Depositional History of Miocene-Age Sediments from the Weddell Sea, Antarctica, Using Sedimentological and Geochemical Proxies
by
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I dedicate this work to my little sister Katherine, who is strongest person I know.
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Abstract

Understanding the stability of Antarctic Ice Sheets is a key to understanding past climates and the response of ice-sheets to warming. In this thesis, I examined the middle through upper Miocene marine sedimentological and geochemical record in the Weddell Sea. Sediments were recovered at Ocean Drilling Program (ODP) Site 694 located in 4653 m of water in the northern Weddell Sea Abyssal Plain, but recovery was poor and many of the recovered sediments were disturbed. Seven lithological units were identified based on composition and sedimentary structures. Preliminary ages were assigned based on diatom datums. Turbidites are present throughout most of the section. Between about 17 and 14.3 m.y. diatoms formed 10 to 40% of the sediment ice-rafted detritus (IRD) was rare. After an interval of glacial-marine sediment with few diatoms, IRD is common. Between 14.2 and 9 m.y. diatoms are absent or present in lower abundance.

The Mid-Miocene Climatic Optimum (MMCO) occurred between ~17 and 14.5 Ma, when \( \delta^{18}O_{/oo} \) lightened to 1.6. From the late Oligocene through the MMCO, the EAIS is assumed to have been ephemeral based on the light isotope values. After the late MMCO, \( \delta^{18}O \) values got heavier by ~0.8 \( _{/oo} \) and by 13.5 m.y. the EAIS became a permanent covered by ice. We postulate that diatomaceous sediments were deposited in the warmer interval of the MMCO, that the glacial marine dominated sediment (Lithologic Unit VI) marked the end of the MMCO, and that the sediments above it were deposited after the EAIS became a permanent feature of the cryosphere. During this time sediments of a mixed provenance of clays, silts and gravels were observed for sediments with ages 10.44, 11.35, 12.51, 14.08, 14.14 and 14.23 Ma.
Considerable work was expended on geochemical proxies to determine provenance and its compositional characteristics. The primary analytical method that was chosen is XRF core scanning. This method is nondestructive, relatively inexpensive, and provides high-resolution data. Data is expressed as elemental intensity. Two different methods were used to convert elemental intensity to weight percent oxide, the Data Reduction Method and the Log Ratio Calibration Equation (LRCE) model. Both methods require actual sample analysis for ground truthing and gave similar weight percent oxide results. In addition to the XRF core scanner, select samples were analyzed for major, minor, trace and rare earth elements.

The geochemical proxies were used to assess the composition, tectonic activity, elemental enrichment and the degree of chemical weathering. All of these proxies indicate a felsic provenance with zircon enrichment most likely due to sediment recycling. The samples displayed similar Upper Continental Crust and Chondrite patterns, which indicates that these sediments have similar compositions and possibly share the same provenance, this being geologically varied regions within East Antarctic. This is expected because the West Antarctic Ice Sheet had not form until ~ 8 m.y.
1. Introduction

This thesis is an investigation of the Miocene (~17-9 m.y.) depositional history of the Weddell Sea Abyssal Plain as recorded at ODP Site 694. The objective is to identify changes in the source area through chemical analysis of the sediments and changes in depositional processes through sedimentary structures. This information is used to interpret the growth and stability of the Antarctic Ice sheets.

1.1 Antarctic Geology

Antarctica is a continent about the size of the United States and Mexico. Over 95% of it is covered by ice that averages a mile in thickness. This makes understanding it’s geology and tectonic history difficult and open to considerable debate. It’s geologic composition has been determined by using 1) outcrops from the few land exposures, especially around the perimeter, 2) what is determined from plate reconstructions to be adjacent geology in other land masses, 3) sediment cores and 4) geophysical investigations. Not surprising, there is some disagreement about the history and the geology (e.g. Harley, 2005, Boger, 2011, Direen, 2011).

Antarctica is divided into two major sections, East Antarctica and West Antarctica; both contain two different geologic entities. East Antarctic consists of a shield and the Transantarctic Mountains (TAM) (Figure 1.1). The shield contains many geologic terranes dating back to the Archean and ending with the breakup of Gondwana (Table 1.1), but most of the orogenies took place in the Precambrian and ended with the Ross Orogeny about 500 my ago. Overlying the shield are Permo-Triassic continental sediments and Jurassic mafic basalts from dyke swarms and a few plateau basalts (Harley, 2005). The Transantarctic Mountains, which separate East and West Antarctica, are underlain by deformed, metamorphosed EAS rocks and
were intruded by granites during the Ross Orogeny. They are overlain by Devonian
to Triassic/Jurassic sedimentary rocks, e.g. the Beacon Supergroup and volcanics,
consisting of dolorite sills and basalt from the Ferrar Group (Harley, 2005).
Figure 1.1A: Antarctica showing the older East Antarctic Shield on the right, the Mesozoic to Cenozoic West Antarctic on the left, with the Trans-Antarctic Mountains in the center (Harley, 2005). The insert gives the location for Figure 1.1B. Figure 1.1B: Antarctic land places surrounding the Weddell Sea with the location of ODP Site 694. Shackleton Range, Theron Mountains, Coats Land and Dronning Maud Land are all considered to be part of East Antarctica. (adapted from Flowerdrew et al., 2012).
<table>
<thead>
<tr>
<th>Orogeny</th>
<th>Occurrence</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gondwana Break-up</td>
<td>175 Ma to 72 Ma</td>
<td>Isolation of Antarctica</td>
</tr>
<tr>
<td>Peninsula Orogeny</td>
<td>250 Ma</td>
<td>Evolution of Antarctic Peninsula</td>
</tr>
<tr>
<td>Ross Orogeny</td>
<td>500 Ma</td>
<td>Extension and intrusion of granite batholiths</td>
</tr>
<tr>
<td>Pan-African Orogeny</td>
<td>600 Ma to 550 Ma</td>
<td>Final formation of Gondwana</td>
</tr>
<tr>
<td>Beardmore Orogeny</td>
<td>633 Ma to 620 Ma</td>
<td>Formation of ancestral Transantarctic Mountains</td>
</tr>
<tr>
<td>Early Ruker Orogeny</td>
<td>2 Ga to 1.7 Ga</td>
<td>Intercratonic basin formation</td>
</tr>
<tr>
<td>Insel Orogeny</td>
<td>2650 ± 150 Ma</td>
<td>Reworking of old crust, final craton building event</td>
</tr>
<tr>
<td>Humbolt Orogeny</td>
<td>3 Ga</td>
<td>Deformation of existing basin material</td>
</tr>
<tr>
<td>Rayner Orogeny</td>
<td>3.5 Ga</td>
<td>Thickening of the craton</td>
</tr>
<tr>
<td>Napier Orogeny</td>
<td>4 Ga ± 200 Ma</td>
<td>Foundation of East Antarctic craton</td>
</tr>
</tbody>
</table>

Table 1.1: Antarctic orogenic events (from Schwarz, 2010).

West Antarctica is formed by an assemblage of microplates, such as the Paleozoic Ellsworth-Whitmore Mountains with little Mesozoic volcanism and microplates such as Marie Byrd Land, Thurston Island and the Antarctic Peninsula, which contain extensive Mesozoic arc-related magmatism. The two marginal seas, the Weddell and Ross Seas, are extensional basins and form the second geologic entity of West Antarctica. Their formation is associated with the uplift of the TAM and some Cenozoic magmatism in East Antarctica (Harley, 2005).
Boger (2011) provides an extensive and detailed history of the tectonic evolution of Antarctica (Figure 1.2). In his simplified map of the tectonic provinces, sediments from Domains 1, 3 and 4 can be expected to provide East Antarctic sediment to the Weddell Sea Basin and ODP Site 694. In contrast West Antarctic sediment will come from Domain 5. Unraveling the complex interplay of these two source areas is an unfulfilled task of this thesis.

1.2 Climate History

The climatic history of Antarctic glaciation is determined from benthic oxygen isotope values from ocean sediments collected around the world (Figure 1.3) and modeling (DeConto and Pollard, 2003, Pollard and DeConto, 2009). This project seeks to understand the glacial history of Antarctica in the Miocene between 17 and 9 m.y. as recorded in the Weddell Sea Abyssal Plain. This is being done by looking at sediment composition, structures and chemistry in cores recovered from ODP Site 694.
This time interval includes the Mid-Miocene Climatic Optimum, a global warming event that occurred between ~17 and 14.5 Ma, when d18O o/oo lightened to 1.6, almost as light as the beginning and end of the Oligocene (Figure 1.3). From the late Oligocene and through the MMCO, the EAIS is assumed to have been ephemeral based on the light isotope values. Following the MMCO, d18O values dropped by ~0.8 o/oo and by 13.5 m.y. the EAIS became a permanent feature. The West Antarctic Ice Sheet (WAIS) did not begin to form until ~ 8 m.y. ago, after the time interval investigated in this project. Therefore any sediment from West Antarctica had to be transported via wind or currents. In contrast, East Antarctic sediment could have traveled by both of those means and through ice rafting.

Figure 1.3: Cenozoic oxygen isotope data from benthic foraminifera showing the hypothesized initiation of Antarctic Ice Sheets. Also included are major climatic tectonic and biotic events (from Zachos et al., 2001).
New satellite data collected during the 2007-2009 polar year has allowed NASA scientists to map present day Antarctic ice drainage areas, velocities and associated stress patterns (Figure 1.4, Rignot et al., 2011). This data provides a new view of ice sheet dynamics with an anastomosing and dendritic drainage basins extending far into the continent and dominated by basal slip. It isn’t clear if basal slip would entrain more sediment that could then be delivered to the marine environment. The map however does clearly show the source areas for sediment to the Weddell Sea.

Figure 1.4: Antarctic drainage basins and velocities (Rignot et al., 2011).
Within the Weddell Sea, there is a strong clockwise current, the Weddell Sea Gyre (Figure 1.5). Today this gyre carries circum-Antarctic water from the east into the Weddell Sea. If this gyre existed in the past, it could have transported additional sediment from the EAS into the Weddell Basin.

Figure 1.5: Surface water flow in the Weddell Sea (awi, 2013)

1.3 Circum-Antarctic Miocene Sediments

Miocene sediments have been recovered by the Ocean Drilling Program (ODP)(Figure 1.6) and by Andrill, a coring program that drilled through the Ross Sea Ice shelf and into continental shelf sediments. Unlike the ODP cores, the Andrill drilling system, which did not have to deal with sea conditions and icebergs, had very high recovery. It is through the enhanced diatom biostratigraphy developed through
the Andrill program, that the sediments recovered during Leg 113 can now provide a more accurate age resolution.

Figure 1.6: Circum-Antarctic cores from DSDP/ODP/IODP that recovered Miocene age sediment (Pierce, 2012).

The Ross Sea has been intensely studied using sediment cores that were recovered by the ANDRILL project. A nearly complete recovery of 98% has allowed for scientists to construct a complete climatic and glacial history of the Ross Sea area.

Fielding et al., 2011 studied the AND-2A drill core that was recovered from the Southern McMurdo Sound. This drill core shows a well-developed stratigraphic cyclicity. Seventy-four high-frequency glaciomarine sequences were recognized, which were grouped into thirteen composite sequences. Composite Sequence 6: 17.35 – 17.3 Ma records a period of ice retreat, which may be associated with the Mid-Miocene Climatic Optimum. Composite Sequence 7: 17.3 – 16.7 Ma records a return to the glacially proximal conditions. Composite Sequence 8: 16.7 – 16.5 Ma shows ice distal conditions and may coincide with a warm period of the MMOC. Composite Sequences 9 – 11: 16.5 – 14.5 Ma records ice-proximal conditions and coincides with
the Mi2 glaciation (Fielding et al., 2011). The changes highlighted by the sequences show that ice sheet growth and retreat varied with climatic changes during the and after the Mid-Miocene Climatic Optimum.

Another study used sedimentary facies distribution to determine the glacial history of the Ross Sea. Passchier et al., 2011 recognized three facies associations; a diamicite dominated facies association, a stratified diamicite facies association and a mudstone-dominated facies association. They found that younger than 15.4 Ma had diamicite-dominated facies associations. This sedimentary facies association has been interpreted as cold glacial regimes. 17.6 - 15.4 Ma had stratified diamicite-mudstone facies and this is indicative of fluctuations in the extent of tidewater draining the East Antarctic Ice Sheet. Ice-retreat phases were found to generally coincide with minima in the delta-O-18 records; and ice advances generally correlated with the delta-O-18 maxima. However, there was a discrepancy between the isotopic records and observed facies around 14.7 – 14.3 Ma. Passchier et al., (2011) found ice advanced on the Antarctic continental margin at proportions greater than today’s.

The AND-2A drill core only constructs the climatic and glacial history for the South Pacific Ocean region off Antarctic; however, no studies have been conducted on the glacial history of the South Atlantic Ocean region of Antarctica. The Ocean Drilling Program (ODP) was the only operation to obtain deep marine sediment from the Weddell Sea. The purpose of this research is to determine the depositional and glacial history of Antarctica using the sediments from the Weddell Sea. In this project, a variety of geochemical proxies have been chosen to observe changes in the deep marine sediments. The X-ray Fluorescence (XRF) core-scanner will be used to
obtain elemental data from the split core sediments. This method has been chosen because it is a non-destructive and inexpensive way of obtaining elemental data. The elemental data is given in intensities, that is, counts per seconds; as a result, compositional data analysis will be used to convert intensities to weight percent. In order to ground truth the elemental intensities, the ICP-MS will be used to obtain percent weight of major and trace elements. A combination of sedimentary facies and the geochemical data will be used to determine the depositional process (turbidity current, IRD or hemipelagic) and ultimately the glacial history.

