XRF-Derived Cyclicity in Pliocene and Pleistocene Sediments from ODP Site 693, Dronning Maud Land, Antarctica

by

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Abstract

Anthropogenic climate change poses great challenges and existential questions to humankind. Communities must be made resilient to the inevitable destructive effects that we are sure to see in the coming decades, and our interactions with the complex, interconnected ecosystems in which we participate need to be restructured in hopes of mitigating continued adverse consequences.

The Pliocene epoch is, in many ways, a climatic analogue to our current world. Atmospheric CO$_2$ levels exceeded 400 ppm during the mid-Pliocene warm period (Haywood et al., 2009), a level that was surpassed in May of 2013 (Blunden, 2014). Therefore, the epoch can shed light on the consequences of current climate change. The Pleistocene epoch, following the Pliocene epoch, is characterized by cycles of Antarctic and Northern Hemispheric glaciation (Pollard and DeConto, 2009), thereby providing important information on the factors necessary in inducing and reducing polar glacial conditions.

The stability of the East Antarctic Ice Sheet (EAIS) is now an area of study experiencing much contention and is one of the focal points of this study. Holding ~26.5 million km$^3$ of ice, the EAIS has the potential to raise global sea levels tens of meter (Gross, 2014). While previously thought to have remained stable during the Pliocene and Pleistocene epochs, it now seems conceivable that the EAIS coastline experienced significant glacial retreat throughout the late Pliocene as well as the early Pleistocene (Raymo et al., 2006, Cook et al., 2013).

Understanding the mechanisms involved in creating the stability of Antarctic ice sheets during these epochs will allow us to more properly estimate the level of
deglaciation that we can expect to see as a result of anthropogenic climate change. This will aid in estimating the magnitude of sea level rise that the world will experience, thereby providing coastal communities with information to prepare appropriately.

Using X-ray fluorescence data from deep-sea sediment cores recovered from the Weddell Sea off the coast of the EAIS (in conjunction with diffuse spectral reflectance and magnetic susceptibility data from the same cores), this study focuses on identifying the roles that Milankovitch cycles had and continue to have on Antarctic climate via the statistical techniques known as Varimax-rotated principal component analysis and wavelet analysis. 100 kyr eccentricity, 41 kyr obliquity, and ~20 kyr precession were identified as the dominant Milankovitch cycles at the time of deposition of Core 8R during the Pliocene, and 400 kyr eccentricity and 100 kyr eccentricity were identified as the dominant Milankovitch cycles at the time of deposition of Core 2R during the Pleistocene. By identifying and applying these Milankovitch cycles to the periodicities obtained from the wavelet spectra, sedimentation rates of 6.58 cm/kyr for Core 8R and ~1.44 cm/kyr for Core 2R were derived.
1. Introduction

1.1 The Ocean Drilling Program

The Ocean Drilling Program (ODP), now the International Ocean Discovery Program (IODP), is a multi-country deep-sea drilling collaboration that provides ocean floor geological data and samples to aid research on the history and dynamics of Earth. The samples used in this research were taken from cores recovered during January and February of 1987 on the 113th expedition of ODP. ODP Expedition 113 traveled to the Weddell Sea, Antarctica, with the goal of acquiring information that could be used in subsequent studies to better understand the processes involved in Antarctic ice sheet formation, Antarctic bottom water formation, and other phenomena.

Cores retrieved by ODP are labeled using the following format: first the expedition number, then the site number, the hole letter, the core number with a letter indicating the type of drilling (where R stands for rotary drilled and X stands for piston cored), and finally the section number (Gross, 2014). The primary cores studied in this research are 113-693A-8R and 113-693A-2R in their entirety, though analyses were also conducted on longer datasets further encompassing Cores 113-693A-9R through 113-693A-14R. All of the cores studied in this paper come from expedition 113, site number 693, and hole A. As such, cores will be referred to using only their core number, e.g. 8R and 2R.

1.2 Expedition 113, Site 693

The site at which our samples were recovered has a geographic coordinate position of -70.8315° latitude, -14.5735° longitude. It is located in the eastern
Weddell Sea in a water depth of 2359 m. It is in close proximity to the Wegener Canyon as well as the coast of the continent. The position of this site, as well as several others from the same expedition, can be seen in Figure 1.1.

The cores from this site include sediments that were deposited during the early Cretaceous at the greatest depth (213.58 meters below sea floor) to the present. The primary focus of this study is on fully recovered core sections from the Pliocene (8R) and the early Pleistocene (2R). Two holes were drilled at Site 693: Hole 693A and Hole 693B. Hole 693A was rotary drilled which resulted in a low recovery of only 44%. Hole 693B, however, was drilled using an extended piston corer, which resulted in a higher recovery rate of 55% (“Shipboard Scientific Party, 1988. Site 693”).

![Figure 1.1. Location of Sites 691, 692, and 693 off the coast of the eastern Weddell Sea and near the Wegener Canyon (Grobe et al., 1990).](image)
1.3 Antarctic Geology

Antarctica resides in the South Pole and is surrounded by the Southern Ocean. Its land area exceeds 14 million km$^2$, making it almost twice the size of Australia. Almost the entirety of Antarctica is covered with ice sheets that are over one mile thick, save the top of the Antarctic Peninsula found in the northwestern most region of the continent (Fretwell et al., 2013). Because of the prominence of the cryosphere in Antarctica, it remains difficult to study the geology of the continent and, as such, scientific debate and research continues to persist on a large number of Antarctic topics.

Nonetheless, using a number of sophisticated research methods (e.g. tectonic plate reconstructions and geochemical studies of sediment cores), geologists have designated two distinct geomorphologic regions of Antarctica: the west and the east. The Transantarctic Mountains (TAM), extending from the Weddell Sea and the Ross Sea, separates West and East Antarctica (Fig. 1.2). The TAM formed during the early Cenozoic from the opening of the West Antarctic Rift. The peaks are composed of various Triassic/Jurassic sedimentary rocks whereas the depths are composed primarily of gneisses made from metamorphosed East Antarctic rock and granite intrusions (Harley, 2005; Chin, 2013).

East Antarctica formed during the Precambrian eon and the Paleozoic era. Dronning Maud Land (Domain 1) is a likely primary sediment source for Site 693 (Fig. 1.2). West Antarctica formed during the Mesozoic and Cenozoic eras. Weathering and erosional processes occurring in distinct sections of Antarctica provide sediment to various basins.
1.4 Plio-Pleistocene Climate

The Pliocene is a geologic epoch within the Neogene Period within the Cenozoic Era. It spanned from 5.33 million to 2.58 million years ago. Paleoclimate reconstruction research in the Pliocene has recently experienced a renewal in activity due to its many climatic similarities to the current industrialized Earth. Haywood et al. (2009) propose, “the warmest intervals of the Pliocene may represent an equilibrium climate response to atmospheric CO$_2$ levels that will be attained approximately by the middle of the twenty-first century.” These warm intervals during the Pliocene likely saw atmospheric CO$_2$ levels that were at least 50-100 ppm higher than preindustrial levels (280 ppm) with many studies placing the estimate at 400 ppm. This resulted in a global average temperature that was 2-4 °C higher than today, as well as an approximate increase of 20 to 25 m in global sea level driven primarily by glacial melt (Dwyer and Chandler, 2009; McKay et al., 2012; Miller et
al., 2012; Fedorov et al., 2013). The National Oceanic and Atmospheric Administration (NOAA) documented the first daily atmospheric CO\textsubscript{2} level averages that reached 400 ppm in 2013 (Blunden, 2014).

The Pliocene can be roughly divided into three separate phases: first, an early period of climatic warming. Then, a short burst of high warmth around 3 Ma, often referred to as the mid-Pliocene warm interval. Finally, a late period of climatic cooling that is characterized by cycles of glaciation and deglaciation (Haywood et al., 2009).

The Pleistocene is a geologic epoch within the Quaternary Period following the Pliocene. It spanned from 2.58 million to 11,700 years ago, up to the beginning of the Holocene epoch. It is the world’s most recent interval of repeating glacial cycles, an interval that ends at the beginning of the Holocene. Unlike the Pliocene, the Pleistocene is not considered a climatic analogue to our current world due to its lower atmospheric CO\textsubscript{2} levels ranging 170-300 ppm (Hansen and Sato, 2012).

1.5 Plio-Pleistocene Antarctic Glacial History

A number of Antarctic paleoclimate reconstruction studies on ice advancement and retreat have been conducted. They commonly use stable isotope ratios, namely benthic $\delta^{16}$O/$\delta^{18}$O ratios. Ice formation uses the lighter of oxygen isotopes, $^{16}$O, and therefore larger benthic $\delta^{18}$O ratios in benthic foraminifera indicate that ice formation is increasing and temperatures are decreasing (Raymo et al., 2006; Pollard and DeConto, 2009).

Results from these studies indicate that large-scale ice sheets first developed on East Antarctica sometime after the mid-Miocene climatic optimum (14.8 to 14.5
West Antarctica, however, experienced glaciation in its mountainous regions but did not experience widespread glaciation until the end of the Miocene epoch (Levitan and Leichenkov, 2014). The West Antarctic Ice Sheet (WAIS) formed when temperatures were cooler and CO₂ levels lower and continues to be more dynamic than the EAIS to this day.

The mid-Pliocene warm period, occurring between 3.3 and 3 Ma, is often considered to be a climate analogue for an impending warmer Earth. Raymo et al. (2006) suggest that much of the EAIS was deglaciated during this interval, challenging the long-held belief that the EAIS was consistently stable throughout the Pliocene and the Pleistocene. The Pleistocene, on the other hand, is a period of cyclical glaciation, especially in the Northern Hemisphere. The extent of deglaciation of West and East Antarctica is under scrutiny (Patterson et al., 2014, Pollard et al., 2015).

