Miocene-Pliocene Weddell Sea Record of Antarctic Glacial and Geologic History

by

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Abstract

Sediments were sampled from Ocean Drilling Program Site 694 in the Weddell Sea. The Middle Miocene to Lower Pliocene interval was sampled in order to better understand the relative timing and depositional sequences between turbidites and ice-rafted debris (IRD). This information will help us to better understand the development and stability of the East and West Antarctic ice sheets, and possibly the geologic history of East Antarctica.

The mineralogy of the sand fraction reveals a granitic source. The granitic material includes quartz, plagioclase and potassium feldspar, albite, biotite, and hornblende, supporting an East Antarctic Ice Sheet (EAIS) origin, while small amounts of augite and zeolites indicate some volcanic/island arc component is also present. Fluid inclusion analysis supports the mineralogy analysis and shows multiple provenances for the quartz grains.

Grain size analysis was performed using two methods: weight percent sieving and laser particle size analyzer. The analysis leads to the conclusion that ice was abundant on East Antarctica from the middle Miocene (~13 Ma) to the early Pliocene (~5 Ma). During the Early Pliocene turbidites are more common, suggesting an unstable ice shelf.
Introduction

The “White Continent” as Antarctica is known, gets its name from the distinct ice sheets that cover its surface: the East Antarctic Ice Sheet (EAIS) and the West Antarctic Ice Sheet (WAIS) by the Trans-Antarctic Mountains (TAM) which run through the center of the continent (Figure 1.). The WAIS is a marine based ice sheet with much of the land under the ice sitting below sea level (Figure 2.), while the EAIS is a primarily land based ice sheet. With global warming becoming an increasing concern, attention is being paid to the possible sea level changes that would occur if the AIS collapsed. The area of the most focus is the WAIS, because if the sea ice were to melt it could cause an acceleration of the land based ice out towards the sea (Bamber et al., 2009).

The primary goal of this research is to better understand the growth and collapse of the AIS during the Miocene-Pliocene transition (~5.3 Ma). There have been many previous studies to understand the stability of the Antarctic Ice Sheets (Table 1.).

<table>
<thead>
<tr>
<th>Ice Sheet Collapse during Pliocene</th>
<th>Ice Sheet Stability during Pliocene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine Diatoms found in 3 Ma volcanic layer, (Barrett et al., 1992)</td>
<td>No change in sedimentation during the Pliocene (Kennett and Hodell, 1993)</td>
</tr>
<tr>
<td>ANDRILL core shows 40 Kyr growth-collapse cycles based on the Earth’s obliquity, (Naish et al., 2009)</td>
<td>Diatoms are of eolian origin, not a collapse indicator, (Burckle and Potter, 1996)</td>
</tr>
<tr>
<td>Computer modeling based on ANDRILL core shows grow and collapse during the Pliocene, (Pollard and DeConto, 2009)</td>
<td></td>
</tr>
</tbody>
</table>
A previous study by Barrett et al. (1992) suggests that there was massive Antarctic deglaciation around 3 Ma. Barrett et al. found marine diatoms in a 3 Ma volcanic layer within the Antarctic interior. They concluded that there had to have been a deglaciation event that caused the glaciers to melt and sea level to rise to a level that would allow for the diatoms to be deposited directly on the continent.

This diatom theory created considerable debate as to whether the diatoms were deposited directly from a high sea level stand or possibly from eolian processes. To determine the method of deposition Burckle and Potter (1996) sampled Paleozoic and Mesozoic surfaces to determine whether the diatoms were unique to the 3 Ma volcanic layer, or if they were deposited randomly across all surfaces. There results showed that, regardless of age, all of the surfaces had diatoms of the same age as those found in the same layer that Barrett et al. (1992) had studied. This definitively showed that the diatoms were of an eolian origin.

In contrast to the suggestion made by Barrett et al. (1992) that there was a collapse of the Antarctic Ice Sheet, others showed that there could have been stability during the Early Pliocene. Kennett and Hodell (1993) used material from Ocean Drilling Program (ODP) Site 704, located in the South Atlantic, to determine ice rafted debris (IRD) fluctuations during the Early Pliocene. Ice rafted debris within a core is an indicator of advanced and stable glaciation because only stable and extensive ice sheets can deposit material far out to sea. Kennett and Hodell (1993) found that there was no change in deposition rates of IRD during the Early Pliocene that would indicate a change in the volume of Antarctic glaciers.
In contrast to the South Atlantic ODP Site used by Kennett and Hodell (1993), Naish et al. (2009) studied the ANDRILL core AND-1B taken from below the Ross Ice Shelf (Figure 1.). They focused on the top 600 m which includes the last 5 Ma of WAIS history. The study of the core revealed 38 unique 40 Kyr sequences of growth and collapse that are aligned with the oscillations in the obliquity, or tilt, of the earth’s axis. The sequences continue from the Early Pliocene through the Pleistocene, showing multiple events of growth and collapse.

