which originates in the North Atlantic Ocean, has been out of physical contact with the atmosphere for more than 1000 years, resulting in decay of \(^{14}C\) without replenishment. Phytoplankton incorporate this old dissolved \(^{14}C\), which produces a surface water age of ~1200 years (Sikes et al., 2000). A reservoir age of 1200-1300 years is considered standard for the western AP region (Domack et al., 2001, 2003).

In the eastern AP region, the radiocarbon age is further influenced by detrital carbon from old terrestrial sources into the marine sediments, for example black shales present on the spine of the peninsula (Domack et al, 1989; Harris et al., 1996). A seasonal effect is the limited exchange of atmospheric CO\(_2\) at the ocean surface. Open marine conditions allow new \(^{14}C\) into the system, but at times it is obstructed by sea ice in the Southern Ocean (Gordon and Harkness, 1992). Additionally, human activities such as combustion of fossil fuels, which formed during the Paleozoic and Mesozoic eras, has added \(^{12}C\) to the atmosphere but no \(^{14}C\), decreasing the \(^{14}C/^{12}C\) ratio in the atmosphere. In contrast, atmospheric nuclear weapons testing added \(^{14}C\) to the atmosphere beginning in
the late 1940s. Consequently, the year 1955 AD is defined as “zero” radiocarbon age (Trumbore, 2000).

In total 13 bulk samples were collected from core JPC40 for radiocarbon dating (Table 2). Due to the lack of biogenic calcite, the bulk sediment’s acid insoluble organic matter (AIOM) was utilized to obtain the uncorrected $^{14}C$ ages (Leventer et al., 2006; Mackintosh et al., 2011). The AIOM samples were prepared at Stanford University by Dr. Robert Dunbar, and analyzed at the Lawrence Livermore National Laboratory Center for Accelerator Mass Spectrometry (CAMS). The uncorrected $^{14}C$ ages were calibrated by using CALIB 7.02 and the Marine 13.14c dataset. The program automatically corrects all ages with an initial global ocean reservoir age of 400 years. An additional $\Delta R$ of 1300 ± 200 years was needed for JPC40 (Mackintosh et al., 2011). Therefore, the local reservoir age for Nielsen Basin is 1700 ± 200 years.

The calibrated ages were used to construct an age model, with the exception of the dates from 2006, 2051, and 2211 cm (Table 2; Figure 17). The uncorrected $^{14}C$ ages at these depths (~14.5 and 19 ka BP) were out of stratigraphic order, and the age at 2211 cm (~25 ka BP) was anomalously high (Table 2). It has been shown in previous reports that these sample depths are subjected to influences from terrestrial carbon in terrigenous sediment (Mackintosh et al., 2011). Several curves were fit to the depth-age data in Figure 18 and examined for the best-fit to the data points. Ultimately, the 3rd-order polynomial equation was decided upon: $y = 9E - 10x^3 + 0.0022x^2 + 1.5554x + 530.45$. This curve produced an $R^2$ value of 0.9984 (Figure 18). In this equation the $y$ signifies the calibrated age (yr BP) and $x$ represents the depth in cm. Confidence in this age model is limited to the diatomaceous sediment, and the depth-age equation was not
applied to the silty mud or diamicton at the base of the core. The diatomaceous sediment extends back to approximately 14 ka BP (Leventer et al., 2006; Mackintosh et al., 2011).

4.2.3 Organic Geochemistry: Pyrolysis-Gas Chromatography-Mass Spectrometer Analysis

NBP01-01 JPC40 is organic-rich and represents open marine conditions. This site contrasts with the sub-ice shelf environments of the AP region. Core JPC40 was also inspected as a potential study area for organic geochemical analysis due to the abundance of diatomaceous mud and ooze. The results from the CNS elemental analyzer were utilized in the depth selection process for JPC40. Sample depths 362, 483, and 553 cm are from laminated diatomaceous horizons and were chosen based on their relatively high wt% carbon (above 1%).

Similar to the AP cores, the qualitative Py-GC/MS analysis did not reveal a large number of peaks or any distinguishing trends down core. The prominent peak observed in the three depths (362, 483, and 553 cm) analyzed contains a base peak of m/z 149, an obvious phthalate (Figure 19). After this prominent contaminant peak an additional phthalate m/z 149 peak emerges, although less pronounced. Similar to the Perseverance Drift data, we believe the m/z 161 peaks observed in JPC40 are true methylindoledione signals and not plasticizers by reason of observed m/z 147,indoledione. Additionally, JPC40 contains other nitrogen compounds such as benzonitriles, indoles and indole-amines, as well as methylated indenes (Figure 19).