Provenance studies conducted by Schwarz (2011) will also be incorporated into this project to determine provenance and associated orogenies of the sediments. Schwarz used U/Pb dating for zircons and $^{40}\text{Ar}/^{39}\text{Ar}$ for the hornblendes.

1.5 ODP Site 694

The Weddell Sea is a bathymetric tongue located between the Antarctic Peninsula and the EAIS. Because of poor recovery and age control, very few studies have been conducted on these cores. However, the use of biosiliceous microfossils, specifically diatoms, has given us better age resolution and allows for better sedimentary analysis.

Site 694 is located within the northern part of abyssal plain of the abyssal plain of the Weddell Sea Basin. The Weddell Sea covers 2.8 million km$^2$ of ocean on the Atlantic side of West Antarctica, opposite the Ross Sea. Ocean Drilling Program (ODP) Leg 113 is the only scientific ocean drilling expedition in the Weddell Sea (Figure 1.1).
ODP Site 694 was cored during Leg 113 in February, 1987 at 66° 50.835’ S, 33° 26.826’ in 4653 m of water, in the northern part of the Weddell Sea Abyssal Plain. Because of its depth, it is well below the calcium carbonate compensation depth (CCD) and no carbonate was recovered. Three holes were drilled. The first Hole (A) recovered a full core barrel, meaning that the sediment-water interface was missed. The B Hole extended to 179.2 m and was abandoned because of equipment failure. The latch assembly in the Extended Core Barrel (XCB) parted and fell into the hole. The C Hole was washed to 179.2 m and then cored to a depth of 391.3 m when equipment failure again caused the hole to be abandoned.
2. Methods:

2.1 Sample selection: Set 1

Two sets of samples were selected for analyses; the first set of samples was selected after using the Proceedings of the Ocean Drilling Program, Initial Reports for Leg 113, Site 694 (Schwarz 2010 and 2011). Samples were selected for coarser sediment and a total of 115 samples were selected for this first set.

2.2 Grain Size Analysis on Sample Set 1

A half of each sample was weighed and placed in a 50 ml centrifuge and filled with 1% Calgon water to approximately 40 ml. The other half of each sample was stored as a library sample. The samples were allowed to sit overnight, then vortexed to break apart fine particles and mix the samples. The samples were then wet sieved into four size fractions; <63 um, 63 – 150 um, 150 – 2000 um and >2000 um. Each size fraction was dried and weighed. The weight percent for each fraction was calculated per sample.

Particle size distribution was determined using the Horiba LA-950 laser particle size analyzer on the total (non-sieved) sample. Particle size is determined by the scattering properties of the individual grains. The particle size analyzer is able to measure grains ranging from 0.01 – 4000 um. This analysis was done three times for each sample.
2.3 Age of Sediments

The age boundaries (Table 2.1) for the Miocene were determined using diatom biostratigraphy (Harwood and Gewecke, 2009).

<table>
<thead>
<tr>
<th>Age Boundary</th>
<th>Gersonde &amp; Burkle (1987)</th>
<th>Harwood Age (Ma)</th>
<th>Magnetics</th>
<th>Florindo et al, 2003 Site 1165</th>
</tr>
</thead>
<tbody>
<tr>
<td>upper Pliocene/lower Pliocene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>lower Pliocene/upper Miocene</td>
<td></td>
<td>5.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>upper/middle Miocene</td>
<td></td>
<td>11.61</td>
<td>C5B-base</td>
<td>C5R-2Rmiddle, 11.15</td>
</tr>
<tr>
<td>middle/lower Miocene</td>
<td></td>
<td>15.97</td>
<td>C5BR/C5CN</td>
<td>16.40</td>
</tr>
<tr>
<td>lower Miocene/upper Oligocene</td>
<td></td>
<td>21.00</td>
<td>23.03</td>
<td>23.90</td>
</tr>
</tbody>
</table>

Table 2.1: Miocene Boundary ages.

Ages were obtained from the set of 115 samples. A graph of age versus depth was plotted, a trend line was added and the equation of the line was obtained. The equation of the line was used to determine the ages (Figure 2.1).

![Diatom Ages vs. Depth](image)

Figure 2.1: Calculation of the linear equation for interpolation at other depths.
2.4 X-Ray Fluorescence (XRF) Core Scanning

X-ray fluorescence (XRF) measurements are used to determine elemental composition. In these analyses X-rays bombard a sample, exciting it’s electrons and causing some electrons to be ejected from the inner atomic shells. These vacancies are filled by outer shell electrons that fall inward. As this happens, energy is emitted. Each element has a characteristic fluorescence energy and wavelength spectra. These are measured in the detector, which determines the element and its relative abundance.

Miocene cores from Holes 694B and 694C were analyzed for elemental data using a third generation Avaatech XRF scanner with a Canberra X-PIPS SDD (silicon drift detector), model SXD. This is a spectroscopy sub-system that is sensitive to X-rays and low-energy gamma rays and has an internal collimator. Measurements were made at the International Ocean Drilling Program (IODP) in the Texas A&M University Research Park, College Station, TX. The XRF core scanner provides elemental identification for elements ranging from Aluminum (Al) to Uranium (U).

This method was chosen because it is a nondestructive way to obtain high-resolution geochemical data for split sediment cores. X-ray excitation is used to produce a response from the elements on the surface of the split core. The response of these elements is dependent on fluorescent radiation. Data was produced as counts per second. Elemental counts were collected for Al, Si, P, S, Cl, Ar, K, Ca, Ti, Cr, Mn and Fe.

Split cores were cleaned by scraping the surface. A 4 um thick SPEXCertifwerp Ultralene film was laid across the core to avoid contaminating the instrument. Measurements were taken every cm except when there were cracks in the
surface or the surface was very irregular. Large dropstones were removed before scanning. Split cores were then placed in a core holder. A rack-mounted, automated X-ray tube and detector moves down the core. At each measuring location the instrument lowers onto the core surface, collects data, rises, and then moves to the next location. A 1 cm$^2$ area of the core surface was irradiated for 20 s, every cm with 800 microamps and 10 kV. It took approximately two and a half hours to measure 150 cm of a sediment core.

2.5 Initial Data Processing

The sediments in these split cores were mostly dry. Although efforts were made to avoid uneven and broken sections not all measurements were taken with a good contact with the sediment. Argon values indicate how much air is present between the helium flushed prism and the surface of the split core. This means that the higher the argon value, the higher the volume of air and the poorer the sediment-detector contact. Measurements with argon values above -500 counts were deleted. In addition, any count with a negative number was converted to zero. This was primarily applied to phosphorous and sulfur.

2.6 Sample selection: Set 2

Twelve samples from Set 1 were analyzed for major elements by XRF. Correlation of these values with core-scanner values was not initially obvious. We thought this might be because the XRF core scanner was sampling a small surface area and the samples were from larger-deeper areas. Additional samples were requested using the method described below.
The Statistical Package for the Social Sciences (SPSS) program was used to analyze geochemical elemental ratios using the XRF core-scanner data. K/Ti and Al/Ti ratios were observed down core and the K/Ti ratios were found to be statistically significant. This was determined using by using the descriptive statistics function and looking at the Sig values for K compared to Ti and Al compared to Ti. Core 694C-14X was used for this analysis because this core has 100% recovery. The K against Ti values had lower Sig values and so this ratio was more statistically significant than Al/Ti. The K/Ti ratios were plotted against depth to observe down core lithologic changes. These graphs were overlain on the high-resolution photos of each section to observe the changes in sediment and elemental ratios. Sample locations were selected from areas that had XRF core-scanner data and displayed a constant value within the given interval. Samples were also selected in areas that showed changes in grain size and/or color. Photographs were marked and sent to the Gulf Coast Repository for resampling. The new samples were taken from the upper few millimeters of the split cores, the area that would have been measured by the X-rays. Figures 3.2 and 3.3 shows sections 694B-22X-2 and 694C-5X-2 overlain with K/Ti ratios (in blue) and argon values (in pink). Argon values were also plotted down core with the K/Ti ratios in order to identify any cracks or uneven surfaces (Figures 2.2 and 2.3).
Figure 2.2: Sections 694B-22X-2 overlain with K/Ti ratios (in blue) and argon values (in pink).
Figure 2.3: Sections 694C-5X-2 overlain with K/Ti ratios (in blue) and argon values (in pink).
2.7 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Eighty samples were selected from sets 1 and 2 for ICP-MS analysis. The sediments were dried overnight at 100 °C and homogenized using an agate mortar and pestle. At least 1 gram of each sample was taken from the homogenized material. Although not part of this thesis, the Minolta CM-2022 spectrophotometer was used to take spectral data for each sample. Three repeat measurements were made for each sample. Samples were then sent to SGS Mineral Services in Canada for analysis. The Sodium Peroxide Fusion ICP-OES and ICP-MS method was used for analysis. The samples were analyzed for 54 major, trace and rare earth elements.

Elemental abundances are determined by the mass spectrometry of ions that are produced in an inductively coupled Ar plasma. A stream of Ar carrier gas, liquid or solid is used to introduce the sample to an inductively coupled Ar plasma. The ions that are produced are extracted from the plasma into a vacuum enclosure using an interface region containing two millimeter-sized apertures. An ion lens system focuses the analyte and the isotopes are separated by mass/charge ratio by the mass spectrometer and measured with a detector.

2.8 X-ray Fluorescence (XRF) Analyzer – Bruker S4 Pioneer

Forty-one samples were selected down core for XRF analysis. The samples were ground until homogenized, dried at 100 °C. Then samples were weighed, heated 1040 °C for 30 minutes and reweighed. This removes any remaining water or volatiles in hydrated minerals and is called Loss on Ignition (LOI).

Then, 2.5 grams of lithium metaborate flux was added to 0.5 grams of sample in order to melt the sample. Each sample was heated for 8 minutes at 1040 °C and
stirred at 3- and 5-minutes. The molten mixture was quenched on a plate heated to 235 °C and molded into a glass disc. The samples were analyzed for Na$_2$O, MgO, Al$_2$O$_3$, SiO$_2$, P$_2$O$_5$, K$_2$O, CaO, Fe$_2$O$_3$, MnO and TiO$_2$ in weight percent. oxide Standards for this analysis included Syenite ST – 1, Rhyolite, Glass Mountain, Granodiorite, Silver Plume, Colorado, GSP-2 and Icelandic Basalt, BIR-1.

2.9 Processing and Calibration of XRF Core-Scanner Data

Relative X-ray intensities (counts) are not a true representation of a sample’s elemental composition. For samples, the weight concentration of an element is determined by a complex formula, which includes factors such as the calibration constant, an element’s sensitivity to detection and the matrix effect and counts/area can be converted to wt% oxide. This is not possible with a core scanner.

Scanner data is given in count rates (counts/unit time/unit area) or as a ratio (e.g. Rothwell et al., 2006). Attempts have been made to convert core scanner data to elemental oxide concentrations by linear regression cross-plots of intensity and concentration (Jansen et al., 1998). Figures 2.4 (a,b,c,d) show cross plots and linear regression equations for Si against SiO$_2$, K against K$_2$O, Fe against Fe$_2$O$_3$ and Ti against TiO$_2$ respectively. Each sample analyzed using the XRF Analyzer represents a 2 cm interval, which is equivalent to 5 XRF results per interval (analysis done at 5 mm intervals). The median was determined for each 2 cm interval and each median to represent the scanner data for its corresponding interval.
(a) SiO$_2$ wt.% against Si counts per second

\[ y = -3E^{-05}x + 79.462 \]

\[ R^2 = 0.0348 \]

(b) K$_2$O wt.% against Si counts per second

\[ y = 2E^{-05}x + 1.0073 \]

\[ R^2 = 0.78153 \]
Table 2.2 Wt% oxide against elemental cps (a). Si against SiO$_2$ (b). K against K$_2$O (c). Fe against Fe$_2$O$_3$ (d). Ti against TiO$_2$. 
1. Elemental ratios

Elemental ratios provide qualitative information about depositional history and are probably the most common use of XRF core scanner data. This works well when there is a distinct lithologic change such as Heinrich Events in the North Atlantic (Hoddell et al., 2008). However, the Site 694 ratios, discussed under results, do not show such obvious depositional changes. Therefore we employed two different analytical methods to convert our data into wt%.

2. Raw and Normalized Elemental Method

Columns were created for elemental scaling and normalized values for the following elements: Al, Si, K, Ti, Mn, Fe, P and Ca. The median intensities were calculated for each element followed by the median values of each oxide obtained from the XRF analyzer. The median intensities were matched with the corresponding median oxide weight percent. Table 2.2 shows a set of 24 samples that are comprised of three major oxides SiO₂, Al₂O₃ and P₂O₅.