1.6 Milankovitch Cycles

One of the largest drivers of climate change is orbital forcing. The quantities of insolation that a given region of the earth is exposed to vary cyclically and are based on several well-documented changes known as Milankovitch cycles, named after the Serbian astronomer Milutin Milankovic. There are three major Milankovitch cycles: obliquity, eccentricity, and precession, all of which are visually depicted in Figure 1.3 (de Boer et al., 1994).

Earth’s ecliptic is the orbital plane that earth follows on its orbit around the sun, i.e. it is the plane that slices both the sun and the earth in half. Obliquity is the change in the angle between the ecliptic and the earth’s equator. This angle varies
between 22.1° and 24.5° and is currently at a tilt of ~23.4°. Obliquity has a cycle length of approximately 41,000 years. The length and magnitude of seasonal changes are a result of obliquity cycles and they are expected to have a significant effect in the onset of ice ages. During periods of low obliquity, summers would receive less insolation and would therefore be less effective at melting the precipitation from the previous winter, thereby accumulating over time.

The orbital forcing known as eccentricity is a consequence of earth’s elliptical orbit around the sun. Because of gravitational interactions with other planets such as Jupiter and Saturn, earth’s orbit around the sun deviates from perfect circularity. This results in minor changes in the amount of solar radiation that the earth receives seasonally. For instance, during periods of high eccentricity, the difference in winter radiation and summer radiation will be larger than during periods of low eccentricity. The change in the magnitude of the earth’s elliptical orbit follows two cycles: one of 100,000 years and the other of 400,000 years.

Precession is a result of the deviation of earth’s shape from that of a perfect sphere. Tidal forces from the Moon and the Sun cause earth to exhibit a bulge at its equator. That earth is an oblate spheroid causes the earth’s rotational axis to change with respect to fixed celestial bearings. Precession periodicities occur in 19,000- and 21,000-year intervals.

It is important to note that orbital forcing redistributes the radiation that earth receives both temporally (i.e. seasonally) and spatially. Under some circumstances, this redistribution affects climate cyclically. Studying how these three cycles work simultaneously on the Antarctic climate and the resulting off-shore deposition can aid
in the understanding of the stability or fragility of the East and West Antarctic Ice Sheets during the Pliocene and Pleistocene epochs.

Figure 1.3. Schematic depictions of the three forms of orbital forcing, also known as the Milankovitch cycles: (a) eccentricity, (b) obliquity, and (c) precession (de Boer et al., 1994).
2. Methods

2.1 X-Ray Fluorescence Core Scanning

X-Ray Fluorescence (XRF) spectroscopy is an analytical technique used to acquire information on the major and trace element concentrations of a material given as element counts per area. XRF spectroscopy is achieved by the firing of high-energy X-rays at the surficial atoms of an object. When the X-rays hit the electrons of these atoms, one or more electrons will be excited and ejected if the energy of the X-ray is larger than the ionization potential of the electron. The ejected electrons are generally removed from the innermost orbital of an atom, causing the atom to become unstable. To restabilize, electrons from the next highest orbital will take the place of the previous electrons and in doing so will emit energy in the form of photons (Fig. 2.1). The emitted energy will be characteristic of that atom, thereby providing information on the surficial elemental composition of a material.

A third-generation Avaatech XRF Core Scanner was used on Leg 113 sediment core sections at the IODP Texas headquarters on the Texas A&M campus in College Station, Texas. Core sections were lightly scraped to produce a smoothed, fresh surface.

Before scanning, core sections were imaged with a Core Imaging Machine developed by the Ocean Drilling Program. The Core Imaging Machine provides both a .tif file of each core section as well as high resolution RGB data in the form of excel files. Dropstones, i.e. pebbles and small rocks, were imaged, but removed from the core prior to XRF scanning. Core sections were then covered with a 4 micron 3525 Ultralene thin film which was taped down to prevent creasing. The core sections were
then placed in the XRF Core Scanner and scanned. Figure 2.2 is a schematic representation of an XRF Core Scanner.

The cores were scanned down their centers in 2 cm intervals, except where gaps or high/low elevated sections within the cores occurred. At each interval, a 1 cm² section of the core was irradiated for 20 seconds. XRF scans were run two or three times per core, depending on the information required. The 10 kV and 30 kV runs were conducted for every core section and 50 kV runs were conducted for core sections from 2R and 8R, as well as several other miscellaneous core sections. 10 kV runs detect the major elements Al, Si, P, S, Cl, Ar, K, Ca, Ti, Cr, Mn, Fe, and Rh and 30 kV runs detect the heavier trace elements Ni, Cu, Zn, Ga, Br, Rb, Sr, Y, Za, Nb, Mo, Pb, and Bi. 50 kV runs allowed for the detection of even heavier elements: Ag, Cd, Sn, Te, and Ba, with our primary interest being the presence or absence of barium. Element counts were recorded in .spe files that were then converted to excel files at IODP using WinAxilBatch. Standards were run after every several core sections to ensure that there was no measurement drift or malfunction.
Figure 2.1. (a) An x-ray bombards a material and an electron from the innermost orbital, the K-shell, is ejected. (b) An electron from the next highest orbital, generally the L-shell, fills the place of the ejected electron to restabilize the atom and a characteristic fluorescence is emitted. (c) An electron from the next highest orbital, generally the M-shell, then fills the place of the electron now residing in the K-shell, resulting in the emission of a characteristic fluorescence (Tjallingii, 2006).

Fig 2.2. Depiction of an XRF core scanning device setup (Tjallingii, 2006).
2.2 Magnetic Susceptibility

Magnetic susceptibility provides a dimensionless value indicating the amount of magnetic material present in a given interval of sediment. A multi-track sensor was used at the IODP Texas headquarters to conduct magnetic susceptibility analyses on the cores used in this study. The cores were scanned down their centers in 0.05 cm intervals for 2R and 0.1 cm intervals for 8R.

2.3 Dataset Preparation

The excel files containing the element counts per area per core section from the XRF Core Scanner were compiled for each core to allow for full downcore elemental analysis. An additional column was added to each excel file to allow for the identification of the Meters Below Seaﬂoor (mbsf) of each interval. Mbsf was determined using the figures given in the Shipboard Reports (see Figs. 2.3 and 2.4). Measurements that had values greater than -140 for argon counts per area were eliminated. These argon values indicate poor contact with the scanner and therefore suggest erroneous measurements.

The divides between the core sections are based solely on the core length of the retrieved cores. Because of this, and in an effort to ensure consistency within the statistical analyses, the following techniques (Sections 2.3 through 2.7) were conducted twice under two separate conditions. First, the analyses were run treating each core section from 2R and 8R as separate entities; that is, the analyses for each of these core section aggregations were conducted separately. Results from these analyses will refer to the cores simply as Cores 2R and 8R.
Next, the analyses were run with the data from the 2R and 8R cores combined with data from Cores 9R through 14R. This formed a longer dataset in which the two groups, i.e. a) 2R, and b) 8R through 14R, are treated as a single entity. Results from these analyses will be referred to as the components derived from the longer dataset, or the Composite Cores Components (C^3). Comparing the results of the analyses under the two separate conditions, it becomes easier to understand the extent to which geological and cyclical processes vary between the two time intervals that are covered by these cores.

The benefits of combining the two datasets (2R and 8R through 14R) and treating them as a single entity include the presence of a greater number of observations within the dataset, which aids in removing noise from the signal. Thus, the components and subsequent interpretations derived from the cores when treated as a single entity (C^3) are given more confidence than the components derived from the cores when treated as separate entities. Furthermore, the C^3 dataset allows us to compare the same components (i.e. components with the same loadings) across the two time intervals. Treating the two cores as separate entities provides us with different components (i.e. components with different loadings) for each time interval, and thus the analyses conducted under the first condition do not allow comparison of identical components across these two time intervals.
Figure 2.3. Shipboard photograph of Core 8R used to identify recovery rates and mbsf for each interval throughout the XRF and magnetic susceptibility datasets.
Figure 2.4. Shipboard photograph of Core 2R used to identify recovery rates and mbsf for each interval throughout the XRF and magnetic susceptibility datasets.
2.4 Calibration of XRF Data to Oxide Weight Percent

The acquisition and analysis of element counts per area from XRF is a popular research method in the geosciences (Marce et al., 2006; Shelley et al., 2014), though it remains hindered by its purely qualitative data. It remains practical for many purposes, such as identifying clear depositional changes within a core, but it may not correctly represent the elemental composition of a material. This is the result of a number of phenomena, including the dependence of the detection of an element’s fluorescence on the mass of sediment in the volume being irradiated. Elements with lower atomic weights release X-rays with lower energies which are consequently more likely to be absorbed by other heavier elements on their departure from the sediment. Because of this, light elements such as Al, Si, P, S, etc. may be underrepresented in the data, which can cause problems when interpreting nonhomogeneous samples (Lyle et al., 2012).

To correct for this, twenty-six samples from Site 693 were selected for XRF analysis at the University of Massachusetts Amherst X-Ray Fluorescence Laboratory (Table 2.1). The samples were ground using an agate mortar and pestle and dried at 70°C. At UMass Amherst, the samples were analyzed for major element oxides “on fused La-bearing lithium borate glass disks using a Siemens MRS-400 multi-channel, simultaneous X-ray spectrometer” (“Facilities at the Ronald B. Gilmore XRF Lab”). This analysis provided weight percent data for the following oxides: SiO₂, TiO₂, Al₂O₃, Fe₂O₃, MnO, MgO, CaO, Na₂O, K₂O, and P₂O₅. Using the median weight percent for each of these oxides for all twenty-six samples, the XRF data in the form of element count per area was calibrated to oxide weight percent data (wt%). Element
counts were collected for Si, Ti, Al, Fe, Mn, Ca, K, and P, and all were calibrated to their respective oxides.