All attempts in this study to discern organic biomarkers and conclusively identify organic sources of Antarctic sediments were unsuccessful. The organic geochemical
signals from the extremely low organic content were overwhelmed by plasticizer contamination. Therefore, this study adopted a new approach to investigate the EAM Holocene record by using both organic and inorganic geochemical proxies to complement a set of magnetic proxies reported by Kacperowski (2009).

4.2.4 Nielsen Basin Element Geochemistry

4.2.4a Carbon-Nitrogen-Sulfur Analysis

CNS analysis was employed to determine organic carbon and sulfur content, which are relevant to both primary production and post-depositional diagenetic processes. The presence of plasticizer contaminants in the sediment may impact the elemental carbon results. JPC40 yielded the following wt% element ranges: 0.23-1.96 wt% C, 0.01-0.44 wt% N, and 0.03-0.74 wt % S (Figure 20). The highest wt% for each element occurred in the diatomaceous SMO (360 and 1025 cm) or varved (2153 cm) sediment sections. The lowest wt% for each element occurred in the sediment section where sand and granules where present (2350 cm). The relative standard deviations (RSD) ranged from 0.04-26.27% for C, 0.06-58.80% for N, and 0.01-19.40% for S. The wide range in RSDs is attributed to minor variability results in duplicate or triplicate samples for intervals with especially low CNS levels. Overall, the averages in wt% CNS for JPC40 are: 1.25 wt% C, 0.25 wt% N, and 0.24 wt% S.

The down core profile of the C/S and C/N ratios are displayed in Figure 21. The ratio for C/N remains relatively constant throughout the core until approximately 12 ka BP (core depth 1975 cm). At this depth the sediment coarsened from a silty-clay SMO to medium-fine grained sandy SMO (Figure 17). The C/N ratio continues to increase below
this depth as the core transitions to diamicton. More variability is observed in the C/S ratio than the C/N ratio. The SMO of the upper core, 800-1100 years BP, contained the highest C/S ratio values, whereas the lowest C/S ratio values were detected in the homogenous and varved sediments of the lower core at approximately 13-14 ka BP. Below this section an increasing trend, similar to the C/N ratio, is observed in the C/S ratio as the core shifts to a diamic bottom.

4.2.4b Inductively-Coupled Plasma Optical Emission Spectrometry Analysis (ICP-OES)

Major and trace element analysis by ICP-OES is useful in revealing sediment source changes through trends in elemental abundances. An observable decreasing trend for Ti, Al, Fe, Mn, Zr, and Ba begins at ~14 ka, the top of the till and diamicet layer, and continues up through ~10.5 ka, the location of a facies change from a sandy SMO to a silty-clay SMO (Figure 22abc). A similar trend is observed in the C/N ratio (Figure 21) and the magnetic susceptibility reported by Kacperowski, 2009. This trend is not discerned for Si, Mg, Ca, Sr, or Ni. The upper silty-clay SMO unit reveals three distinctive features occurring at ~1.7, 4.3, and 7.9 ka BP (Figure 22abc). At ~1.7 ka the elements Ti, Al, Fe, Mn, Ba, and Zr all display a sharp increase in abundance while a sudden decrease in abundance is observed at ~4.3 and 7.9 ka for these elements as well as Si.

An inverse relationship is observed for Mg and Si in the down core profiles (Figure 23). The Pearson correlation coefficient for the Mg and Si profiles is -0.71. Pearson correlation coefficients for Ti, Al, Fe, and Mn profiles ranged from 0.87-0.98
(Table 3). The trace elements Ba and Zr also exhibit a positive correlation with Ti, Al, Fe, and Mn (0.78-0.95) (Table 3).

Between ~9 and 10.5 ka BP distinctive pulses are observed in the terrigenous and biogenic ratios including Si/Al, Si/Ti, Al/Ti, Fe/Ti, Ni/Al, and Sr/Al (Figure 24ab). Si and Ba sources include both terrigenous and biogenic input. Therefore, Si/Al and Ba/Al ratios can evaluate Si and Ba excesses derived from biogenic input, since Al sources are strictly terrigenous (Figure 24ab). The Si/Al and Ba/Al ratios confirm the lithological observations that significant inputs of Si and Ba are attributed to biogenic sources down core until ~10.5 ka BP. Al/Ti values range from 14-26 and Fe/Ti range from 8-13, with the highest values occurring between ~9 and 10.5 ka BP. The entire core mean values for Al/Ti and Fe/Ti, 16.5 ± 1.8 and 9.1 ± 0.9, were consistent with the mean values for the till and diamict unit, 15.8 ± 1.9 for Al/Ti and 9.8 ± 1.0 for Fe/Ti (Figure 24a and Table 4).
5. DISCUSSION

