Diffuse Spectral Reflectance-derived Pliocene and Pleistocene Periodicity from Weddell Sea, Antarctica Sediment Cores

by

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Abstract

With climate change presenting the very real threat of sea level rise as one of many side effects, it is important in planning for future changes to understand how it changed in the past. With the potential to raise sea level by ~60 meters if it melted completely, the East Antarctic Ice Sheet and its responses to changing climate is an critical relationship to study. In this thesis I analyze two marine sediment cores of Pleistocene and Pliocene age from the same site off the coast of Dronning Maud Land, East Antarctica, for signs of climate change-related fluctuations in the fine fraction (<63um) of sediment. Using changes in mean grain size and reflectance-derived mineral assemblages I identify warm and cold periods within the cores. Wavelet analysis provides likely sedimentation rates, which help constrain the timing of the climate fluctuations.
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First and foremost I'd like to acknowledge Jamie Hall, who has been working beside me with his own thesis from the very beginning. Without you to share ideas/victories/struggles with, this whole process would have been so much more difficult.

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Thanks to Joe Ortiz at Kent State for teaching me how to analyze my samples so my thesis could be more than “This is really old dirt from far away” and for responding to many long e-mails full of questions. Also thanks to Sushma Parab for showing me my way around the lab and Fangyu Zheng for running many of the samples I could not bring to Ohio myself.

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A special shout out to Jason, whose own thesis served as a guide for writing this one (this acknowledgement section is not worthy of the comparison). And thanks for sticking around for an extra year and giving a lot of great advice about this whole process.

Thanks to anyone who is reading this. It is great to think that after all the effort that went into this, it is being read, and hopefully used and appreciated. If you’re using it to help with your thesis, good luck!

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Introduction

1.1 Project Context

While politicians continue to debate whether human actions are changing the climate, in the scientific community the debate is less about if we are causing change and more about what the nature of that change will be. The discussion of future sea level rise is one of the most pressing topics of climate change discussion, with the most recent IPCC report predicting that in a high emissions scenario, it is very likely that sea level at the end of the century will be up to 0.98m higher than present levels, and continuing to rise (J. A. Church et al., 2013). While Antarctic ice is currently contributing the least out of the land ice reservoirs (Antarctic and Greenland Ice Sheets, alpine glaciers), accounting for about 10% of observed rise (J. A. Church et al., 2013) (Table 1.1), the combination of the West and East Antarctic Ice Sheet (WAIS and EAIS) have the potential to raise sea level on the order of 56m (Allison, Alley, Fricker, Thomas, & Warner, 2009) so it is very important to understand how both ice sheets might behave in a warming climate. New models are being developed that make use of our growing understanding of the physical properties that govern our climate, providing better predictions of what might be coming. Still, understanding how the ice sheets behaved in the past remains a critical part of looking towards the future.

From the geologic record, we know that Earth’s climate can be highly variable, from global glaciation (Kirschvink, 1992) to arctic temperatures of over 15°C during the Paleocene-Eocene Thermal Maximum (Weijers, Schouten, Sluijs, Brinkhuis, & Sinninghe Damsté, 2007), and past sea level has been variable as
well, as shown by Miller (2011). During the Cenozoic, the most recent geologic era spanning from 65.5Ma to the present, climate has been variable as well, with warming and cooling trends driven by tectonic processes on the order of $10^6$ to $10^7$ years, orbital cycles operating on timescales of $10^4$ to $10^6$ years, and aberrant rapid changes lasting $10^3$ to $10^5$ years (J. Zachos, Pagani, Sloan, Thomas, & Billups, 2001).

In the context of our current climate change issues, we should restrict our focus to climate variability during time periods when the basic climate parameters are similar to what they are now. As we live in an “ice house” world, with polar ice sheets, we should first look to past climates with this condition to understand our future.

In regards to sea level projections J. A. Church, J.M Gregory, N.J. White, S.M. Platen, and J.X. Mitrovica (2011) suggest “the major challenge is the response of ice sheets, particularly those parts grounded below sea level,” showing the importance of understanding the impact of ice sheets. The particular interest in ice sheets grounded below sea level stems from the potential they have for “ice-sheet rapid dynamics” or in other words, a rapid collapse, which would lead to much higher than predicted sea level in a relatively short time span. Much of the WAIS is grounded below sea level, and the Greenland Ice Sheet (GRIS) is not buttressed by an ice shelf (Schoof, 2007), so there has been more concern about their catastrophic melting, while the EAIS is generally considered stable in part due to its high elevation (Denton, Sugden, Marchant, Hall, & Wilch, 1993; Huybrechts, 1993). Figure 1.1(a) shows how Antarctica is divided into two ice sheets as well
as the path melting ice from the continent makes its way to the oceans surrounding it. Figure 1.1(b) shows the elevation of the continent, highlighting how low the WAIS is both relative to the EAIS, as well as to sea level.

That the EAIS is relatively stable may be the general assumption, but it is certainly up for debate. and Cook et al. (2013) present an argument for a dynamic EAIS during at least one period. In addition to a global sea level high stand that suggests the possibility of a partially melted EAIS, they present a sedimentary record deposited off Adelie Land from 5.3 to 3.3 ma during the Pliocene warm period that indicates warmer Antarctic waters and glacial retreat in East Antarctica.

The purpose of this research is to further investigate the stability of the EAIS through the investigation of Pliocene and Pleistocene age sediments from the opposite side of East Antarctica, with implications regarding future projection of sea level changes. Changes in the cryosphere lead to changes in the ocean currents that move the sediments around the ocean, thereby controlling the sedimentation pattern in our cores, providing a record we can use to trace back the steps, and ultimately create a picture of the ongoing ice sheet dynamics at the time of deposition.
<table>
<thead>
<tr>
<th>Source</th>
<th>1993-2010</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Expansion</td>
<td>1.1 [0.8 10 1.4]</td>
</tr>
<tr>
<td>Glaciaers except in Greenland and Antarctica</td>
<td>0.76 [.39 to 1.13]</td>
</tr>
<tr>
<td>Glaciers in Greenland</td>
<td>0.10 [0.07 to 0.13]*</td>
</tr>
<tr>
<td>Greenland ice sheet</td>
<td>0.33 [0.25 to 0.41]</td>
</tr>
<tr>
<td>Antarctic ice sheet</td>
<td>0.27 [0.16 to 0.38]</td>
</tr>
<tr>
<td>Land water storage</td>
<td>0.38 [0.26 to 0.49]</td>
</tr>
<tr>
<td>Total of contributions</td>
<td>2.8 [2.3 to 3.4]</td>
</tr>
<tr>
<td>Observed GMSL rise</td>
<td>3.2 [2.8 to 3.6]</td>
</tr>
</tbody>
</table>

**Table. 1.1** This table shows the measured (not modeled) contribution to sea level rise (in meters) from various processes over the period from 1993-2010. (Recreated from Church et al., 2013) *Only through 2009.*
Figure 1.1 (a) This image shows how the Antarctic continent is divided into eastern and western halves, with the Transantarctic Mountains essentially serving as the border (Naish et al., 2009). (b) The image on the left shows the current elevation of the continent, with the right modeling elevation after isostatic rebound. Note how low the western half is in both scenarios (Wilson et al., 2012).

1.2 Antarctic Glacial History

While the massive ice sheets covering the entire continent of Antarctica are now it’s most defining feature, these were not always there. Because of their current significance to Antarctic environment, it is important to understand how and when these ice sheets appeared on the continent, and one means of accomplishing that is by using the oxygen isotope record, one of the major tools used to reconstruct past climate. Oxygen isotopes are drawn from planktonic and benthic foraminifera that take oxygen out of the water to create their calcite shells. These shells, called tests, preserve a snapshot of the $\delta^{16}O/\delta^{18}O$ ratio of the ocean at the time they were formed. While there are intricacies involved, due to the different types of organisms, generally this oxygen isotope ratio can be used to reconstruct past climate, as the two isotopes occur at a specific standard ratio in
the environment. Furthermore, changes in this ratio reflect changes in the environment (Mix, 1987).

