

Environmental interpretation of Marine Isotope Stage
M2 (3.312-3.264 Ma) and Turnover Pulse D (3.55-3.4
Ma) through the use of diatoms in the Weddell Sea,
Antarctica

by

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Abstract

Over the last 5 million years, the global benthic foraminiferal $\delta^{18}\text{O}$ record shows a $\sim+1.5\%$ shift reflected by colder temperatures and increase ice cover. The Marine Isotope Stage M2 (3.312-3.264 Ma) is a global glaciation event that corresponds to a $\sim+0.5\%$ shift. This 50 thousand year event, associated with a 20 to 60 m sea level drop, precedes Arctic glaciation and is associated with the onset of the glacial-interglacial cycles of the Quaternary. Turnover Pulse D (3.55-3.40 Ma) is an enigmatic Southern Ocean diatom turnover event that correlates with rising temperatures and ice retraction. The focus of this study is to quantify the environmental characteristics of these two major mid-Pliocene events.

The samples used in this study are from ODP Site 697 from ~ 3.6 - 3.2 Ma. We examined the diatom community of 31 samples for their use as paleoenvironmental proxies. Diatom assemblages through our ~ 400 kyr sample interval are generally characterized by open ocean related species and record a period of decreasing warmth. Species associated with Cold/ Sea-Ice related conditions comprise only a small percentage of the diatom assemblages, but indicate the presence of icebergs throughout the entire study interval. The high abundance of the warm species *S. oestrupii* demonstrates that the modern cold conditions attributed to the Weddell Sea are not yet established, even during the MIS M2 glaciation event. Future studies should implement the diatom assemblage data presented here to further constrain the paleo-latitudinal position of the major Antarctic fronts.

I. Introduction

The goal of this research is to quantify the environmental characteristics of two major events from the mid-Pliocene: diatom turnover pulse D (Pulse D) (3.55–3.40 million years ago (Ma)) and Marine Isotope Stage M2 (MIS M2) (3.312-3.264 Ma). It is unclear whether Pulse D and MIS M2 are connected in any way, since these two events are relatively understudied. Here we use the ODP Site 697 diatom record, off the Weddell Sea margin of Antarctica, to describe the environmental conditions present during this short and eventful mid-Pliocene interval. The central hypothesis underpinning this research is that Pulse D was caused by a warming event that decreased sea-ice cover, in turn driving open ocean diatoms to dominate the assemblages. MIS M2 is a global glaciation event, correlated to a 20-60 m sea-level drop, which we hypothesize will result in significant changes to the diatom record associated with cooler conditions.

Our analysis will help determine the impacts associated with these two events, and will also help further constrain the paleo-latitude position of the major oceanic fronts within the Southern Ocean. The relative abundance of sea-ice adapted and non-sea-ice adapted diatoms is also supplemented by biosilica weight percent (wt. %) and coarse fraction (ice-rafted detritus, IRD) analysis (Kaufman, 2016; Luna, 2018).

i. Background

A. The Pliocene Epoch (5.33-2.58 Ma)

According to the International Committee of Stratigraphy, the Pliocene Epoch includes two stages: the Zanclean (5.33-3.6 Ma) and the Piacenzian (3.6-2.58 Ma)[Gibbard et al., 2010]. During this span of time, Earth's climate was transitioning

from the relatively warm conditions of the early Pliocene to a cooler climate (Liseicki and Raymo, 2005).

Relative to today, the Pliocene was a generally warm and wet interval (Salzmann et al., 2011). Elevated atmospheric CO₂ concentrations have been suggested to be the main reason for higher global temperatures during the Pliocene (e.g. Pagani et al., 2010). Based on the interpretations from the carbon isotope composition of marine organic matter, atmospheric CO₂ levels averaged 380 parts-per-million (ppm) and peaked at 425 ppm, making it the most recent interval in Earth's history when atmospheric CO₂ concentrations were at or slightly above modern levels (Raymo et al., 1996). Global mean annual surface temperature (MAT) during the Piacenzian are estimated to have been 2 to 3°C higher than today, with a reduced equator to pole gradient (Haywood et al., 2000; Lunt et al., 2010). Furthermore, paleogeography, ocean bathymetry and paleobiology during the Pliocene were very similar to current conditions (Salzmann et al., 2009). Therefore, the warm conditions experience in the Pliocene provides a plausible analog for future climate warming during the 21st century.

B. ODP Leg 113, Site 697

The Ocean Drilling Program (ODP) was an international cooperative effort that conducted 110 expeditions and drilled 2000 drill holes (“History”). Site 697 (61°48.626'S, 40° 17.749'W) is a drill hole located in the Weddell Sea within the Jane Basin and is 3480 meters below sea level. Site 697 is the deepest of a three-site depth transect of the South Orkney microcontinent (SOM) drilled during ODP Leg 113 (Barker et al., 1988)[Fig. 1.1].