As part of the same study of the AND-1B core, Pollard and DeConto (2009) created a simulation of how the observation seen in the core could be modeled. The model consisted of four parameters: sub-shelf oceanic melting, change in sea level, change in precipitation, and change in temperature. These four parameters were then run as a function of changes in $\delta^{18}O$ over the last 5 Ma. Oxygen isotope ratios are used as a proxy for paleoclimate, since they fractionate based on temperature, with the lighter $^{16}O$ evaporating and causing a high $^{18}O$ signature in times of colder. The model was able to accurately recreate the 40 Kyr oscillations seen in the ANDRILL core as well as many of the major glaciation and deglaciation events at 1.094 and 1.079 Ma, respectively.

Though most of the concern with the threat of global warming is centered on the WAIS, most of the study of the glacial history of WAIS has been done in only one basin. The WAIS has two large floating sea ice components: the Ross Ice Sheet in the Ross Shelf on the Pacific Ocean side, and the Ronne Ice Self in the Weddell Sea on the Atlantic side (Figures 1. and 2.). Barrett et al. (1992), Licht et al. (2005), Naish et
al. (2009) and Santis et al. (1999) all focus their glacial history studies and conclusions about the WAIS on sediments and work done concerning the Ross Sea and the Ross Sea Ice Shelf. Though Kennett and Hodell (1993) used material from Ocean Drilling Program (ODP) sites in the Atlantic, these sites were a significant distance from the Weddell Sea, along the same latitude as the Southern tip of South America, while my samples are located within the Weddell Sea Basin. Additionally, these studies only looked at ice rafting as the method of transport for sediment. Turbidites, or submarine debris flows, can send material thousands of meters out along the ocean floor. This study will look to see if turbidites can be identified along with IRD from core samples. IRD deposits material all at once and should have a varied grain size, while turbidites have a fining up stratigraphy and should have a homogenous grain size.

A secondary goal of this research hopes to further the understanding of the geology of the continent by characterizing the mineralogy of the sand fraction of the samples being studied. Glacial history will be determined looking at changes in the sand size fraction. By looking at the size distribution and composition of the sand, general times of increasing glaciations can be determined. Geologic history will be determined through two different techniques: grain counting using a Scanning Electron Microscope (SEM), and fluid inclusion analysis of quartz grains. By using an SEM with an EDAX X-Ray analyzer, exact chemistry of the grains can be determined, and from that, their mineralogy. Fluid inclusion analysis determines the type of fluids inside the inclusions and from that their metamorphic origins.
Previous work by Kanfoush et al. (2002) in the South Atlantic used sediment from the ODP Site 1094 piston core and the ODP Site 1094 core (in conjunction with the Vostok ice core) to identify IRD within cores and determine glaciation changes through time. Their study found that the best sediment parameter for identifying IRD was weight percent >150 µm. Additionally, Licht et al. (2005) used Ross Sea sediments and compared them to sediment taken from different glaciers flowing off of both East and West Antarctica. They found that there were unique signatures in the particle size and mineralogy that allowed them to identify the original source areas of the Ross Sea till and ice contribution during the last glacial maximum (LGM). The East Antarctic till samples contained mostly mafic intrusive lithic fragments and mudstones, while the West Antarctic till contained mostly quartz and felsic intrusive lithic fragments. The particle size analysis showed that the West Antarctic till was generally finer grained than the East Antarctic. No such studies have been done on Weddell Sea material. If the sand from the Weddell Sea does show distinct IRD and mineralogy, then a characterization of the WAIS can be done for both basins.
Physical Setting

The Weddell Sea is a 2.8 million square kilometer section of ocean extending from the area between East Antarctica and the Antarctic Peninsula (Figure 1.). Floating atop the Weddell Sea is the Ronne Ice Shelf. The Ronne-Filchner Ice Shelf is separated into the Ronne Ice Shelf, which extends from the Antarctic Peninsula to Berkner Island, and the Filchner Ice Shelf, which extends from Berkner Island to East Antarctica (Figure 2.). The Ronne Ice Shelf is larger than the Ross Sea ice shelf, drains 20% (or 3x10^6 square kilometers) of the total Antarctic Ice Sheet, and reaches a thickness of 1600 m (Jenkins and Doake, 1991).

East Antarctica is made of older cratonic rock, formed over several billion years (3 Ga - 1.7 Ga) (Figure 3.). West Antarctica, by contrast, is relatively young (less than 1 Ga) and composed of volcanic island arc terrains (Roy et al., 2009). Both are covered completely by ice (WAIS and EAIS) and very few rock outcrops exist, with the existing ones being along the tops of the TAM and the coasts.

Geology of the Weddell Sea Area

Antarctic Peninsula

The youngest rocks within the Weddell Sea area are located at the tip of the Antarctic Peninsula. The tip of the Antarctic Peninsula is made up of the Jurassic Botany Bay Group (Rees, 1993). The Botany Bay Group is made up of interbedded conglomerates, sandstones, silt stones, and mud stones, as well as lapilli and crystal tuffs and silicic ignimbrite. The U-Pb zircon dates give the group an age of 167.1
±1.1 Ma (within the Middle Jurassic), before the rifting that opened up the Weddell Sea basin (Hunter et al., 2005).