Evaporation preferentially takes lighter isotopes from the ocean, and so it is $\delta^{16}$O enriched water that is then precipitated on land. During ice-free conditions, this water is quickly returned to the ocean, maintaining a stable $\delta^{16}$O/$\delta^{18}$O ratio. However, when ice sheets are present, the isotopically light water is trapped on land, leading to ocean water that is enriched in the heavier $\delta^{18}$O isotope, which is recorded by the foraminifera (Fig. 1.2). A temperature-dependent fractionation also exists between water and the calcite in the tests that has the same trend of higher $\delta^{18}$O values with lower temperatures (M E Raymo, 1994), but it is not enough to account for the abrupt change that happened at the Eocene/Oligocene boundary. This all leads to the conclusion that this period is when substantial ice first appeared on Antarctica (J. Zachos et al., 2001) (Fig 1.3).

Thus the oxygen isotope record suggests Antarctic glaciation began 34 million years ago, but it does not provide insight as to why this onset occurred. Kennett (1977) proposed that the climatic isolation created separation of Antarctica and subsequent creation of the Antarctic Circumpolar Current (ACC) would have led to the glaciation. However this hypothesis has been challenged by several shortcomings, with Goldner, Herold, and Huber (2014) pointing out three notable examples: the timing of the separation is poorly constrained and does not seem to match with ice sheet formation; the ACC hypothesis cannot account for rapid change without assuming tipping point dynamics, and it fails to lead to ice sheet formation in models. General circulation models such as the one used by
(DeConto & Pollard, 2003) indicate that falling atmospheric CO$_2$ concentrations were the primary driver, and the opening of the Southern Ocean and subsequent isolation of the continent by the Antarctic Circumpolar Current were merely secondary components. While most models based on the CO$_2$ reduction hypothesis could not account for the stratification of ocean temperatures observed in $\delta^{18}$O records Goldner et al. (2014) suggest that the inclusion of simple feedbacks can account for this problem.

The CO$_2$ drawdown hypothesis is supported in the geologic record as well as in models. Boron isotope pH proxy data presented by Pearson, Foster, and Wade (2009) suggest that during the Oligocene transition, carbon dioxide concentrations were close to the 750 ppm level that would lead to glaciation, as suggested by models. These palaeo-CO$_2$ reconstructions are also supported by the Tex$_{86}$ alkenone proxy (Pagani et al., 2011).

The most widely suggested mechanism for this reduction in CO$_2$ is increased silicate weathering as a result of the Himalayan orogeny. M. E. Raymo and Ruddiman (1992) link this generally to continental glaciation and J. C. Zachos and Kump (2005) use this orogeny as the initial forcing for their CO$_2$ drawdown model. However they expand the model to incorporate the role of increased carbon burial spurred on by increased ocean mixing. By including this positive feedback mechanism, their model accounts for the anomalies in both the oxygen and carbon isotope records.

These studies all show that 34 million years ago the conditions were right for the formation of continental ice on Antarctica, but the formation process itself
was complex. Levitan and Leichenkov (2011) use sedimentary records from numerous locations around the continent to reconstruct a six-stage history of primarily East Antarctic glaciation. They find evidence of glaciation in the highest Antarctic mountains during the late Eocene (stage 1), followed by the growth of a continental ice sheet that reached an extent similar to today during the Oligocene (stage 2). Stage 3, during the early Miocene, is characterized by a loss of ice volume, but the appearance of ice shelves, and ends with ice near the present day extent. This was followed by the middle Miocene thermal maximum, characterized by polythermal glaciers (parts are above freezing). The late Miocene early Pliocene stage saw intense glaciation of the entire continent, and ended at the Pliocene thermal optimum that led to an almost complete melting of the WAIS. The final stage is the Pliocene-Quaternary stage during which the polythermal glaciers reverted to polar glaciers (consistently frozen) and distinct glacial/interglacial cycles.

Glaciation of West Antarctica and the Antarctic Peninsula began around the same time as East Antarctica, and was also confined to alpine regions (Anderson et al., 2011). Seismic stratigraphic and drill data from Bart (2012) indicates that West Antarctic glaciation had appeared by the late Oligocene, with continental ice in some of the highland regions. At this time local ice caps were forming in Central Ross Sea, and by the end of the middle Miocene, glaciation had intensified and grounded ice extended across the Ross Sea (Bart, 2012). The Antarctic Peninsula retained coniferous woodlands and tundra throughout the Oligocene, with local regions of tundra persisting until 12.8 ma, and the
northernmost region of the peninsula was not overrun with ice until the early Pliocene (Anderson et al., 2011)

Figure 1.2 This illustrates how the buildup of land ice leads to an ocean enriched in respect to δ18O. (Figure created by Hannes Grobes, acquired from http://commons.wikimedia.org/wiki/File:Glacial_effect_hg.png)
Figure 1.3 This figure shows a ~65 million year $\delta^{18}O$ curve. The red box highlights the rapid change when ice first appeared in Antarctica. More sharp changes also occur at the appearance of the EAIS and the onset of N Hemisphere glaciation. (From J. Zachos et al. (2001)).
1.3 Pliocene Epoch

The Pliocene epoch lasted from about 5.33 to 2.68 ma and its climate is characterized by two contrasting trends. The first trend being an early Pliocene warming extending from 4.5 to 3 ma (McKay et al., 2012), and the second being a gradual cooling of the environment that lasted into the Pleistocene (M E Raymo, 1994).

Reconstructions from various archives such as alkenones, boron isotopes (Fedorov et al., 2013) and stomata (McKay et al., 2012) have shown that during the warmest Pliocene periods atmospheric pCO$_2$ levels were similar to current values (~400 ppm). Models show that during this period, global temperatures were 2-4°C warmer than today (Fedorov et al., 2013), and the GRIS and WAIS were substantially diminished with corresponding sea level rise 20-25m above current levels (McKay et al., 2012). During this period maximum ocean temperatures were also similar to those today, but meridional and zonal gradients were substantially lower than they are at present (Fedorov et al., 2013).

Numerous mechanisms have been proposed to account for this warming, but Fedorov et al. (2013) suggest that no one factor can account for both the temperature change and structural change (gradients), proposing instead a combination of three forcing mechanisms: pCO$_2$ increase of 100ppm, increased subtropical ocean mixing due to enhanced cyclone activity, and low extratropical cloud albedo. The model generated using these forcing parameters leads to results that are a fair complement to palaeo-reconstructions.
The Pliocene warm period was followed by a cooling period starting around 3.1 ma. From 3.1 to 2.95 ma temperatures oscillated, but even the cold periods were warmer than current temperatures. It was not until after 2.95 ma that cold episodes were colder than present. This cooling trend eventually led to the onset of Northern Hemisphere glaciation ~2.7 ma, with further intensification until 2.4 ma (M E Raymo, 1994). McKay et al. (2012) link this cooling to the expansion of ice sheets, which began 3.3 ma. They propose cooling Southern Ocean temperatures increased seasonal sea ice persistence, which led to reduced interhemispheric heat transfer by slowing down the AMOC. Additionally, the potential reduction of atmospheric CO$_2$ by ~120 ppm, and feedbacks such as increased albedo, all worked together to create a cooling climate.

Because of our concern regarding sea level rise in the face of a warming climate, and because early Pliocene climate was similar to what we might see in the future, there is a strong interest in studying how the Antarctic ice sheets responded to these environmental conditions. Based on the study of core AND-1B taken in the Ross Sea, Naish et al. (2009) find that during this period melting Antarctic ice contributed to 7 m of sea level rise, with models attributing most of this to the collapse of the WAIS, and the remainder, up to 3 m coming from marginal melting of the otherwise stable EAIS (Pollard, 2009). However a recent study by Cook et al. (2013) suggests that the EAIS was not as stable as previously believed during this period. Using evidence from Pliocene-age marine sediments recovered off of Adélie Land, East Antarctica, they conclude that the EAIS was dynamic during the mid-Pliocene warm period. Warming ocean temperatures
caused glacial retreat hundreds of kilometers inland, especially in areas where the ice was grounded below sea level. This amount of retreat would lead to 3-10 m of sea level rise, and perhaps serve as a dire warning as to what may come if our climate continues to warm.