5.1 Pyrolysis-GC/MS

Organic carbon content preserved in modern marine settings generally ranges from < 0.25-2% (Killops and Killops, 2009). In order for organic carbon to be preserved various criteria need to converge: availability of primary producers, settling of particulate matter in low energy depositional environments, higher ratios of organic to inorganic inputs, high sedimentation rate, and development of anoxic conditions (Killops and Killops, 2009). The Antarctic cores in this study are located in deep basins, troughs, or sediment drifts. These sites are ideal settings for preserving organic-rich sediment because they meet several criteria for preservation (Harris et al., 1999). They contain low energy depositional environments, high sedimentation rates, and develop anoxic conditions. Additionally, Antarctica surface waters are rich in nutrients due to aeolian dust and upwelling inputs (Kumar et al., 1995). However, Antarctica’s sediment is extremely low in total organic content despite this nutrient-rich upper water.

Production rate variations in time and space are attributed to sea ice and seasonal blooms. The species variability of Antarctic primary producers is restricted by spatial variations and physical water properties (Killops and Killops, 2009). Furthermore, particles suspended in the water column are exposed to degradation and may never reach the sea floor. Suspended organic particulates’ settling velocity can range from ~0.15-160 m day^{-1}, with rate increasing or decreasing as a result of particle density (Killops and Killops, 2009). The shallow CCD around Antarctica reduces the accumulation of biogenic carbonate on the sea floor, and decomposers on and below the sediment water interface will consume deposited particulates. The harsh environment restricts production
and the complex water dynamics obstruct organic deposition, therefore, the preservation of organic matter in the Antarctic sediment record is limited (TOC ~0.2-1%) despite the ideal preservation settings (Domack et al., 2003).

For these reasons, identifying biomarkers in Antarctic sediments posed a challenge for the Py-GC/MS method utilized in this study. Several cores, LMG05-02 KC5A, NBP06-03 KC5, and NBP12-03 KC36, display even number carbon dominance for short chain n-alkanes. Marine phytoplankton have a preference for short chain n-alkanes with odd number carbons (Harada et al., 1995). This preference is in contrast with the observed results, however, microalgae are known to be the biomarker source for long-chain alkanes with no odd or even preference and fatty acids with an even carbon number dominance (Volkman et al., 1998). The two ringed aromatic hydrocarbons, naphthalenes, are distinctly displayed in NBP12-03 KC36 and NBP06-03 KC5. The exact source of the naphthalenes in the cores is unknown. However, resistant proteins, such as plant cuticular waxes, are known sources for naphthalenes in other sediment locations (Gillam and Wilson, 1985; Peulve et al., 1996). Antarctica lacks higher order waxy plants, therefore, the transported method of this source is most likely aeolian.

The presence of different alkylphenols and alkylbenzenes in NBP12-03 KC36 and NBP01-01 JPC40 suggests each core has a varying macromolecular source. Previous studies of marine sediments in other global locations have concluded alkylphenols are attributed to non-lignin sources, such as carbohydrates and alkylbenzenes, and are thought to derive from highly resistant algal macromolecules (Gillam and Wilson, 1985; Peulve et al., 1996). However, these signals are observed early in the scan and are possible pyrolysis remnants. Several cores (NBP10-01 JPC127, NBP12-03 KC36, and
NBP01-01 JPC40) contained aromatic and aliphatic nitriles. Similarly, the assemblages of these compounds include triple bonded nitrogen to either a ringed or chained carbon configuration. Nitriles derive from biopolymer such as proteins and polysaccharides (Gillam and Wilson, 1985; Peulve et al., 1996). Continuing with nitrogen compounds the previous three cores (JPC127, KC36, and JPC40) presented evidence of indoles, a five-membered pyrrole ring fused to benzene ($C_{8}H_{7}N$). Indoles derive from the amino acid tryptophan in proteins, and are thus a marker for microbial organic matter in sediments (Peulve et al., 1996). Interestingly, KC36 and JPC40 revealed an indole derivative bearing two attached ketone groups (indole-dione, Figure 25ab). Indoledione has been identified in the pyrolyzate of marine diatoms (Gillam and Wilson, 1985). The indoledione and methylindoledione detected in the pyrolyzates of diatomaceous Antarctic sediments could thus be interpreted as molecular markers for diatoms. This appears to be true in both Antarctic Peninsula and Nielsen Basin samples, even if they are relatively organic-lean.

NBP12-03 KC36 had the greatest pyrolysis product yield of all six analyzed cores. On its chromatograms, the most prominent peak was elemental sulfur, $S_{8}$.