The samples are scaled using the following series of equations:

\[ S_e = \text{Med}\%_e \times \left( \frac{\text{PeakArea}_e}{\text{PeakArea}_{e, \text{med}}} \right) \]

Where,
\[ \text{Med}\%_e = \text{median of the weight percent of each oxide obtained from the XRF Analyzer, for example, for Al, Al}_2\text{O}_3 \text{ was used.} \]
\[ \text{PeakArea}_e = \text{intensity of an element at a given interval} \]
\[ \text{PeakArea}_{e, \text{med}} = \text{median for each element obtained from the XRF core - scanner} \]
Sample scaling is needed to better match the range of chemical composition along the scan (Lyle, et al., 2012). This method reduces the domination of one element. Errors were observed in the absolute scaling, in that there were elemental scaling values greater than 100. Normalizing the data assigns a percentage value to the specific interval out of 100%. This method was chosen because the X-ray results of different elements do not scale linearly with elemental ratios for the sample in question. Scaling to the summed peak area was not chosen because one element will dominate.

The data was then normalized so that the sample composition is equivalent to 100%. The following calculation was performed for each component:

$$\text{NMS}_i = \frac{C \times 100}{(\text{raw sum})}$$

Where $C = \text{component}

\text{Raw sum} = \text{sum of components after elemental scaling}
3. Log-ratio Transformation Method

Weltje and Tjallingii. (2008) proposed a method based on the statistical theory of compositional data analysis known as the log ratio calibration model. This method is used here. Log ratios are used because it makes the ratios independent of each other, i.e. log-ratios preserve all compositional information and the value of one log ratio can be changed independently of the other log-ratio values derived from the same composition. Because Al$_2$O$_3$, SiO$_2$, P$_2$O$_5$, K$_2$O, CaO, Fe$_2$O$_3$, MnO and TiO$_2$ were the oxides obtained from the XRF sample analyzer, Al, Si, P, K, Ca, Fe, Ti and Mn intensities were selected for the log-ratio transformations.

The data was represented in Euclidian real space of reduced dimensionality using additive log-ratio transformations (alr), i.e. $y = \text{alr}(x)$. The XRF core scanner (element) and XRF sample data (oxide) was input into the “CoDaPAct v2 Additive Log-ratio Transformation (ALR or alr)” function. This was repeated for each element and elemental oxide. This produced intensity log-ratios and elemental oxide log ratios. Table 2.4 shows 12 of the 41 samples with the corresponding elemental oxide and element log-ratio transformations for Si/Fe and Ti/Fe.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Depth (m)</th>
<th>Age (Ma)</th>
<th>alr(Si Area_Fe Area)</th>
<th>alr(SiO2 (%)_Fe2O3 (%))</th>
<th>alr(Ti Area_Fe Area)</th>
<th>alr(TiO2 (%)_Fe2O3 (%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>694-B-1H-1, 59-61</td>
<td>112.1</td>
<td>7.45</td>
<td>0.04</td>
<td>2.90</td>
<td>-1.76</td>
<td>-1.51</td>
</tr>
<tr>
<td>694-B-22X-1, 24-26</td>
<td>150.65</td>
<td>8.80</td>
<td>0.74</td>
<td>3.23</td>
<td>-1.76</td>
<td>-1.54</td>
</tr>
<tr>
<td>694-B-22X-1, 39-41</td>
<td>150.8</td>
<td>8.81</td>
<td>0.91</td>
<td>3.83</td>
<td>-1.46</td>
<td>-1.14</td>
</tr>
<tr>
<td>694-B-22X-2, 69-71</td>
<td>152.6</td>
<td>8.87</td>
<td>-0.59</td>
<td>2.35</td>
<td>-2.45</td>
<td>-2.15</td>
</tr>
<tr>
<td>694-B-23X-2, 69-71</td>
<td>163.7</td>
<td>9.26</td>
<td>-0.02</td>
<td>2.95</td>
<td>-2.02</td>
<td>-1.85</td>
</tr>
<tr>
<td>694-B-23X-2, 69-71</td>
<td>167.9</td>
<td>9.41</td>
<td>-0.01</td>
<td>2.84</td>
<td>-2.08</td>
<td>-1.55</td>
</tr>
<tr>
<td>694-B-23X-6, 39-41</td>
<td>170.3</td>
<td>9.49</td>
<td>-0.35</td>
<td>2.40</td>
<td>-2.10</td>
<td>-1.85</td>
</tr>
<tr>
<td>694-B-24X-3, 69-71</td>
<td>173.3</td>
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<td>-0.43</td>
<td>2.38</td>
<td>-2.28</td>
<td>-1.98</td>
</tr>
<tr>
<td>694-C-2X-1, 60-62</td>
<td>179.81</td>
<td>9.83</td>
<td>0.48</td>
<td>3.46</td>
<td>-1.78</td>
<td>-1.34</td>
</tr>
<tr>
<td>694-C-5X-2, 38-40</td>
<td>210.19</td>
<td>10.89</td>
<td>0.09</td>
<td>3.08</td>
<td>-2.14</td>
<td>-1.77</td>
</tr>
<tr>
<td>694-C-6X-1, 106-108</td>
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<td>-2.38</td>
<td>-2.05</td>
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<tr>
<td>694-C-6X-2, 60-62</td>
<td>220.01</td>
<td>11.24</td>
<td>-0.71</td>
<td>2.25</td>
<td>-2.47</td>
<td>-2.15</td>
</tr>
</tbody>
</table>
Table 2.4: Oxide wt.% and element log-ratio transformations for the ratios Si/Ti and Ti/Fe.

The Standardized Major Axis Tests & Routines (SMATR) program was used to calculate the slope, intercept and R-squared value for each element and elemental oxide log ratio (Table 3.3). The X-axis value was assigned the element’s log ratio and the Y-axis value was assigned the elemental oxide log ratio. These values were assigned based in the Log-ratio Calibration Equation (LRCE):

\[
\ln \left( \frac{W_{ij}}{W_{iD}} \right) = A_{jD} \ln \left( \frac{I_{ij}}{I_{iD}} \right) - B_{jD}
\]

Where,

- \( W_{ij} \) = net oxide weight percent of element j
- \( W_{iD} \) = net oxide weight percent of denominator element D
- \( I_{ij} \) = net intensity of element j
- \( I_{iD} \) = net intensity of denominator element D
- \( A_{jD} \) = slope of log-ratio j/D
- \( B_{jD} \) = intercept of log-ratio j/D

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>SiO2 (%)</th>
<th>K2O (%)</th>
<th>CaO (%)</th>
<th>Fe2O3 (%)</th>
<th>MnO (%)</th>
<th>TiO2 (%)</th>
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<td>Slope</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Al</td>
<td>1.28</td>
<td>0.8631</td>
<td>1.2</td>
<td>0.8452</td>
<td>1.163</td>
<td>0.7495</td>
<td>1.089</td>
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<td>Si</td>
<td>0.8631</td>
<td>1.2</td>
<td>0.7578</td>
<td>0.8122</td>
<td>0.851</td>
<td>1.163</td>
<td>0.7578</td>
</tr>
<tr>
<td>K</td>
<td>0.6326</td>
<td>0.8452</td>
<td>0.7578</td>
<td>0.8122</td>
<td>0.851</td>
<td>1.163</td>
<td>0.7578</td>
</tr>
<tr>
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<td>0.5922</td>
<td>1.097</td>
<td>0.5922</td>
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<tr>
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<tr>
<td>Mn</td>
<td>0.9977</td>
<td>1.48</td>
<td>1.089</td>
<td>0.7137</td>
<td>1.097</td>
<td>0.901</td>
<td>0</td>
</tr>
<tr>
<td>Ti</td>
<td>0.9977</td>
<td>1.48</td>
<td>1.089</td>
<td>0.7137</td>
<td>1.097</td>
<td>0.901</td>
<td>0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>SiO2 (%)</th>
<th>K2O (%)</th>
<th>CaO (%)</th>
<th>Fe2O3 (%)</th>
<th>MnO (%)</th>
<th>TiO2 (%)</th>
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<td>Intercept</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>-1.954</td>
<td>0</td>
<td>3.077</td>
<td>3.095</td>
<td>3.998</td>
<td>4.484</td>
<td>3.716</td>
</tr>
<tr>
<td>Si</td>
<td>-3.077</td>
<td>-1.978</td>
<td>0</td>
<td>0.4439</td>
<td>0.928</td>
<td>1.65</td>
<td>0.3068</td>
</tr>
<tr>
<td>K</td>
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<td>-2.828</td>
<td>-0.4439</td>
<td>0</td>
<td>0.0375</td>
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<td>0.2145</td>
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<tr>
<td>Ca</td>
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<td>-0.0375</td>
<td>0</td>
<td>1.89</td>
<td>-0.5451</td>
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<tr>
<td>Fe</td>
<td>-4.484</td>
<td>-1.163</td>
<td>-1.65</td>
<td>-0.9182</td>
<td>-1.89</td>
<td>0</td>
<td>-0.7407</td>
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<tr>
<td>Mn</td>
<td>-3.716</td>
<td>-1.601</td>
<td>-0.3068</td>
<td>-0.2145</td>
<td>0.5451</td>
<td>0.7407</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2.5: Slope and intercept values calculated using major axis regression.
The values highlighted in bold numbers and box indicate the slope and intercept values for the Si/Fe ratio, while the values highlighted in color indicate the slope and intercept values for the Ti/Fe ratio.

The LRCE was then used to predict oxide wt.% log-ratio values:

Si/Fe Equation: \[ \ln \left( \frac{W_{Si}}{W_{Fe}} \right) = A \ln \left( \frac{I_{Si}}{I_{Fe}} \right) - B \]

Ti/Fe Equation: \[ \ln \left( \frac{W_{Ti}}{W_{Fe}} \right) = A \ln \left( \frac{I_{Ti}}{I_{Fe}} \right) - B \]

Using sample 694B-14H-1, 59 – 61 cm:

Si/Fe Equation: \[ \ln \left( \frac{W_{Si}}{W_{Fe}} \right) = 1.222 (0.04) + 2.955 \]

Ti/Fe Equation: \[ \ln \left( \frac{W_{Ti}}{W_{Fe}} \right) = 1.097 (-1.76) +0.5451 \]

Si/Fe Equation: \[ \ln \left( \frac{W_{Si}}{W_{Fe}} \right) = 3.0038 \]

Ti/Fe Equation: \[ \ln \left( \frac{W_{Ti}}{W_{Fe}} \right) = -1.3862 \]

Table 2.6 shows the elemental oxide log-ratio predictions. This is a dimensionless unit and can be used to show qualitative changes in geochemical data. The dimensionless units can be converted to wt% oxide. In order to do this, a common denominator should be chosen. The denominator that shows the least variation is selected. This is determined by the R-squared value.

The R-squared value is determined by plotting the estimated oxide wt% against the known log ratio oxide wt.% value. The equation of the line and R-squared values were determined using a linear trendline. Figure 2.2 shows the plot of predicted oxide wt.% log ratio against known weight percent oxide, with Si as the numerator and Fe as the denominator.
Figure 2.2: Plot of predicted oxide wt.% log ratio against known oxide weight, with Si as the numerator and Fe as the denominator.

The R-squared values for each element as a denominator was determined by averaging the R-squared values determined by plotting the predicted oxide wt.% log ratio against the known log ratio weight percent oxide. The denominator that shows the least variation (highest R-Squared value) is used as the common denominator. Table 2.6 shows the R-squared values for each elemental denominator. The ‘X’ values are used when the element in question is both the denominator and numerator.
Table 2.6: R-squared values for each elemental denominator

Fe has the highest R-squared value and was selected as the common denominator. The dimensionless oxide wt.% log ratio can then be converted to weight percent oxide. This is done calculating the inverse of the log ratios with Fe as the common denominator. After calculating the inverse of the predicted oxide wt.% log ratio, the values are normalized to 1 or 100. The percentage of each element was then calculated by determining the fraction or percentage of the sum of predicted weights. This method was applied to the XRF core-scanner data.

The equation \( \ln \left( \frac{W_{ij}}{W_{iD}} \right) = A_{jD} \ln \left( \frac{I_{ij}}{I_{iD}} \right) - B_{jD} \) was applied to the XRF core-scanner data, with Fe counts per second as the denominator. The slope and intercept values were selected from the values determined by major axis regression (Table 2.6). The predicted oxide weight percent was then subjected to the inverse of the log ratio transformation and normalized to produce oxide weight percent values.
3. Results:

3.1 Lithostratigraphy

Introduction

A lithostratigraphic column (Figure 4-1) was created based on the core
descriptions from the Proceedings of the Ocean Drilling Program, Initial Reports for
Leg 113, Site 694 ((Shipboard Scientific Party, Site 694, 1988), henceforth SSP,
1988) and describing, imaging and measuring cores at the IODP core repository in
College Station, TX. The descriptions are hampered by overall poor recovery,
averaging 37% at Hole 694B and 34% at Hole 694C, but ranged from less than 2%
over 30 m to 100% in a few cores. The low recovery includes cores that were highly
disturbed and the core catcher, so the percentage of usable material is even lower.
Interpretation is especially difficult as the recovered sediment could have come from
anywhere in the cored 9.5-9.7 m interval.