Ice sheet volume during this period was obliquity forced (Naish et al., 2009; Pollard, 2009), in contrast to the eccentricity forcing that controls present ice sheet fluctuations. In the context of current changes this difference is occurring at a time scale that is too long to be imminently relevant to the future. However Pollard (2009) points out that some of the modeling results are independent of these long term forcing. The models show the WAIS’s tendency to undergo rapid transitions on the order of $10^3$ years despite smooth forcing. They trace this behavior to the how the ice sheet responds to sub-ice ocean melting, and calculate that in the current conditions WAIS collapse would be initiated with a warming of around 5° C.

1.4 Pleistocene Epoch

The Pleistocene Epoch lasted from the end of the Pliocene 2.58 million years ago to the beginning of the current Holocene epoch 11,700 years ago, at the end of the most recent glacial period (Gibbard, Head, & Walker, 2010)

Pleistocene climate is known for ice ages, with the onset of Northern Hemisphere glaciation occurring only slightly before the beginning of the Pleistocene (2.7 ma). While glaciation occurred periodically throughout the Pleistocene, the character of the ice ages changed. One particularly noteworthy event during this period is the mid-Pleistocene transition, an event that took place
1.4 million years ago and saw the timing of glaciations switch from the 41kyr cycle of obliquity to following the 100kyr cycle of eccentricity. In addition, these ice ages increased in amplitude, and the shape of the glaciation (when presented graphically) became more saw-toothed, meaning the rate of deglaciation exceeds the rate of ice sheet growth (Lisiecki & Raymo, 2007).

Despite its closeness in time to the present day and the switch to the 100kyr cycle, the Pleistocene is not necessarily a good of a paleo-analogue to the present. Unlike the Pliocene, during which CO₂ concentrations were similar to the levels today and what we might see in the near future, Pleistocene concentrations were low, between 170-300 ppm (Hansen & Sato, 2011).

1.5 Weddell Sea

The Weddell Sea sits at the southernmost reaches of the Atlantic Ocean, situated between the Antarctic Peninsula to the west, Coats Land and Dronning Maud Land to the East, and bounded on the south by the Filchner-Ronne Ice Sheet, comprising a total area of 2.8 million km² (Hellmer, 2007). Within the Weddell Sea, many ocean currents of varying temperature and salinity come together and mix their waters. The Antarctic Circumpolar Current (ACC) flows clockwise around the continent, while closer in, the Antarctic Coastal Current (ACoC) travels in the opposing direction. North Atlantic Deep Water (NADW) mixes with the ACC creating Warm Deep Water (WDW), which then flows in a clockwise gyre around the Weddell Sea, becoming Western Shelf Water (WSW), which in turn can sink to become Weddell Sea Bottom Water (WSBW), which mixes a final time to become Weddell Sea Deep Water (WSDW) and then exits
the gyre (Núñez-Riboni & Fahrbach, 2007). These current interactions are illustrated in Figure 1.4. One critical component of this cycle is the formation of Antarctic Bottom Water (AABW). This water is the coldest, densest water in the world, and about 80% is formed in the Weddell Sea (Foldvik & Gammelsrød, 1988). Antarctic Bottom Water can be formed in two ways. The classical formation process from the first studies that bottom water formed when dense water generated by the process of sea ice formation formed WSW which when mixed with Modified Weddell Deep Water (MWDW) formed a bottom water current. However subsequent studies found that much of the AABW formed in the Weddell Sea was coming from Ice Shelf Water (ISW). Water flowing under the massive ice shelves is supercooled to a temperature of -2° C. Plumes of this ISW exit from under the ice sheets and flow downhill, mixing with WDW to form AABW (Foldvik & Gammelsrød, 1988). Figures 1.5 and 1.6 show how cold Antarctic bottom water, including AABW and CDW, are spread around the world, influencing water masses across in all regions except the northernmost Atlantic and Arctic Oceans (Mantyla & Reid, 1983), and the majority of the AABW is produced in the in the Weddell Sea, making critical component to Global Thermohaline Circulation (Orsi, Johnson, & Bullister, 1999).
Figure 1.4 This figure shows the surface currents near the Weddell Sea. Green arrows show the ACC, magenta arrows represent Antarctic Coastal Current, red arrows are Circumpolar Deep Water, and blue arrows show the path of Weddell Sea Bottom Water. The blue oval shows the approximate location of the Weddell Sea Gyre. (Modified from http://www.awi.de/en/research/research_divisions/climate_science/physical_oceanography_of_polar_seas/projects/acocibow/)
Figure 1.5 This figure show the currents around Antarctica, both surface and deep water, and how they interact with the waters of the rest of the world’s oceans. The Pacific arm has been cut off to focus on the Weddell Sector. Note the AABW being formed in the Weddell Sea and circulated far north. Modified from Schmitz Jr (1996).
Figure 1.6 This figure shows the pattern of global thermohaline circulation (THC). This circulation is critical in maintaining the climate patterns we are used to, and the formation of AABW in the Weddell Sea is critical, as this is one of only a few places in the world where deep water is formed, a process that drives the “conveyor belt” of THC (From http://www.ncdc.noaa.gov/paleo/abrupt/images/story2-salt-feedback.gif)
1.6 Sites and cores

In this study I use two sediment cores drilled at ODP site 693A from expedition 113. The site is in the Weddell Sea, just off the coast of Dronning Maud Land, and is one of only a handful of deep-sea core sites in the entire Weddell Sea. Additionally 693 is very close to the continent, in a location that is generally ice covered, making it a particularly unique core (Fig. 1.7-1.8). The drilling that collected the samples used in this study was completed during an unusually ice-free year. Core 693A was drilled at 70°49.892'S, 14°34.410'W at a water depth of 2359m. The length of the cored section was 483.9m with 213.5m recovered for a recovery rate of 44% (Shipboard Scientific Party, 1988).

The cores used were obtained using a rotary drill, with core 2R having a recovery rate of 99.1% and consisting of 9.51m of middle Pleistocene age sediment. Core 8R was 100% recovered and is 9.64m long and along with other sections from 693 contains the only Pliocene age sediment recovered from the Weddell Sea. Figure 1.9 shows images of the cores analyzed in this study.

The Initial Shipboard Report puts Core 2R within lithostratigraphic unit I which is composed of foraminifer-bearing clayey and silty mud. The top of Core 2R has a relatively high percent of sand (20%), which diminished to 5% by the bottom of the core. The terrigenous fraction consists mostly of clay and quartz, with minor amounts of feldspar. Core 8R falls within unit III subunit A, in the middle to late Pliocene, and consisting of clayey mud, diatom mud, and silty and clayey diatom-bearing mud. Initial XRD measurements showed that both Core 2R and 8R fall within
the same clay mineral unit (C1) dominated by illite and smectite, with smaller amounts of chlorite and kaolinite.

In terms of biogenic content, Core 2R has only rare and poorly preserved siliceous nanofossils, while Core 8R is barren of calcareous microfossils, and biostratigraphy is reliant on diatoms and radiolarians (Shipboard Scientific Party, 1988).

Figure 1.7 This figure shows the location of ODP leg 113 site 693, from which the cores for this study were drilled. Even in February, the height of the summer, sea ice is still present at the site. (Modified from http://earthobservatory.nasa.gov/Features/WorldOfChange/images/sea_ice_south/spseaice_woc_201402.jpg)
Figure 1.8 This shows the bathymetry near site 693, showing its location relative to Wegener’s Canyon and the continental shelf. (Modified from (Fütterer, Kuhn, & Schenke, 1990)).