Interestingly, all three KC36 depths (88, 298, and 504 cm) analyzed contained three distinctive peaks beginning ~2.3 min after the $S_{8}$ peak. These peaks indicate the presence of three $C_{20}$ isoprenoid thiophene isomers, which are alkyl-substituted aromatic sulfur compounds ($C_{20}H_{36}S$). Isoprenoid thiophenes can participate in the formation of kerogens and are thought to be produced by the reaction between $H_{2}S$ and algal phytol ($C_{20}H_{40}O$) or bacterial phytadiene ($C_{20}H_{38}$) (Brassell et al. 1986; Fukushima et al., 1992). At least one phytene compounds are found in organic rich marine sediments, source
rocks, and crude oils (Haven et al., 1990; Katsumata and Shimoyama, 2001). One of the possible precursor compounds (a phytadiene isomer) was detected in pyrolysis products from KC36 (Figure 15 and 16). Additionally, the presence of the short chained isoprenoid thiophenes is a good indication that Perseverance Drift is a prime location for the production of sulfurous kerogens. This is evidence for the diagenetic interaction of the abundant sulfur with the isoprenoids (such as phytol derived from microbial chlorophyll) in these sediments.

Unfortunately, the detected biomarkers for the Antarctic cores (NBP00-03 KC23, NBP10-01 JPC127, NBP01-01 JPC40), by pyrolysis-GC/MS method, were eclipsed by the overwhelming phthalate peaks. The jumbo piston cores contain an inner polyvinyl chloride (PVC) tube. The sediment core is retained in this inner tube, which is sliced lengthwise to create archive and working halves. This possibly exposes the sediment to shavings of PVC. The kasten core is a metal coring device without a plastic liner. However, the sediment sampled from both KC and JPC cores for magnetic and geochemical analysis was placed in low density polyethylene (LDPE) vials in which they were freeze-dried and stored. Overtime the sediment samples could have absorbed compounds degrading from the vial. Additionally, the elemental carbon results can be affected by plasticizers in the sediment.

The amount of sample placed into the GC/MS system is limited by the quartz pyrolysis tube. The sample masses for the cores evaluated in this study ranged from 1-1.5 mg (Nielsen Basin) and 11-15 mg (AP region). The extremely lean TOC values (~0.2-1%) in the Antarctic cores render these weights insufficient for adequate detection by the Py-GC/MS method. Therefore, the next attempt for organic geochemical analysis should
take extra steps to extract the organic material within the sediment and use a liquid injection input system. Additionally, when samples for organic geochemical analysis are collected the subsample should be collected from underneath the top exposed layer and away from the edges of the PVC core. Lastly, depositing samples in glass vials instead of polyethylene vials will eliminate possible phthalate contamination during storage.

5.2 Nielsen Basin Element Analysis

A previous study (Kacperowski, 2009) explored the magnetic properties of Nielsen Basin core NBP01-01 JPC40. The goal was to study the Holocene stability of the East Antarctic Ice Sheet. Magnetic proxies were used to search for intervals of intense melting. Meltwater plumes would supply abundant terrigenous sediment to the ocean. Terrigenous sediment contains iron-bearing minerals. Therefore, Kacperowski, 2009 looked for peaks in parameters such as magnetic susceptibility and induced remanences to identify terrigenous-rich horizons. Such peaks were observed and originally interpreted as cyclical input of magnetite from terrigenous sediment (Kacperowski, 2009). However, a follow-up electron microscopy analysis of magnetic particles extracted from Nielsen Basin sediment revealed only iron sulfides, which are products of diagenesis (Brachfeld et al., 2011). This necessitated revisiting JPC40 with a new set of tools capable of differentiating terrigenous and diagenetic inputs.

Pyritization is a complicated process (Figure 26) involving the dissolution of strongly magnetic (i.e., ferrimagnetic) iron oxides such as magnetite and maghemite ($\text{Fe}_3\text{O}_4$ and $\gamma\text{Fe}_2\text{O}_3$) (Berner, 1984; Canfield and Berner, 1987). The ferric iron from the dissolved minerals is reduced to ferrous iron, which interacts with hydrogen sulfide
(H$_2$S), created during bacterial metabolization of organic matter and the anion sulfate (SO$_4^{2-}$), to create paramagnetic pyrite (FeS$_2$) (Berner, 1984; Canfield and Berner, 1987). Paramagnetic minerals are very weakly magnetic, and the magnetite dissolution zones can be identified by abrupt drops in the intensity of magnetic susceptibility and remanent magnetization (Leventer et al., 1996; Brachfeld et al., 2002). However, if this process is incomplete then there may be preservation of the intermediate iron sulfide greigite (Fe$_3$S$_4$), which is ferrimagnetic (Liu et al., 2004; Rowan and Roberts, 2006; Rowan et al., 2009). This is the case in several intervals in core JPC40 where Kacperowski, 2009 originally believed that magnetite was present. Therefore, CNS and ICP-OES analysis will contribute to reinterpreting the magnetic data by examining organic carbon abundance and iron abundance, respectively, two of the main factors that limit pyrite formation in sediment.