Considering its deep open-ocean location and distance from Antarctica, Site 697 is located beyond the reach of glacial erosion, allowing for the preservation of the climatic and glaciation event MIS M2 in the sediment record. Its distance from the Antarctic margin restricts our ability to record a direct proximal biological response to Antarctica's glacial history, but provides an opportunity to assess the relative influence of, and changes in, the Antarctic Circumpolar Current's major circumpolar fronts (i.e. the Antarctic Polar Front (PF) and the sub-Antarctic Front (SAF)).

C. Proxy Records

Proxy records are used to study the climate of the Pliocene, or any span of time that predates human record-keeping. Proxy records preserve information about Earth's history, which enable scientists to reconstruct past climatic conditions.

This study implements multiple proxy records found in marine sediment cores in the Antarctic region that provide insight into the climatic conditions that characterize this important time period.

D. Diatoms

Diatoms are the main biogenic tracer for past surface ocean water conditions and sea surface temperature (SST) at Site 697 during the mid-Pliocene, since other microfossil groups are virtually absent due to ecological exclusion and poor preservation. The first physical remains of diatoms date back to the Jurassic Period, but may have been present much earlier (Sims et al., 2006). They are extremely diverse, with estimates of the number of species on the order of 10^5 (Mann and Droop, 1996). They are also sensitive to environmental conditions and are able to inhabit virtually any environment with moisture and sunlight, making them an especially versatile and accessible paleoclimate indicator (Crosta and Koc, 2007).

Diatoms are of critical interest today because they contribute an estimated 45% of total oceanic primary production; they are the dominant living marine phytoplankton group, and their macroevolutionary history is linked to changes in climate (Yool and Tyrell, 2003; Lazarus, 2014).

E. Ice Rafted Detritus/ Biosilica

Near the Polar Regions, marine sediment cores preserve unique terrigenous sediment known as ice-rafted detritus (IRD). These IRD grains are eroded from the continental bedrock by calving glaciers and are trapped within floating icebergs, which carry the sediment out into the open ocean (Alley et al., 1997). Ocean currents can transport these icebergs for thousands of miles before they completely melt, depositing the IRD grains far away from their original terrigenous locations (e.g. Williams et al., 2010). Our minimum grain-size threshold for distinguishing IRD is defined as coarse fraction sand: 63 μm and above (Kaufman, 2016). Mineralogical analysis from Diekmann & Kuhn (1999) demonstrated that coarse fraction deposition to hemipelagic/pelagic ocean depths is only possible through ice rafting. Therefore, IRD is used as an index for ice-rafting intensity and glacial variability and has been suggested to record glacial cycle fluctuations (e.g. Patterson et al., 2014; Naish et al., 2009).

Biosilica, also known as biogenic opal, is deposited in the Southern Ocean by organisms whose skeletons are formed using dissolved silicate available in the water column (e.g. radiolarian, silicoflagellates, ebridians, chrysophycean cysts, and siliceous sponges). However, the main source of biosilica in Site 697 comes from sinking diatoms, whose ornate skeletal structures are also made of silica. The biosilica

record provides paleoproductivity information, as the abundance of diatoms should increase in response to increased light, nutrient availability, and SST (Zielinski and Gersonde, 2000). Comparing the changes in the diatom assemblages to our biosilica and IRD data gives us a holistic perspective with which to consider the changing conditions within this study interval .

ii. Chapter I Figures
A. Bathymetric map of the three-site transect of the Jane Basin