Following the method developed by Lyle et al. (2012), the data were calibrated using a two-step process in which the raw element count data is scaled and then normalized. Elemental scaling consists of calculating the median value for an elemental oxide for the twenty-six analyzed samples as well as the median of the element representative of that oxide for the interval being calibrated (e.g. Al$_2$O$_3$ and Al counts per area, respectively). The median of the weight percent for that oxide is then multiplied by the element count per area at each interval within the core and divided by the median element count for that element. The method is more clearly represented by the following equations:

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

Where,

- $S_e$ = non-normalized oxide wt% at a given interval,
- $\text{Med} \%_e$ = median of the wt% of each oxide obtained from the XRF Analyzer (for example, for Al, the median of the wt% of Al$_2$O was used),
- $\text{PeakArea}_e$ = intensity of an element at a given interval,
- $\text{PeakArea}_e, \text{med}$ = median for each element obtained from the XRF core scanner (Lyle et al., 2012).

Sample scaling with the Lyle et al. (2012) method provides a more accurate representation of the elemental composition of a material as it reduces the dominance of the heavier elements within the data.

After scaling, the oxide wt% for each oxide should sum to 100%. However, this was usually not the case. Therefore the data were normalized such that the sum of the oxide wt% values for each sample would be 100. The first step to achieve this is to sum the raw oxide wt% values at each interval. Then, the scaled oxide wt% for each individual oxide at a specific interval is multiplied by 100 and divided by the
summed raw oxide wt% at that interval. The following series of equations explain the method used for each interval:

\[ \text{NMS}_o = \left( \frac{S_e \times 100}{\text{raw sum}} \right) \]

Where,

\[ \text{NSM}_o = \text{normalized median-scaled data for a specific oxide at a specific interval, e.g. Fe}_2\text{O}_3 \text{ at 21.2 mbsf,} \]

\[ S_e = \text{oxide wt% of a specific oxide at a specific interval,} \]

\[ \text{Raw sum} = \text{sum of the raw oxide wt% at an interval (Lyle et al., 2012).} \]

After normalizing the complete datasets for Cores 2R and 8R, the oxide wt% values were summed at each mbsf interval and each mbsf interval returned a summed total of 100%, indicating that the conversion process was successful.

The following example provides a demonstration of the two-step method for SiO$_2$:

Step 1: Med\%$_e$ = 67.2 wt% SiO$_2$, PeakArea$_e$ = 78,922 at 60.62 mbsf, and PeakArea$_{med}$ = 107,650. Thus, \( S_e = 67.2 \times \left( \frac{78,922}{107,650} \right) = 49.27 \) wt%.

Step 2: \( S_e = 49.27 \) wt%, raw sum = 68.02 wt%. Thus, \( \text{NMS}_o = \left( \frac{49.27 \times 100}{68.02} \right) = 72.43 \) wt% SiO$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$</th>
<th>TiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MnO</th>
<th>MgO</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>P$_2$O$_5$</th>
<th>Total</th>
</tr>
</thead>
<tbody>
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<td>0.98</td>
<td>11.88</td>
<td>6.92</td>
<td>0.08</td>
<td>3.82</td>
<td>2.92</td>
<td>5.49</td>
<td>2.61</td>
<td>0.21</td>
<td>100.11</td>
</tr>
<tr>
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<td>14.87</td>
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<td>3.30</td>
<td>0.53</td>
<td>99.43</td>
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<td>10.51</td>
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<td>4.68</td>
<td>2.81</td>
<td>4.30</td>
<td>2.89</td>
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<tr>
<td>693B-4H-2</td>
<td>67.75</td>
<td>0.75</td>
<td>12.89</td>
<td>5.74</td>
<td>0.08</td>
<td>2.83</td>
<td>2.85</td>
<td>4.10</td>
<td>3.06</td>
<td>0.19</td>
<td>100.24</td>
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<tr>
<td>693A-7R-2</td>
<td>59.61</td>
<td>1.51</td>
<td>13.14</td>
<td>9.62</td>
<td>0.13</td>
<td>5.22</td>
<td>3.42</td>
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<td>3.26</td>
<td>0.25</td>
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</tr>
<tr>
<td>693A-8R-1</td>
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<td>1.00</td>
<td>12.94</td>
<td>7.20</td>
<td>0.11</td>
<td>3.45</td>
<td>3.05</td>
<td>3.35</td>
<td>3.19</td>
<td>0.25</td>
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<td>5.13</td>
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<td>2.81</td>
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<td>3.67</td>
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<td>3.19</td>
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<td>0.21</td>
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<td>13.00</td>
<td>7.55</td>
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<td>3.68</td>
<td>2.80</td>
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<td>3.52</td>
<td>0.83</td>
<td>99.60</td>
</tr>
<tr>
<td>693A-12R-1</td>
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<td>12.74</td>
<td>9.02</td>
<td>0.11</td>
<td>5.08</td>
<td>3.04</td>
<td>3.51</td>
<td>3.06</td>
<td>0.25</td>
<td>99.68</td>
</tr>
<tr>
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<td>9.08</td>
<td>6.00</td>
<td>0.08</td>
<td>3.82</td>
<td>1.92</td>
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<td>0.62</td>
<td>99.41</td>
</tr>
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<td>693A-12R-7</td>
<td>63.78</td>
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<td>10.84</td>
<td>8.65</td>
<td>0.11</td>
<td>5.14</td>
<td>3.62</td>
<td>3.54</td>
<td>2.24</td>
<td>0.25</td>
<td>99.68</td>
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<td>693A-15R-4</td>
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<td>0.17</td>
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<td>11.04</td>
<td>6.52</td>
<td>0.09</td>
<td>3.52</td>
<td>2.58</td>
<td>3.72</td>
<td>2.73</td>
<td>0.16</td>
<td>100.11</td>
</tr>
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<td>693A-16R-1</td>
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<td>0.75</td>
<td>11.10</td>
<td>5.99</td>
<td>0.08</td>
<td>2.68</td>
<td>2.30</td>
<td>2.35</td>
<td>2.86</td>
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<td>693B-1X-5</td>
<td>68.76</td>
<td>0.81</td>
<td>12.03</td>
<td>5.52</td>
<td>0.10</td>
<td>2.53</td>
<td>3.29</td>
<td>3.13</td>
<td>2.74</td>
<td>0.50</td>
<td>99.41</td>
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<tr>
<td>693A-17R-2</td>
<td>69.70</td>
<td>0.81</td>
<td>11.58</td>
<td>5.39</td>
<td>0.08</td>
<td>3.09</td>
<td>2.52</td>
<td>3.55</td>
<td>2.73</td>
<td>0.16</td>
<td>99.61</td>
</tr>
<tr>
<td>693A-18R-3</td>
<td>71.47</td>
<td>0.85</td>
<td>11.05</td>
<td>5.87</td>
<td>0.08</td>
<td>2.96</td>
<td>2.44</td>
<td>2.35</td>
<td>2.57</td>
<td>0.20</td>
<td>99.84</td>
</tr>
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<td>693A-18R-5</td>
<td>70.71</td>
<td>0.87</td>
<td>10.40</td>
<td>5.96</td>
<td>0.08</td>
<td>3.13</td>
<td>2.54</td>
<td>3.44</td>
<td>2.53</td>
<td>0.15</td>
<td>99.81</td>
</tr>
<tr>
<td>693A-19R-1</td>
<td>70.36</td>
<td>0.75</td>
<td>11.13</td>
<td>5.43</td>
<td>0.07</td>
<td>2.83</td>
<td>2.38</td>
<td>3.80</td>
<td>2.67</td>
<td>0.14</td>
<td>99.56</td>
</tr>
<tr>
<td>693A-28R-1</td>
<td>76.89</td>
<td>0.57</td>
<td>9.34</td>
<td>4.27</td>
<td>0.05</td>
<td>2.04</td>
<td>1.96</td>
<td>2.19</td>
<td>2.20</td>
<td>0.15</td>
<td>99.66</td>
</tr>
<tr>
<td>693A-31R-1</td>
<td>66.31</td>
<td>0.86</td>
<td>12.68</td>
<td>6.61</td>
<td>0.09</td>
<td>3.02</td>
<td>3.06</td>
<td>3.86</td>
<td>3.13</td>
<td>0.22</td>
<td>99.84</td>
</tr>
<tr>
<td>693A-34R-1</td>
<td>64.25</td>
<td>0.84</td>
<td>13.36</td>
<td>7.60</td>
<td>0.11</td>
<td>3.50</td>
<td>2.78</td>
<td>3.95</td>
<td>3.43</td>
<td>0.22</td>
<td>100.04</td>
</tr>
<tr>
<td>693A-38R-1</td>
<td>72.53</td>
<td>0.63</td>
<td>11.64</td>
<td>3.79</td>
<td>0.05</td>
<td>1.94</td>
<td>2.58</td>
<td>3.78</td>
<td>2.71</td>
<td>0.19</td>
<td>99.84</td>
</tr>
</tbody>
</table>

Table 2.1 List of XRF samples from Site 693 that were analyzed at the University of Massachusetts Amherst X-Ray Fluorescence Laboratory.
2.5 Varimax-rotated Principal Component Analysis

Principal component analysis (PCA) is an exploratory statistical technique used to reduce large, cryptic datasets to more easily interpretable "components" with the goal of elucidating an underlying structure behind the dataset. Principal components, i.e. combinations of uniquely weighted variables in the original dataset, are created such that each principal component is orthogonal to the others, thereby removing any correlation that may exist between the initial variables. The first principal component attempts to explain the largest possible amount of variance within the dataset, the second explains the second largest possible amount of variance (with the stipulation that it is orthogonal to the first principal component), and so on. The principal components can then be used in scatterplots, regressions, and other statistical techniques.