Further south is the 170 Ma volcanic Mapple Formation that erodes into the Larsen Basin in the western part of the Weddell Sea (Hunter et al., 2006). The Mapple Formation consists of rhyolite lava, ignimbrites, and epiclastic deposits interbedded with lava flows (Riley and Leat, 1999). The final basin on the Weddell Sea side is the Latady Basin in the south western corner of the Weddell Sea (Figure 4.). This basin receives material from the 183 Ma volcanic Brennecke Formation and the 183 Ma Ellsworth Land Volcanic Group. The Brennecke Formation consists of rhyolitic lava flows, pyroclastic rocks, black shales, and basaltic lavas (Pankhurst et al., 2000). The Ellsworth Land Volcanic Group consists of mostly amygdaloidal basalt (Hunter et al., 2006).

The formation of the Weddell Sea Basin and the Antarctic Peninsula began with intra-continental rifting during the Early Jurassic, separating the Ellsworth Land Volcanic Group from the Trans-Antarctic Mountains. This rifting continued until the Botany Bay Group was separated from the mainland East Antarctica. Rifting and back arc volcanism continued, causing the peninsula to move to its current location (Hunter and Cantrill, 2006).

**South Eastern Weddell Sea Coast**

Two mountain ranges make up the south eastern coast of Antarctica: the Shackleton Range and the Pensacola Mountains (Figure 1.). The Shackleton Range is made up ophiolites, granite, and ultramafic rocks, specifically garnets, pyroxenes,
and olivine. The age of the metamorphism of the rocks in the Shackleton range is between 525 Ma and 520 Ma (Romer et al., 2009). The Pensacola Mountains are composed of five different sequences of sedimentary, volcanic, and metamorphic rocks that range in age from the Precambrian to the Jurassic. The first sequence consists of turbidites and mafic lavas, as well as a granitic protolith of the gneiss within the formation. The second sequence consists of limestone capped by felsic volcanic rocks. The third sequence consists of mudstones, sandstones, and limestone. Sequence four is an unconformity that sits on top of the previously mentioned three sequences and contains mostly the same sedimentary features found in sequence three. Sequence five consists of sandstone overlaid by mudstone (Storey et al., 1996).

Glacial History: Eocene to the Present

The glacial history of Antarctica in the Eocene begins at 36 Ma, when small ephemeral ice sheets began to appear on Antarctica (Figure 5., Table 2.). They continued to form 12 Ma (in the Middle Miocene), when the East Antarctic Ice Sheet became stable. This was followed by the final formation of the West Antarctic Ice Sheet 6 Ma, in the Late Miocene (Zachos et al., 2001, Table 2.).
Table 2. Major Glacial Events since the Eocene.

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>36 Ma (Eocene)</td>
<td>First ephemeral ice sheets appear, (Zachos et al., 2001)</td>
</tr>
<tr>
<td>19 Ma (Miocene)</td>
<td>First evidence for glaciation on Ross shelf, (Santis et al., 1999)</td>
</tr>
<tr>
<td>12 Ma (Miocene)</td>
<td>East Antarctic Ice Sheet becomes stable on the continent (Zachos et al., 2001)</td>
</tr>
<tr>
<td>6 Ma (Miocene)</td>
<td>West Antarctic Ice sheet becomes fully formed (Zachos et al., 2001)</td>
</tr>
<tr>
<td>5 Ma to Present</td>
<td>Growth and collapse events (Table 1.)</td>
</tr>
<tr>
<td>(Pliocene to present)</td>
<td></td>
</tr>
</tbody>
</table>

Though Zachos et al. (2001) used δ¹⁸O to determine Antarctic Ice Sheet events, other studies focused on alternate ways of determining the onset of glaciation. Santis et al. (1999) used seismic profiles of the Ross Sea Shelf to determine when the WAIS had formed. They based their study on the theory that natural continental shelves slope gradually, while the ice sheets would cause not only sharp drop offs, but the shelf would also be inclined due to the weight of the ice. With a combination of computer modeling and seismic profiling, Santis et al. (1999) found evidence for ice on the Ross Shelf between 19 Ma and 13 Ma, during the Early to Middle Miocene.
Methods

Sample Selection

Samples were selected by a review of the *Proceedings of the Ocean Drilling Program, Initial Reports* from Leg 113. Site 694 was selected because of its location in the central Weddell Sea basin, the long age interval, and the availability of material. Samples were preferentially selected for those that would yield the coarse material most likely to contain IRD and would therefore be the most useful for grain counting and other analyses.

Particle Size Analysis

For each sample approximately half (~15 grams) were weighed to get an initial dry weight. They were placed in a 50 ml centrifuge tube with ~30ml of Calgon water, to separate the silt and clay particles, for at least 24 hours. The samples were then vortexed for 30 seconds to break up remaining silt and clay. After vortexing, the samples were wet sieved and separated into four different size fractions: less than 63µm, 63 to 150 µm, 150 µm to 2 mm, and greater than 2 mm. The sieved samples were then transferred into weighing dishes and excess water was pipetted out. When completed, the three coarse fractions were then weighed and stored in vials.