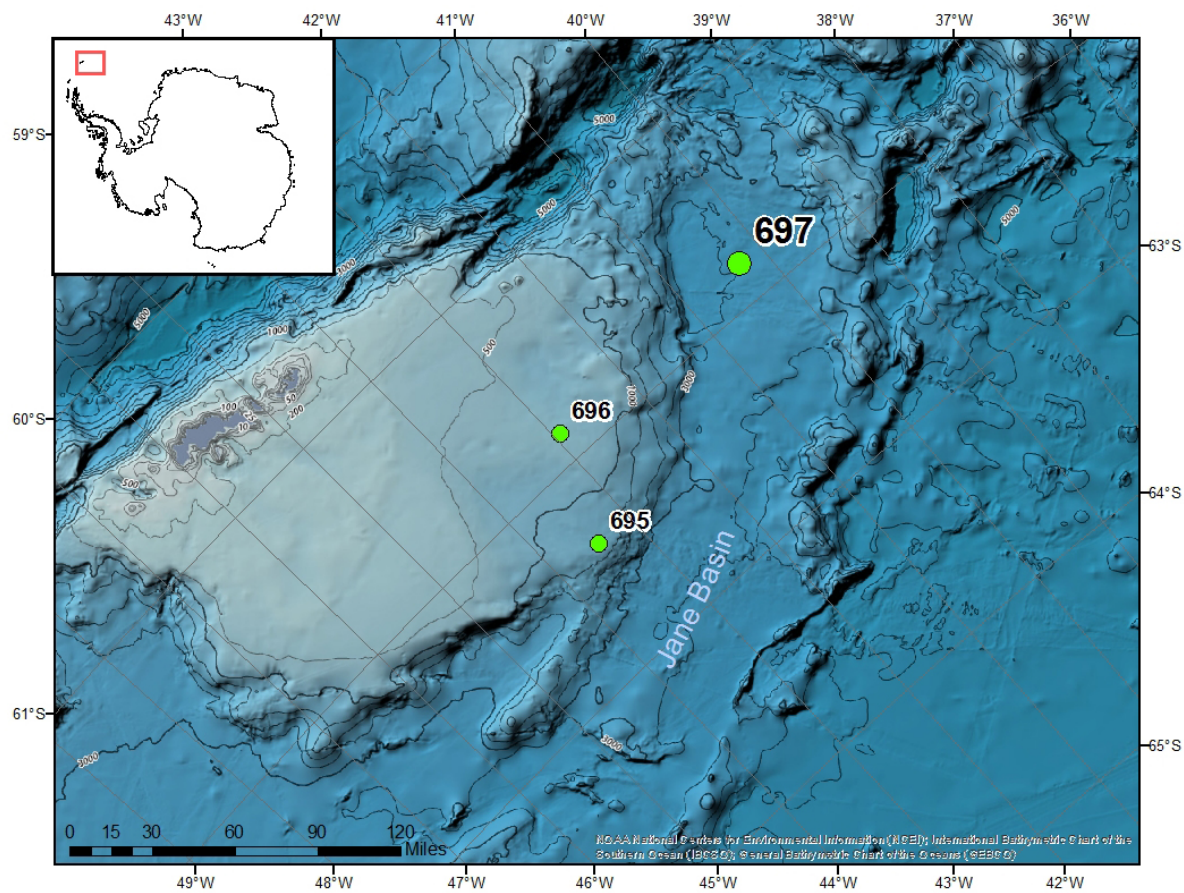


Figure 1.1. Bathymetry (meters) of the Jane Basin (labeled). Sites 697, 696, and 695 are marked with a green symbol.

II. Previous Studies

i. Southern Ocean Phytoplankton Turnover

A. CONOP

Constrained Optimization (CONOP) is a quantitative biostratigraphic method that uses biostratigraphy and teprostratigraphy data from 32 Neogene sections around the Southern Ocean and Antarctic continental margin (Cody et al., 2008). CONOP combines data from geomagnetic polarity reversals, volcanic ash layers, and successions of local First and Last Occurrences of diatom taxa to create a high resolution biostratigraphic age model (Cody et al., 2008). The comprehensive data set used in the model makes it applicable to onshore and offshore paleoenvironmental records around the Antarctic.

B. Southern Ocean Diatom Turnover Events

Crampton et al. (2016) used the CONOP model to identify five major episodes of Southern Ocean diatom species turnover (origination rate plus extinction rate) linked to times of cooling and ice expansion in the last 15 million years (Ma)(Figure 1.2A). The ages of the five major pulses are approximately 14.65–14.45 Ma (A), 13.75–13.55 Ma (B), 4.90–4.40 Ma (C), 3.55–3.40 Ma (D), and 3.00–1.95 Ma (E) (Crampton et al., 2016). Diatom species are highly endemic in the Southern Ocean and form two distinct biomes: a specialized flora occupying the sea-ice zone (Armand et al., 2005) and a high-nutrient, low-chlorophyll flora occupying the open ocean (Crosta et al. 2005). Past plankton turnover has been inferred to occur when a warmer-than-present climate state is terminated by a major period of glaciation that

results in loss of open-ocean habitat due to increase sea-ice cover, driving non-ice adapted diatoms to regional or global extinction (Crampton et al., 2016).