Figure 1.9 This figure shows the sections recovered from Core 2R (left) and Core 8R (right). Image from (Shipboard Scientific Party, 1988).
1.7 Project Goals

The goal of this research is to present new mineralogical and grain size data from Pleistocene and Pliocene-age Weddell Sea sediments. These data, in conjunction with ice rafted debris (IRD), dropstone, foraminifera, and elemental data collected in separate studies of the core, will be used to piece together the depositional history of the cores. With the understanding of the palaeo-currents provided by the depositional history, further study will be able to reconstruct the environmental conditions (ice sheet behavior) of the surrounding area at the time of the sediment deposition.
Methodology

2.1 Introduction to Methods Used

2.1.1 Diffuse Spectral Reflectance

Identifying mineral composition of a sample is critical in marine sedimentology, with X-ray Diffraction (XRD) being the most common method. However, Diffuse Spectral Reflectance (DSR) is a quick and effective method that can be used to the same end as XRD, using a portable machine and less sample preparation (J. D. Ortiz, 2011). Using this method, light is bounced off the target sediment and reflected back into the sensors of a spectrometer. These sensors measure the varying percent of light that is being reflected across a wide range of wavelengths. Taken together these create a reflectance spectrum that is shaped by the physical properties of the minerals reflecting the light. Thus the spectrum from a sample can be compared to a library of known mineral spectra to identify the composition of the sample.

In particular derivative spectroscopy can be a particularly useful form of DSR. Reflectance spectra can be modified by grain size and moisture differences in the sample, but taking the derivative of the spectrum can minimize this effect (J. D. Ortiz, 2011).

2.1.2 Principal Component Analysis

Using raw reflectance data for sample identification does have a few drawbacks. Mineral assemblages are not as clearly identified as pure minerals, as the reflectance pattern of one mineral can counteract that of another (Yurco, Ortiz, Polyak, Darby, & Crawford, 2010). Additionally a raw dataset of many samples has a
correspondingly large number of spectra and individual reflectance measurements, which can be overwhelming to analyze (J. D. Ortiz, 2011). Fortunately the use of Principal Component Analysis (PCA) can help with both these problems. This technique breaks down all the downcore samples into a manageable number of discrete, non-correlated components. These components are generated to represent the fractions of the data that account for the most variability. Their loadings can be plotted against wavelength and be compared to the derivative reflectance spectra in a mineral library, while the scores can be plotted downcore to show the variability of the different components over time (J. D. Ortiz, 2011).

2.1.3 Grain Size Analysis

In marine environments, the relationship between flow power and sediment transport is well understood, with faster currents able to keep larger particles in suspension (Pudsey, 1992). Sediment is sorted during deposition or resuspension. As sediments are carried by a current, some fall out of suspension based on their settling velocity, so an originally unsorted mixture is sorted as the grain size distribution narrows downstream. The resuspension of particles by currents also contributes to sorting, as the critical speed of the current is reliant on grain size, with a particular speed only resuspending sediments up to a certain size (I. N. McCave, Manighetti, & Robinson, 1995). This means sediments deposited by bottom currents are a valuable source of information for palaeo-current reconstruction. The fine fraction (<63µm) is commonly used for these reconstructions, but when considering the deposition of such small particles, it is important to note that the smallest silt and clay-sized grains are prone to aggregation, and that the disaggregated state in which they are analyzed
is not necessarily representative of the way they were deposited. To minimize this issue, palaeo-current reconstruction is often done with the “sortable silt” (SS) fraction (10-63µm) which is more likely to be deposited as individual grains (I.N. McCave, 2008).

The interpretation of the sortable silt fraction is straightforward. Due to the processes of sediment suspension, transportation, and settling discussed above, larger mean SS size indicates faster currents. Few studies have attempted to correlate grain size with absolute speed; instead the changes in grain size are interpreted as relative changes in current speed, which is sufficient for most analyses. An example of this type of analysis is shown in Figure 2.1, which is used by I.N. McCave (2008) to highlight the information that can be extracted from the mean SS data.
Figure 2.1 This figure from I.N. McCave (2008) illustrates the interpretation of grain size data. The grain size profiles from two cores (Gardar Drift and Bermuda Rise) are presented. The lettered arrows highlight notable increases and decreases in grain size that are found in both cores. These are then interpreted as climate-induced changes in current speed, and related to a benthic isotope curve for age and correlation with specific climate events (MIS 6, 5e, and 5d).

2.1.4 Wavelet Analysis

Wavelet analysis is a tool that is used to find signals within a time series. By decomposing the time series into time-frequency space, wavelet analysis makes it possible to determine the dominant modes of variability within a time series and how the modes vary in time. Windowed Fourier transforms are another common tool used in similar applications, but have been found to be an inaccurate and inefficient method of time-frequency localization due to their imposition of a scaled response.
time and the need for the use of several windows to determine the most appropriate window size to capture the variability of the record (Torrence & Compo, 1998).

To carry out the analysis, the basic, or “mother” wavelet is transformed to match the original time series. The mother wavelet can come in many forms, which are suited to particular applications. Different types of wavelet functions include orthogonal and non-orthogonal, real or complex, and can differ in width and shape as well (Torrence & Compo, 1998). After the wavelet is chosen, the scale on which the power analysis will occur must be determined, with powers of two a commonly chosen scale. Finally, since the transform assumes a cyclical pattern despite a finite time series, the ends are padded with zeroes to improve the calculations, then removed once the transform is complete. The region affected by these edge effects is referred to as the cone of influence (Torrence & Compo, 1998).

2.2 Sample Acquisition and Preparation

Samples from ODP cores 113-693A-2R and 113-693A-8R were obtained from the IODP Gulf Coast Repository at Texas A&M in College Station, Texas. Most samples were 1cm, taken at 2cm intervals, although this initial analysis is performed on every other sample. The samples were dried in an oven at 60° C for at least 24 hours. They were then weighed and their masses were recorded. Each sample was put into a 50 mL tube with Calgon water (water + 0.1% sodium hexametaphosphate), which acts as a dispersing agent to dissipate aggregated sediment. Samples were left in these tubes overnight to allow the sediment to disperse, then they were physically mixed using a Vortex Genie 2 to complete the disaggregation. The contents of the tubes were then wet sieved into four sediment fractions (>500µm, 150-500µm, 63-
150µm, and <63µm). Each fraction was appropriately labeled and left to air dry, with
the fine fraction (<63µm) sitting under heat lamps to speed the drying. Once dry, the
fine fraction was scraped from the bottom of the containers onto weigh paper to be
were reweighed, with the weight of each sample recorded and used to calculated the
percentage of the whole sample it composed. After weighing, each sample was placed
into a Whirlpak labeled with its sample ID and weight to await analysis.

2.3 Initial Laboratory Methods

2.3.1 Homogenization

To return the fine fraction sediment to particles rather than clay sheet flakes,
each sample was homogenized. This was accomplished using an agate mortar and
pestle. Each sample was emptied into the mortar and gently ground until it was once
again composed of a homogenous grain size. Losses were minimized by crushing the
samples by hand while still within the Whirlpak, which reduced the amount of
grinding needed with the mortar and pestle, reducing the amount of spillage. The
mortar and pestle were wiped clean using a cotton ball and isopropyl alcohol between
each sample. Each sample was weighed after homogenization and the new weight
was recorded on the Whirlpak. For most samples the amount of sediment lost (from
spills or samples left in containers during transfer and homogenization) was less than
2 percent.

2.3.2 Visual Near-Infrared Diffuse Spectral Reflectance

VNIR reflectance measurements were taken in Dr. Joseph Ortiz’s lab at Kent
State University using a Minolta CM-2600D handheld photospectrometer, which
measures reflectance at 10nm intervals from 360-740nm. To take measurements each
homogenized sample was emptied onto a piece of plain white paper and covered with a sheet of Glad® cling wrap. The spectrometer was held over the sample and the measurement was taken. A white reference image was taken every 5 samples, and the machine was recalibrated using both zero (black) and white references every 24 samples. The reflectance data was exported from the machine using specialized software, and transferred to Excel for analysis.