Additionally particle size analyses were done using a Horiba LA-950 laser particle size analyzer. The LA-950 works on the principle that particles of different sizes scatter light in different ways. By measuring the angle and intensity of the scattered light it can determined if a particle is large (high intensity at low angles) or
small (low intensity at low angles). The LA-950 employs a second shorter wavelength laser which is better for determining the size of nano scale particles. Three analyses of each sample were run to check for reproducibility and compared via printouts. The sample material used for this analysis was taken from the material that was not sieved.

Sand Petrography Analysis

Five samples were selected for grain mounts. The grains were mounted in epoxy, polished, and left uncovered for use in Wesleyan University’s Scanning Electron Microscope. The samples were coated with approximately 100 Å of carbon per slide using a Balzers Cold Sputtering Coater with a carbon-thread attachment. Carbon coating provides a conductive layer for the slide to prevent sample charge. Slides were viewed under a JEOL 6390LV Scanning Electron microscope with an accelerating voltage of 20 kV. The sample was viewed at 33x magnification and once a field of view had been selected the atomic composition was determined using an EDAX X-Ray Microanalysis tool.

For each sample, grain counting began at the lower left corner of the slide’s label and continued diagonally right of that point down the slide. At total of 300 grains were analyzed per slide. This method of slide analysis was chosen because it allowed for a method that was reproducible on each slide, due to the standardized location of the slide labels. Additionally, starting at the corner of the slide label allowed for a recognizable starting point for petrographic microscope analysis.
Grain counting was done by the method described by Suttner (1974) and Suttner and Mack (1981) which involved counting for multiple minerals as opposed to counting only for quartz, feldspar, and lithic fragments. Additionally, SEM analysis has been used in provenance studies in the past (Kwon and Boggs, 2002) with positive results compared to petrographic analysis.

Fluid Inclusion Analysis

Fluid inclusion analyses were done for 15 to 20 grains from three samples. Grains were ground and polished on both sides for viewing under a petrographic microscope. Two methods were used to select quartz grains for the fluid inclusion study. The first method was to mount a group of mixed >150 µm sized grains on a slide and individually pick out the quartz after the grains had been ground and polished. The second method, the one that was used for the majority of the study, involves mounting 50 randomly chosen quartz grains. The grains were preferentially selected by the maximum number of visible inclusions for use in the 15 to 20 grain subset and analyzed in the fluid inclusion microscope stage.

The grain is heated until the vapor bubble within the fluid inclusion homogenizes with the fluid in the inclusion (118-354 °C). This is the homogenization temperature. The grain cools naturally to ~50°C, at which point liquid nitrogen is used to cool the grain to -115±5°C in order to freeze the fluid in the inclusion. The grain warms back to room temperature and the temperature at which the fluid is completely melted is a salinity indicator.
Results

Due to the lack of microfossils and poor recovery at Site 694, there is very poor age resolution. The age of the samples located at depths 121.96 and 131.2 mbsf are not actually known as being either from the Lower Pliocene or the Upper Miocene. For the purposes of this study it was decided that they were Lower Pliocene samples, and the first Upper Miocene sample was at 150.64 mbsf.

Particle Size Analysis

Particle size analysis focused on the wt. % (Figure 6.) and grain size distribution data. Horiba particle size distribution was done by separating the particle distribution graphs into different size groups as follows: clay = 1 to 4 microns, silt = 4 to 63 microns, sand = 63 microns to 4 millimeters. Pebble size particles (>2 millimeter) were rare and thus were grouped with the sand fraction for particle size distribution. Because Site 694 covers the Middle Miocene to the Lower Pliocene the analysis will be discussed in terms of the three major time periods covered in the data: the Middle Miocene, the Upper Miocene, and the Lower Pliocene.
Middle Miocene Particle Size Analysis

Coarse Fraction

The Middle Miocene section of Site 694 includes material from the bottom 135 meters of core material (Figure 7.). There is a general trend towards increasing percent of the sand fraction going up core in the Middle Miocene. No samples contained material >2 mm. The wt. % 150 µm – 2 mm of the bottom 40 meters of core material is near zero (<3%) until rising up to above 35% at the top of the section. The wt. % 63 µm – 150 µm follows the same trend, except it fluctuates between 10% and 40% for the top 100 meters as opposed to generally increasing in weight percent.

Horiba Particle Size Distribution Analysis

The particle size distribution follows a similar pattern to the weight percent distribution (Figure 8.). The samples from the bottom 40 meters all contain less than 15% sand sized particles and greater than 80% silt sized particles. The top 95 meters of samples contain greater than 40% sand sized particles, with the exception of one sample at 287.78 mbsf, which has a large clay fraction. Additionally, the Middle Miocene section contains the samples with the largest fractions of clay. The coefficient of variation (CV) for the bottom two samples is nearly the same (at 58% and 59%), while the CV for the top 115 meters of the section fluctuates between 80% and 120%. This trend follows the particle size distribution graphs, with the bottom two samples being unimodal and the top 115 meters of samples multimodal.
Upper Miocene Particle Size Analysis

Coarse Fraction

The Upper Miocene section of Site 694 includes material from the next 106 meters (Figure 9.). There was no >2 mm material (>1%) in the Upper Miocene. The bottom 76 meters contain between 30% and 55% material 150 µm – 2 mm, with the exception of one sample at 227.8 mbsf that is below 10%, while the top two samples contain <1% material 150 µm – 2 mm. The wt. % 63 µm – 150 µm follows the same trend, fluctuating between 20% and 35% for the bottom 76 meters, before dropping below 4% for the top two samples.