Many variations of this technique exist, with the most popular being Varimax-rotated principal component analysis (VPCA). Rotated PCA methods allow variance to be more widely distributed across principal components, thereby increasing the number of "loadings" for variables on the components that follow the leading component. This allows the components to be more easily interpreted. Professor Joseph Ortiz of Kent State University and several of his students have used VPCA extensively to examine orbital loadings in XRF and visible near-infrared (VNIR) data from Ohio and the Arctic (Cope, 2009; Siriwardana, 2011). Similar applications have been conducted in this thesis using both of the XRF datasets (count ratios and calibrated oxide weight percents) and magnetic susceptibility. It should be noted that
PCA (including VPCA) is exploratory and not confirmatory, and thus inferences and
general trends, not conclusions, can be drawn from these methods.

VPCA analyses were conducted in RStudio, a free and open source statistical
software. Sample codes are included in Appendix B. These techniques were
conducted primarily on two cores: 2R and 8R, deposited during the Pleistocene and
Pliocene, respectively, as well as on a larger dataset composed of 2R combined with
8R through 14R (C3) to examine changes in component composition over longer
timescales. The component values were split back into the two intervals (2R and 8R
through 14R) following the VPCA procedure. Components were created and
compared using the raw element count per area ratio data and oxide weight percent
data.

The element ratios used in creating the components for the raw element count
per area data were Ag/Ti, Ba/Ti, Ca/Ti Cd/Ti, Cl/Ti, Cr/Ti, Cu/Ti, Fe/Ti, K/Ti,
Mn/Ti, Mo/Ti, Ni/Ti, P/Ti, Rb/Ti, S/Ti, Sn/Ti, Sr/Ti, Zr/Ti, and Zn/Ti. Element
counts were normalized with Ti as the denominator to account for terrigenous sources
as titanium is an element that comes predominantly from land and is not important in
biogeochemical cycles. Aluminum was another possible normalization factor, but Ti
was deemed a more suitable choice in accordance with previous studies (e.g.
Jorgensen, 2012; Chin, 2013). The oxides used in creating the component for the
oxide weight percent data were Al2O3, CaO, Fe2O3, K2O, MnO, P2O5, SiO2, and TiO2.

2.6 Wavelet Analysis

Wavelet analysis is a statistical analysis technique used to identify
periodicities within a time-series dataset (Terrence and Compo, 1998). It is widely
used within the paleoclimate reconstruction and geophysics communities, as Earth’s climate is reliant on many periodicities (e.g. those driven by eccentricity, precession, and obliquity).

Wavelet analysis attempts to correct two problems with the more traditional running variance technique, namely time localization (i.e. the shape of the curve being dependent on the size of the window being used) and frequency localization (i.e. information not being given on the frequency of the curve, only on the amplitude). As explained by Balu and Padmanabhan (2007), "Wavelet analysis attempts to solve these problems by decomposing a time series into time/frequency space simultaneously. One gets information on both the amplitude of any ‘periodic’ signals within the series, and how this amplitude varies with time." Wavelet analysis assumes that the time-series data contain nonstationary power at specific frequencies, i.e. the XRF count ratio and oxide weight percent data contain trends and are created by periodicities of differing lengths. This is a valid assumption for the datasets being used, as they should be capturing the effects of the different Milankovitch cycles on the depositional environment of Site 693.

To prepare the datasets for wavelet analysis, they were interpolated and subsequently detrended. The XRF datasets were interpolated (that is, expanded to intervals not captured in the actual XRF scanning procedure due to the presence of gaps, etc.) to provide measurements for every 2 cm interval, as wavelet analysis requires the use of a constant interval between observations. The data were then detrended by creating a 2nd-degree polynomial trendline for the cores, inserting the depth at each interval into the equation for the trendline, and subtracting the trendline
equation value from the original value at each interval. After detrending, cyclical patterns become more easily identifiable. Both the interpolation and the detrending methods were conducted in RStudio. Sample codes are in Appendix B.

The data from each component created from the element count and oxide weight percent data, as well as the non-VPCA magnetic susceptibility data, were then inputted into Interactive Wavelet Plot (http://ion.exelisvis.com/). This is a free, online program that provides wavelet power spectra to aid in the identification of cycles within a dataset. The settings were adjusted such that zeroes were padded to the end of the datasets to offset edge effects, a cone of influence was included, and a line representing 30% red noise was included to better identify cycles from misleading spikes.

2.7 Linear Sedimentation Rates and Accumulation Rates

Using the wavelet power spectra, linear sedimentation rates were calculated using the period length of a cycle and the lengths of Milankovitch cycles for Cores 2R and 8R through 14R. By experimenting with Milankovitch cycle lengths, trends were identified in the linear sedimentation rates and wavelets within the dataset were matched with Milankovitch cycles. The estimated linear sedimentation rates and matched Milankovitch cycles were compared with those from a similar study by True-Alcala (2015) using diffuse spectral reflectance (DSR) data to further increase confidence in the conclusions being drawn.

Using the derived linear sedimentation rates well as bulk density data provided in the Shipboard Report, accumulation rates were derived for Cores 2R and
8R through 14R. Accumulation rates (g/cm$^2$/kyr) are calculated by multiplying linear sedimentation rate (cm/kyr) by the average bulk density of a given core (g/cm$^3$).
3. Results

3.1 Varimax-rotated Principal Component Compositions

Twenty-eight Varimax-rotated principal components were created for this study:

a. five from the raw element count ratio data for each core in which each core was treated as a separate identity (ten total; five for 2R and five for 8R),

b. five from the raw element count ratio data in which Cores 2R and 8R through 14R were treated as a single entity (C\(^3\)),

c. four from the oxide weight percent data for each core when treating each core as a separate identity (eight total; four for 2R and four for 8R), and

d. five from the oxide weight percent data when treating Cores 2R and 8R through 14R as a single entity (C\(^3\)).

Figures 3.1 through 3.4 compare downcore component values from Core 8R with the corresponding C\(^3\) values. The graphs exhibit strikingly similar patterns, thereby suggesting that either set of component values is sufficient for analysis and interpretation. Still, our preference remains with the latter due to its ability to be compared with identical components during 2R.

The component loadings for each component can be found in the second columns of Tables 3.1 through 3.6, where DR indicates a detrended and rotated component. The larger the absolute value of a given component loading, the more influence it holds within a component, e.g. in the first row of Table 3.1 Ba has a value of 0.95 and therefore it holds the most influence in the first component. The sign of a relationship matters: values with a positive sign are positively correlated with the
principal component while those with a negative sign are negatively correlated. The third column of Tables 3.1 through 3.6 gives the percent of total variance that each component explains.

Figure 3.5 is a graphical depiction of select component loadings for components created from the XRF element count ratios data in which Cores 2R and 8R were treated as separate entities. Though 2R and 8R were deposited during the Pleistocene and Pliocene, respectively, there are several underlying element ratio combinations that explain large amounts of each dataset’s variance regardless of the epoch in which it was deposited. The second component from 2R and the first component from 8R share six of the same element count ratios as their primary component loadings (Ba, Sr, Zr, Rb, K, Zn), and the first component from 2R and the third component from 8R share seven of the same element ratios as their primary component loadings (Sn, Ag, Cu, Ni, Cd, Fe, Mo). Unsurprisingly, both of the selected components from 2R include Ca/Ti as a component loading as the core contains foraminifera.

Interpretation of the components created from the XRF element count ratio data requires making inferences using the known geochemical properties of the elements that form a component. Examining both positive and negative correlations between components and element count ratios can also aid in the interpretation of the created components, and interactive crossplots have been created to show the presence or absence of correlations between component and element count ratios (see Section 3.3).
Figure 3.1. Comparison of 8R-DR1 component values with C³-DR1 component values.
Figure 3.2. Comparison of 8R-DR2 component values with C$^3$-DR2 component values.
Figure 3.3. Comparison of 8R-DR3 component values with C³-DR3 component values.
Figure 3.4. Comparison of 8R-DR4 component values with $C^3$-DR4 component values.
### Table 3.1. Composition of components created from 8R element count ratio data

<table>
<thead>
<tr>
<th>Component of 693-A-8R</th>
<th>Composition/Component scores (all are count ratios over Ti)</th>
<th>% Variance (after rotation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8R-DR1</td>
<td>Ba (0.95), Sr (0.91), Zr (0.85), Rb (0.78), K (0.76), Zn (0.71), Sn (0.56), Ag (0.51), Cu (0.50)</td>
<td>27%</td>
</tr>
<tr>
<td>8R-DR2</td>
<td>P (-0.8), Cr (0.51), S (0.50)</td>
<td>9%</td>
</tr>
<tr>
<td>8R-DR3</td>
<td>Ag (0.81), Sn (0.77), Ni (0.75), Cd (0.67), Fe (0.63), Mo (0.54)</td>
<td>19%</td>
</tr>
<tr>
<td>8R-DR4</td>
<td>Cl (0.76), S (0.56)</td>
<td>9%</td>
</tr>
<tr>
<td>8R-DR5</td>
<td>Mn (0.91), Ca (0.86)</td>
<td>11%</td>
</tr>
</tbody>
</table>

Table 3.2 Composition of components created from the 8R element oxide weight percent data.