2.3.3 Grain Size Measurements

Grain size was also measured in Dr. Ortiz’s laboratory. They were collected using a Malvern Mastersizer 2000 particle size analyzer. This machine measures grain size with a laser by running sediment samples suspended in water through a window. As the light hits sediment particles it is reflected at different angles based on the size of the particle. To collect these measurements, a small portion of a sample was transferred from the Whirlpak to into a 1L beaker of distilled water using a Scoopula. The beaker was then placed in the machine’s intake mechanism. Each sample was sonically disaggregated using the system’s ultrasonic dispersion feature for one minute to isolate individual particles in the sample to ensure measurements were of individual and not clumped grains. After each run the machine was flushed with several liters of distilled water until the background measurements reached normal, indicating the system was clean and ready to run another sample. The beaker and the Scoopula were rinsed and wiped clean between each run. The window was periodically sprayed with distilled water and wiped down to ensure its clarity and cleanliness. For each sample the machine took 3 measurements, which were included
in the output as well as the average of all three measurements. These results were exported as a text file to be opened in Excel for analysis.

2.4 Initial Data Analysis

2.4.1 Data Sheet Setup

The spreadsheets generated from the raw data collected from the spectrometer and particle size analyzer included some unnecessary data, so the relevant information from each dataset was extracted and input into a new data sheet, with separate sheets for Core 2R and Core 8R samples. For the reflectance data the values from each sample are so similar that differences would be difficult to distinguish for the principle component analysis. The raw reflectance data were therefore converted to first derivative values, calculated by dividing the difference of two sample values on either side of the sample in question by the difference in wavelength (e.g. value for 420nm would be reflectance of 430nm-410nm/20). For the grain size data, only particle sizes that were present in all samples were used, as including sizes not present in all samples could skew the results. The measurements were then organized according to the depth profile in each section, which was translated into depth in core by adding 150cm to the depth in core value for each section after 1 (e.g. core section 2, 14-15 cm becomes 164.5cm deep in core, core section 5, 106-107 becomes 706.5 deep in core).

2.4.2 Principal Component Analysis

Varimax-Rotated Principal Component Analysis was used to transform the data from hundreds of individual values into several meaningful components for more effective interpretation. The Varimax rotation ensures there will no correlation
between generated components by rotating the data after each component is generated so that the next component is orthogonal to the rest. The VPCA was run using SPSS, which requires specific formatting for data input, so in the Excel spreadsheet headers spaces and left parentheses were replaced by underscores, right parentheses were deleted, and periods/decimal points were replaced with the letter p. Thus formatted, the spreadsheets were opened in SPSS, and the “factor” feature was used to generate the principal component analysis, with initial settings including all components that account for more than 1% of the variance. The scree plot was analyzed to determine the number of components that were above the noise floor, and the analysis was run again and told only to generate the specified number of components.

2.4.3 Wavelet Analysis

Wavelet analysis was used to determine periodicity within our component loading dataset. For this analysis to work, the data must have a constant change interval, which the samples used in this study do not. The interpolate function in Excel was used to generate a dataset that matches the collected data, but with even spacing intervals. These data were than de-trended by subtracting their second order polynomial trend from the data values. This is done to remove any trend caused by periodicity occurring at a time scale that is too long to be captured within the range of data used. These interpolated and de-trended values were then input into an online wavelet generator (http://ion.exelisvis.com/) that output the resulting power spectrum and wavelet plot. The periodicities of the wavelets generated were compared to Milankovitch cycles, which are climate cycles driven by regular changes in the Earth’s orbit around the sun (Fig. 2.2). Converting periodicity in cm given by the
wavelets to Milankovitch periodicity in years allowed us to calculate average sedimentation rate within the cores.

Figure 2.2 An illustration of the three Milankovitch cycles showing how changes in Earth’s orbit around the sun can affect the amount of solar insolation received at critical latitudes. Eccentricity can have a 400 or 100kyr period, obliquity is 41kyr, and precession has either 23 or 19kyr cycles. (from J. Zachos et al. (2001))
2.4.4 Mineral Identification

To identify the mineralogical composition of the components generated by the VPCA the loadings of each component was plotted in excel and compared to mineral spectra from the USGS spectral library. A correlation matrix was created to match each component with a few of the most closely matching minerals. The spectra of these closely matched minerals were then mixed in a linear fashion at different ratios to yield the highest possible correlation, providing an identification of the mineral assemblage of each component.

2.5 Revised Methods

2.5.1 Data Collection

After the initial round of data collection, more samples were made available for analysis. The grain size methods remain unchanged, as the samples were sent to Dr. Ortiz’s lab where they were run by Fangyu Zheng. However the new spectral data was collected in Dr. Martha Gilmore’s lab at Wesleyan University using a ASD FieldSpec FR® spectrometer which measures reflectance at every wavelength from 350-2500nm, increasing the dataset not in both number of samples and wavelength range. Different methods were used to collect these data. First the difference in reflectance between homogenized and non-homogenized samples was tested. Eight samples, representing both cores, were divided. Half of each sample was homogenized while the other half was left flakey. Reflectance of both halves were taken and plotted against each other in Excel. Six out of the eight samples showed a high degree of correlation (>0.95) between homogenized and flakey samples, while two did not. However after inputting these two samples into ENVI Classic and using
the continuum removed function, which takes away trends in the data and highlights the valleys in the reflectance curve, the correlation between homogenized and flakey samples were in the range of the other six samples. This gave us confidence to proceed using non-homogenized samples for the spectral data collection. To collect the reflectance measurements the machine was turned on and optimized for the light conditions. Each sample was poured onto weigh paper, and the spectrum was taken by pointing the sensor at the sample. The machine took 10 measurements per sample, and a white reference was taken every ten minutes. The data were exported as text files and opened in Excel, where the average of the 10 spectra taken was calculated. The data were then uploaded to ENVI, subjected to continuum removal, and re-exported as text files. For reasons yet to be determined, the FieldSpec FR® data led to compromised components in the principal component analysis stage, and were not used in this study. The samples missing from the original data were measured in Dr. Ortiz’s lab by Fangyu using the Minolta CM-2600D.

2.5.2 Data Analysis

The data processing (VPCA, interpolation, and detrending) on the completed dataset was carried out using an “R” template created by James Hall. The results were identical to those generated by running the VPCA in SPSS and the interpolation and detrending in Excel, but more streamlined as it is all carried out on the same platform. While R does also have the ability to generate wavelets, the graphics for the online generator are superior, so that step remained the same.
Results

3.1 Methodology Comparisons

3.1.1 SPSS vs. R

As discussed in methods, two programs were used to accomplish the VPCA, first SPSS, then R to compare with a similar study being undertaken by James Hall. These two different methods lead to essentially identical results. Table 3.1 provides one example, showing the first four components generated by each method are nearly identical. In the downcore loading of these components also showed 0.99+ correlation between SPSS and R. The full results for components and scores from both methods can be found in the supplementary materials.

3.1.2 Individual vs. Combined Analysis

Initially the VPCA was carried out separately on the data from 2R and 8R due to the large difference between their times of deposition and lithology. The VPCA was later carried out on the combined data from both cores to test whether the components would be different. Comparison of the results generated by individual and combined results show that the first two components, which account for 80+% of variance, are very similar whether they are generated from the individual cores, or by the combined samples. Components 3 and 4 are less correlated across these methods, however these account for <5% of variance, and would not have been considered in the further analysis, so the combined components are used for the remainder of the study as representative of both cores. Figure 3.1 shows the spectral curves generated by the three different methods for four components, while the scree plot in Figure 3.2 shows components 1 and 2 are the only ones significantly above the noise floor.
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Table 3.1 This Table shows the VPCA results from R (blue columns) and SPSS (purple columns). The correlation between the two methods is shown in the bottom row, and is very high (>0.99) in all cases.
Figure 3.1 The four most significant components generated by VPCA comparing the curves generated from only Core 2R (blue), only Core 8R (red) and both combined (green). In plot C3, the combined curve (C3, in green) is graphed on an inverse axis relative to the other two.
This scree plot shows the relative proportion of variance explained by successive components generated by the VPCA. Only 1 and 2 are above the noise.