However, it is unclear why the turnover pulse that occurred between 3.55–3.40 Ma (Pulse D) - the highest of all five turnover rates - correlates with an increase in biosiliceous activity (Fig. 1.2D), rising CO₂ concentrations (Fig. 1.2 E), warming temperature and ice retraction (Fig. 1.2 C) [Crampton et al., 2016]. Furthermore, the end of Pulse D coincides with the transition from subpolar to polar conditions on the Antarctic margin, and marks the termination of early to mid-Pliocene warm conditions (McKay et al., 2012).

ii. Marine Isotope Stage M2 and Turnover Pulse D

Over the last 5 million years, the global benthic foraminiferal $\delta^{18}\text{O}$ record shows a $\sim+1.5\%$ shift caused by colder bottom water temperatures and increased ice cover (Liseicki and Raymo, 2005). The Marine Isotope Stage M2 (3.312-3.264 Ma) is a global glaciation event that corresponds to a $\sim+0.5\%$ shift, interrupting a period of high global temperatures and CO₂ concentrations. Several proxy estimates show this 50 thousand year (kyr) event caused a 20 to 60 m sea level drop, which represents between one sixth and nearly half of the sea level drop during the Last Glacial Maximum despite lasting half the duration of the recent Quaternary glacial cycles (Dwyer and Chandler, 2009; Miller et al., 2012; Naish and Wilson, 2009).

De Schepper et al. (2013) suggests that a brief re-opening and then closing of the shallow Central American Seaway may have catalyzed and also terminated the M2 glaciation event. Early modelling studies from Dolan et al. (2015) and Tan et al. (2017) show the re-opening of the CAS led to global ice sheet build-up, but cannot

alone explain the onset of M2. Thus, the M2 glaciation is an enigma, occurring at the beginning of the mid-Pliocene Warm Period (ca. 3.3 to 3.0 Ma), which is well documented in the marine (Dowsett et al., 2012) and continental records (Salzmann et al., 2008), and model studies (Haywood et al., 2016).