Five litho-sedimentary facies were identified based on grain-size, sedimentary
structures, lithology, clay mineralogy and biogenic abundance; 1) clayey, silty mud,
2) silty and sandy mud, 3) laminated sand, silt and clay, 4) diatom-bearing mud (clay
and silt), and 5) mud with sand and gravel Table 4-1. These sediments define seven
lithologic units (Table 4-2 and 4-3, Figure 4-1). Lithologic units are distinguished by
presence or absence of diatoms, laminations and graded beds, dropstones and clay
mineralogy. They are modified from the shipboard initial reports (SSP, 1988). A
distinction is not made between fine and coarse grain turbidite layers, as grain-size
differences can vary over short distances in channeled deep-sea fan and abyssal plain
deposits (OConnell et al., 1991).
### Figure 3.1: Lithostratigraphy column showing sediment types between 179.2 and 391.3 mbsf.

<table>
<thead>
<tr>
<th>Age (Ma)</th>
<th>Unit</th>
<th>Depth (mbsf)</th>
<th>Grain Size</th>
<th>Clay</th>
<th>Silt</th>
<th>Sand</th>
<th>Gravel</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.8 - 10.8</td>
<td>179.2 - 208.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Barren muds, silts and coarse sands. Top of lithology unit = 9.806 Ma Drilling disturbances range from slightly to very disturbed.</td>
</tr>
<tr>
<td>10.8 - 13.98</td>
<td>208.3 - 298.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Diatom-bearing muds, silts sands. Top of lithology unit = 10.827 Ma Drilling biscuits are present in this unit.</td>
</tr>
<tr>
<td>14.2 - 17.00</td>
<td>298.2 - 304.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gravel-bearing sandy and silty mud.</td>
</tr>
<tr>
<td>14.2 - 17.00</td>
<td>304.3 - 391.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Diatom and diatom-bearing claystones with silts near the base. Top of lithology unit = 14.197 Ma Drilling biscuits are present in this unit.</td>
</tr>
</tbody>
</table>
Table 3.1: Summary of sedimentary features from shipboard lithologic and smear-slide descriptions (SSP, 1988). Column headings are as follows: Lam/GB = laminations and graded beds, Drpst=dropstones, Diatm=Diatoms, y=present, above 9% the estimated percentage is given, Rad=Radiolaria, BT= Bioturbation. Within column information is, y=present, n=absent, y-t = dropstone only in the upper 40 cm of Section one, and therefore probably fell into the hole during coring, y-unc = layers, but probably produced by different types of sediments being adjacent because of lost material, nx = not enough recovery to say.

<table>
<thead>
<tr>
<th>Hole</th>
<th>Core</th>
<th>Section</th>
<th>Lam/GB</th>
<th>Drpst</th>
<th>Diatm</th>
<th>Rad</th>
<th>BT</th>
<th>Lithology</th>
<th>Unit</th>
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</thead>
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<td>22X</td>
<td>1</td>
<td>Y</td>
<td>n</td>
<td>y</td>
<td>y</td>
<td>n</td>
<td>clayey mud</td>
<td>IV</td>
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<tr>
<td></td>
<td></td>
<td>2</td>
<td>y</td>
<td>y</td>
<td>y</td>
<td>y</td>
<td>y</td>
<td>silty mud</td>
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<tr>
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<td>y</td>
<td>y</td>
<td>y</td>
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<td>y</td>
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</tr>
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<td>y</td>
<td>silty mud</td>
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<td>y</td>
<td>y</td>
<td>y</td>
<td>y</td>
<td>silty mud</td>
<td></td>
</tr>
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<td></td>
<td>3</td>
<td>n</td>
<td>y</td>
<td>10</td>
<td>y</td>
<td>n</td>
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<td>y</td>
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</tr>
<tr>
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<td></td>
<td>2</td>
<td>nx</td>
<td>n</td>
<td>n</td>
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<td>y</td>
<td>clayey mud</td>
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<tr>
<td></td>
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<td>n</td>
<td>n</td>
<td>14</td>
<td>y</td>
<td>n</td>
<td>silty mud</td>
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</tr>
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<td>34</td>
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</tr>
<tr>
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<td>5 y</td>
<td>n</td>
<td>na</td>
<td>n</td>
<td></td>
<td></td>
<td></td>
<td>diatomaceous clayey mud</td>
<td>VIIC</td>
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<td>23X</td>
<td>2 y</td>
<td>n</td>
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Table 3.1 (cont.)

<table>
<thead>
<tr>
<th>Unit</th>
<th>Depth (mbsf)</th>
<th>Cores</th>
<th>Ht (m)</th>
<th>% Rev.</th>
<th>Age</th>
</tr>
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<tbody>
<tr>
<td>I</td>
<td>0-21.1</td>
<td>A-IH to B-3H-5</td>
<td>21.1</td>
<td>98%</td>
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<tr>
<td>II</td>
<td>21.1-111.5</td>
<td>B-3H-5 to B-14H</td>
<td>90.4</td>
<td>23%</td>
<td></td>
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<tr>
<td>IIIA</td>
<td>111.5-113.0</td>
<td>B-14H-1</td>
<td>1.5</td>
<td>100%</td>
<td></td>
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<tr>
<td>IIIIB</td>
<td>113.0-150.4</td>
<td>B-14H-2 to B-22X</td>
<td>37.4</td>
<td>55%</td>
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</tr>
<tr>
<td>IV</td>
<td>150.4-179.3</td>
<td>B-22X to C-2X</td>
<td>28.9</td>
<td>72% / 34%</td>
<td>9.7-10.8</td>
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<tr>
<td>VA</td>
<td>179.3-208.3</td>
<td>C-2X to C-5X</td>
<td>29</td>
<td>71% / 34%</td>
<td>10.8-13.8</td>
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<tr>
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<td>208.3-294.7</td>
<td>C-5X to C-14X</td>
<td>86.4</td>
<td>30%</td>
<td>13.8-14.2</td>
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<tr>
<td>VI</td>
<td>294.7-304.3</td>
<td>C-14X to 15X</td>
<td>9.6</td>
<td>100%</td>
<td>14.2-14.3</td>
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<tr>
<td>VIIA</td>
<td>304.3-343.0</td>
<td>C-15X to C-19X</td>
<td>38.7</td>
<td>53%</td>
<td>14.3-15.5</td>
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<tr>
<td>VIIIB</td>
<td>343.0-378.0</td>
<td>C-19X to C-22X-5</td>
<td>35</td>
<td>59%</td>
<td>15.5-16.8</td>
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<tr>
<td>VIIIC</td>
<td>378.0-391.3</td>
<td>C-22X-5 to C-23X</td>
<td>13.3</td>
<td>27%</td>
<td>16.8-17.1</td>
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</table>

Table 3.2: Depth, core, height, recovery and age for lithologic units. See text for Subunit VA’s two different percent recovery values.
Lithologic Units I-IIIA are from the Initial Results of ODP Leg 113 (SSP, 1988), have not been investigated as part of this study. Boundaries between lithologic units are hampered by the very low recovery and core disturbance. Most boundaries are placed between cores. However for the few that occur within a core, the boundary is located within the recovered material near the top of the core, but in reality could be located any where with the core. No downhole logs were collected at this site, so it isn’t possible to try match well-log and sediment characteristics to place the recovered sediment at its correct depth.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Lithology</th>
<th>Biogenic component</th>
<th>Sedimentary structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>hemipelagic muds</td>
<td>diatoms in discrete layers</td>
<td>silt lams, graded beds, IRD</td>
</tr>
<tr>
<td>II</td>
<td>coarse to fine sands, mud</td>
<td>diatoms present in discrete layers</td>
<td>graded beds</td>
</tr>
<tr>
<td>IIIA</td>
<td>sandy mud</td>
<td>Few diatoms</td>
<td></td>
</tr>
<tr>
<td>IIIB</td>
<td>clayey and silty mud, sand</td>
<td>diatoms, radiolaria</td>
<td>graded silt</td>
</tr>
<tr>
<td>IV</td>
<td>clayey muds</td>
<td>baren</td>
<td></td>
</tr>
<tr>
<td>VA</td>
<td>silty mud, sand</td>
<td>diatoms abundant, radiolaria</td>
<td>Bioturbation, no dropstones</td>
</tr>
<tr>
<td>VB</td>
<td>silty, clayey and sandy mud</td>
<td>diatoms, radiolaria</td>
<td>Bioturbation, no dropstones</td>
</tr>
<tr>
<td>VI</td>
<td>gravel and sandy bearing mud</td>
<td>diatoms, radiolaria</td>
<td>Disturbed silt layering</td>
</tr>
<tr>
<td>VIIA</td>
<td>clayey and silt mud</td>
<td>15-40% diatoms, radiolaria</td>
<td>none</td>
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<tr>
<td>VIIB</td>
<td>finer-grained clayey mud</td>
<td>15-35% diatoms, some radiolaria</td>
<td>silt lams, thin graded beds, IRD rare</td>
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<tr>
<td>VIIIC</td>
<td>finer-grained clayey mud, no smectite</td>
<td>&gt;10% diatoms, no radiolaria</td>
<td>silt lams, thin graded beds, no visible bioturbation, dropstones rare</td>
</tr>
</tbody>
</table>

Table 2.3: Sediment composition and features for each lithologic unit.

Lithologic Unit IV (150.4-179.3 mbsf, 72% recovery) is 28.9 m thick. It consists of clay, clayey mud, clayey silt and diatomaceous clayey and silty mud. Like the units above and below, it contains graded silts, but unlike those, diatoms and radiolarian are present in the clayey mud. Graded silt beds, 1-15 cm thick form about 30% of B-Core 22X (35.4% recovery) and 15% of Core B-23X (90.6% recovery).

Some of the silt layers contain parallel lamination. Bioturbation is present in Core B-24X. Scattered sand grains and ice-rafted debris are present through out most of the unit (Table 4-1).
Two large dropstones from this Unit were selected for thin-sectioning and petrographic examination. These were a 5 x 6 cm subrounded hornfels at 165.51 mbsf and a subrounded 4 x 4 cm kyanite-sillimanite schist at 165.55 mbsf (SSP, 1988).

Lithologic Unit V (179.3-294.7 mbsf) is poorly recovered and subdivided into two subunits, distinguished primarily by the absence (VA) or presence (VB) of diatoms and radiolaria. Clay mineralogy in this unit has wide variations in smectite and chlorite ranging from 10-50% to 15 to 40% respectively with fairly constant amounts of illite and kaolinite (Robert and Maillot, 1990). Bioturbation is also more common in VA. The rest of the sediment is silty and clayey mud with graded beds. The graded beds have erosional bases extending from 20 to 100 cm in thickness. In Lithologic Subunit VA (179.3-208.3 mbsf) official recovery is 70%, but actual recovery is about half that because Core C-3X, recovered a small amount of sediment at the top and bottom of the core liner and the seven empty m in between are counted as recovered sediment. A subangular, 3 x 3 cm, amphibole-biotite gneiss was recovered at 198.67 mbsf and examined petrographically (SSP, 1988). As this is within the top 10 cm of section 1, this was probably not in place. Lithologic Subunit VB (208.3-294.7 m) was also poorly recovered, with the exception of Core C-6X. Core catchers contained sand, so it is likely that sand was present and washed away during the coring process.

Lithologic Unit VI (294.7-304.3 mbsf, 100% recovery) contains clayey, silty and sandy mud with diatoms. Gravel, sand and mud clasts are present throughout. Millimeter-sized, well-sorted, quartz-rich sand pockets suggest bioturbation, but might also be dropstones. The poorly sorted matrix is somewhat finer near the top,
coarsest in the middle and silty towards the bottom. There are some deformed silt beds and at 300.2 mbsf an undeformed silty diatom layer suggesting original deposition.

Lithologic Unit VII (304.3-391.3 mbsf) is subdivided into three. Subunit VIIA (304.3 – 343.0 mbsf, 53% recovery) consists of diatomaceous clayey and silty mud with radiolarian, but lacks sedimentary structures. Subunit (343.0-378.0 mbsf, 59% recovery is finer grained than VIIA, and contains thin graded beds, silt laminations, and some IRD. The core-catcher at 363.82 mbsf, contained a 6 x 6 cm subrounded, pyroxene tholeite (SSP, 1988). Subunit VIIC (378.0 – 391.3 mbsf, 27% recovery) is similar to the overlying layer but is distinguished by the lack of the clay mineral smectite (Robert and Maillot, 1990).

3.2 Consecutive Number Depth Scale (CNDS)

Approximately 36% of sediments was recovered at Site 694. Due to the poor recovery, the data when plotted against depth and age scales is discontinuous. The data is clustered into small sections and trends in the down core data could not be identified (Figure 4.2). As a result, a consecutive number depth scale (CNDS) was used to make continuous down core plots. Therefore, each depth was assigned a consecutive number from 1 – 11177 (Table 4-5).

<table>
<thead>
<tr>
<th>Lith. Unit</th>
<th>CNDS</th>
<th>Age (m.y.)</th>
<th>Depth (mbsf)</th>
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<td>IV</td>
<td>2703</td>
<td>9.7</td>
<td>150.4</td>
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<td>304.3</td>
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</tr>
<tr>
<td>VIIC</td>
<td>11176</td>
<td>16.8</td>
<td>378.0</td>
</tr>
</tbody>
</table>

Table 4.5. Shows the Continuous Number Depth Scale (CNDS) with age and mbsf boundary for each lithologic unit.
3.2 Arbitrary Depth

Approximately 36% of sediments was recovered at Site 69. Due to the poor recovery, the data when plotted against depth and age scales is discontinuous. The data is clustered into small sections and trend in the down core data could not be identified. An example of these plots is shown in figure 4.1. As a result, an arbitrary depth scale was used to make continuous down core plots. Therefore, each depth was assigned a number from 1 – 11 177. Consecutive numbers were used in order to make the data continues.