3.2 Reflectance Curve Principal Component Analysis

Initially the first four components generated by the VPCA were taken for further analysis, based on the SPSS default to select components with eigenvalues above one. The first two components in terms of variance explained accounted for 59% and 28% respectively, while the latter two were 5% and 2%. This suggest that only the first two are significant, which is supported by the scree plot of all components generated.
(Figure 3.2) which shows that components three and four are very close to the noise floor. Even including only the first two components most (87%) portion of the downcore variation is included in the study. Component 1 (Fig. 3.3) was matched with high (0.97) correlation with a mixture of 70% Kaolinite (CCJB25) and 30% Smectite (BKR1JB005). Component 2 (Fig. 3.4) was matched with high correlation (0.98) with a mixture of 65% Illite (LAIL01) and 35% Chlorite (LACL14). The standard mineral curves were attained from the Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) spectral library (speclib.rsl.wustl.edu).

**Component 1**

0.3*Smectite+0.7*Kaolinite=0.97 Correlation

![Component Loading](image)

**Figure 3.3** The loadings of the first component generated by the VPCA plotted against a spectrum created by combining the spectra of kaolinite and smectite. The y-axis is flipped for the component due to the rotations that occur during the VPCA. The correlation between components is based on the positions of peaks and valleys, which is based on the minerals in the sample. The absolute reflectance values are also dependent on the size of particles measured, which explains why the two curves appear different despite the high correlation.
Component 2
0.35*Chlorite+0.65+Illite=0.98 Correlation

Figure 3.4 Component 2 is plotted against the combined spectra of chlorite and illite.

3.3 Downcore Component Loading

Interpreting the loading of the components in each sample down the core is important for determining how the deposition of the different components varied over time, an important clue in determining their climatic significance. Figures 3.5 and 3.6 show the downcore trends of the components in Core 2R and Core 8R respectively. For Core 2R, component 2 has a larger range in loadings, and the components display some degree of an inverse relationship, both looking at particular depths (the first peak/valley) as well as the more general trend. Core 8R components are similar in both respects, with component 2 having a larger range of loading values. It is more difficult to see the inverse variability at specific depths, although the changes at the gap (~68-69.4 mbsf) does provide an example.
Figure 3.5 The downcore loadings of Core 2R component 1 (red) and 2 (blue).
3.4 Wavelet Analysis

The wavelets presented here were generated from the downcore loadings generated by the principal component analysis discussed above, after the raw data was interpolated and detrended as described in the methods section. Because of the five-core gap between the cores analyzed in this study time series analysis treating
both cores as a continuous entity is impractical. Therefore to generate the wavelets, the scores were calculated separately for each core.

The wavelets generated by the two Core 2R components (Fig. 3.7a and 3.7b) show fairly similar shapes, with component 2 showing a greater power decrease between the two prominent peaks. The first component shows high power at intervals of approximately 375 cm, 140 cm, and 64 cm, with the longer two periods generating peaks above the 30% red noise level. The second component has shows peaks at 500 cm, 130 cm, and 64 cm, however only the 500 cm peak is above the 30% red noise level. In both wavelets the longest period peak has the largest power. We attribute the peaks in both components to 400 kyr eccentricity, 100 kyr eccentricity, and 41 kyr precession.

The wavelets from Core 8R (Fig. 3.7c and 3.7d) have peaks that indicate longer periods than their counterparts from Core 2R. The first Core 8R component has peaks at 600 cm, and 180 cm. Both peaks are above the red noise level. In contrast to this wavelet, the wavelet from component 2 has a reduced long “peak” at 500 cm is below red noise spectrum. The second peak is the strongest, at 200 cm and is above the red noise. The longest period in both these wavelets in attributed to the 100 kyr precession cycle, while the shorter represents 41 kyr obliquity.

Assigning Milankovitch cycles to the peaks in the wavelet allows us to translate the periodicity from a frequency in space to a frequency in time, which can be used to calculate average sedimentation rates. This is accomplished by dividing the length of the period in centimeters by the years in the assigned Milankovitch cycle, resulting in a cm/kyr value for the sedimentation rate. We would expect the calculated
sedimentation rates from the different cycles and components to be the same, as they are all representations of the patterns recorded by the same sediment. This can be used as a check for our assigned cycles. Figure 3.8 shows the rates calculated from the various components plotted against each other for comparison. The Milankovitch cycle assignments, peak lengths, and sedimentation rates are shown in Table 3.2(a) (2R) and 3.2(b) (8R) along with the rates generated from 3 other datasets analyzed by Hall (2015).
Figures 3.7 (a-d) These wavelet plots show the downcore loading of the VPCA scores (a) as well as the wavelet power spectrum (b). Black lines connect the wavelet peaks with the period to make the connection easier to visualize. (plots generated using ion.excelis.com)
Table 3.2 (a) The sedimentation rates calculated for Core 2R are based on two long eccentricity peaks and average of about 1.37\text{cm/kyr}. Rates calculate from all four datasets combined are higher, averaging 1.44\text{cm/kyr}. 

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<th>Sed. Rate (cm/kyrs)</th>
<th>Ave. Sed. Rate</th>
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Table 3.2 (b) The DSR-derived sedimentation rates for Core 8R average 6.44 cm/kyr, with dominant eccentricity and precession forcing. The additional datasets see more obliquity forcing than eccentricity, and indicate a sedimentation rate ~0.14 cm/kyr higher than the data used in this study.

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Figure 3.8 The average sedimentation rates calculated from the peaks in both components for Cores 2R and 8R. Core 2R peaks are consistent across all peaks and components, while 8R sedimentation rates vary between the two components.

3.5 Grain Size Analysis

The sortable silt (SS) fraction (10-63µm) is the best indicator of palaeo-current speeds (I.N. McCave, 2008). However Figures 3.9 (a and b) show the relative percentages of the sortable sediment and the fine silt and clay (<10µm). In both cores the 10µm fraction is more abundant, but whereas 2R shows very little variability in the ratio between this and the SS, in 8R the relationship fluctuates more, with one point having slightly more in the SS fraction.

The sedimentary data from Core 2R displays relatively consistent fluctuation throughout, both in in the average SS size (Fig. 3.10) and in the clay and fine silt to sortable silt ratio (Fig. 3.9a). The SS average shows several large and rapid changes at the top of the core. There are some notable longer-term changes within the core, with small peaks occurring cyclically approximately every 1.7m, with peaks lasting
roughly half a meter. Fitting a polynomial trendline to the data also reveals a longer-term period of ~6m.

The variation of average SS size in Core 8R (Fig. 3.11) also lacks large magnitude, rapid changes in grain size, and unlike Core 2R, the data itself does not readily show any cyclicity. However, the longer trend does reveal notable fluctuations in the SS mean, with a period of ~6m. This core also shows greater variability in the sortable silt/clay and fine silt ratio, with one section ~67.5 mbsf having a higher proportion of SS than of the smaller fraction. Overall Core 8R trends to slightly smaller particle sizes throughout the length of the core with a difference of ~2 µm.

Both cores have very similar average SS sizes, ranging from 18-28 µm in Core 2R, and from 17-27 in Core 8R.
A  Downcore SS vs <10um fraction
Figures 3.9 (a and b) show the downcore percentages of the SS and <10µm fractions of Core 2R and Core 8R respectively. The <10µm fraction (in blue) is dominant in both cores.
Figure 3.10 This downcore plot showing the average grain size of the sortable silt fraction (10-63µm) for Core 2R reveals a rather flat trend, but more short term fluctuations.
Figure 3.11 The average grain size of the sortable silt fraction (10-63μm) of Core 8R.
Discussion

4.1 Discussion of Methods

As the comparison between R and SPSS yielding nearly identical results, the discussion as to which is the preferable method is an issue of the process itself. Between the two, R appears to be, as with the script already written and ready to run with few modifications (code in supplementary material), it is very easy to generate the desired results even with next to no knowledge of the program. Additionally the steps to carry out the wavelet analysis after the VPCA are built into the code, and can also be accomplished along with the initial run, whereas using SPSS there is no easy way to combine the VPCA with further processing, and subsequent steps must be carried on in a different program such as Excel. In addition, R is a free and open source software, which in many cases can be beneficial for those who do not have or wish to spend money on SPSS.