iii. Chapter II Figures

A. Southern Ocean diatom turnover pulse history

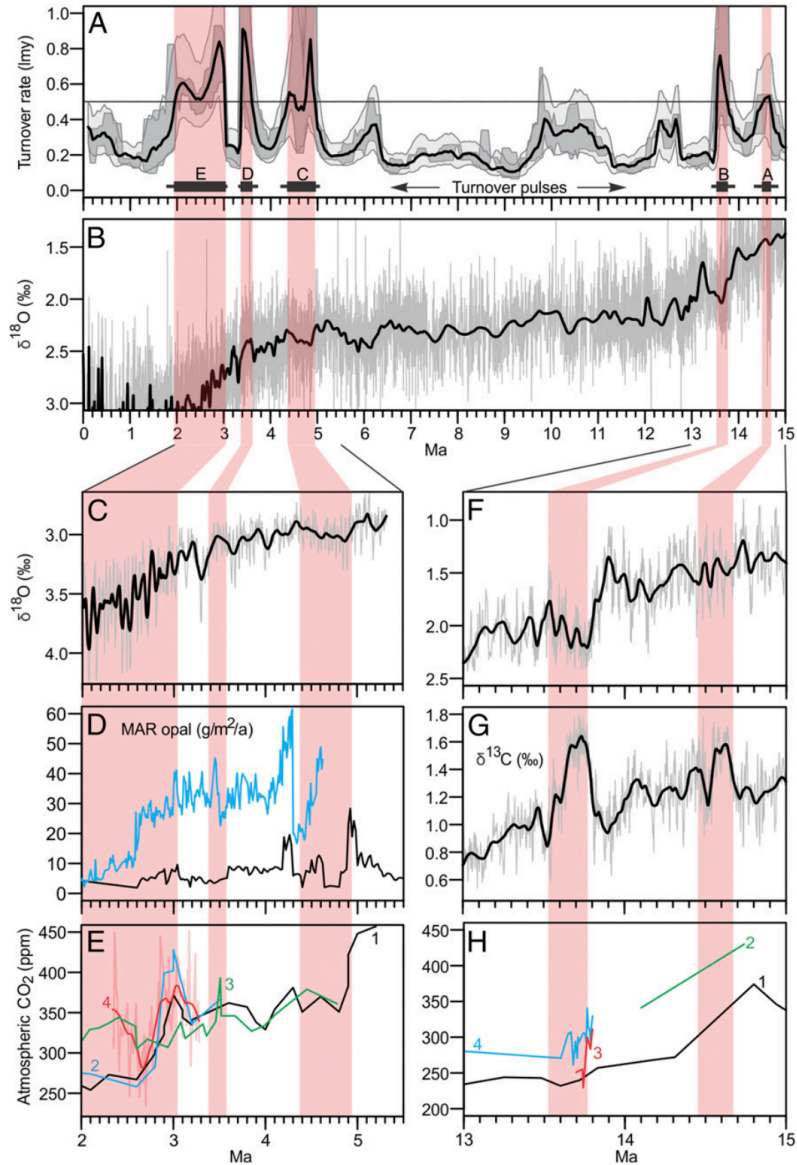


Figure 2.1. Turnover pulses of diatoms in the Southern Ocean and Antarctic margin over the past 15 My compared with key paleoenvironmental proxies. (A) A plot of species lineage-million-year (*lmy*) turnover rate, with major pluses identified by pink bars. (B) Benthic $\delta^{18}\text{O}$ curve for the time interval 15-0 Ma. (C) Benthic $\delta^{18}\text{O}$ curve for the time interval 5-2 Ma. (D) Opal accumulation rates, which acts as a proxy for sea-ice extent on the Antarctic margin for the time interval 5-2 Ma. Declining opal accumulation indicates an expansion in sea-ice. (E) Estimate of atmospheric $p\text{CO}_2$ for the time interval 5-2 Ma, based on alkenone (1 and 2) and boron (3 and 4) proxies. (F) Benthic $\delta^{18}\text{O}$ curve for the time interval 15-13 Ma. (G) Benthic $\delta^{13}\text{C}$ curve for the time interval 15-13 Ma. (H) Estimates of atmospheric $p\text{CO}_2$ based on alkenone (2 and 4), boron (1), and B/Ca (3) proxies (Crampton et al., 2016).

B. Benthic foraminiferal $\delta^{18}\text{O}$ record (~3.6-3.2 Ma)

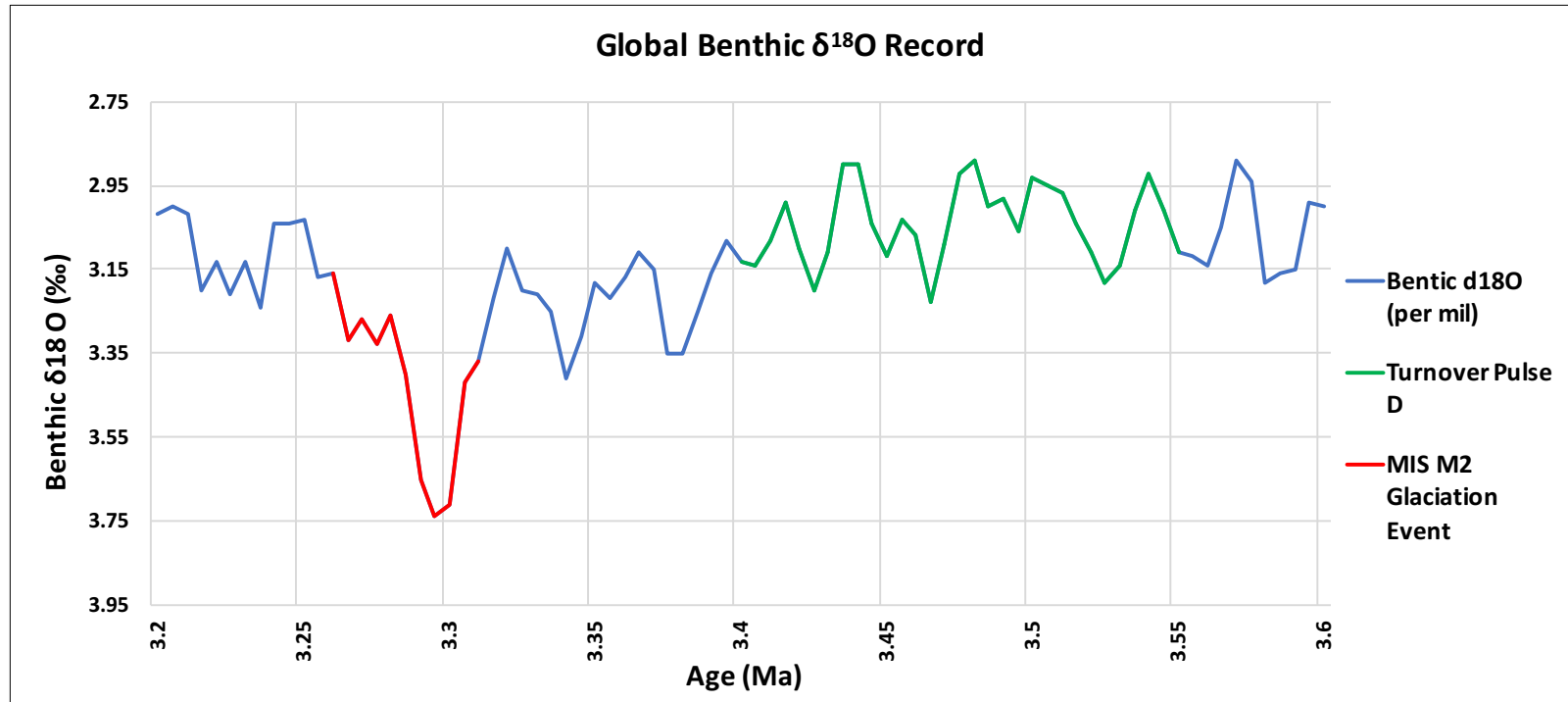


Figure 2.2. Modified benthic foraminiferal $\delta^{18}\text{O}$ stack (blue) is plotted from ~3.6 to 3.2 Ma (cores 14x-17x from Site 697), which is an average of 57 globally distributed $\delta^{18}\text{O}$ records (Lisiecki and Raymo, 2005). The interval corresponding to Turnover Pulse D is highlighted in green, while the interval corresponding to MIS M2 is highlighted in red.