Figure 3.2: Ti-normalized ratios plotted against depth (mbsf).
3.3. Major Elements

The values for major elements were determined using the XRF core scanner. Values were obtained for Al, Si, P, K, Ca, Ti, Mn and Fe. These values were then converted to oxide weight percent using the data reduction and log ratio calibration equation methods (see methods section).

4.3.1 Descriptive Statistics: XRF Raw Counts

The XRF raw counts for Al range from 1797–25936 and have a mean of 11722.84 ± 3957.40. The XRF raw counts for Si range from 46625 – 428291 and have a mean of 202065.62 ± 44737.26151. The XRF raw counts for P range from 0 – 2603 and have a mean of 262.09 ± 215.23. The XRF raw counts for K range from 18517 – 180351 and have a mean of 76964.19 ± 26795.02. The XRF raw counts for Ca range from 17434 – 461648 and have a mean of 80825.38 ± 49556.54. The XRF raw counts for Ti range from 8011 – 118371 and have a mean of 28857.04 ± 8710.60. The XRF raw counts for Mn range 714 – 59764 and have a mean of 4517.93 ± 2393.44. The XRF raw counts for Fe range from 55615 – 625494 and have a mean of 291735.39 ± 107519.86.

Figure 4.3 shows the XRF raw counts for each element plotted against arbitrary depth. The elements Mn and Ca do not show a distinct trend. Between 9200 and 11117 arbitrary units, the values of Al, Si, P, K, Ti and Fe are relatively high in comparison to values between 7000 and 9200 arbitrary units.

Arbitrary units 9200 - 11177 correspond with depths 344. 47 – 384.37 mbsf. The age range for these depths is 15.61 – 17.01 Ma. The highest values are observed between 15.61 and 15.96 Ma. This is also observed in the statistical data for the
corresponding sections, this being 694-C-19X-1 to 694-C-19X-3. Sections 694-C-19X-1 to 694-C-19X-3 have the highest mean values for depths 344.47 -384.37 mbsf.

XRF raw counts then decrease between 7000 and 9200 arbitrary units. The values correspond with 13.91 – 14.24 Ma. This is also observed in the statistical data, where XRF raw counts in sections 694-C-14X-1 to 694-C-15X-2 are lower than XRF raw counts in sections 694-C-19X-1 to 694-C-19X-3. In sections 694-C-14X-1 to 694-C-15X-2, Al has a mean value of 8494.58 ± 2481.42, Si has a mean of 166901.24 ± 38047.18, P has a mean of 94.42 ±139.07, K has a mean of 55583.76 ± 17503.96, Ca has a mean of 82721.64 ±35512.92, Ti has a mean of 21363.11 ± 4805.13, Mn has a mean of 3271.95 ± 839.23 and Fe has a mean of 208526.94 ± 67077.89.

In sections 694-C-19X-1 to 694-C-19X-3, Al has a mean value of 13598.38 ± 3133.44, Si has a mean of 220822.92 ±39838.40, P has a mean of 337.75 ± 231.97, K has a mean of 93198.81 ±19787.61, Ca has a mean of 103015.48 ± 59080.23, Ti has a mean of 31445.29 ±4969.94, Mn has a mean of 4022.06 ± 921.35 and Fe has a mean of 385045.77 ± 76584.31.

The XRF raw counts are relatively steady between ~3000 and 7000 arbitrary units. Between ~1 – 3000, the XRF raw counts increase when compared to values between ~3000 – 7000 arbitrary units. A significant change in elemental values is observed between sections 694-C-2X-1 to 694-C-2X-2 and 694-B-23X-1 to 694-B-24X-4, where in Al, Si, K, Ti and Fe increase in sections 694-B-23X-1 to 694-B-24X-4.

Sections 694-B-23X-1 to 694-B-24X-4 correspond with 8.80 – 9.66 Ma. Al has a mean value of 11330.30 ± 3949.69, Si has a mean of 217988.52 ± 43374.65, P has a mean of 153.51 ± 208.13, K has a mean of 74904.83 ± 32492.97, Ca has a mean
of 90107.74 ± 66306.70, Ti has a mean of 26316.21 ± 7115.84, Mn has a mean of 5445.66 ± 2519.68 and Fe has a mean of 213093.36 ± 115471.78.

Sections 694-C-2X-1 to 694-C-2X-2 correspond with 9.81 – 9.90 Ma. Al has a mean value of 14154.65 ± 3708.85, Si has a mean of 228680.58 ± 40364.70, P has a mean of 419.52 ± 172.75, K has a mean of 85917.62 ± 21812.01, Ca has a mean of 72951.94 ± 24004.63, Ti has a mean of 38350.96 ± 6827.09, Mn has a mean of 5037.27 ± 1545.21 and Fe has a mean of 346155.25 ± 77780.99.
3.3.2 Descriptive Statistics: Data Reduction Method

The data reduction was used to normalize the XRF raw counts. This method converts the raw counts to weight percent. The weight percent of $\text{Al}_2\text{O}_3$ ranges from 5.81–18.40 % and has a mean of 12.34 ± 1.99 %. The weight percent of $\text{SiO}_2$ ranges from 55.14 –90.74% and has a mean of 76.90 ± 3.63%. The weight percent for $\text{P}_2\text{O}_5$
ranges from 0 –1.55 % and has a mean of 0.18 ± 0.14%. The weight percent for K$_2$O ranges from 1.16 – 4.70 % and has a mean of 2.71 ±0.59 %. The weight percent for CaO ranges from 0.46– 29.92% and has a mean of 2.41 ± 1.72%. The weight percent for TiO$_2$ ranges from 0.23–3.14% and has a mean of 0.80 ± 0.14%. The weight percent for MnO ranges 0.02 – 0.91 % and has a mean of 0.07 ± 0.04 %. The weight percent for Fe$_2$O$_3$ ranges from 0.84 – 9.69 % and has a mean of 4.59 ± 1.29%.

Figure 4.4 shows the oxide weight percentages plotted against arbitrary depth. The elements Mn and Ca do not show a distinct trend. Between 9200 and 11117 arbitrary units, the oxide values of Al$_2$O$_3$, P$_2$O$_5$, K$_2$O, TiO$_2$ and Fe$_2$O$_3$ are relatively high in comparison to the values between 7000 and 9200 arbitrary units. This trend is opposite for SiO$_2$.

Arbitrary units 9200 - 11177 correspond with depths 344.47 – 384.37 mbsf. The age range for these depths is 15.61 – 17.01 Ma. The highest values are observed between 15.68 and 16.25 Ma.

Oxide weight percent values for Al$_2$O$_3$, P$_2$O$_5$, K$_2$O, TiO$_2$ and Fe$_2$O$_3$ then decrease between 7000 and 9200 arbitrary units. The opposite trend is observed for SiO$_2$. The values correspond with 13.91 – 14.24 Ma. This is also observed in the statistical data for corresponding sections, in that oxide weight percent values in sections 694-C-14X-1 to 694-C-15X-2 are lower in comparison to oxide weight percent values for sections 694-C-19X-1 to 694-C-19X-3. In sections 694-C-14X-1 to 694-C-15X-2, Al$_2$O$_3$ has a mean value of 11.19 ± 1.21%, SiO$_2$ has a mean of 78.39 ± 2.39 %, P$_2$O$_5$ has a mean of 0.08 ± 0.11 %, K$_2$O has a mean of 2.45 ± 0.43 %, CaO has a mean of 3.00 ± 1.45 %, TiO$_2$ has a mean of 0.74 ± 0.08%, MnO has a mean of 0.06 ± 0.01 % and Fe$_2$O$_3$ has a mean of 4.09 ±0.83%.
In sections 694-C-19X-1 to 694-C-19X-3, Al₂O₃ has a mean value of 12.92 ± 1.23 %, SiO₂ has a mean of 74.74 ± 2.59%, P₂O₅ has a mean of 0.22 ± 0.15 %, K₂O has a mean of 2.97 ± 0.42%, CaO has a mean of 2.77 ± 2.30 %, TiO₂ has a mean of 0.78 ± 0.07%, MnO has a mean of 0.06 ± 0.02 and Fe₂O₃ has a mean of 5.52 ± 1.02%.

The oxide weight percent values are relatively steady between ~3000 and 7000 arbitrary units. Between ~1 – 3000, the elemental values increase in comparison to values between ~3000 – 7000 arbitrary units. A significant change in elemental values is observed between sections 694-C-2X-1 to 694-C-2X-2 and sections 694-B-23X-1 to 694-B-24X-4, where in Al₂O₃, K₂O, TiO₂ and Fe₂O₃ increase in sections 694-B-23X-1 to 694-B-24X-4 and SiO₂ decreases.

Sections 694-B-23X-1 to 694-B-24X-4 correspond to 8.80 – 9.90 Ma. Al₂O₃ has a mean value of 13.19 ± 1.87%, SiO₂ has a mean of 76.16 ± 2.79%, P₂O₅ has a mean of 0.27 ± 0.10%, K₂O has a mean of 2.69 ± 0.48 %, CaO has a mean of 1.84 ± 0.64 %, TiO₂ has a mean of 0.94 ± 0.15 %, MnO has a mean of 0.07 ± 0.02 % and Fe₂O₃ has a mean of 4.85 ± 0.95%.
Sections 694-C-2X-1 to 694-C-2X-2 correspond with 8.80 – 9.66 Ma. Al2O3 have a mean value of 11.33 ± 2.76 %, SiO2 have a mean of 79.54 ± 4.84 %, P2O5 have a mean of 0.10 ± 0.13 %, K2O have a mean of 2.51 ± 0.76 %, CaO have a mean of 2.59 ± 2.21, TiO2 have a mean of 0.70 ± 0.12, MnO have a mean of 0.08 ± 0.04 % and Fe2O3 have a mean of 3.15 ± 1.35%.

Figure 3.3: Arbitrary depth against oxide weight percent values for Al2O3, SiO2, P2O5, K2O, CaO, TiO2, MnO and Fe2O3. Oxide weight percent values have been determined using the data reduction method.
3.3.3 Descriptive Statistics: Log Ratio Calibration Method

The log ratio calibration method was used to normalize the XRF raw counts. This method converts the raw counts to oxide weight percent. The weight percent for $\text{P}_2\text{O}_5$ was not calculated because some of the values were less than zero, which produced erroneous results when the log ratio calibration method was applied. $\text{Al}_2\text{O}_3$ ranges from 4.81–20.48 % and has a mean of 13.56 ± 2.65 %. The weight percent $\text{SiO}_2$ ranges from 55.83–9.67 % and has a mean of 74.12 ± 5.33 %. The weight percent for $\text{K}_2\text{O}$ ranges from 1.13–6.02 % and has a mean of 3.20 ± 0.81 %. The weight percent for $\text{CaO}$ ranges from 0.36–22.81 % and has a mean of 2.23 ± 1.33 %. The weight percent for $\text{TiO}_2$ range from 0.18–3.78 % and have a mean of 0.82 ± 0.17 %. The weight percent for $\text{MnO}$ ranges 0.01–0.48 % and has a mean of 0.08 ± 0.02 %. The weight percent for $\text{Fe}_2\text{O}_3$ ranges from 0.77–13.85 % and has a mean of 6.01 ± 1.94 %.

Figure 4.5 shows the oxide weight percent values plotted against arbitrary depth. The elements Mn and Ca do not show a distinct trend. Between 9200 and 11117 arbitrary units, the oxide weight percent values of $\text{Al}_2\text{O}_3$, $\text{K}_2\text{O}$, $\text{TiO}_2$ and $\text{Fe}_2\text{O}_3$ are relatively high in comparison to the oxide weight percent values between 7000–9200 arbitrary units. The trend is the opposite for $\text{SiO}_2$. Arbitrary units correspond with depths 344.47–384.37 mbsf. The age range for these depths is 15.61–17.01 Ma. The highest values are observed between 15.68 and 16.25 Ma.

Oxide weight percent values for $\text{Al}_2\text{O}_3$, $\text{K}_2\text{O}$, $\text{TiO}_2$ and $\text{Fe}_2\text{O}_3$ then decrease between 7000 and 9200 arbitrary units. The opposite trend is observed for $\text{SiO}_2$. The values between 7000 and 9200 arbitrary units correspond with 13.91–14.24 Ma. This is also observed in the statistical data for individual sections, in that oxide
weight percent values in sections 694-C-14X-1 to 694-C-15X-2 are lower in comparison to oxide weight percent values in sections 694-C-19X-1 to 694-C-19X-3.

In sections 694-C-14X-1 to 694-C-15X-2, Al₂O₃ has a mean value of 12.09 ± 1.57%, SiO₂ has a mean of 76.41 ± 3.34 %, K₂O has a mean of 2.84 ± 0.58 %, CaO has a mean of 2.60 ± 1.05 %, TiO₂ has a mean of 0.75 ± 0.09%, MnO has a mean of 0.07 ± 0.01 % and Fe₂O₃ has a mean of 5.24 ± 1.25%.