Horiba Particle Size Distribution Analysis

The particle size distribution follows a similar trend to the weight percent analysis (Figure 10.). The bottom 76 meters contains a mix of clay to sand, with all samples having around 50% sand sized material. The first two samples contain exclusively silt, 100% and 93% respectively. The coefficient of variation of the samples within the Upper Miocene fluctuates between 65% and 110%, except for the top sample which has a CV of 54%. All of the samples have multimodal particle size distributions, except for the top sample, which has a unimodal distribution.
Lower Pliocene Particle Size Analysis

*Coarse Fraction*

The Lower Pliocene sample section of Site 694 encompasses the top 131 meters of core material (Figure 11.). The Lower Pliocene is the only section that has any significant >2 mm contribution, with three samples above 5% (Figure 6.). The bottom 110 meters fluctuate between 5% and nearly 100% material 150 µm – 2 mm, until the top 20 meters, where there is <1%. The wt. % 63 µm – 150 µm follows no trend and changes between 0% and 40% going up the whole section, with the exception of 21.7 mbsf at 58%.

*Horiba Particle Size Distribution Analysis*

The particle size distribution follows a similar trend as the wt. % 150 µm – 2 mm, with the bottom 110 meters dominated by >70% sand-sized particles, with the exception of 121.96 mbsf, which only has 20%. The top 20 meters contain >70% silt-sized particles. The coefficient of variation varies from 30% to 120% throughout the entire core and does not show any difference between the bottom 110 meters and the top 20 meters. The particle size distributions also vary through the core in a similar fashion to the CV.

Mineralogical Analysis

The samples used cover the time from the Lower Pliocene (19.14, 36.08, and 113.2 mbsf) to the Upper Miocene (198.82, and 237.05 mbsf). There were no samples from the Middle Miocene.
The samples all show a similar mineralogical composition with some differences (Figure 13.). More than 60% of the grains are quartz, the most abundant mineral observed. The next most abundant mineral species were feldspars, in the forms of potassium feldspar, plagioclase feldspar, and albite. Only the sample at 36.08 mbsf had less than 20% of its composition made up of mixed feldspars. The amount of plagioclase feldspar was between 5% and 10%, while amounts of potassium feldspar ranged from 5% to 15%, with the 36.08 mbsf sample containing the 5% potassium feldspar composition.

The remaining minerals were: augite, biotite, calcite, clays, hornblende, muscovite, and zeolites, all in abundances of less than 5% of the sample. Lithic fragments were not counted separately because the SEM is not able to distinguish lithics from minerals.

*Statistical Analysis of Mineral Counts*

Analysis of the difference between two proportions was done to determine if the differences between the compositional counts were in fact statistically significant. This technique is used to tell if the difference between two proportions is significant or not by calculating if zero is within its upper and lower bounds. If zero is within the upper and lower bounds of the calculation, then the two proportions are not statistically significant. The sample at 36.08 mbsf contained a different particle size distribution than the other mineralogical samples. I looked at a single mineral and compared the percentage at 36.08 mbsf to the sample with the next lowest/highest percentage. If there was a statistical difference between the
sample at 36.08 mbsf and the sample with the next closest percentage of that mineral, then the sample at 36.08 mbsf would be statistically different than all the rest of the samples.

For example, the quartz percentage at 36.08 mbsf (84.33% quartz) was compared to the sample 198.82 mbsf (75.33% quartz) and the differences were statistically significant. The potassium feldspar percentage at 36.08 mbsf (5.00% potassium feldspar) was compared to the sample at 19.14 mbsf (8.00% potassium feldspar) and the differences were not statistically different. When repeated with the other three samples, a statistical difference was found for each. The total feldspar percentage at 36.06 mbsf (13.33% feldspars) was compared to the sample at 237.05 mbsf (20.00%) and the differences were statistically significant (Table 3.).

Table 3. Statistical differences between sample 36.06 mbsf for different minerals.

<table>
<thead>
<tr>
<th>Sample Depth in mbsf</th>
<th>Stat. different than 36.06 mbsf for quartz?</th>
<th>Stat. different than 36.06 mbsf for potassium feldspar?</th>
<th>Stat. different than 36.06 mbsf for total feldspars?</th>
<th>Stat. different than 36.06 mbsf for all other minerals?</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.14</td>
<td>YES</td>
<td>NO</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>113.2</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>198.82</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
</tr>
<tr>
<td>237.05</td>
<td>YES</td>
<td>YES</td>
<td>YES</td>
<td>NO</td>
</tr>
</tbody>
</table>

Fluid Inclusion Analysis

Fluid inclusion analysis was done in order to find another way to characterize the provenance of the sand-sized fraction of the samples at depths of 26.9 mbsf, 92.48 mbsf, and 107.9 mbsf from Site 694 from the >150 µm fraction of sand.
Homogenization Temperatures

The homogenization temperatures vary across all samples from a low of 27.1 °C to a high of 381.5 °C (Figure 14.) making it difficult to identify any notable patterns within the data. However, 75% of the homogenization temperatures fall between 150 °C and 275 °C. Only the sample at 92.48 mbsf does not have any homogenization temperatures above 300 °C and the sample at 107.9 mbsf is the only sample to not have any homogenization temperatures below 125 °C.