III. Methods

Samples from the working half of sediment cores of Site 697 (Hole 697B) were collected at the Integrated Ocean Discovery Program (IODP) Gulf Coast Core Repository at Texas A&M University. Excluding areas of the core with poor recovery, 10-20 cubic centimeters (cc) samples were brought back to the Wesleyan University campus for further study. The ages for this study are based on the magnetic reversal stratigraphy given in Pudsey (1990) and then tied to the Gee and Kent (2007) timescale (Table 3.1). Between reversals, ages are extrapolated.

i. Preparing Diatom Slides

For each sample, approximately 0.5 g of sediment was placed in a desiccator for at least 24 hours to ensure they were completely dry. Next, 0.3 g of sample was placed in a 50 mL centrifuge tube with 10 mL of deionized water and then treated with 20 mL of 35% hydrogen peroxide to oxidize organic material. After effervescence stopped, samples were rinsed multiple times with deionized water and centrifuged at 1500 rpm for 10 minutes. To further disaggregate sediments, samples are treated with a dilute Calgon (sodium hexametaphosphate) solution and rinsed again with deionized water.

For quantitative analysis, a random settling method was used to evenly distribute the diatoms in suspension over three cover slips per sample. For each sample, 5 mL of randomized suspended sediment was extracted and added to a small beaker containing 45 mL of deionized water, to allow for good dissemination. The diluted solution was then poured into a petri dish containing 20 mL of deionized water. After waiting 30 minutes for the sediment to settle in the petri dish, short strips

of paper towel were inserted into the water and connected to a sponge under the petri dish. Through capillary action this step drains the water and expedites drying. After allowing for all of the water in the petri dish to dry, coverslips were removed from the petri dish, dried on a hot plate, and mounted to glass slides using Norland Optical Adhesive #61.

ii. Identifying and Counting Diatoms

One slide per sample was examined under a light microscope at 1,000x magnification. Random traverses are made across the coverslip until at least 500 diatom valves are counted for each sample, to ensure an accurate representation of the fossil assemblage (Chang, 1967).

Diatoms were only counted when at least half of a valve was visible. Each diatom was identified to the species level unless diagnostic features were missing, in which case they were categorized at the generic level. Diatoms from the lineolate genera, such as *Thalassiothrix* and *Thalassionema*, are usually fractured along their length, in which case two ends counted as one valve. *Chaetoceros* resting spores (rs) were included in the results because they are often associated with high levels of productivity in a stratified ocean setting.

iii. Diatom Abundance

Diatom Total Abundance (DTA) was calculated as microfossils per gram using the following formula:

$$n = (V * (v * (x * A/a)^{-1})^{-1}) * m^{-1}$$

In this equation, V is the total volume of the sample suspension after chemical treatment; v is the volume of the aliquot of the sample added to the Petri dish; x is the

number of microfossils counted; A is the area of the Petri dish in which the coverslips were evaporated; a is the area examined on a coverslip; and m is the original mass of the sample processed (Witkowski et al., 2012).

iv. Statistical Analysis

Diatom relative abundance data were analyzed using orthogonal rotated (Varimax) principal component (PC) analysis, according to Malmgren and Haq (1982). PC analysis helps to reduce the number of variables (i.e. species) to a manageable number without a significant loss of information. The dataset used did not include *Chaetoceros* spp., since its dominance in more than half of the samples suppresses the contribution of other ecologically significant but less abundant species. Species with relative abundance of less than 2% in a single sample are not interpreted to be statistically significant and were also removed from statistical analyses, leaving 27 species for statistical treatment (Kato, 1993).

Scores were calculated for each species, which reflect their contribution for each PC. Species that favor similar environmental conditions, which observe coincident changes in the assemblages, are expected to show high scores together on one PC. PC loadings are also included to show similarities between the assemblages from different depths. PC loadings that exceed a value of 0.4 are interpreted to be statistically significant (Malmgren and Haq, 1982).

iv. Chapter III figures

A. Magnetic Polarity Reversal boundaries used between 3.6-3.2 Ma

Magnetic Boundaries	Sample	Depth (mbsf)	G&K (2007) model age [Ma]	Pudsey (1990) model age [Ma]
C2AN-2, base	697B-14X-1-50	138.7	3.22	2.99
C2AN-3, top	697B-14X-7-40	147.6	3.33	3.13
Gauss chron, base/ C2AN-3, base	697B-16X-4-50	162.25	3.58	3.40

Table 3.1. The age model used in this study relies on the absolute ages from magnetic boundaries. Pudsey (1990) was the first to establish magnetic ages for 697, however, this study uses the ages from the more recently redeveloped by Gee and Kent (2007).