In sections 694-C-19X-1 to 694-C-19X-3, Al₂O₃ has a mean value of 14.67 ± 1.46 %, SiO₂ has a mean of 70.78 ± 3.55 %, K₂O has a mean of 3.55 ± 0.56%, CaO has a mean of 2.69 ± 0.09 %, TiO₂ has a mean of 0.81 ± 0.09%, MnO has a mean of 0.08 ± 0.02% and Fe₂O₃ has a mean of 7.42 ± 1.59%.

The oxide weight percent values are relatively steady between ~ 3000 and 7000 arbitrary units. Between ~1 – 3000, the oxide weight percent values increase when compared to values between ~3000 – 7000 arbitrary units. A significant change in elemental values is observed between sections 694-C-2X-1 to 694-C-2X-2 and sections 694-B-23X-1 to 694-B-24X-4, where in Al₂O₃, K₂O, TiO₂ and Fe₂O₃ increase in sections 694-B-23X-1 to 694-B-24X-4 and SiO₂ decreases.

Sections 694-B-23X-1 to 694-B-24X-4 correspond with 8.80 – 9.90 Ma. Al₂O₃ has a mean value of 14.64 ± 2.36 %, SiO₂ has a mean of 72.91 ± 4.13%, K₂O has a mean of 3.15 ± 0.65 %, CaO have a mean of 1.86 ± 0.54 %, TiO₂ has a mean of 0.99 ± 0.18%, MnO have a mean of 0.08 ± 0.02 % and Fe₂O₃ has a mean of 6.38 ± 1.43%.
 Sections 694-C-2X-1 to 694-C-2X-2 correspond with 8.80 – 9.66 Ma. Al2O3 have a mean value of 11.364 ± 3.68 %, SiO2 have a mean of 78.76 ± 6.85 %, K2O have a mean of 2.91 ± 1.05 %, CaO have a mean of 2.03 ± 1.52, TiO2 have a mean of 0.69 ± 0.14, MnO have a mean of 0.07 ± 0.03 % and Fe2O3 have a mean of 3.90 ± 1.97%.

Figure 3.5: Arbitrary depth against oxide weight percent values for Al2O3, SiO2, P2O5, K2O, CaO, TiO2, MnO and Fe2O3. Oxide weight percent values have been determined using the log ratio calibration method.
3.4 Grain Size Proxies

Si/Al, Ti/Al and K/Al are ratios that are generally used as grain size proxies. The descriptive statistics for the ratios have been determined and the ratios plotted against arbitrary depth.

3.4.1 Descriptive Statistics: XRF Raw Counts

The Si/Al ratios range from 10.87 – 43.87 and have a mean of 18.21 ± 3.77. The Ti/Al ratios range from 1.42 – 11.69 with a mean of 2.54 ± 0.54. The K/Al ratios range from 4.15 – 12.69 with a mean of 6.59 ± 0.81.

Figure 4.9 shows the elemental ratios plotted against arbitrary depth. Between 9200 and 11117 arbitrary units, the elemental ratios for K/Al and Ti/Al are high in comparison to the elemental ratios between 7000 – 9200 arbitrary units. The opposite trend is observed for Si/Al. 9200 – 11177 arbitrary units correspond with depths 344.47 – 384.37 mbsf. The age range for these depths is 15.61 – 17.01 Ma. The highest values are observed between 15.95 and 16.73 Ma.

Elemental ratio values then decrease for K/Al and Ti/Al between 7000 and 9200 arbitrary units. The opposite trend is observed for Si/Al. The values between 7000 and 9200 arbitrary units correspond with 13.91 – 14.17 Ma.

The elemental ratios are relatively steady between ~ 3000 and 7000 arbitrary units. Between ~1 – 3000 arbitrary units, the elemental values increase when compared to values between ~3000 – 7000 arbitrary units.
Figure 3.6: Arbitrary depth against Si/Al, Ti/Al and K/Al elemental ratios. These values are in XRF raw counts.
3.4.2 Descriptive Statistics: Data Reduction Method

The SiO$_2$/Al$_2$O$_3$ ratios range from 3.84 – 15.51 and have a mean of 6.44 ± 1.33. The TiO$_2$/Al$_2$O$_3$ ratios range from 0.04 – 0.30 with a mean of 0.07 ± 0.01. The K$_2$O/Al$_2$O$_3$ ratios range from 0.14 – 0.42 with a mean of 0.22 ± 0.03.

Figure 4.7 shows the oxide weight percent ratios values plotted against arbitrary depth. Between 9200 and 11117 arbitrary units, the K$_2$O/Al$_2$O$_3$ and TiO$_2$/Al$_2$O$_3$ ratios are high in comparison to the oxide weight percent ratios between 7000 – 9200 arbitrary units. The opposite trend is observed SiO$_2$/Al$_2$O$_3$. Arbitrary units 9200 and 11117 correspond with depths 344.47 – 384.37 mbsf. The age range for these depths is 15.61 – 17.01 Ma. The highest values are observed between 15.95 and 16.73 Ma.

Oxide weight percent ratios for K$_2$O/Al$_2$O$_3$ and TiO$_2$/Al$_2$O$_3$ then decrease between 7000 and 9200 arbitrary units. The opposite trend is observed for SiO$_2$/Al$_2$O$_3$. The arbitrary units 7000 – 9200 correspond with 13.91 – 14.17 Ma.

The oxide weight percent ratios are relatively steady between ~ 3000 and 7000 arbitrary units. Between ~1 – 3000 arbitrary units, the elemental values increase when compared to values between ~3000 – 7000 arbitrary units.
Figure 3.7: Arbitrary depth against SiO$_2$/Al$_2$O$_3$, TiO$_2$/Al$_2$O$_3$ and K$_2$O/Al$_2$O$_3$ ratios. These oxide weight percent values were determined using the data reduction method.

3.4.3 Descriptive Statistics: Log Ratio Calibration Method

The SiO$_2$/Al$_2$O$_3$ ratios range from 3.19 – 19.16 and have a mean of 5.78 ± 1.67. The TiO$_2$/Al$_2$O$_3$ ratios range from 0.04 – 0.31 with a mean of 0.06 ± 0.01. The K$_2$O/Al$_2$O$_3$ ratios range from 0.14 – 0.42 with a mean of 0.23 ± 0.03.

Figure 4.8 shows the oxide weight percent ratios values plotted against arbitrary depth. Between 9200 and 11117 arbitrary units, the oxide weight percent ratios of K$_2$O/Al$_2$O$_3$ and TiO$_2$/Al$_2$O$_3$ are relatively high in comparison to oxide weight percent ratios between 7000 – 9200 arbitrary units. The opposite trend is observed for
SiO$_2$/Al$_2$O$_3$. 9200 – 11177 arbitrary units correspond with depths 344. 47 – 384.37 mbsf. The age range for these depths is 15.61 – 17.01 Ma. The highest values are observed between 15.96 and 16.70 Ma.

Oxide weight percent ratios then decrease for K$_2$O/Al$_2$O$_3$ and TiO$_2$/Al$_2$O$_3$ between 7000 and 9200 arbitrary units. The opposite trend is observed for SiO$_2$/Al$_2$O$_3$. The oxide weight percent ratios between 7000 and 9200 arbitrary units correspond with 13.91 – 14.17 Ma.

The elemental ratios are relatively steady between ~3000 and 7000 arbitrary units. Between ~1 – 3000 arbitrary units, the elemental values increase when compared values between ~3000 – 7000 arbitrary units.

Figure 3.8: Arbitrary depth against SiO$_2$/Al$_2$O$_3$, TiO$_2$/Al$_2$O$_3$ and K$_2$O/Al$_2$O$_3$ ratios. These oxide weight percent values were determined using the log ratio calibration method.
3.5 Ti-normalized major elements

Ti-normalized ratios are used to observe chemical changes down core. The descriptive statistics for the ratios have been determined and the ratios have been plotted against arbitrary depth.

3.5.1 Descriptive Statistics: Raw XRF Counts Ti-Normalized Majors

Ti-normalized ratios were determined for Al, Si, K, Ca, Mn and Fe and the results were plotted against arbitrary depth. The elemental ratios for Al/Ti range from 0.09–0.07 and have a mean of 0.41 \pm 0.07. The elemental ratios for Si/Ti range from 1.69–28.38 and have a mean of 7.29 \pm 1.55. The elemental ratios for K/Ti range from 0.46–4.95 and have a mean of 2.69 \pm 0.57. The elemental ratios for Ca/Ti range from 0.68–42.74 and have a mean of 3.08 \pm 2.32. The elemental ratios for Mn/Ti range from 0.06–2.09 and have a mean of 0.16 \pm 0.8. The elemental ratios for Fe range from 2.46–17.38 and have a mean of 10.06 \pm 2.28.

Figure 4.9 shows the elemental ratios plotted against arbitrary depth. The elemental ratios for Mn/Ti and Ca/Ti do not show a distinct trend. Between ~9200 and 11117 arbitrary units, the elemental ratios of Al/Ti, K/Ti and Fe/Ti are relatively high when compared to the elemental ratios between 7000–9200 arbitrary units. Si/Ti shows an opposite trend. 9200–11177 arbitrary units correspond with depths 344.47–384.37 mbsf. The age range for these depths is 15.61–17.01 Ma. The highest values for elemental ratios Al/Ti, K/Ti and Fe/Ti are observed between 15.63 and 15.95 Ma. This is also observed in the statistical data for the corresponding sections, this being 694-C-19X-1 to 694-C-19X-3. Sections 694-C-19X-1 to 694-C-
19X-3 have the highest mean values for the elemental ratios of Al/Ti, K/Ti and Fe/Ti when compared to other sections other sections between 344.47 - 384.37 mbsf.

Elemental ratios then decrease between 7000 and 9200 arbitrary units for Al/Ti, K/Ti and Fe/Ti and increase for Si/Al. The values between 7000 and 9200 arbitrary units correspond with 13.91 – 14.24 Ma. This is also observed in the statistical data of individual sections, in that the elemental ratios for Al/Ti, K/Ti and Fe/Ti are lower in sections 694-C-14X-1 to 694-C-15X-2 in comparison to elemental ratios in sections 694-C-19X-1 to 694-C-19X-3. Elemental ratios for Si/Al are higher in sections 694-C-14X-1 to 694-C-15X-2 in comparison to elemental ratios in sections 694-C-19X-1 to 694-C-19X-3.

In sections 694-C-14X-1 to 694-C-15X-2, Al/Ti ratios have a mean value of 0.39 ± 0.05, Si/Ti ratios have a mean of 7.85 ± 0.96, K/Ti ratios have a mean of 2.59 ± 0.39 and Fe have a mean of 9.66 ± 1.42.

In sections 694-C-19X-1 to 694-C-19X-3, Al/Ti ratios have a mean value of 0.43 ± 0.05, Si/Ti ratios have a mean of 7.03 ± 0.79, K/Ti ratios have a mean of 2.95 ± 0.33 and Fe have a mean of 12.28 ± 1.77.

Elemental ratios are relatively steady between ~ 3000 and 7000 arbitrary units. Between ~1 – 3000 arbitrary units, the elemental ratios for Al/Ti, K/Ti and Fe/Ti and the Si/Al decrease when compared to values between ~3000 – 7000 arbitrary units. A significant change in elemental values is observed between sections 694-C-2X-1 to 694-C-2X-2 and sections 694-B-23X-1 to 694-B-24X-4. Al/Ti, K/Ti, Fe/Ti and the Si/Al ratios decrease in sections 694-B-23X-1 to 694-B-24X-4.

Sections 694-B-23X-1 to 694-B-24X-4 correspond with 8.80 – 9.90 Ma. In sections 694-B-23X-1 to 694-B-24X-4, Al/Ti ratios have a mean value of 0.37 ± 0.07,
Si/Ti ratios have a mean of 6.02 ± 0.79, K/Ti ratios have a mean of 2.25 ± 0.48 and Fe/Ti ratios have a mean of 9.06 ± 1.59.

Sections 694-C-2X-1 to 694-C-2X-2 correspond with 8.80 – 9.66 Ma. In sections 694-C-2X-1 to 694-C-2X-2, Al/Ti ratios have a mean value of 0.42 ± 0.09, Si/Ti have a mean of 8.51 ± 1.55 ratios, K/Ti ratios have a mean of 2.78 ± 0.69 and Fe have a mean of 7.78 ± 2.83.

Figure 3.9: Arbitrary depth against Ti-normalized elemental ratios. XRF raw counts were used to calculate these ratios.
3.5.2 Descriptive Statistics: Ti-Normalized Majors using Data Reduction Method

Ti-normalized ratios were determined for Al$_2$O$_3$, SiO$_2$, K$_2$O, CaO, MnO and Fe$_2$O$_3$ and the results were plotted against arbitrary depth. The Ti-normalized ratios for Al$_2$O$_3$/TiO$_2$ range from 3.32 – 27.25 and have a mean of 15.80 ± 2.82. The Ti-normalized ratios for SiO$_2$/TiO$_2$ range from 23.18 – 389.07 and have a mean of 100.00 ± 21.30. The Ti-normalized ratios for K$_2$O/TiO$_2$ range from 0.59 – 6.37 and have a mean of 3.46 ± 0.74. The Ti-normalized ratios for CaO/TiO$_2$ range from 0.69 – 43.30 and have a mean of 3.12 ± 2.35. The Ti-normalized ratios for MnO/TiO$_2$ range from 0.03 – 1.18 and have a mean of 0.09 ± 0.05. The Ti-normalized ratios for Fe$_2$O$_3$/TiO$_2$ range from 1.41 – 9.94 and have a mean of 5.76 ± 1.30.