<table>
<thead>
<tr>
<th>Component of 693-A-8R</th>
<th>Composition/Component scores (all are oxide wt% values)</th>
<th>% Variance (after rotation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8R-DR1</td>
<td>Fe₂O₃ (0.95), SiO₂ (-0.93), TiO₂ (0.90), CaO (0.65), MnO (0.62)</td>
<td>43%</td>
</tr>
<tr>
<td>8R-DR2</td>
<td>K₂O (-0.93), CaO (0.73), MnO (0.61)</td>
<td>23%</td>
</tr>
<tr>
<td>8R-DR3</td>
<td>Al₂O₃ (0.99)</td>
<td>14%</td>
</tr>
<tr>
<td>8R-DR4</td>
<td>P₂O₅ (0.98)</td>
<td>13%</td>
</tr>
</tbody>
</table>
### Table 3.3. Composition of components created from 2R element count ratio data

<table>
<thead>
<tr>
<th>Component of 693-A-2R</th>
<th>Composition/Component scores (all are count ratios over Ti)</th>
<th>% Variance (after rotation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2R-DR1</td>
<td>Ag (0.92), Ni (0.89), Sn (0.88), Cd (0.76), Cu (0.69), Mo (0.69), Fe (0.60), Ca (0.50)</td>
<td>28%</td>
</tr>
<tr>
<td>2R-DR2</td>
<td>K (0.91), Ba (0.89), Sr (0.81), Rb (0.84), Zn (0.73), Ca (0.61), Zr (0.54)</td>
<td>25%</td>
</tr>
<tr>
<td>2R-DR3</td>
<td>P (-0.87), S (0.86), Cl (-0.50), Zr (0.49)</td>
<td>13%</td>
</tr>
<tr>
<td>2R-DR4</td>
<td>Mn (0.89), Cl (-0.49)</td>
<td>7%</td>
</tr>
<tr>
<td>2R-DR5</td>
<td>Cr (0.73), Fe (0.60)</td>
<td>7%</td>
</tr>
</tbody>
</table>

### Table 3.4. Composition of components created from 2R oxide weight percent data

<table>
<thead>
<tr>
<th>Component of 693-A-2R</th>
<th>Composition/Component scores (all are oxide wt% values)</th>
<th>% Variance (after rotation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2R-DR1</td>
<td>Fe₂O₃ (0.97), Al₂O₃ (-0.93), TiO₂ (0.91)</td>
<td>37%</td>
</tr>
<tr>
<td>2R-DR2</td>
<td>SiO₂ (0.97), CaO (-0.72)</td>
<td>22%</td>
</tr>
<tr>
<td>2R-DR3</td>
<td>P₂O₅ (0.82), K₂O (0.54), CaO (-0.53)</td>
<td>16%</td>
</tr>
<tr>
<td>2R-DR4</td>
<td>MnO (0.95)</td>
<td>14%</td>
</tr>
<tr>
<td>Component of C³</td>
<td>Composition/Component scores (all are count ratios over Ti)</td>
<td>% Variance (after rotation)</td>
</tr>
<tr>
<td>----------------</td>
<td>----------------------------------------------------------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>C³-DR1</td>
<td>Rb (0.91), Sr (0.91), K (0.89), Cl (0.56), Zr (0.47)</td>
<td>23%</td>
</tr>
<tr>
<td>C³-DR2</td>
<td>P (-0.93), S (0.90), Ca (0.67)</td>
<td>17%</td>
</tr>
<tr>
<td>C³-DR3</td>
<td>Fe (-0.87), Ba (-0.8), Mn (0.76), Ni (0.56), Ca (-0.51)</td>
<td>20%</td>
</tr>
<tr>
<td>C³-DR4</td>
<td>Cr (0.85), Cl (0.62), Ni (0.48)</td>
<td>12%</td>
</tr>
<tr>
<td>C³-DR5</td>
<td>Cu (0.92)</td>
<td>8%</td>
</tr>
</tbody>
</table>

Table 3.5. Composition of components created from C³ element count ratio data

<table>
<thead>
<tr>
<th>Component of C³</th>
<th>Composition/Component scores (all are oxide wt% values)</th>
<th>% Variance (after rotation)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C³-DR1</td>
<td>K₂O (0.89), Al₂O₃ (0.88)</td>
<td>21%</td>
</tr>
<tr>
<td>C³-DR2</td>
<td>Fe₂O₃ (0.98), SiO₂ (-0.93)</td>
<td>25%</td>
</tr>
<tr>
<td>C³-DR3</td>
<td>CaO (0.83),</td>
<td>12%</td>
</tr>
<tr>
<td>C³-DR4</td>
<td>MnO (0.86), TiO₂ (0.85)</td>
<td>21%</td>
</tr>
<tr>
<td>C³-DR5</td>
<td>P₂O₅ (0.94)</td>
<td>13%</td>
</tr>
</tbody>
</table>

Table 3.6. Composition of components created from C³ oxide weight percent data
3.2 Principal Component Downcore Plots

Downcore plots for each component were created to aid in identifying cycles and/or lithologic changes. The plots are color-coded to highlight areas with low component values, medium component values, and high component values. Additionally, identical online interactive graphs were built using Shiny, a user-built package for R, to allow readers to examine the data in a more user-friendly way. Sample codes can be found in the appendix. The graphs can be found in the Supplementary Information files or using the following web addresses:

- [http://jthall.shinyapps.io/components_lyle_2R](http://jthall.shinyapps.io/components_lyle_2R) (2R, oxide weight % plots)
3.3 Crossplots of Principal Components and Element/Oxide Variation

To aid in the interpretation of the principal components (using correlations between components and elements/oxides) and to identify stratigraphic variation throughout the core, crossplots were created such that principal component data can be compared with element count ratio or oxide weight percent data. Online interactive crossplots were built, again using Shiny, and are the preferred method of data visualization due to the ability of users to choose which components and element count ratios/oxides to compare, as well as the option for users to select the number of clusters they wish to view within the plots. Clusters were created using k-means clustering, a data visualization and exploration technique that places \( n \) observations into \( k \) clusters such that each observation is placed into the cluster with the nearest mean. Sample codes can be found in Appendix B. The graphs can be found in the Supplementary Information files or using the following web addresses:


3.4 Wavelet Power Spectra

The data for each detrended/interpolated Varimax-rotated component were inputted into Interactive Wavelet Plot and wavelet power spectra were returned and analyzed for each of the twenty-eight components. All of the wavelet power spectra created using the principal component data from the C\(^3\) element count ratios and
oxide weight percent datasets, as well as the wavelet power spectra created using the magnetic susceptibility data for 2R and 8R, can be found in Appendix A.

In these figures, (a) shows the interpolated and detrended data for the component, (b) shows the wavelet power spectrum, color-coded based on each wavelet’s power, and (c) shows the variance of each wavelet (another way to represent the power of a wavelet) overlaid on a line representing 30% red noise.

3.5 Extrapolation of Milankovitch Cycles and Sedimentation/Accumulation Rate using Power Spectra

The dominant wavelets were identified using the variances found in part (c) of the wavelets included in Appendix A and the wavelet’s length (in centimeters) was identified using the y-axis in part (b) of the same figures. Using the wavelet’s length, the dominant Milankovitch cycles for each core could be identified.

Tables 3.7 and 3.8 show the linear sedimentation rates (centimeters/thousand years) for each Pliocene and Pleistocene component, respectively, calculated by dividing the length of each of the two most dominant periodicities by the length of the assigned Milankovitch cycle and multiplying that value by 1,000. Note that Table 3.8 does not include component 3 for the XRF element count ratio data, nor does it include component 4 for the XRF oxide weight percent data. This is because interpretation of these two components was obscured throughout 2R due to the presence of a marine sand burrow. They were therefore excluded from the linear sedimentation rate calculations (see Section 4.2 for more on the presence of the marine sand burrow).
The derived linear sedimentation rates from the XRF element count ratio data, XRF oxide weight percent data, and magnetic susceptibility data are then compared with the derived linear sedimentation rates from DSR data (True-Alcala, 2015). The same statistical techniques were used to derive sedimentation rates from this fourth dataset, i.e. Varimax-rotated principal component analysis followed by wavelet analysis and Milankovitch cycle assignments.

Finally, Figures 3.6 and 3.7 show the calculated linear sedimentation rates and accumulation rates, respectively, across Cores 8R through 14R.

<table>
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<tr>
<th>8R Dataset</th>
<th>Component</th>
<th>Peak</th>
<th>Milankovitch Cycle (kyr)</th>
<th>Length (cm)</th>
<th>Sedimentation Rate (cm/kyrs)</th>
<th>Average Sedimentation Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffuse Spectral Reflectance</td>
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<td>6.44</td>
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<td>Component 1</td>
<td>Peak 2</td>
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<td>160</td>
<td>6.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Component 2</td>
<td>Peak 1</td>
<td>100</td>
<td>500</td>
<td>5.00</td>
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</tr>
<tr>
<td></td>
<td>Component 2</td>
<td>Peak 2</td>
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<td>8.70</td>
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</tr>
<tr>
<td>XRF Count Data</td>
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<td>Peak 1</td>
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<tr>
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<td>Component 2</td>
<td>Peak 1</td>
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<td>Component 4</td>
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<tr>
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<td>Component 5</td>
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<td>Component 2</td>
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Table 3.7. Comparison of average Pliocene sedimentation rates from diffuse spectral reflectance (DSR) data, $C_3^3$ XRF element count ratio data, $C_3^3$ XRF oxide wt.% data, and magnetic susceptibility data.
<table>
<thead>
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<th>Milankovitch Cycle (kyr)</th>
<th>Length (cm)</th>
<th>Sedimentation Rate (cm/kyrs)</th>
<th>Average Sedimentation Rate</th>
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<tr>
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<td>100</td>
<td>160</td>
<td>1.60</td>
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<tr>
<td></td>
<td></td>
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</tr>
<tr>
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<td>Component 2</td>
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<tr>
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<td>Peak 2</td>
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<td>140</td>
<td>1.40</td>
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</tr>
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<td>1.46</td>
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<td>2.00</td>
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</tr>
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</table>

Table 3.8. Comparison of average Pleistocene sedimentation rates from diffuse spectral reflectance (DSR) data, C\(^3\) XRF element count ratio data, and C\(^3\) XRF oxide wt. % data.
Figure 3.6. Graphical depiction of linear sedimentation rate (cm/kyr) over time using rates derived from $C^3$.

Figure 3.7. Graphical depiction of accumulation rate (g/cm$^2$/kyr) over time using rates derived from $C^3$. 
4. Discussion

4.1 Interpretation of Principal Components

Interpretations of the components created from the XRF element count ratio data and the oxide weight percent data for Cores 2R and 8R were created using known geochemical information of the elements and oxides included in the formation of a component. Correlations between components and element count ratios or oxides were also used in the interpretations of the created components (see the interactive crossplots in Section 3.3).