IV. Results

Since this 400 kyr interval studied here does not extend across multiple biostratigraphic diatom zones, this interval is subdivided into five parts:

- Before Pulse D (165.32-162.45 mbsf; 16X-6, 32-34 cm to 16X-4, 45-47 cm)
- Within Pulse D (162.15-153.27 mbsf; 16X-4, 15-17 cm to 15X-4, 87-88 cm)
- Between Pulse D and MIS M2 (151.97-148.36 mbsf; 15X-3, 107-109 cm to 15X-1, 46-48 cm)
- MIS M2 (146.05-143.38 mbsf; 14X-6, 35-37 cm to 14X-4, 68-70 cm)
- Post-MIS M2 (141.1-139.2 mbsf; 14X-2, 140-142 cm to 14X-1, 100-102 cm).

These five intervals provide a basis for interpretation of the relationship between changes in the record and these two events.

i. Preliminary Results

The three records produced by our laboratory (Figure 3.1) (diatom total abundance [DTA], wt. % biosilica and IRD) seem to follow similar trends through the interval of this study. Ideal interpretation is hampered by the different resolution of the three records. There are 31 diatom samples, 62 biosilica samples, and 100 IRD samples.

A. Before Pulse D

The DTA, biosilica, and IRD records all show relatively low values during the 150 kyr interval before Pulse D with only minor changes.

B. Pulse D

DTA values remain relatively low at the start of Pulse D. Starting at 160.02 mbsf our record shows a dramatic 5% increase, reaching the highest values at 156.2

and 155.3 mbsf with 4.07×10^6 and 4.61×10^6 microfossil per gram of sediment, respectively.

These DTA record peaks are roughly coeval with increases in the biosilica record. During Pulse D, the biosilica record contains four peaks at 156.02, 154.97, 153.08, and 152.23 mbsf. The greatest increase during this interval at 153.08 mbsf represents a $\sim 7.5\%$ increase in biosilica wt.%. Only two peaks that appear in the biosilica record are also present in the DTA record.

The higher resolution coarse fraction record (IRD) also demonstrates abrupt increases during the Pulse D interval. Three sharp peaks occur in the IRD record at 158.92, 155.8, and 152.78 mbsf. These three peaks are more spread out than the peaks in the DTA and biosilica records, occurring >50 kyr apart from each other.

The aforementioned peaks in the biosilica and DTA records, that occur during the second half of pulse D, are generally coeval with the sharp increase in the MAR of Opal in the Southern Ocean at ~ 3.45 Ma (See Figure 2.1)

C. Between Pulse D and MIS M2

Between pulse D and MIS M2, a sharp increase in all three records interrupts a period of relatively low values at ~ 149 mbsf (Biosilica 149.34 mbsf; DTA 148.95; IRD 148.72 mbsf). This sharp increase is also in conjunction with an increase in the $\delta^{18}\text{O}$ record at ~ 3.34 Ma. The IRD record also shows an increase before 148.72 mbsf at 149.71 mbsf (11.32 wt. %). This is followed by lower IRD wt.% from 148.16-139.85 mbsf, which corresponds to decreases in DTA and biosilica wt.% from 148.36 and 148.72 mbsf, respectively. In fact, our extend coarse fraction record, which

extends into the Pleistocene (~2.0 Ma), shows that coarse fraction wt.% never fully recovers after this abrupt decrease (Figure 4.3).

D. MIS M2

We observe relatively low results for all three records during M2 interval, but biosilica and DTA records peak mid-M2 close to the coldest interval in the M2 glaciation event (Biosilica 147.48 mbsf; DTA 144.12 mbsf). IRD record doesn't observe a peak mid-M2, but does decrease from 148.16-139.85 mbsf. This decrease corresponds with a decrease in DTA from 148.36-141.10 mbsf. The biosilica record shows variability from 148.72 mbsf to the end of the M2 interval, unlike the IRD and DTA records.