Figure 4.10 shows the Ti-normalized ratios plotted against arbitrary depth. The Ti-normalized ratios for MnO/TiO$_2$ and CaO/TiO$_2$ do not show a distinct trend. Between ~ 9200 and 11117 arbitrary units, the elemental ratios of Al$_2$O$_3$/TiO$_2$, K$_2$O/TiO$_2$ and Fe$_2$O$_3$/TiO$_2$ are relatively high when compared to the Ti-normalized ratios between 7000 – 9200 arbitrary units. SiO$_2$/TiO$_2$ shows an opposite trend. 9200 – 11177 arbitrary units correspond with depths 344.47 – 384.37 mbsf. The age range for these depths is 15.61 – 17.01 Ma. The highest values for Ti-normalized ratios of Al$_2$O$_3$/TiO$_2$, K$_2$O/TiO$_2$ and Fe$_2$O$_3$/TiO$_2$ are observed between 15.60 and 15.97 Ma. This is also observed in the statistical data for the corresponding sections, this being 694-C-19X-1 to 694-C-19X-3. Sections 694-C-19X-1 to 694-C-19X-3 have the highest mean values for the elemental Ti-normalized ratios of Al$_2$O$_3$/TiO$_2$, K$_2$O/TiO$_2$ and Fe$_2$O$_3$/TiO$_2$ when compared to other sections that are between 344.47 -384.37 mbsf.
Ti-normalized ratios then decrease between 7000 and 9200 arbitrary units for 
$\text{Al}_2\text{O}_3/\text{TiO}_2$, $\text{K}_2\text{O}/\text{TiO}_2$ and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ and increase for $\text{SiO}_2/\text{Al}_2\text{O}_3$. The values 
between 7000 and 9200 arbitrary units correspond with 13.91 – 14.24 Ma. This is 
also observed in the statistical data of individual sections, in that Ti-normalized ratios 
for $\text{Al}_2\text{O}_3/\text{TiO}_2$, $\text{K}_2\text{O}/\text{TiO}_2$ and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ are lower in sections 694-C-14X-1 to 694-
C-15X-2 when compared to Ti-normalized ratios in sections 694-C-19X-1 to 694-C-
19X-3. Ti-normalized elemental ratios for $\text{SiO}_2/\text{Al}_2\text{O}_3$ are higher in sections 694-C-
14X-1 to 694-C-15X-2 compared to Ti-normalized ratios in sections 694-C-19X-1 to
694-C-19X-3.

In sections 694-C-14X-1 to 694-C-15X-2, $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios have a mean 
value of 15.30 ± 1.95, $\text{SiO}_2/\text{TiO}_2$ ratios have a mean of 107.58 ± 13.12, $\text{K}_2\text{O}/\text{TiO}_2$
ratios have a mean of 3.33 ± 0.50 and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ have a mean of 5.52 ± 0.81.

In sections 694-C-19X-1 to 694-C-19X-3, $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios have a mean 
value of 16.61 ± 1.94, $\text{SiO}_2/\text{TiO}_2$ ratios have a mean of 96.36 ± 10.80, $\text{K}_2\text{O}/\text{TiO}_2$
ratios have a mean of 3.80 ± 0.42 and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ ratios have a mean of 7.02 ± 1.01.

Ti-normalized ratios are relatively steady between ~ 3000 and 7000 arbitrary 
units. Between ~1 – 3000 arbitrary units, the Ti-normalized ratios for $\text{Al}_2\text{O}_3/\text{TiO}_2$, 
$\text{K}_2\text{O}/\text{TiO}_2$ and $\text{Fe}_2\text{O}_3/\text{TiO}_2$ and the $\text{SiO}_2/\text{Al}_2\text{O}_3$ decrease when compared values 
between ~3000 – 7000 arbitrary units. A significant change in elemental values is 
observed between sections 694-C-2X-1 to 694-C-2X-2 and sections 694-B-23X-1 to
694-B-24X-4, where in $\text{Al}_2\text{O}_3/\text{TiO}_2$, $\text{K}_2\text{O}/\text{TiO}_2$, $\text{Fe}_2\text{O}_3/\text{TiO}_2$ and $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios
decrease in sections 694-B-23X-1 to 694-B-24X-4.

Sections 694-B-23X-1 to 694-B-24X-4 correspond with 8.80 – 9.66 Ma. In 
sections 694-B-23X-1 to 694-B-24X-4, $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratios have a mean value of 14.30
± 2.85, SiO$_2$/TiO$_2$ ratios have a mean of 82.58 ± 13.26, K$_2$O/TiO$_2$ ratios have a mean of 2.90 ± 0.61 and Fe$_2$O$_3$/TiO$_2$ ratios have a mean of 5.18 ± 0.91.

Sections 694-C-2X-1 to 694-C-2X-2 correspond with 9.81 – 9.90 Ma. In sections 694-C-2X-1 to 694-C-2X-2, Al$_2$O$_3$/TiO$_2$ ratios have a mean value of 16.33 ± 3.57, SiO$_2$/TiO$_2$ ratios have a mean of 116.65 ± 21.28, K$_2$O/TiO$_2$ ratios have a mean of 3.58 ± 0.89 and Fe$_2$O$_3$/TiO$_2$ ratios have a mean of 4.45 ± 1.62.

Figure 3.10: Arbitrary depth against Ti-normalized elemental ratios. The data reduction method was used to determine the oxide weight percent.

3.5.3 Descriptive Statistics: Ti-Normalized Majors using Log Ratio Calibration Method

Ti-normalized ratios were determined for Al$_2$O$_3$, SiO$_2$, K$_2$O, CaO, MnO and Fe$_2$O$_3$ and the results were plotted against arbitrary depth. The Ti-normalized ratios
for Al₂O₃/TiO₂ range from 3.27 – 30.06 and have a mean of 16.96 ± 3.19. The Ti-normalized ratios for SiO₂/TiO₂ range from 17.94 – 524.67 and have a mean of 95.78 ± 27.21. The Ti-normalized ratios for K₂O/TiO₂ range from 0.54 – 7.89 and have a mean of 3.99 ± 0.94. The Ti-normalized ratios for CaO/TiO₂ range from 0.75 – 27.77 and have a mean of 2.80 ± 1.68. The Ti-normalized ratios for MnO/TiO₂ range from 0.03 – 0.46 and have a mean of 0.09 ± 0.03. The Ti-normalized ratios for Fe₂O₃/TiO₂ range from 1.56 – 13.30 and have a mean of 7.32 ± 1.81.

Figure 4.11 shows the elemental values plotted against arbitrary depth. The elemental ratios for MnO/TiO₂ and CaO/TiO₂ do not show a distinct trend. Between 9200 and 11117 arbitrary units, the elemental ratios of Al₂O₃/TiO₂, K₂O/TiO₂ and Fe₂O₃/TiO₂ are relatively high when compared to Ti-normalized ratios between 7000 – 9200 arbitrary units. SiO₂/TiO₂ shows an opposite trend. 9200 – 11177 arbitrary units correspond with depths 344.47 – 384.37 mbsf. The age range for these depths is 15.61 – 17.01 Ma. The highest values for Ti-normalized ratios of Al₂O₃/TiO₂, K₂O/TiO₂ and Fe₂O₃/TiO₂ are observed between 15.60 and 15.97 Ma. This is also observed in the statistical data for the corresponding sections, this being 694-C-19X-1 to 694-C-19X-3. Sections 694-C-19X-1 to 694-C-19X-3 have the highest mean values for the Ti-normalized ratios of Al₂O₃/TiO₂, K₂O/TiO₂ and Fe₂O₃/TiO₂ when compared to other section between 344.47 -384.37 mbsf.

Ti-normalized ratios then decrease between 7000 and 9200 arbitrary units for Al₂O₃/TiO₂, K₂O/TiO₂ and Fe₂O₃/TiO₂ and increase for SiO₂/Al₂O₃. The values between 7000 and 9200 arbitrary units correspond with 13.91 – 14.24 Ma. This is also observed in the statistical data of individual sections, in that Ti-normalized ratios for Al₂O₃/TiO₂, K₂O/TiO₂ and Fe₂O₃/TiO₂ are lower in sections 694-C-14X-1 to 694-
C-15X-2 when compared to Ti-normalized ratios in sections 694-C-19X-1 to 694-C-19X-3. Ti-normalized ratios for SiO$_2$/Al$_2$O$_3$ are higher in sections 694-C-14X-1 to 694-C-15X-2 when compared to Ti-normalized ratios in sections 694-C-19X-1 to 694-C-19X-3.

In sections 694-C-14X-1 to 694-C-15X-2, Al$_2$O$_3$/TiO$_2$ ratios have a mean value of 16.36 ± 2.13, SiO$_2$/TiO$_2$ ratios have a mean of 104.45 ± 17.00, K$_2$O/TiO$_2$ ratios have a mean of 3.82 ± 0.64 and Fe$_2$O$_3$/TiO$_2$ ratios have a mean of 6.98 ± 1.13.

In sections 694-C-19X-1 to 694-C-19X-3, Al₂O₃/TiO₂ have a mean value of 18.21 ± 2.08, SiO₂/TiO₂ have a mean of 88.56 ± 13.22, K₂O/TiO₂ have a mean of 4.38 ± 0.53 and Fe₂O₃/TiO₂ have a mean of 9.09 ± 1.43.

Ti-normalized ratios are relatively steady between ~3000 and 7000 arbitrary units. Between ~1–3000 arbitrary units, the Ti-normalized ratios for Al$_2$O$_3$/TiO$_2$, K$_2$O/TiO$_2$ and Fe$_2$O$_3$/TiO$_2$ and the SiO$_2$/Al$_2$O$_3$ decrease when compared values between ~3000–7000 arbitrary units. A significant change in elemental values is observed between sections 694-C-2X-1 to 694-C-2X-2 and sections 694-B-23X-1 to 694-B-24X-4, where in Al$_2$O$_3$/TiO$_2$, K$_2$O/TiO$_2$, Fe$_2$O$_3$/TiO$_2$ and SiO$_2$/Al$_2$O$_3$ decrease in sections 694-B-23X-1 to 694-B-24X-4.

Sections 694-B-23X-1 to 694-B-24X-4 correspond with 8.80 – 9.66 Ma. In sections 694-B-23X-1 to 694-B-24X-4, Al$_2$O$_3$/TiO$_2$ ratios have a mean value of 15.22 ± 3.19, SiO$_2$/TiO$_2$ ratios have a mean of 76.31 ± 15.75, K$_2$O/TiO$_2$ ratios have a mean of 3.27 ± 0.77 and Fe$_2$O$_3$/TiO$_2$ ratios have a mean of 6.52 ± 1.24.

Sections 694-C-2X-1 to 694-C-2X-2 correspond with 9.81 – 9.90 Ma. In sections 694-C-2X-1 to 694-C-2X-2, Al$_2$O$_3$/TiO$_2$ ratios have a mean value of 17.02 ±
4.24, SiO$_2$/TiO$_2$ ratios have a mean of 120.01 ± 29.91, K$_2$O/TiO$_2$ ratios have a mean of 4.22 ± 2.13 and Fe$_2$O$_3$/TiO$_2$ ratios have a mean of 5.54 ± 2.22.

Figure 3.11: Arbitrary depth against Ti-normalized elemental ratios. The log ratio calibration method was used to determine the oxide weight percent.
4. Discussion

The results section described the changes observed down core based on the major oxide composition. While major oxides can reveal changes in sedimentary processes, the results can sometimes be erroneous and not a true representation of the processes taking place.

4.1 Rare Earth Elements

Fourteen trace elements were normalized to the upper continental crust (UCC) using the McLennan et al. (1989) values. Based on the lithologic units described in the results section, the mean values for each lithologic unit were normalized to the UCC (Figure 4.1). The sediments normalized to the upper continental crust all have a similar pattern. The pattern indicates that the sediments deposited at Site 694 are similar in composition to the upper continental crust as the normalized values are close the value 1. A composition similar to the upper continental crust indicates a provenance that has a felsic component.
Fourteen trace elements were then normalized to chondrite using the Boynton (1984) values. Based on the lithologic units described in the results section, the mean values for each lithologic unit were normalized to the chondrite values (Figure 4.2). The sediments normalized to the chondrite all have a similar pattern. The $\Sigma$ REE ranges from 129.67 – 198.3 ppm, with the highest value being observed in unit VIIC and the lowest $\Sigma$ REE being observed in Unit IIIB. The Units IIIB, IV, VA, VB, VI, VIIB and VIIIC are 129.67 ppm, 168.69 ppm, 135.74 ppm, 145.17 ppm, 140.55 ppm, 174.21 ppm and 193.83 ppm respectively. The $\Sigma$REE values for units IIIB and VA are lower than the total $\Sigma$REE of the UCC, while units VIIB and VIIC have $\Sigma$REE values greater than the UCC total REE. The UCC has a $\Sigma$REE value of 143 ppm.
(Taylor and McLennan, 1985). All units show slight light rare earth element (LREE) enrichment, and a relatively flat heavy rare earth element (HREE) pattern, with a negative Eu anomaly.