Melting Point Temperatures

Over 75% of the melting temperatures are between 2 °C and -4 °C (Figure 15.). Additionally, all of the melting points are >-22 °C, with the exception of one with a melting point of -55.7 °C. The depression of the melting point is related to the salinity of the fluid inside the inclusion; the higher the salinity, the lower the melting point, as seen in Figure 16. Seventy-five percent of the inclusions contain fluids that have a salinity of 5% or lower.

Comparison of Melting Temperatures to Homogenization Temperatures

When plotted against each other in Figure 17, it is easy to see the great variety and range of the different fluid inclusions observed in the quartz grains sampled. The inclusions from the grains at 92.48 mbsf cluster within the same general area between 120 °C and 220 °C for homogenization temperatures and between 1 °C and -5 °C for melting temperatures. The inclusions from the grains at 107.9 mbsf all have relatively similar melting temperatures, and therefore similar salinities, but encompass a wide range of homogenization temperatures. The
inclusions from 26.9 mbsf have the widest array of both temperatures of homogenization and melting point. Sixty inclusions had both homogenization temperatures and melting point temperatures recorded.
Discussion

Particle Size

Horiba data was compared with the wt. % from the sieve data and for both methods wt. % >63 µm data were almost an exact match (Figure 18). Particle size analysis included grain size distribution to better understand the composition of the samples. Particle size distribution graphs belong in two general categories: a unimodal distribution of particle sizes, and a multimodal distribution. Since turbidites settle fining up, the unimodal distributions were interpreted to be parts of turbidites, while the samples with multimodal distributions were interpreted to be IRD deposits. Because turbidites have a uniform grain size, it would be possible that a sample could be a turbidite even with high weight percent >150 µm, if the grain size was uniform. Grain size analysis was done in order to determine if the Kanfoush et al. (2002) method of high wt. % >150 µm as a proxy for IRD was an accurate analysis method. When interpretation of the size distribution graphs was compared to the coefficient of variation data, it was found that all samples with a CV of lower than 60% had unimodal distributions and all those above 60% had multimodal distributions.

Based on the Kanfoush et al. (2002) method, the general interpretation of the Middle Miocene section could be an increasing amount of IRD. Since the lower interval of the Middle Miocene section contains little to no wt. % material >150 µm, the conclusion would be that there was no IRD during this time period. However, only the bottom two samples have CV values less than 60%, while the rest going up
section are above 60%. This leads to the interpretation that there was a large amount of IRD, and therefore a stable, growing ice sheet during the Middle Miocene-Upper Miocene boundary, as evidence by the increasing CV value.

The Upper Miocene section of core contained little IRD, since half the samples have less than 10% wt. % >150 µm (Figure 9.). An interpretation of the data for the Late Miocene would be that it was a time of ice sheet instability with a severe instability event or collapse near the Late Miocene-Early Pliocene boundary, but since the CV is above 60% for all but the top most sample, the conclusion would be that the ice sheet was stable. The declining CV percentage to below 60% at 150.64 mbsf could indicate a general decline in overall stability of the ice sheet during this time.

The majority (13 out of 21) of Lower Pliocene samples with greater than 30% >150 µm suggest an abundance of IRD (Figure 11.). The fluctuation during the lower part of the Lower Pliocene material could mean a change in the ice sheet or some mild instability. Additionally, the lack of wt. % >150 µm material in the top 20 meters of the Lower Pliocene section probably means a reduction in ice sheet stability or collapse. The fluctuating CV value for the Lower Pliocene indicates that there were times of ice sheets and turbidites. The interpretation of this section would be that the ice sheet was very unstable and that there were fluctuations between growth and collapse events. This interpretation is similar to the ANDRILL data interpretation from Naish et al. (2009).
Taken as a whole, based on the CV data, the ice sheet began to form some time during the Middle Miocene with some instability going through the Late Miocene, as evidence by the lack of abundant wt. % >150 µm (IRD) peaks in the graph and declining CV (Figure 19.). This is followed by the Early Pliocene where the ice sheet was in a constant state of flux with a combination of IRD and turbidites.

Mineralogy

Sample Composition and Provenance

The abundance of quartz and feldspars and the trace amounts of biotite, hornblende, and muscovite lead to the conclusion that these minerals most likely came from a granitic source (Press and Siever, 1986). I come to this conclusion because the composition of granites is usually quartz and feldspars, and albite is especially abundant. The small amount of zeolites and augite suggest a minor volcanic source for the minerals.