Table 3.1 presents the composition of the 8R principal components created from the XRF element count ratio data when treating 8R as a separate identity. Due to the dominance of land-based elements in forming the components, e.g. Ba (Li et al., 1973) and dissolved trace metals Ni, Cu, and Cd (Saager et al., 1997), 8R-DR1 and 8R-DR3 are assumed to be proxies for terrigenous sources, likely two different terrigenous sources. In other words, they represent the weathering of the continent and can be indicative of source areas during glacial advance and retreat. More specifically, 8R-DR1 contains many elements that Luttinen et al. (1998) have identified in CT3 lavas from Vestfjella, Dronning Maud Land (namely Rb, Ba, K and Sr), and therefore 8R-DR1 is assumed to represent sources from or similar to these lavas of Vestfjella, Dronning Maud Land (Fig 4.1). 8R-DR2 and 8R-DR4 are both related to biogenic processes. 8R-DR2 is heavily composed of Cr, an element that precipitates predominantly during anoxic periods (Calvert and Pederson, 1993). High 8R-DR2 scores likely indicate times of high levels of primary productivity and high 8R-DR4 scores indicate times of low levels of primary productivity. Thus, 8R-DR2
and 8R-DR4 have an inverse relationship as can be see in Figure 4.1. They are therefore instrumental in identifying interstadial periods. Finally, DR5 is also likely a biogenic proxy as it is positively correlated with DR2 and contains high loadings of Mn/Ti and Ca/Ti, indicators of the deposition of sediments under oxic bottom water conditions (Calvert and Pederson, 1993).

Comparison of Tables 3.1 and 3.3 shows that many of the 2R and 8R components created from the element count ratio data are comparable in composition, and this comparability has aided in the interpretation of these components. 2R-DR2 and 8R-1 are both heavily composed of Ba, Sr, Zr, Rb, K, and Zn ratios. 2R-DR1 and 8R-DR3 are both heavily composed of Sn, Ag, Ni, Cd, Fe, and Mo ratios. 2R-DR1 and 8R-DR1 are both composed of Cu ratios. 2R-DR3 and 8R-DR2 and both composed of P and S ratios. 2R-DR4 is similar to 8R-DR4 (Cl/Ti) and 8R-DR5 (Mn/Ti). Finally, 2R-DR5 is similar to 8R-DR2 (Cr/Ti) and 8R-DR3 (Fe/Ti).

Using this comparability, as well as the literature referenced in the preceding paragraphs, I interpret the first and second components from 2R (DR1 and DR2) as representing terrigenous sources, likely two separate terrigenous sources. More specifically, 2R-DR2 (similar to 8R-DR1) likely represents sources from or similar to those of Vestfjella, Dronning Maud Land. 2R-DR3, with its similarities to 8R-DR2, appears to be related to biogenic processes. 2R-DR4 is similar to 8R-DR4 and 8R-DR5, both of which have been interpreted as biogenic proxies, and therefore 2R-DR4 is also assumed to represent a combination of biogenic processes. Finally, 2R-DR5, containing only Cr/Ti and Fe/Ti, is interpreted as yet another biogenic proxy.
Tables 3.2 and 3.4 present the composition of the 8R and 2R principal components created from the oxide weight percent data. 8R-DR1 is composed of both Fe$_2$O$_3$ and MnO. Mn and Fe precipitate under oxidizing conditions and therefore 8R-DR1 is interpreted as an indicator of oxidation (Howe et al., 2007). Furthermore, 8R-DR1 includes a negative loading of SiO$_2$, which, in contrast to Fe$_2$O$_3$, is commonly present in turbidites (Levitan et al., 2008). Thus, 8R-DR1 is interpreted as being an indication of both the lack of turbidites and the presence of oxidation. 8R-DR2 is also composed of MnO and is therefore interpreted as a second indicator of oxidation. 8R-DR3 is composed solely of Al$_2$O$_3$, which, similarly to Fe$_2$O$_3$, is known to be absent from turbidites, and therefore 8R-DR3 is interpreted as an identifier of periods lacking turbidites and periods containing turbidites. Finally, 8R-DR4 contains only P$_2$O$_5$, an oxide likely representing biogenic processes, and therefore 8R-DR4 has been interpreted as an indication of primary productivity.

2R-DR1 includes Fe$_2$O$_3$ and 2R-DR4 includes MnO, both of which are oxides indicative of oxidizing conditions, and therefore these two components have been interpreted as indicators of oxidation. 2R-DR2 is primarily composed of SiO$_2$ and is therefore interpreted as representing the presence or absence of turbidites. 2R-DR3 is composed of P$_2$O$_5$, K$_2$O, and CaO, all of which likely represent biogenic processes, and therefore 2R-DR3 is interpreted as being a proxy for some form of biogenic processes. Finally, 2R-DR4 is composed solely of MnO, which, as stated previously, is indicative of oxidation. Thus, 2R-DR4 is assumed to represent periods of oxidation.

Table 3.5 presents the composition of the C$^3$ principal components created from the element ratio count data. C$^3$-DR1, with its similarities to 8R-DR1 and 2R-
DR1, is likely representative of sources from Vestfjella, Dronning Maud Land. C³-DR2, with its similarities to 8R-DR2 and 2R-DR3, suggest that it is related to biogenic processes. C³-DR3 is similar to 8R-DR1, 8R-DR3, 2R-DR1, and 2R-DR2 and thus likely represents terrigenous sources, though presumably separate terrigenous sources than those represented by C³-DR1. C³-DR4 and C³-DR5 do not appear to be strongly similar to any of the 2R and 8R components and therefore have not been interpreted.

Table 3.6 presents the composition of the C³ principal components created from the oxide weight percent data. C³-DR1 is largely composed of Al₂O₃, an oxide known to be absent from turbidites. Therefore, C³-DR1 is interpreted as an indicator of the presence or absence of turbidites. C³-DR2 includes Fe₂O₃ and C³-DR4 includes MnO, both of which have been previously identified as indicators of oxidizing conditions. Thus, these two components are interpreted as representing conditions of oxidation. Furthermore, C³-DR2 contains a negative loading of SiO₂, thereby suggesting that this component is also indicative of the presence or absence of turbidites. Finally, C³-DR3 is composed only of CaO and C³-DR5 is composed only of P₂O₅, and therefore both of these components have been interpreted as being biogenic proxies.

The collected interpretations of all of the previously mentioned components can be found in Table 4.1.
Figure 4.1. Map of Dronning Maud Land, Antarctica, including Vestfjella.
Figure 4.2. Graphical comparison of DR2 and DR4 from 8R, depicting their inverse relationship and a half-cycle length of ~4 meters.
<table>
<thead>
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<th>Principal Component</th>
<th>Interpretation</th>
</tr>
</thead>
<tbody>
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<td>8R-DR1, Element Count Ratio</td>
<td>Dronning Maud Land</td>
</tr>
<tr>
<td>8R-DR2, Element Count Ratio</td>
<td>Biogenic proxy</td>
</tr>
<tr>
<td>8R-DR3, Element Count Ratio</td>
<td>Terrigenous sources</td>
</tr>
<tr>
<td>8R-DR4, Element Count Ratio</td>
<td>Biogenic proxy</td>
</tr>
<tr>
<td>8R-DR5, Element Count Ratio</td>
<td>Biogenic proxy</td>
</tr>
<tr>
<td>8R-DR1, Oxide Weight Percent</td>
<td>Turbidites, oxidizing environments</td>
</tr>
<tr>
<td>8R-DR2, Oxide Weight Percent</td>
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</tr>
<tr>
<td>8R-DR3, Oxide Weight Percent</td>
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</tr>
<tr>
<td>8R-DR4, Oxide Weight Percent</td>
<td>Biogenic proxy</td>
</tr>
<tr>
<td>2R-DR1, Element Count Ratio</td>
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<tr>
<td>2R-DR2, Element Count Ratio</td>
<td>Dronning Maud Land</td>
</tr>
<tr>
<td>2R-DR3, Element Count Ratio</td>
<td>Deposition of redox-sensitive metals</td>
</tr>
<tr>
<td>2R-DR4, Element Count Ratio</td>
<td>Biogenic proxy</td>
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<td>2R-DR5, Element Count Ratio</td>
<td>Biogenic proxy</td>
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<tr>
<td>2R-DR1, Oxide Weight Percent</td>
<td>Oxidizing environments</td>
</tr>
<tr>
<td>2R-DR2, Oxide Weight Percent</td>
<td>Turbidites</td>
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<tr>
<td>2R-DR3, Oxide Weight Percent</td>
<td>Biogenic proxy</td>
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<tr>
<td>2R-DR4, Oxide Weight Percent</td>
<td>Oxidizing environments</td>
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<td>C³-DR1, Element Count Ratio</td>
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<td>C³-DR2, Element Count Ratio</td>
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<td>C³-DR4, Element Count Ratio</td>
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<td>Turbidites, oxidizing environments</td>
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<td>C³-DR3, Oxide Weight Percent</td>
<td>Biogenic proxy</td>
</tr>
<tr>
<td>C³-DR4, Oxide Weight Percent</td>
<td>Oxidizing environments</td>
</tr>
<tr>
<td>C³-DR5, Oxide Weight Percent</td>
<td>Biogenic proxy</td>
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Table 4.1. General interpretation of the twenty-eight principal components used throughout this study.