The diamict and sandy-mud in JPC40 represents deglaciation following the LGM (Leventer et al., 2006; Mackintosh et al., 2011). The diamict unit was not analyzed for CNS due to the presence of detrital carbon from terrestrial sources (Mackintosh et al., 2011). The sandy mud, as expected, presented the lowest wt% carbon of all three elements as a result of the sand and granules in this unit. There is an enrichment of terrigenous elements (Al, Ti, Fe) for the diamict and sandy mud units.

Taylor and McLennan (1985) determined elemental ratios for different types of crust, which can be used as provenance indicators. For example, Al/Ti values $\leq$ 10 are typical of basalts and continental crust = 15.8 (Taylor and McLennan, 1985). Upper continental crust is characterized by Al/Ti values of near 26.8 and Fe/Ti values of 11-14 (Taylor and McLennan, 1985). Fe/Ti ratios for the diamict in JPC40 are $9.8 \pm 1.0$ and
Al/Ti values are 15.8 ± 1.9, representing a continental crust provenance. Petrology studies have determined Mac.Robertson Land consists predominately of Precambrian Charnokites, massif-type anorthosites, (Young et al., 1997; Mikhalsky et al., 2006; Winter, 2010) with occurrences of metamorphic granulite facies and mafic dyke intrusions (Sheraton et al., 1981; Sheraton et al., 1984; Mikhalsky et al., 2006). The diamicton data for Nielsen Basin is consistent with these previous petrology studies. We reason that the terrigenous sediment in JPC40 was derived from the local charonckites, specifically orthopyroxene granitoids and monzodiorites, together with tonalitic to granodioritic gneisses and tholeiitte intrusions (Sheraton et al., 1981; Sheraton et al., 1984; Mikhalsky et al., 2006). Additionally, the other lithological units in JPC40 largely agree with this assessment as well, suggesting the sediment inputs are locally derived at this location, even during open marine conditions.

An interval of particular interest to Kacperowski (2009) was the strongly magnetic early to middle Holocene zone at 7.7 to 10.4 ka. The CNS and ICP-OES analyses reveal that incomplete pyritization was a factor in generating the magnetic signals. Within this interval iron concentrations fluctuate between 7.5 to 22 kppm. Carbon remains more stable and low from 10.4 to 8.4 ka (Figure 27). The availability of carbon limits pyritization in this interval. Carbon content peaks at 7.7-8 ka, at which time iron content is low. Therefore, lack of carbon and/or iron from 7.7-10.4 ka interrupted the pyritization process and preserved the ferrimagnetic greigite (Fe3S4), leading to the enhanced remanences in this interval.

The ICP-OES data confirms Nielsen Basin experienced an early Holocene warm period immediately after deglaciation and a mid-Holocene Climate Optimum. These
periods of climatic warming are characterized by high Si concentrations due to the abundance of diatoms in an open marine environment, and low concentrations of Fe, Ti, and Al, attributable to decreases in terrigenous inputs (Figure 28). These were followed by a cooler Neoglacial period marked by substantial increases in the terrigenous element (Fe, Ti, and Al) concentrations combined with lower Si concentration. However, the timing of these intervals is offset from other sites around Antarctica (Domack et al., 2001). This could be a function of uncertainties in radiocarbon chronologies or these events could be time transgressive around Antarctica.

Research on the Palmer Deep places deglaciation at 12 ka, the early Holocene warmth at 11-9 ka, the middle Holocene Climate Optimum at 3.4-9 ka and the Neoglacial at 3.4 ka - present (Domack et al., 2001). Deglaciation in JPC40 is represented by the varved sediments at ~14 ka, roughly 2,000 years earlier than seen in the Palmer Deep and other inner shelf basins and fjords on the western AP (Domack et al., 2001; Brachfeld et al. 2002; Heroy and Anderson 2007). The early deglaciation may be a function of Nielsen Basin’s location on the middle continental shelf and earlier removal of ice as the ice margin retreated landwards. A neighboring inner-shelf basin on Mac.Robertson Shelf, Iceberg Alley (core NBP01-01 JPC43B), correlates with the Palmer Deep timing of deglaciation, ~12 ka (Mackintosh et al., 2013). Evidence of delayed deglaciation around Antarctica suggests the melting of the Antarctic ice sheet did not contribute to meltwater pulse 1a (MWP1a). However, the timing of deglaciation in JPC40 indicates that retreat of the Antarctic ice sheet may have been accelerated by sea level rise resulting from MWP1a, which could have cause the ice sheet to lift off the seafloor and retreat more rapidly (Leventer et al., 2006, Mackintosh et al., 2011).
6. CONCLUSIONS

6.1 Pyrolysis-GC/MS

Phthalate contamination was detected by the Py-GC/MS method used in this study. The sample retrieval and storage method contained PVC and LDPE plastics that possibly transferred into the sediment, causing phthalate signals, m/z 149 and 161, that dwarfed the biomarker peaks in the Antarctic cores. However, in two cores, NBP01-01 JPC40 and NBP12-03 KC36, we concluded the suspect m/z 161 signal was not a plasticizer, but a true methylindoledione signal due to the co-occurrence of its indole (m/z 147). Despite the overwhelming presence of phthalate signals and limited peak abundance due to the lean TOC we were still able to discern a number of the other peaks.