Since East Antarctica contains older granitic and cratonic rocks, it is most likely that it is the source for the granitic minerals, while the volcanic minerals are probably from West Antarctica which is younger and made up of island arcs.

Differences between IRD and Turbidite Sample Mineralogy

The unimodal grain size distribution of sample 36.08 indicates that it is a turbidite. Notable trends for the mineralogy of the sample as a turbidite include an abundance of quartz and a scarcity of feldspars.
One of the ways of identifying a turbidite deposit in an ocean core versus an IRD core would be to look at the abundance of quartz and the scarcity of feldspars. The ratio of feldspar to quartz in the turbidite deposit was 0.15 while the average ratio of the other four samples was 0.31. While one turbidite sample is not enough to characterize all of them, the low feldspar to quartz ratio when compared to other samples would be a definite indicator of turbidite rather than IRD deposit.

Fluid Inclusions

Though no definitive conclusion can yet be drawn from the homogenization temperatures alone, when combined with the melting point temperatures there is a possible indication of multiple quartz sources. The first conclusion is that for the majority of the samples the fluid within the inclusions is brackish water. This conclusion is made by the fact that the salinities were mostly below 10%, which would be considered brackish. The higher salinities could be considered saline or even brine, but the majority of the fluid in the quartz inclusions, regardless of homogenization temperature, is brackish water.

The second conclusion that can be drawn from the melting points is based on the salinity of the fluids, more specifically, the conditions that could produce such fluids. Low salinity (<5%) brackish water is typically found in midcontinent metamorphism, while high salinity brines (>10%) are typical of basinal brines (Hanor, 1994 and Yardley and Graham, 2002). This means that most of the quartz contains fluids that would have come from a midcontinent metamorphic region, like East
Antarctica. The quartz grains with the higher salinity are most likely from West Antarctica or from the volcanic Antarctic Peninsula.

Though nothing can be determined about the quartz grains as a whole, there were some remarkable differences between the samples. The sample at 26.9 mbsf had the lowest melting temperatures, which correlate to highest salinity and most likely an island arc origin. The youngest sample contains the most inclusions of possible volcanic origin, meaning there might have been active volcanism during deposition in the Early Pliocene.

Figure 17 shows that the inclusions from 92.48 mbsf cluster between 120 °C and 220 °C for homogenization temperatures and between 1 °C and about -5 °C for melting point temperatures. This tight distribution is not seen in the other two samples, which could mean that this sample’s provenance is different from the other two. Since the sample is IRD, these quartz grains could have come from the same rock source, pulled off as the ice was cutting through, and deposited together.
Conclusions

There was EAIS growth and stability during the Middle Miocene within the Weddell Sea as evidenced by the CV >60% and the East Antarctic origin of the mineralogy samples. This led to continued stability through the Late Miocene and ice sheet instability during the Early Pliocene, based on the fluctuations of IRD and turbidite deposits as indicated by the CV values.

This study additionally shows the important contribution of total grain size to distinguish IRD from turbidites. Though the weight percent data can give an accurate answer, it is biased by coarse grained material and therefore cannot accurately distinguish between IRD and the coarse section of turbidite deposits. This is why it is important to determine the particle size distribution of the sample material, to better understand the fluctuations between IRD and turbidite deposits.

Two different sources were observed for the sand material in the Weddell Sea basin. The analysis of the mineralogy of the >150 µm sized fraction of several samples revealed a granitic/metamorphic provenance for the majority of the sample, with a minor contribution from a volcanic/island arc source, as evidenced by the zeolites and augite in the samples. In addition to using the observed mineralogy, the fluid inclusion analysis reveals that there are multiple quartz source areas within Antarctica. The fluid inclusion analysis also supports the mineralogy conclusion that there is a large metamorphic source for the sand fraction as well as a minor volcanic source. Through the use of these two analyses, the conclusion can be made that the majority of the material being deposited within the Weddell Sea basin originates
from the craton of East Antarctica and was transported by both ice rafting and 
turbidites.

The distinction between IRD and turbidites was made from many different 
analyses (Table 4.). Turbidite deposits had low feldspar to quartz ratios, unimodal 

grain size distributions, CV values below 60%, and multiple sources for the quartz 
within the sample. IRD deposits had higher feldspar to quartz ratios, multimodal 

grain size distributions, CV values above 60%, and possibly one source for the quartz 
within the sample.

Table 4. Summary of results.