Since the significant components generated separately and by the combined dataset were so similar, the combined results were used, as in a situation in which the data from the cores bridging the gap were also available, they would be used. In this case, the differences, if any, between Core 2R and 8R would be the same as they are now, and would not be artificially separated, therefore in this steady they remain combined as well.

The fact that the lesser components varied more between cores could be a result of their being so close to the noise floor they incorporate some random variation and do not represent a completely pure component. However it could suggest these
components are real and could reveal more about the more short term and local changes that are present in one core and no the other.

4.2 Primary Components and Downcore Loading

The minerals that make up the components analyzed in this study (smectite, kaolinite, illite, and chlorite) were among the main clay minerals identified in the Shipboard Report on clay mineralogy. While at glance, it may seem problematic that the ratios found in the this study vary from the percentages found in the initial analysis of the Site 693 cores, it is important to remember that the components discussed here do not represent the overall character of the sediment. The component represents the variation from the mean and standard deviation of the optical curve (J. Ortiz, 2015). Therefore the assemblages identified show the minerals that account for variation from the standard curve, rather than the composition of the sample as a whole.

At high latitudes, where erosional processes are pronounced, variations in clay mineral changes in marine sediments can provide a record of climatic changes by reflecting the fluctuation of ice volume (Junttila, Ruikka, & Strand, 2005). Clay minerals in marine sediments can come from a variety of sources, including physical weathering of rocks on land, submarine weathering of volcanic material, and from early diagenic processes (Robert & Maillot, 1990). Of the minerals that make up the components in this study, illite and chlorite are especially common in high latitude areas, and are predominantly detrital, coming from a continental origin. Kaolinite is not formed in the cold conditions that currently characterize the high latitudes, but it
is resistant to erosion, so it is assumed to also have a continental origin, remaining as a relic of warmer times thanks to its resistant nature. Smectite can form from a number of different processes, and is often associated with hydrolysis, but in Antarctic Ocean sediments it is also assumed to be continental (Ehrmann, Melles, Kuhn, & Grobe, 1992). As products of physical weathering and glacial erosion, illite and chlorite are associated with cold climatic conditions (Juntila et al., 2005) which is in agreement with their prevalence in high latitude marine sediments today. In contrast, smectite and kaolinite result from more chemical weathering, and are therefore associated with warmer climatic regimes when chemical weathering would increase and physical weathering due to glaciation would subside (Juntila et al., 2005).

Based on this interpretation of the clay minerals, component 1 from this study, consisting of smectite and kaolinite, would clearly represent a warm climate clay mineral assemblage. Component 2 consists of an assemblage of illite and chlorite, both of which are indicators of a cold climate. Since the first component consists of two minerals that indicate warm climate conditions, and the second is an assemblage of two cold climate minerals, one would expect to see the components vary inversely in the downcore plot, and as Figure 4.1 (a and b) shows, this relationship is in fact recorded. The trends are not completely in sync, as they often show a slight offset from one another. However in Core 2R, the warm component seems to lead, while in 8R the cold component changes first. This suggests that rather than representing a lag in the response of one component relative to the other that the offset is merely the
result of inaccuracies from the processing of the data, such as the assignment of a polynomial trend to represent the changes in the individual sample points.

![Figure 4.1](image)

**Figure 4.1** (a and b) The downcore components of 2R (a) and 8R (b) plotted against one another (component 1 in red, 2 in blue). The trend lines show the inverse relation between the two components.

### 4.3 Wavelet Analysis

In Core 2R, the wavelet plots indicate that the Milankovitch cycles which were exerting influence on the deposition of the fine fraction were 400 and
100kyr eccentricity and 41kr obliquity, with the power of their effects also in that order. While various studies (Lisiecki & Raymo, 2007; Naish et al., 2009) indicate Pliocene glaciation was dominated by obliquity forcing, a transition to the current 100kyr glacial cycle occurred during the Pleistocene ~0.8 ma. Grobe, Fütterer, and Spiess (1990) identified the Bruhnes/Matayama boundary, a magnetic reversal that occurred 730ka, at 8 mbsf at Site 693, indicating that much of Core 2R was likely deposited during this eccentricity-dominated period, agreeing with the timing the wavelets in this study suggest.

The sedimentation rates calculated for Core 2R using the Milankovitch cycles assigned to the wavelet peaks is very low, at an average of 1.37cm/kyr. The additional datasets from Hall (2015) also have this low sedimentation rate, and it is also in agreement with the Initial Shipboard Report, which suggest that during the Pleistocene, approximate sedimentation rates were less than 1.0/kyr (Shipboard Scientific Party, 1988).

Core 8R wavelets suggest forcing from 100kyr eccentricity and 41kyr obliquity, however they are not in agreement as to which was the dominant forcing. While the wavelet generated by Component 1 shows eccentricity as the dominant forcing, with an obliquity peak that also crosses the red noise spectrum, component 2 shows next to no long 100 kyr peak, and a very strong obliquity signal. Component 2 is more in agreement with previous studies that indicate strong obliquity forcing during the Pliocene.

The average sedimentation rate calculated from the Core 8R wavelets averages 4.95cm/kyr, which is lower than the rates calculated by Hall (2015),
which averaged 6.64 cm/kyr. However, the rates calculated in this study are more in line with the Initial Shipboard Report, which reported average sedimentation rates for the Pliocene between 2.6-4.6 cm/kyr.

4.4 Grain Size

The grain size measurements in this study are used as a proxy for palaeocurrent speeds at the time of deposition. Following the suggestion of I.N. McCave (2008), only the sortable silt section is analyzed to attain the best representation of the currents.

Based on the results of Pudsey, Barker, and Hamilton (1988), Pudsey (1992), and I.N. McCave (2008), we interpret the periods of higher grain size to be periods of warmth, whereas low grain size averages indicate slower currents and colder periods. In particular, the 1988 study suggests that during warmer periods there is a larger reservoir for production of Ice Shelf Water, which leads to increased bottom water production and stronger currents. The opposite of this mechanism is in operation during the colder periods. Figure 4.2 shows the second VPCA components from Cores 2R and 8R plotted against their respective grain size graphs. Since the mineral assemblage in the second component represents a cold regime, the inverse relationship they show with the grain size data is expected. The grain size data appears to peak earlier than the components, indicating that it is more sensitive to the climatic changes that are being recorded.

In the previously mentioned studies, Pudsey assigns the warm and cold periods identified to glacial and interglacial periods. This interpretation fits the SS variations described in Core 2R, with the 0.5m peak representing the interglacials and the whole
cycle comprising of a full glacial period. The sedimentation rate of \( \sim 1.7 \text{cm/kyr} \) this would lead to, based on a 100kyr cycle, is also similar to the 1.37cm/kyr sedimentation rate calculated from the wavelet generated by the reflectance data.

Core 8R is more difficult to interpret in this manner, as the only the trendline showed cyclical variability, and this does not present enough resolution to see glacial and interglacial periods. However, assigning the \( \sim 6.5 \text{m} \) period to the 100kyr eccentricity cycle leads to a sedimentation rate of 6.5cm/kyr, which is also in good agreement with the wavelet-derived rate.

**Figure 4.2** The downcore trend in average SS size (blue) is inverse to that of Component 2 (red) in both Core 2R (on the left) and Core 8R (on the right).
4.5 Synthesis of Analyses

Having identified likely warm and cold periods within the core, the next step is to put some time constraint on these periods, as well as investigate the forcing that is leading to the changes. This is accomplished by comparing the trends to the wavelet plots (Figure 4.3).

In Core 2R, the trend lines of both components show cyclicity with a period of approximately 6m. Based on the sedimentation rate calculated from the wavelet plot, the fluctuations of both components and the mean SS size are occurring on a 400kyr cycle. This would indicate that rather than representing glacial-interglacial changes, the clay mineral variability and inferred shifts in climatic regime are responding more to the longer-term eccentricity forcing which modulates the strength of the 100kyr cycle.