For example, n-alkanes and n-alkenes were detected in AP cores NBP12-03 KC36, LMG05-02 KC5A, and NBP06-03 KC5. The C₅-C₁₈ aliphatic compounds displayed prevalence toward even number carbon dominance suggesting a stronger influence by microbes than algae. Additionally, several nitrogen bearing compounds, indoles (C₈H₇N) coupled with aromatic and aliphatic nitriles (R–C≡N), were detected in NBP10-01 JPC127, NBP12-03 KC36, and NBP01-01 JPC40. As mentioned above, cores KC36 and JPC40 also contained signals for the nitrogen bearing compounds indoledione and methylindoledione, interpreted as pyrolysis markers for diatoms.

The most significant findings were in the strong sulfurous odor emitting core, KC36, located in Perseverance Drift. The Py-GC/MS data displayed a significant elemental sulfur peak, S₈, at approximately 25.7 min for the three analyzed depths (88, 298, and 504 cm). Additionally, KC36 contained three isoprenoid thiophene isomers
(C$_{20}$H$_{36}$S). These organosulfur compounds document diagenetic reactions between sulfur and phytoplankton-derived organic matter.

6.2 Nielsen Basin Element Analysis

Deglaciation in Nielsen Basin began at $\sim$14.3 ka, which is 2,000 years earlier than deglaciation in the AP region. This is possibly due to its location on the middle continental shelf. Stratigraphically above the diamict open marine sediment dominates JPC40. By comparing the geochemistry of the diamict unit to previous petrology studies, this work establishes the terrigenous sediment sources in JPC40. Local charnockites, specifically orthopyroxene granitoids and monzodiorites, together with tonalitic to granodioritic gneisses and tholeiite intrusions (Sheraton et al., 1981; Sheraton et al., 1984; Mikhalsky et al., 2006) are the most likely sources of terrigenous sediment in JPC40. The elemental ratios Al/Ti and Fe/Ti in the diamict are consistent with continental crust provenance as outlined in Taylor and McLennan (1985). The elemental ratios in the open marine section are similar to those in the diamict unit. This similarity indicates the sediment input is locally derived during both ice covered and open marine conditions.

This core was previously investigated by magnetic proxies and was revisited in this study by geochemical proxies. The CNS and ICP-OES results reveal a sequence of warm-cold alternations that is similar to the pattern observed on the WAP, though with different timing. An indication of a warmer environment is observed in Si concentrations. In an open marine environment diatom abundance increases and is reflected by high Si/Al values. On the other hand cold environments are less diatom-rich due to sea ice cover that limits photosynthesis. Therefore, Si/Al values are lower. Additionally,
increased Fe, Al, and Ti concentrations are an indication of a colder environment due to IRD from glacial sedimentation. This study demonstrates that incomplete pyritization was a factor in generating the magnetic signals observed by Kacperowski, 2009. The lack of carbon and/or iron from 7.7-10.4 ka interrupted the pyritization process and preserved the ferrimagnetic greigite (Fe₃S₄), leading to the enhanced remanences in this interval.
REFERENCES


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### Table 1. Antarctic Peninsula and East Antarctica samples analyzed by Py-GC/MS

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Core No.</th>
<th>Core Depth (cm)</th>
<th>Region</th>
<th>Latitude</th>
<th>Longitude</th>
<th>Water Depth (m)</th>
<th>Lithology</th>
</tr>
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<tr>
<td>NBP00-03</td>
<td>K23</td>
<td>0</td>
<td>East Antarctic Peninsula;</td>
<td>64.357</td>
<td>-0.3594</td>
<td>901</td>
<td>Clay-Silt, Diatom Rich</td>
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<tr>
<td>NBP00-03</td>
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<td>East Antarctic Peninsula; Larsen-A; Greenland Trough</td>
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<td>810</td>
<td>Clay-Silt, Diatom Rich</td>
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<tr>
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<td>810</td>
<td>Clay-Silt, Diatom Rich</td>
</tr>
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<tr>
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<td>East Antarctic Peninsula</td>
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<td>810</td>
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<td>810</td>
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<td>LMG05-02</td>
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<tr>
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<td>Grey Laminated Clay-Silt</td>
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<tr>
<td>NBP06-03</td>
<td>KCS</td>
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<td>East Antarctic Peninsula; Larsen-B; Crane Glacier Trough</td>
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<td>NBP10-01</td>
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<td>88</td>
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<td>750</td>
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**Note:** Lithology descriptions are indicative of the predominant sediment type and may vary slightly depending on the specific analysis and context.
Table 2. Radiocarbon Dates for NBPOl-01 JPC40