Figure 4.2: Rare earth elements normalized to the Boynont et al. (1989) model.

Elemental ratio averages for each unit also supports the observed chondrite-normalized patterns. The \((\text{La}_n/\text{Sm}_n)\) ratio represents LREE, where ‘n’ means that the values are chondrite-normalized. \((\text{La}_n/\text{Sm}_n)\) values that are less than 5 are enriched in LREE. The \((\text{Gb}_n/\text{Yb}_n)\) ratio represents HREE, where ‘n’ means that the values are chondrite-normalized. Values that fall within the range of 1.5 – 2, indicate an HREE flat pattern (Jorge et al., 2013). Units IIIB, IV, VA, VB, VI, VIIB and VIIIC \((\text{La}_n/\text{Sm}_n)\) values are 3.13, 3.16, 3.17, 3.15, 3.25, 3.23 and 3.27 respectively. This
indicates LREE enrichment. Units IIIB, IV, VA, VB, VI, VIIB and VIIIC (Gb\textsubscript{n}/Yb\textsubscript{n}) values are 1.67, 1.82, 1.66, 1.74, 1.73, 1.76 and 2.01 respectively.

Gb\textsubscript{n}/Yb\textsubscript{n} ratios that are less than 2, such as the samples in this study, were derived from less HREE-depleted Archaean, post-Archaean sources or a combination of both (Armstrong-Altrin, et al., 2004). Figure 4.3 shows that sediments within units IIIB, IV, Va, Vb, VI, and VIIA plot in the post-Archaean quadrant, close to the upper continental crust region. The sediments in units VIIB and VIIC plot closer the region where (Gy/Yb)\textsubscript{cn} is equal two. This indicates a source somewhat depleted in HREE.

Figure 4.3: Plot of Eu/Eu* against (Gy/Yb)\textsubscript{cn} for 41 sediment samples. The upper continental is plotted on the graph (black star). This figured was adopted from Taylor and McLennnan (1985).
4.2 Geochemical Indicators of Weathering

The chemical index of alteration and major oxide discrimination plots were created using the 41 sediment samples that were analyzed using the Bruker S4 Pioneer XRF Analyzer. These samples were chosen because the samples analyzed using ICP-MS were not analyzed for Na and Si, which are needed for the CIA calculations. Samples analyzed using the XRF Bruker are comparable to the samples analyzed using ICP-MS because these sediment samples have similar ages, if not, the same ages.

4.2.1 Chemical Index of Alteration (CIA)

Chemical weathering alters siliciclastic sediments (Nesbitt and Young, 1982). These changes can be used to determine source-area weathering. The chemical index of alteration (CIA) is measures the chemical alterations to sediments using the formula CIA = [Al$_2$O$_3$ / (Al$_2$O$_3$ + K$_2$O + Na$_2$O + CaO*)] × 100, where as CaO* belongs to the silicate fraction and it is not of a biogenic source (Nesbitt and Young, 1982).

The CIA values for the 41 samples range from 58.90 – 66.96, with a mean of 63.25 ± 2.05. Sediments with a CIA range of 50 – 70 are classified as incipiently weathered. Therefore, the CIA values for the sediments indicate that the source area has not undergone intense chemical weathering.

The Al$_2$O$_3$, Na$_2$O + K$_2$O and CaO* values were also plotted on a A–CN–K triangular diagram in molecular proportions (Figure 5). All samples plot below the A$_{50}$ line known as the feldspar join (adopted from Fedo et al., 1995). Incipiently weathered sediments plot near the feldspar join line. These sediments plot below the feldspar join, close to the granite region, suggesting a granitic source.
Figure 4.4: A–CN–K diagram (in molecular proportions) for 41 samples (Nesbitt and Young, 1982). Legend: A – Al₂O₃; C – CaO; N – Na₂O; K – K₂O; CN – CaO + Na₂O. This block is designate rock and mineral compositions. Gr – granite; Ms – muscovite; Il – illite; Ka – kaolinite; Ch – chlorite; Gi – gibbsite; Sm – smectite; Bi – biotite; Ks – K-feldspar; Pl – plagioclase (figure adopted from Perri et al., 2012).
4.2.2 Major Oxide Discrimination Diagram

The samples were then plotted on the major-element distribution ternary diagram, with Al₂O₃ – K₂O- Fe₂O₃. The samples plot along the mixing line defined by illite-muscovite and chlorite end-members; however, the samples are centered in the region of the North American Shale Composite (NASC) (example adopted from Wronkiewicz and Condie 1989). This supports the observations from the CIA values and the A-CN-K diagram, in that, sediments that plot in the NASC region have undergone moderate chemical weathering.

Figure 4.5: Al₂O₃ – K₂O- Fe₂O₃ ternary diagram showing discrimination of 41 samples into NASC and residual clays regions with illite-muscovite and chlorite end-members. The black star is represents the composition of the North American Shale Composite (NASC).
4.3 Sediment Sorting and Recycling

Sediment sorting and recycling can be determined by looking at the distribution of the chemical components and the mechanical properties of the host minerals. Mechanical transport fractionates clay minerals (Al$_2$O$_3$) from quartz and feldspars (SiO$_2$). The sorting process also fractionates TiO$_2$ and Zr from zircons, which are then sorted with quartz. Ternary plots of Al$_2$O$_3$, TiO$_2$, and Zr eliminate the effects of chemical weathering and can be used to identify fractionations related to sorting processes (Mongelli et al., 2005). The end members Al$_2$O$_3$ and TiO$_2$ are multiplied by 15 and 300 respectively, in order to create a centered plot on the ternary diagram. The diagram was modeled after Garcia et al. (1994).

Figure 4.6 shows individual samples that were assigned a color based on lithologic units. The sediments samples are dispersed on the Al$_2$O$_3$ - TiO$_2$ - Zr ternary and show a wide range of TiO$_2$/Zr variations. This indicates that these sediments are possibly mature and recycled (Perri et al., 2011).
Figure 4.6: 15Al$_2$O$_3$–300TiO$_2$–Zr ternary plot showing relationship between Zr, TiO$_2$ and Al$_2$O$_3$. The samples are dispersed on the plot, indicating that the samples are mature (Perri et al., 2011; Garcia et al., 1994).

The Zr/TiO$_2$ variations are also observed in a Th/Sc vs. Zr/Sc plot (Figure 4.7). Th and Sc are useful for constraining source area composition of siliciclastic rocks because these minerals do not fractionate during sediment recycling. The is enriched in felsic rocks, while Sc is enriched in basic rocks, and any compositional changes in source areas can be determined using these elements (McLennan et al., 1990). The Th/Sc vs. Zr/Sc plot shows sediments that plot to the UCC and PAAS value. This trend represents zircon enrichment and sediment recycling.
4.4 Provenance

Elements such as La, Th and Sc can be used to differentiate source of the sediments. Th is highly incompatible, whereas Sc is relatively incompatible, and all three elements are transferred from source to into terrigenous sediments during deposition (Taylor and McLennan 1985). In Figure 4.8, elements were plotted on the
La-Th-Sc ternary plot. This plot can distinguish mafic/ultramafic and felsic sources in the absence of recycling.

Sediments that plot within the clay silt and gravel from mixed sources region have the ages 10.44, 11.35, 12.51, 14.08, 14.14 and 14.23 Ma. The other sediments that plot within the granite region as well as these the PAAS region. The granite region indicates a felsic source, while the PAAS indicates an intermediate felsic source (Perri et al., 2011).

The years 14.08, 14.14 and 14.23 coincide with 14 Ma, a period when the EAIS had become stable, dry-based ice sheet in the Middle Miocene Marchant et al., 1993; Sudgen and Denton, 2004). Therefore, mixture of sources could indicate that ice sheets were advancing and causing physical erosion of multiple sources. Each
sample was then assigned a color based lithologic units and mixing between the different aged sediments was observed, in that, the samples plot in the same region (Figure 4.8).

Figure 4.8: Sediments plotted on La-Th-Sc diagrams. Most of the sediment samples plot within the region close the Post-Archaean Australian Shale compositions. Other sediments plot in the mixed source and granitic gneiss sources regions. This indicates intermediate felsic and felsic sources. Black stars represent Granodiorite, andesite and basalt compositions.
Figure 4.9: Average values for each lithologic unit were plotted on La-Th-Sc diagrams. Most of the sediment samples plot within the region close to the Post-Archaean Australian Shale compositions. Other sediments plot in the mixed source and granitic gneiss sources regions. This indicates intermediate felsic and felsic sources. Black stars represent Granodiorite, andesite and basalt compositions.

Elemental ratios such as the Eu/Eu*, La/Sc, Th/Sc, Th/Co, Th/Cr and Cr/Th are used to distinguish between mafic and felsic sources. The data from this study was compared to the defined UCC and PAAS values (Table 4.1). The values from this study all fall in the felsic source range and therefore support the findings from the La-Th-Sc plots.
Table 4.1: Comparison of elemental ratios to mafic and felsic sources as well as the UCC and PAAS. The range of felsic and mafic sediments were taken from Cullers (2000), the UCC values were taken from McLennan et al. (2006) and the PAAS value were taken from Taylor and McLennan 1995.

Figures 4.10 and 4.11 are plots showing provenance characteristics. Figure 4.10 shows an Eu/Eu* against Th/Sc plot. These ratios are used to distinguish between a felsic and mafic contribution. The sediments all plot near the evolved felsic sources. These sources are rich in K, Na, Si, and quartz. Th/Sc vs Cr/Th is another plot that is used to distinguish between felsic and mafic sources. The plot indicates that there is a felsic contribution.
Figure 4.10: Eu/Eu* vs. Th/Sc plot discriminating between felsic and mafic sources (adopted from McLennan et al., 1990).

Figure 4.11: Th/Sc vs. Cr/Th plot discriminating between felsic and mafic sources (adopted from Condie & Wronkiewicz, 1990).
4.5 Tectonic Setting

The tectonic setting can be determined for sediments using a plot proposed by Bhatia and Crook (1986). Two plots were created, one with the individual sediment sediments and the other with mean values for each lithological unit (Figures 4.12 and 4.13). For both plots, sets of data plotted in the mostly in continental island arc region.

![Tectonic Setting Diagram](image)

Figure 4.12: Plot of average elemental values in tectonic discriminant setting diagram. A = Ocean island, B = continental island arc, C = active continental margin and D = passive continental margin. Figure was adapted from Bhatia and Crook (1986).
Figure 4.13: Elemental values plotted on tectonic setting discriminant diagram. A = Ocean island, B = continental island arc, C = active continental margin and D = passive continental margin. This figure was adapted from Bhatia and Crook (1986).
5. Conclusion

Various geochemical methods have been used in order to study Site 694 sediments and determine the depositional history and provenance of the sediments. Normalizing the data to the Upper Continental Crusts and Chondrite were useful for determining the composition of the provenance. In addition to this, other important elemental ratios such as Eu/Eu* were necessary to confirm the composition of the provenance(s).

During 9 – 17 m.y. it is expected that the terrigenous sediment input would only come from East Antarctica as the West Antarctic Ice Sheet formed after this period. The results of this study support this theory. The sediments have a chemical signature that is almost identical for each geochemical proxy used. All the proxies indicated a source that is felsic in composition. It is also important to note that these sediments displayed a recycling trend marked by the addition of zircon.

East Antarctica comprises of different suites of rocks including deformed, metamorphosed rocks that form a part of the TAM. Based on the drainage pattern map of Antarctica, the TAM could have been a sediment supply to the Weddell Sea. The sediments could also have come from a granitic gneiss suite, which would be felsic in composition and metamorphosed.

It is also important to note that the sediments from Units VIIB and VIIC had higher (Gy/Yb)$_{cn}$ in comparison to the other sediments. In fact, these averages were on the border of the Archean sediment region and coincide with the Middle Miocene Climatic Optimum. This signature could indicate a change in provenance, which coincides with the Miocene warming.
5.1 Future Work

The analysis for this study provided interesting preliminary data. It must be noted however that the data set was small and there was an uneven distribution of sediments per lithologic unit. This could have created biases and skewed the data. Therefore, the next step of this project should be to obtain more samples per lithologic unit.

For this study, the geochemical analyses were not conducted for one specific grain size fraction and this can affect the signatures seen amongst sediments. Jorge et al. (2013) conducted a study on coarse and fine fractions from different sediments and they found that the elemental ratios such as La/Sc, Th/Sc, La/Co, Cr/Th and Eu/Eu* are affected by grain size. Therefore, future analysis should be carried out on uniformed grain sizes.

This study was not successful in identifying the actual provenance of the sediments, in that a specific source area could not be located. Isotope geochemistry can be used to address this problem. Flowerdew et al. (2012) used Pb analyses of Kfeldspars (Kfs) from Archaean–Mesozoic crystalline rocks from across the Weddell Sea region. Kfs has different signatures associated with different geographical regions and this method has been used to define five basement provenances. This method could be used to identify provenance basements during the Middle Miocene.

The XRF core scanner data reveals interesting results, in that, changes are observed throughout the Middle Miocene period. Because the XRF dataset is large, more samples should be taken down core to represent the area of interest and further geochemical analyses should be performed.
References