4.2 Anomalous Spike in 2R-DR3

The third component for 2R made from the XRF element count ratio data exhibits a spike of an anomalous magnitude in the downcore plot, occurring from ~11.52 to 11.64 mbsf. A similar spike, though with a lesser magnitude, occurs in the downcore plot for the fourth component made from the same data. After identifying
these spikes, the .tif file from 2R-7 (starting at 11.5 mbsf) was examined (Fig. 4.2). At around 11.57 mbsf there is a marine sand burrow that is likely the cause of these spikes. 2R-DR3 is composed primarily of –P, S, and Zr ratios, whereas 2R-DR4 is composed primarily of Mn and –Cl ratios. During anoxic conditions, phosphorus is used up (hence the negative correlation with P) and sulfur is then used as an energy source (hence the positive correlation with S). Additionally, redox-sensitive metals such as Mn are “solubilized during reduction and precipitated under oxidizing conditions” and “are often enriched along the oxic-anoxic boundary” (Blackburn and Sørensen, 1988). Therefore, 2R-DR3 is thought to represent anoxic conditions whereas 2R-DR4 may represent the deposition of redox-sensitive metals, likely via biogenic processes.

Figure 4.3. Cropped image of core section 2R-7A exhibiting a marine sand burrow around 22.25 cm.
4.3 Comparison of 2R and 8R Components with C³

Tables 3.1 through 3.6 provide the component loadings for each of the twenty-eight principal components and can be used to identify similarities and differences between the components. Figures 4.3 through 4.6 provide examples of the many similarities that exist between the components created from Cores 2R and 8R as treated as separate entities and the components created from C³. Most of the components created from these different datasets are either strongly positively correlated—e.g. Figure 4.2 in which both components exhibit strong CaO, K₂O, and P₂O₅ loadings in the same direction—or strongly negatively correlated—e.g. Figure 4.3 in which both components exhibit strong Al₂O₃ and K₂O loadings but in the opposite direction.

Due to these similarities, as well as the ability of the same components created from the longer dataset (C³) to be compared across 2R and 8R, the components created from C³ have been chosen as being those that are given the most confidence and attention in the interpretations of the results.
Figure 4.4. Graphical depiction of similarities and positive correlation between $C^3$-DR3 and 2R-DR3.

Figure 4.5. Graphical depiction of similarities and negative correlation between $C^3$-DR5 and 2R-DR1.
Figure 4.6. Graphical depiction of similarities and positive correlation between $C^3$-DR2 and 8R-DR1.

Figure 4.7. Graphical depiction of similarities and positive correlation between $C^3$-DR5 and 8R-DR3.
4.4 Deriving Sedimentation Rates

Comparison across the results from all four of the 8R datasets—i.e. oxide weight percent, XRF element count ratio, magnetic susceptibility, and diffuse spectral reflectance—shows fairly comparable sedimentation rates, ranging from 6.02 cm/kyr to 7.03 cm/kyr (see Table 3.7). Still, there is a noticeable difference between the rates calculated using the XRF oxide weight percent and element count ratio data and the rates calculated using the DSR and magnetic susceptibility data. A possible explanation for this disparity is that the two XRF-derived rates were created using a largely continuous dataset encompassing 2R and 8R through 14R (C3), whereas the DSR-derived rates were created using a smaller, more widely spaced dataset encompassing 2R and 8R. However, nearly all of the components across the four datasets were assigned 100,000 year eccentricity as well as 41,000 obliquity or 23,000 precession as the dominant Milankovitch cycles. Furthermore, though the order of dominance varies per component (eccentricity most commonly being more dominant), the levels of dominance of these three cycles are nearly always comparable (see the wavelet power spectra in Appendix A).

Figure 4.5 compares component values of 8R-DR2 and 8R-DR4, two components that represent inverse levels of primary productivity. Each exhibits a half-cycle of ~4 meters, which, when extended, suggests a total cycle length of ~8 meters. Applying 100 kyr eccentricity as the dominant Milankovitch cycle throughout this core puts the sedimentation rate at 8 cm/kyr (800 cm/100 kyr = 8 cm/kyr). Though this value is higher than the sedimentation rates estimated via the wavelet analysis spectra, it remains comparable, especially to those derived using the C3 XRF
data. Thus, by comparing downcore variation in component values, it is possible to constrain sedimentation rates, identify dominant Milankovitch cycles, and presumably identify interglacial/glacial periods.

Comparison across the results from all four of the 2R datasets shows more consistent and significantly smaller sedimentation rates, ranging from 1.37 cm/kyr to 1.55 cm/kyr (see Table 3.8). These values are similar to the sedimentation rates identified in the Shipboard Reports, thereby increasing our confidence in the derived values. Furthermore, nearly all of the components across the four datasets are assumed to have 400,000 year eccentricity as the most dominant Milankovitch cycle, followed by 100,000 year eccentricity.

A recent study by Patterson et al. (2014) identified the dominance of 100 kyr eccentricity and precession during the Pliocene after 3.5 Ma and the dominance of obliquity prior to 3.5 Ma. The strong presence of all three of these Milankovitch cycles suggests that Core 8R is close to the transition from an obliquity-dominated Pliocene to an eccentricity- and precession-dominated Pliocene, i.e. ~3.5 Ma. Furthermore, the top of Core 8R is assumed to be close to the Gauss-Gilbert geomagnetic reversal documented by Grobe et al. (1990). This then suggests that 8R was deposited sometime between 3.6 Ma and 4.2 Ma, a time interval that approaches the Milankovitch cycle switch at 3.5 Ma. A reason as to why the data used in this study show both eccentricity and obliquity as being dominant whereas Patterson et al. (2014) do not is that their data were astronomically tuned and our data are not. Were our data astronomically tuned, it is possible that we may no longer see eccentricity as a dominant Milankovitch cycle throughout Core 8R.
The results from the wavelet power spectra suggest that the long-term changes in the depositional environment at Site 693 during the Pliocene epoch were driven primarily by eccentricity (100 kyr) and obliquity (41 kyr), with precession (~20 kyr) also playing a significant role. Figure 4.8 shows the differences between average linear sedimentation rates across the four datasets using the 100 kyr and 41 kyr peaks. Again, the rates were comparable, though the 41 kyr peak averages were higher than the 100 kyr peak averages for the continuous, split-core measurements.

The results from the wavelet power spectra suggest that the long-term changes in the depositional environment at Site 693 during the Pleistocene epoch were driven primarily by eccentricity, both the 400 kyr and 100 kyr periodicities. Figure 4.9 shows the differences between average linear sedimentation rates across the four datasets using the 400 kyr and 100 kyr peaks. Again, the rates were comparable, though the 100 kyr peak averages were consistently higher than the 400 kyr peak averages. These conclusions indicate that the EAIS was moderated predominantly by 400 and 100 kyr eccentricity during this section of the Pleistocene. The moderation by these Milankovitch cycles likely produced minor differences between interglacial and glacial periods in terms of sedimentation patterns, a hypothesis further supported by the relatively small changes in component values throughout Core 2R (see Section 3.2).
Figure 4.8. Comparison of average sedimentation rates from the four datasets using 100 kyr and 41 kyr peaks.

Figure 4.9. Comparison of average sedimentation rates from the four datasets using 400 kyr and 100 kyr peak.
4.5 Sedimentation and Accumulation Rates Over Time

Figure 3.8 shows the sedimentation rates derived from 8R to 14R principal components from the C^3 XRF oxide weight percent dataset. From 14R to 10R, there is a fluctuating sedimentation rate keeping within the 3.5 cm/kyr to 5 cm/kyr range. From 10R to 9R, the sedimentation rate experiences a significant increase, followed by an even larger increase from 9R to 8R. Figure 3.9 shows the accumulation rates derived from 8R to 14R principal components from the C^3 XRF oxide weight percent dataset. Again, there is a fluctuating accumulation rate from 14R to 10R, keeping within the 6 g/cm\(^2\)/kyr to 8 g/cm\(^2\)/kyr range. Then, after 10R, there is an increase in the accumulation rate to ~12 g/cm\(^2\)/kyr at 9R and 8R.

The increase in both the sedimentation rate and accumulation rate at Cores 9R and 8R suggest that temperatures and atmospheric CO\(_2\) levels began increasing around the time these sediments were deposited, thereby driving up the speed of sedimentation at our site. It is possible that the increase in sedimentation and accumulation rates could be an indication that 9R and 8R are approaching the increase in surface temperatures that has been identified by Hansen et al. (2013) in Figure 4.10. This increase in surface temperature begins ~3.6 Ma, near the Gauss-Gilbert geomagnetic reversal which occurred near 3.6 to 4.2 Ma. This would explain the poor recovery in Cores 3R through 7R, as these would have presumably been deposited during times of decreasing surface temperatures and therefore increased glaciation. This also fits nicely with the previously suggested placement of these cores at the transition from the obliquity-dominated Pliocene to the eccentricity- and precession-dominated Pliocene around 3.5 Ma. Furthermore, Lindeque et al. (2013)
have identified higher sedimentation rates in the central and northwestern Weddell Sea during transitional regimes as compared to sedimentation rates during pre-glacial and full glacial regimes, further supporting the hypothesis that 9R and 8R were deposited during a transitional regime.

The dominant Milankovitch cycles remained consistent throughout Cores 14R to 8R in that we continue to see strong eccentricity (100 kyr), obliquity (41 kyr), and precession (~20 kyr) responses. Thus, I conclude that the EAIS was moderated by these three Milankovitch cycles throughout the early Pliocene (at least for the time interval in which these cores fall) and that sedimentation rates experienced spikes as the Pliocene became warmer and atmospheric CO$_2$ levels rose.
Figure 4.10. Surface temperature estimates for (a) the past 65.5 Ma, (b) the Pliocene and Pleistocene, and (c) the past 800,000 years. Part (b) includes a line representing the estimated time of deposition of Core 8R, i.e. ~3.6 Ma (Hansen et al., 2013).
5. Conclusion

5.1 Cores 8R and 2R

Obliquity has been identified as the dominant pacer of the West Antarctic Ice Sheet during the Pliocene (Naish et al., 2009), but this is the first time it has been identified for the Weddell Sea portion of the EAIS. This study also identifies eccentricity (100 kyr) and precession (~20 kyr) as dominant drivers of climate during the Pliocene in the Weddell Sea. In accordance with the results from the Patterson et al. (2014) study, the identification of these dominant Milankovitch cycles points towards the dominance of obliquity in shaping EAIS glaciation/deglaciation during the early Pliocene, i.e. pre-3.5 Ma, with a subsequently strong precession response that is modulated by 100 kyr eccentricity. However, that this study identifies all three of these cycles simultaneously suggests that Core 8R falls somewhere close to 3.5 Ma, the time in which Patterson et al. identified a shift in dominance from obliquity to 100 kyr eccentricity and precession. The estimated placement of this core is between 3.6 and 4.2 Ma, a period which Hansen et al. (2013) have identified as one of increasing surface temperatures (Fig. 4.7).