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<th>Lab ID</th>
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<th>Core number</th>
<th>Depth interval (cm)</th>
<th>Carbon Source</th>
<th>$^{14}$C Age (yr BP)</th>
<th>Calibrated Age (cal. yr BP)</th>
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<td>134382</td>
<td>NBP01-01</td>
<td>JPC40</td>
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<td>AIOm</td>
<td>2400 ± 35</td>
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<td>27667 ± 164</td>
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$^a$ AIOm = acid insoluble organic material

$^b$ Calibrated with CALIB 7.02 Marine 13.14c Dataset; ∆R = 1300 ± 200 yrs and the built-in R = 400 yrs; Total Reservoir Age = 1700 ± 200 yrs

$^c$ One-sigma error

$^d$ These dates were not used in the development of the age model
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Table 4. Element ratio mean and standard deviation for NBP01-01 JPC40 lithologic units and entire core

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<th>Depth (m)</th>
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<th>Al/Ti Mean</th>
<th>Al/Ti STDEV</th>
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<td>16.5</td>
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Figure 1. The Transantarctic Mountains (TAM) separate the continent of Antarctica into western and eastern sections (IBCSO Version 1.0). East Antarctic Margin and Antarctic Peninsula study areas are indicated (Figure generated using GeoMapApp).
Figure 2. Antarctic Peninsula core locations (listed clockwise): Barilari Bay, NBP10-01 JPC127; Perseverance Drift, NBP12-03 KC36; Greenpeace Trough, NBP00-03 KC23; Hektoria Basin, LGM05-02 KC5A; Crane Glacier Trough, NBP06-03 KC5. See Figure 1 for geographic context (Figure generated using GeoMapApp).
Figure 3. East Antarctic study area showing Mac.Robertson Land and the core location for Nielsen Basin. See Figure 1 for geographic context (Figure generated using GeoMapApp).
Figure 4. Mac.Robertson shelf geomorphic zones (from Harris and O’Brien, 1996).
Figure 5. Bathymetry of Mac. Robertson shelf, Nielsen Basin (Mackintosh et al., 2013).
Figure 6. Schematic of sediment sources and transport methods on Mac.Robertson shelf (Harris and O’Brien, 1996; Sedwick et al., 2001).
Figure 7. Modified stratigraphic columns for Greenpeace Trough, NBP00-03 KC23; Crane Glacier Trough, NBP06-03 KC5; and Barilari Bay, NBP10-01 JPC127.
Figure 8a. Total ion current for NBP00-03 KC23 core depth 0 cm.

Figure 8b. Mass spectrum for retention time 13.9 min; base peak m/z 161, methylindoledione.
Figure 9. Mass range m/z 57 for NBP00-03 KC23 core depth 65 cm. Identified peaks are n-alkanes: a) C_{12}; b) C_{14}; c) C_{16}; d) C_{18}.
Figure 10. Mass range m/z 57 for LMG-05-02 KC5A core depth 90 cm. Identified peaks are \( n \)-alkanes: a) \( C_{12} \); b) \( C_{14} \); c) \( C_{16} \); d) \( C_{18} \); e) \( C_{20} \).
**Figure 11.** Naphthalene series, mass range m/z 128, 142, and 156 for NBP06-03 KC5 core depth 70 cm: a) naphthalenes; b) methylnaphthalenes; c) dimethylnaphthalenes; d) trimethylphenylindane. Co-eluting compounds include indane, indole, naphthalenol, and other unidentified compounds containing a base peak of m/z 141.
Figure 12a. Mass range m/z 55 and 57 for NBP06-03 KC5 core depth 25 cm. Identified peaks are n-alkanes (C) and methylated hydrocarbons (brHC): a) C12; b) C13; c) C14; d) brHC; e) C16; f) brHC; g) C18.

Figure 12b. Mass range m/z 55 and 57 for NBP06-03 KC5 core depth 70 cm. Identified peaks are n-alkanes (C) and methylated hydrocarbons (brHC): a) C12; b) brHC; c) C13; d) brHC; e) C14; f) brHC; g) C15; h) brHC; i) C16; j) brHC; k) C17; l) brHC; m) C18.
Figure 13a. Total ion current for NBP06-03 KC5 core depth 0 cm.