<table>
<thead>
<tr>
<th>Sample Depth (mbsf)</th>
<th>Age (MM, UM, LP)</th>
<th>Wt. % &gt; 150</th>
<th>CV</th>
<th>Mineralogy (% quartz, % feldspar, % zeolite, % augite)</th>
<th>Felds:Quartz</th>
<th>Fluid Inc.</th>
<th>Mode of Particle Size Distribution</th>
<th>Turbidite or IRD?</th>
</tr>
</thead>
<tbody>
<tr>
<td>19.14</td>
<td>LP</td>
<td>30%</td>
<td>75%</td>
<td>74%, 22%, 2%, 1%</td>
<td>0.29</td>
<td>NA</td>
<td>Multimodal</td>
<td>IRD</td>
</tr>
<tr>
<td>26.9</td>
<td>LP</td>
<td>97%</td>
<td>34%</td>
<td>NA</td>
<td>NA</td>
<td>Multiple possible sources</td>
<td>Unimodal</td>
<td>Turbidite</td>
</tr>
<tr>
<td>36.08</td>
<td>LP</td>
<td>44%</td>
<td>37%</td>
<td>84%, 13%, 0%, 1%</td>
<td>0.15</td>
<td>NA</td>
<td>Unimodal</td>
<td>Turbidite</td>
</tr>
<tr>
<td>92.48</td>
<td>LP</td>
<td>77%</td>
<td>89%</td>
<td>NA</td>
<td>NA</td>
<td>Possibly one source</td>
<td>Multimodal</td>
<td>IRD</td>
</tr>
<tr>
<td>107.9</td>
<td>LP</td>
<td>68%</td>
<td>32%</td>
<td>NA</td>
<td>NA</td>
<td>Multiple possible sources</td>
<td>Unimodal</td>
<td>Turbidite</td>
</tr>
<tr>
<td>113.2</td>
<td>LP</td>
<td>5%</td>
<td>71%</td>
<td>75%, 20%, 1%, 1%</td>
<td>0.27</td>
<td>NA</td>
<td>Multimodal</td>
<td>IRD</td>
</tr>
<tr>
<td>198.82</td>
<td>UM</td>
<td>9%</td>
<td>106%</td>
<td>65%, 27%, 3%, 2%</td>
<td>0.41</td>
<td>NA</td>
<td>Multimodal</td>
<td>IRD</td>
</tr>
<tr>
<td>237.05</td>
<td>UM</td>
<td>36%</td>
<td>88%</td>
<td>67%, 20%, 5%, 1%</td>
<td>0.3</td>
<td>NA</td>
<td>Multimodal</td>
<td>IRD</td>
</tr>
</tbody>
</table>
Future Work

For future studies, more samples will be requested from Site 694 to better understand the trends seen in the data. For example, there are many sections where tens of meters are defined by one or two samples. In order to better constrain these observations more samples will be requested. Additionally, new techniques will be employed to analyze the samples including: searching for zircons, dating of hornblendes, and bulk chemistry through the use of Wesleyan’s new XRF.

In addition to more samples from ODP Site 694, there will be samples requested from ODP Sites 693 and 696. Site 693 contains core material from the Middle Miocene to the Middle Oligocene, and Site 696 contains material from the Middle Oligocene to the Late Eocene. With these samples and the samples from Site 694, I will be able to create a more complete glacial record from the Late Eocene through the Early Pliocene.
Figure 1: Map of Antarctica showing ice flows, location of Trans-Antarctica Mountains, and locations of relevant study areas (Naish et al., 2009). Green Triangle represents location of the Shackleton Range and the orange triangle represents the location of the Pensacola Mountains.
Figure 2: Map of West Antarctic Ice Sheet depicting whether the ice is grounded above, at or below sea level (Mercer, 1978).
Figure 3: Depictions of the orogenies that formed East Antarctica (Grikurov, 1982). The darkest grays depict pre-existing crust.
Figure 4: Map showing the Basins and relevant formations in and around the Antarctic Peninsula (Hunter et al., 2006).
Figure 5: Graph showing changes in $\delta^{18}O$ and major climatic events over the last 65 Ma (Zachos et al., 2001).
Figure 6: Weight percentage of the three different sized sand fractions for the entirety of Site 694.
Figure 7: Weight percentage of two different sized sand fractions for the Middle Miocene section of Site 694.
Figure 8: Graph of the coefficient of variation within the particle sizes of the Middle Miocene samples (left) and the distribution of three different particle sizes (right).
Figure 9: Weight percentage of two different sized sand fractions for the Upper Miocene section of Site 694.
Figure 10: Graph of the coefficient of variation within the particle sizes of the Upper Miocene samples (left) and the distribution of three different particle sizes (right).
Figure 11: Weight percentage of two different sized sand fractions for the Lower Pliocene section of Site 694.
Figure 12: Graph of the coefficient of variation within the particle sizes of the Lower Pliocene samples (left) and the distribution of the three different particle sizes (right).
Figure 13: Percentages of different minerals identified from counting using the SEM. The asterisks denote a sample with a unimodal particle size distribution.
Figure 14: Frequency of homogenization temperatures from fluid inclusions found inside quartz grains at different depths.
Figure 15: Frequency of freezing point temperatures from fluid inclusions found inside quartz grains at different depths.
Figure 16: Graph showing the relationship between freezing point of the fluid inclusions and the salinity derived from the freezing point depression.
Figure 17: Plot of the fluid inclusions that have both homogenization and melting point temperatures.
Figure 18: Plot of weight percent >63 µm determined via manual sieving and the percent >63 µm determined from the Horiba Particle Size Analyzer.
Figure 19: Comparison of weight percent >150 µm to the coefficient of variation of the grain sizes going down core of Site 694.
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