The results from this study indicate that the long-term changes at Site 693 during the Pleistocene were driven primarily by eccentricity, both the 400 kyr and 100 kyr periodicities, though the 100 kyr periodicity to a lesser extent. The dominance of these longer Milankovitch cycles suggests that changes in sedimentation patterns at our site during the Pleistocene were less dramatic than those during the Pliocene.
5.2 Sedimentation Rates

Sedimentation rates at our site have been identified as being ~6.58 cm/kyr during the early Pliocene epoch and ~1.44 cm/kyr during the Pleistocene epoch (found by averaging the sedimentation rates across all four of the datasets used in this study). Furthermore, spikes in sedimentation and accumulation rates have been identified from Cores 10R to 8R, suggesting that these cores are in temporal proximity to an increase in surface temperatures identified by Hansen et al. (2013), ~3.6 Ma. The observed increase in sediment delivery in this stable part of the EAIS indicates that melting of this portion of the EAIS continued to increase as it approached the mid-Pliocene warm period.

5.3 Significance and Future Work

This study claims that the early Pliocene, a climatic analogue of our current world, exhibits an EAIS environment in the Weddell Sea that is moderated simultaneously by 100 kyr eccentricity, 41 kyr obliquity, and ~20 kyr precession. Furthermore, sedimentation and accumulation rates experienced an increase from Cores 10R to 9R to 8R, presumably increasing due to deglaciation of the EAIS as these cores approach the mid-Pliocene warm period. I hypothesize that our current, post-industrialization world and its increased atmospheric CO₂ levels will experience continued deglaciation of this portion of the EAIS, similar to the deglaciation that occurred during the early Pliocene.

Future work should use both the component interpretations and values as well as sedimentation and accumulation rates to a) further constrain the temporal position of these cores within the Pliocene and Pleistocene, and b) better identify periods of
glaciation/deglaciation, primary productivity/lack of primary productivity, oxic conditions/anoxic conditions, and so on to draw more specific conclusions on the cyclical conditions of this depositional environment. Furthermore, the methods in this study should be applied to the recovered core sections throughout the Oligocene, as well as to other regions of Antarctica including Maud Rise.
Appendix A
Wavelet Power Spectra

The titles of these wavelet power spectra take the following form: first the core section, next the type of data used to create the principal component in which the wavelet power spectrum was generated, and finally the number of the component used to generate the wavelet power spectrum. 2R stands for Core 693A-2R, deposited during the Pleistocene epoch. 8R through 14R stand for Cores 693A-8R through 693A-14R, deposited during the Pliocene epoch. Black bars were added

Fig. 1: (a) 2R Oxides: DR1. (b) The wavelet power spectrum. The contour levels are chosen so that 75%, 50%, 25%, and 5% of the wavelet power is above each level, respectively. The cross-hatched region is the cone of influence, where zero padding has reduced the variance. Black contour is the 30% significance level, using a red-noise (autoregressive lag1) background spectrum. (c) The global wavelet power spectrum (black line). The dashed line is the significance for the global wavelet spectrum, assuming the same significance level and background spectrum as in (b) (Torrence and Compo, 1998).
a. 8R Oxides: DR2

b. Wavelet Power Spectrum

c. Global Wavelet

Powered by IDL
a. 8R Oxides: DR4

b. Wavelet Power Spectrum

c. Global Wavelet

Powered by IDL

a. 8R Oxides: DR5

b. Wavelet Power Spectrum

c. Global Wavelet

Powered by IDL
a. 10R Oxides: DR2

Data (units)

mbsf (meters)

b. Wavelet Power Spectrum

Period (meters)

mbsf (meters)

0.062
0.064
0.37
2.0
10.0

Power (units)²

C. Global Wavelet

Variance (units)²

Powered by IDL

a. 10R Oxides: DR3

Data (units)

mbsf (meters)

b. Wavelet Power Spectrum

Period (meters)

mbsf (meters)

0.062
0.064
0.37
2.0
10.0

Power (units)²

C. Global Wavelet

Variance (units)²

Powered by IDL
Appendix B
Sample RStudio Scripts

1. Creating principal components using the principal() function

```r
wavelet_693A8R <- read.delim("file_name", na.strings="#N/A")
VPCA1 <- principal(wavelet_693A8R[,2:20], nfactors=5, rotate="varimax")
VPCA1 #view the component loadings
plot(VPCA1$values)
wavelet_693A8R$RC1 <- VPCA1$scores[,1]
wavelet_693A8R$RC2 <- VPCA1$scores[,2]
wavelet_693A8R$RC3 <- VPCA1$scores[,3]
wavelet_693A8R$RC4 <- VPCA1$scores[,4]
wavelet_693A8R$RC5 <- VPCA1$scores[,5]
```

2. Interpolating and detrending the data

```r
wavelet1 <- aspline(wavelet_693A8R$mbsf, wavelet_693A8R$RC1, wavelet_693A8R$mbsf_interpolate) #interpolating the data using specified intervals
wavelet <- data.frame(wavelet1)
wavelet$mbsf <- wavelet$x
wavelet$R1 <- wavelet$y
wavelet <- wavelet[,3:4]
p1 <- polyfit(wavelet$mbsf, wavelet$R1, 2) #creating a polynomial trend line
wavelet$TR1 <- polyval(p1, wavelet$mbsf)
wavelet$DR1 <- wavelet$R1-wavelet$TR1
```

3. Creating downcore plots for the principal components using Shiny

**User interface script:**
```r
shinyUI(fluidPage(
    titlePanel("Principal Components from 693A-8R"),
    sidebarPanel(
        selectInput("DR1", "Select Component",
            choices=list("DR1","DR2","DR3","DR4","DR5"), selected="DR1"),
        mainPanel(align="center",
            plotOutput('plot', height=650, width=450))
    ))
)
```

**Server script:**
```r
cbPalette <- c("#999999", "#E69F00", "#56B4E9", "#0072B2", "#D55E00", "#CC79A7") #creating a colorblind-friendly palette
wavelet <- read.csv("file_name", na.strings="#N/A")
shinyServer(function(input, output, session){
    dataset <- wavelet
```
4. Creating crossplots with components and elements/oxides using Shiny

**User interface script:**
```r
shinyUI(fluidPage(
  titlePanel("Principal Components and Element Crossplots for 693A-8R"),
  sidebarPanel(
    selectInput("RC1", "Select Component or Element Ratio",
                choices=list("RC1","RC2","RC3","RC4","RC5",
                              "Fe.Ti","Ba.Ti","Ca.Ti","K.Ti","Rb.Ti",
                              "Cr.Ti","P.Ti","Cl.Ti","S.Ti","Mn.Ti",
                              "Ni.Ti","Cu.Ti","Sr.Ti","Zr.Ti","Sn.Ti",
                              "Cd.Ti","Ag.Ti","Mo.Ti","Zn.Ti"),
                selected="RC1"),
    selectInput("RC2", "Select Second Component or Element Ratio",
                choices=list("RC1","RC2","RC3","RC4","RC5",
                              "Fe.Ti","Ba.Ti","Ca.Ti","K.Ti","Rb.Ti",
                              "Cr.Ti","P.Ti","Cl.Ti","S.Ti","Mn.Ti",
                              "Ni.Ti","Cu.Ti","Sr.Ti","Zr.Ti","Sn.Ti",
                              "Cd.Ti","Ag.Ti","Mo.Ti","Zn.Ti"),
                selected="RC2"),
    numericInput("clusters", "Number of clusters", 3,
                 min=1, max=6)
  ),
  mainPanel(align="center",
            plotOutput('plot', height=650, width=450))
))
```

**Server script:**
```r
wavelet_693A8R <- read.csv("file_name", na.strings="#N/A")
waveletplot <- wavelet_693A8R[1:328,]
shinyServer(function(input, output, session) {
```

selectedData <- reactive({
  waveletplot[, c(input$RC1,input$RC2)]
})

clusters <- reactive({
  kmeans(selectedData(), input$clusters)
})

output$plot <- renderPlot({
  plot(selectedData(),
       col=clusters()$cluster)
})
}
Appendix C
Table of Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Meaning</th>
</tr>
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<tbody>
<tr>
<td>C³</td>
<td>Composite Cores Component; components created from the longer dataset in which 2R and 8R through 14R are treated as a single entity</td>
</tr>
<tr>
<td>DR</td>
<td>Detrended and Varimax-rotated principal components</td>
</tr>
<tr>
<td>DSR</td>
<td>Diffuse spectral reflectance</td>
</tr>
<tr>
<td>EAIS</td>
<td>East Antarctic Ice Sheet</td>
</tr>
<tr>
<td>IODP</td>
<td>International Ocean Discovery Program</td>
</tr>
<tr>
<td>MBSF</td>
<td>Meters Below Sea Floor</td>
</tr>
<tr>
<td>NOAA</td>
<td>National Oceanic and Atmospheric Administration</td>
</tr>
<tr>
<td>ODP</td>
<td>Ocean Drilling Program</td>
</tr>
<tr>
<td>PCA</td>
<td>Principal Component Analysis</td>
</tr>
<tr>
<td>TAM</td>
<td>Transantarctic Mountains</td>
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<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
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References Cited


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