Figure 13b. Mass spectrum for retention time 14.0 min; base peak m/z 161.
Figure 14. Total ion current for NBP10-01 JPC127 core depth 465 cm. Identified peaks: a) 1-methyl,4(1-methylethyl)benzene; b) dimethylindene; c) iso-dimethylindenes; d) indole; e) base peak m/z 161, methlyindoledione; f) base peak m/z 147, indoledione; g) tetrahydrodimethylnaphthalene; h) tetramethylnaphthalene and branched alkane coeluting; i) base peak m/z 149, phthalate; j) C<sub>16</sub> n-alkane; k) tetradecanenitrile; l) prist-2-ene; m) branched alkane; n) C<sub>18</sub> n-alkane; o) hexadecanenitrile; p) phthalate; q) C<sub>20</sub> n-alkane; r) C<sub>22</sub> n-alkane.
Figure 15a. Total ion current for NBP12-03 KC36 core depth 88 cm. Identified peaks: a) benzopropanenitrile; b) indole; c) methylindole and dimethylnaphthalenes; d) base peak m/z 161, methylindoledione; e) base peak m/z 147, indoledione; f) base peak m/z 149, phthalate; g) diketodipyrrole; h) tetradecanenitrile; i) prist-2-ene; j) pentadecanenitrile; k) phytene isomer; l) phytadiene isomer; m) hexadecanenitrile; n) elemental sulfur, S₈; o) thiophenes (identified in Figure 15b). See Figure 16 for a list of identified n-alkenes and n-alkanes.
Figure 15b. Chromatogram modified from the total ion current graph for NBP12-03 KC36 core depth 504 cm. A zoomed in view of a) elemental sulfur peak, S₈; b) 2,3-dimethyl-5-(2,6,10-trimethylundecyl)thiphene c) 3-methyl-2-(3,7,11-trimethylldodecyl)thiophene; d) 3-(4,8,12-trimethyltridecyl)thiophenes (Katsumata and Shimoyama, 2001).
Figure 16. Mass range m/z 55 and 57 for NBP12-03 KC36 core depth 298 cm. Identified peaks are n-alkenes (C) and n-alkanes (C) unless otherwise stated: a) \(^\text{11}\text{C}\); b) \(^\text{12}\text{C}\); c) \(^\text{13}\text{C}\); d) \(^\text{14}\text{C}\); e) \(^\text{15}\text{C}\); f) \(^\text{16}\text{C}\); g) tetradecanenitrile; h) \(^\text{17}\text{C}\); i) prist-1-ene; j) prist-2-ene; k) \(^\text{18}\text{C}\); l) iso-phytadiene; m) hexadecanenitrile; n) \(^\text{19}\text{C}\); o) S; p) \(^\text{20}\text{C}\)
Figure 17. Stratigraphic Column for Nielsen Basin (after Kacperowski, 2009).
Figure 18. Nielsen Basin Age Model generated by utilizing calibrated radiocarbon calibrated ages from Mackintosh et al., 2011 (see Table 2, Radiocarbon Dates).
Figure 19. Total ion current for NBP01-01 JPC40 core depth 362 cm. Identified peaks: a) benzolnitrile; b) methylnaphthalenes and indole-amines; c) phthalic anhydride; d) indene; e) base peak m/z 161, methylindoledione; f) base peak m/z 147, indoledione; g) and h) base peak m/z 149, phthalate.
Figure 20. Nielsen Basin down core results from CNS element analysis.
Figure 21. Nielsen Basin C/S and C/N ratios vs. age (ka BP).
Figure 22a. Nielsen Basin ICP-OES abundance results in ppm vs. age. From left to right: Si, Ti, Al, and Fe.

Figure 22b. Nielsen Basin ICP-OES abundance results in ppm vs. age. From left to right: Mn, Mg, Ca, and P.
Figure 22c. Nielsen Basin ICP-OES abundance results in ppm vs. age. From left to right: Ba, Sr, Ni, and Zr.
Figure 23. NPB01-01 JPC40 displays an inverse relationship between Si and Mg.
Figure 24a. Nielsen Basin element ratios: Si/Al, Si/Ti, Al/Ti, and Fe/Ti.

Figure 24b. Nielsen Basin element ratios: Ba/Al, Sr/Al, and Ni/Al.
Figure 25a. Methylindoledione (m/z 161) mass spectrum and chemical structure (webbook.nist.gov).

Figure 25b. Indoledione (m/z 147) mass spectrum and chemical structure (webbook.nist.gov).
Figure 26. Schematic of the pyritization process (from Rowan et al., 2006).
Figure 27. Nielsen Basin Fe (ppm) and C (wt%). The strongly-magnetic interval (7.7-10.4 ka) detailed in Kacperowski, 2009 is shown in red.
Figure 28. Five distinctive Holocene intervals and the radiocarbon-based ages for Nielsen Basin.