However, an alternate explanation is also feasible if the two major peaks are interpreted as 100kyr and 41kyr respectively. These assignments would lead to an average sedimentation rate of 4.11 cm/kyr. With this rate, the period of the cycle found in the components would be ~145kyr, most likely representing glacial-interglacial variation. This could fit with the switch to 100kyr that is believed to have occurred ~0.8 ma, although the 145kyr length is a longer than the eccentricity forced variation would suggest. Huybers (2007) presents a model that could explain this longer cycle as well as incorporate presence of an obliquity cycle in the wavelet plots. He suggests that rather than a switch from obliquity to eccentricity forced glacial cycles, the forcing (obliquity) remained the same, and only the likelihood of a skipped termination changes. In this model, the glacial fluctuations are based on
either two or three obliquity cycles grouped together before a termination, which he claims is well supported in the record, as well as a simpler explanation for the shift to longer glacial cycles. He also makes the point that averaging the length of double and triple obliquity glaciations (~80 and 120kyr) yields the familiar 100kyr average cycle.

This theory would explain the long cycle suggested by our components by attributing it to a triple obliquity period. The relationship between the wavelet power spectra and the component variation would also fit with this theory. The power of obliquity forcing is strongest at times when component 1 is lowest, and decreases in power when component 1 goes up, suggesting potential obliquity control on the fluctuations despite the longer cycle.

In Core 8R, the dominant forcing has been assigned to 100kyr and 23kyr cycles, which goes against the prevailing consensus that Pliocene glaciations were obliquity forced, as proposed by Lisiecki and Raymo (2007) and Naish et al. (2009), among others. However, it is worth noting that these studies make inferences based on the proxies they investigate, which are different both in nature and location to the proxies used in this study. While some degree of extrapolation is expected, it is also reasonable to suggest that the signals found from Liesicki and Raymo’s global δ¹⁸O record and Naish’s WAIS fluctuations responded differently than the EAIS, to which the proxies used in this study relate. Initial assignment of the 100kyr and 23ky cycles to the wavelet periodicities was done to match the sedimentation rates with those calculated by Hall (2015). Beyond this comparison, this assignment is justified by the findings of a recent study of similar scope to this one. Using mass accumulation rate of iceberg rafted debris from the coast of East Antarctica, Patterson et al. (2014) infer
the influence of the orbital cycles on deposition, which is associated with iceberg calving and ice sheet retreat. While the study finds the familiar 41kyr forcing through much of the Pliocene, they note that a reduction in obliquity power starting ~3.5ma. At this time the power of the 100kyr eccentricity cycle also increases, with 23kyr precession also showing power of significance above red noise (Fig 4.4). Even in the LR04 benthic $^{18}$O stack, the 100kyr appears stronger while obliquity is relatively weak. When combined with an eccentricity-tilted precession solution, the LR04 shows both 100kyr and 23kyr cycles of significant power. In their argument they suggest that the cooling and subsequent growth of sea ice might have lessened EAIS sensitivity to orbital forcing, and further hypothesize that it is comparable to the global shift to 100kyr cyclicity during the late Pleistocene, a colder climate regime. While Core 8R does not have ideal age constraints, the Gilbert/Gauss magnetic reversal is placed in the upper part of the core, giving that section an approximate age of 3.6ma. This is close enough to the decrease in obliquity found by Patterson et al. (2014) that we suggest the forcing suggested by our data is representative of the beginning of the transition to this alternate power regime. Accepting the sedimentation rate of 6.44cm/kyr as calculated by the peaks assigned above, the ~7m cycle between 62-69 mbsf (Fig. 4.3 c and d) would represent a period of approximately 110kyr. With this timing it is most likely attributed to a glacial/interglacial cycle.

If the assumption that obliquity is the dominant Pliocene forcing cannot be put aside, an alternative interpretation is still possible using the Huybers (2007) model as discussed in regards to Core 2R above. While his main argument is in regards to the
Pleistocene transition, he mentions several occasions before the transition when obliquity-paced deglaciations were skipped. While none of the intervals mentioned reach back this far, it suggests that this missed deglaciations did occur before the transition, indicating it would be possible that this is another example of a skipped obliquity-forced termination. Using the sedimentation rate of 4.73 cm/kyr calculated by assigning 41 kyr to the second peak rather than 23 kyr, the 6.5 m period in the core corresponds to a ~130 kyr cycle, which could represent a long, triple obliquity glacial cycle.

It should be noted that the glacial and interglacial periods of the cycle shown by our data appear to be of equal length, which is in contrast to the current paradigm. However, Lisiecki and Raymo (2007) noted that during the Pliocene glacial/interglacial transitions were more evenly paced, with the transition to the familiar “sawtooth” shape of the glacial curve being a later occurrence. This would explain why Core 8R does not exhibit this pattern, but it would still be expected in Core 2R. The most likely reason is that we are identifying the glacial cycles based on periodicity from the trendline fit to the data, which does not have enough resolution to differentiate between the two modes of the glacial cycle.
By comparing the downcore component loading to the wavelets they generate, we can see how the components react to the power of the signal. Core 2 components (a and b) respond to 100kyr forcing while core 8 (c and d) responds to 23kyr.
Figure 4.4 These figures, from Patterson et al. (2014) show the power of various orbital cycles from that study’s IRD mass accumulation rate data (a) as well as from the LR04 benthic stack. This period shows 100kyr and 23kyr cyclicity, rather than 41kyr obliquity as in most of the Pliocene.
Conclusions

5.1 Core 2R

Core 113-693A-2R consists of Pleistocene age sediments, constrained somewhat in time by the presence of the Bruhnes/Matayama boundary at 8 mbsf, part way through the core. It is characterized by a low sedimentation rate, with the wavelet suggesting 1.37 cm/kyr and the grain size putting it at ~1.7 cm/kyr. The predominant orbital cycles during its deposition were 400 and 100 kyr eccentricity. The fine fraction of sediment within the core has two main components that account for most of the variability, a cold climate assemblage consisting of illite and chlorite, and a warm climate assemblage consisting of smectite and kaolinite. These components vary inversely throughout the core, and along with the sortable silt variations, indicate that the climate at the top of the core was in a warming state, and that the core contains slightly more than one full cycle of warm and cool periods, which likely traces the power of 100 kyr eccentricity modulated by the 400 kyr cycle. The average SS data reveals provides a finer resolution picture, which shows glacial/interglacial variation within the longer-term changes indicated by the component trends.

5.2 Core 8R

Core 113-693A-8R contains Pliocene age sediments. Although the absolute dating of the core is not well constrained, it is presumed to be in Chron 2r (Gilbert), older than 3.6 ma. The average sedimentation rate during this time was a 6.44 cm/kyr, and the dominant orbital forcing came from the 100 kyr eccentricity and the 23 kyr
precession cycles. Like Core 2R, the fine fraction has two clay mineral assemblages consisting of illite and chlorite, and smectite and kaolinite that vary inversely throughout the core, representing colder and warmer periods respectively. The components, in conjunction with variations in the mean size of sortable silt, show the core begins in the cooling portion of a climate cycle, then proceeds to complete slightly over one full cycle over the length of the core. Based on the sedimentation rate calculated in this study, the length of this climate cycle would be approximately 110 kyr, and so could be identified as potentially representing glacial/interglacial changes.

5.3 Future Work

The research presented in this thesis is only one piece of the puzzle. In order to see the big picture, further work will focus on synthesizing the findings of this paper with the results of other studies on the cores we have discussed here. Taken together, these studies will provide a more detailed story about the environmental conditions at the time when the sediments were deposited.

Supplementary Material:

Supplementary materials, including datasets, additional figures, spectral curves, and the R script used in this study can be found on the Wes Scholars page (wesscholars.wesleyan.edu).
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**Online Sources:**

Interactive Wavelet Generator—ion.exelisvis.com

CRISM Spectral Library—speclib.rsl.wustl.edu