E. Post-MIS M2

The biosilica record contains some of its highest values (13.4%) during this entire ~400 kyr interval after the M2 glaciation event at 140.49 mbsf. The DTA and IRD records remain low.

ii. Diatom Relative Abundance

A total of 68 diatom taxa were identified and quantified during this interval (139.2-165.32 mbsf; ~3.59-3.22 Ma). *Chaetoceros* rs dominated, accounting for ~27% of all counted valves, and exceeding 50% of the total assemblage in the sample at 148.36 mbsf. The most abundant non-*Chaetoceros* rs taxa included *Eucampia antarctica*, *Thalassiothrix antarctica*, *Thalassiosira teres*, *Thalassiosira striata*, *Shionodiscus oestrupii*, *Fragilariopsis barronii*, *Rouxia antarctica*, and diatoms belonging to the genus *Stephanopyxis*. The complete data set is available on request.

A. Before Pulse D

Before Pulse D, the characteristic species include *Stephanopyxis* spp. (average 24%) and *Chaetoceros* rs (avg. 20%). Present in lower abundances are *T. striata* (average of 7%), *T. inura* (avg. 5%), *T. oliverana* (avg. 4%), *Thalassiothrix antarctica* (avg. 4%) and *S. oestrupii* (avg. 3%). Also in this unit is the peak abundance of *T. oliverana* (8%; 164.8 mbsf) and *Stephanopyxis* spp. (39%; 164.8 mbsf).

B. Pulse D

Chaetoceros rs (avg. 26%) is the dominant species in this interval, but experiences considerable variability throughout this interval. *Stephanopyxis* spp. (avg. 10%) decreases in total abundance together with *T. oliverana* (avg. 1%). The abundance of *S. oestrupii* reaches a peak abundance of 10 and 8% at 156.20 and 154.21 mbsf, respectively. During the DTA peak ca. 156.20 and 155.3 mbsf, *T. teres* (16%), *S. oestrupii* (10%), *Chaetoceros* rs (33%) experience an increase, whereas *F. barronii* (>0.1%), *Thalassiothrix antarctica* (4%), and *Stephanopyxis* spp. (5%) all decrease in abundance. *F. curta* (0.57-0.16%) abundance is low but consistent throughout pulse D.

C. Between Pulse D and MIS M2

In this interval, *Stephanopyxis* spp. (17%) and *Thalassiothrix antarctica* (13%) have peak abundances at 148.95 mbsf. *Chaetoceros* rs has its peak abundance after this (51%; 148.36 mbsf), which is coeval with the sharp decrease in biosilica, DTA, and IRD. Both *Eucampia antarctica* (7%) and *S. oestrupii* (5%) increase in this interval.

D. MIS M2

The most striking change in the M2 interval is the decrease in *Stephanopyxis* (avg. >1%). The dominant taxa are *Chaetoceros* rs (avg. 26%) and silicoflagellates *Stephanocha speculum* (avg. 12%). Other important species in the assemblages are *E. antarctica* (9%), *T. teres* (6%), and *S. oestrupii* (4%). Slightly before the DTA peak (3.278 Ma) at 144.75 mbsf, *Thalassiothrix antarctica* abundance increases to 10%, while *Chaetoceros* rs abundance decreases to 10%.

E. Post-MIS M2

The dominant species immediately after M2, as in Pulse D, is *Chaetoceros* rs (avg. 21%). Also abundant are *E. antarctica* (avg. 13%), and *S. speculum* (avg. 11%). However, *Chaetoceros* rs values drop to a minimum abundance of 5% at 140.36 mbsf. Present in low abundance are *R. antarctica* (6%), *Thalassiothrix antarctica* (avg. 6%), *T. teres* (avg. 4%), and *F. barronii* (avg. 3%).

iii. PCA Results

Principle Components (PCs) are defined by single dominant species with the highest PC scores accompanied by two or more accessory species (PC score >1.0). For clarity, the calculated PCs, which are mathematical models of real assemblages, are referred to as diatom assemblages (DAs) using the names of the dominant taxa for each PC. They are (1) the *Stephanopyxis* spp. DA (43% of the total variance explained, with accessory *Thalassiothrix antarctica*), (2) *S. speculum* DA (23.12% with accessory *E. antarctica* and *Thalassiothrix antarctica*), (3) the *T. teres* DA (7.89% with accessory *S. oestrupii* and *E. antarctica*), and (4) *T. striata* DA (6.29%

with accessory *T. teres*, *R. antarctica*, *T. complicata*, and *Thalassiosira* spp.). These four PCs explain 80.5% of the total variance of the diatom abundance.

The interval before Pulse D is dominated by the *Stephanopyxis* spp. DA. This dominance extends into the first half of the Pulse D zone (162.15-156.2 mbsf; ~3.55-3.46 Ma). The second half of Pulse D has the most variability in the studied interval, but is primarily characterized by the *T. teres* and *T. striata* DAs. The *Stephanopyxis* spp. DA mainly characterizes the zone between Pulse D and M2, while the M2 and post-M2 zones are characterized by the *S. speculum* DA (See Table 4.1).

iv. Chapter IV Figures

A. Preliminary Results

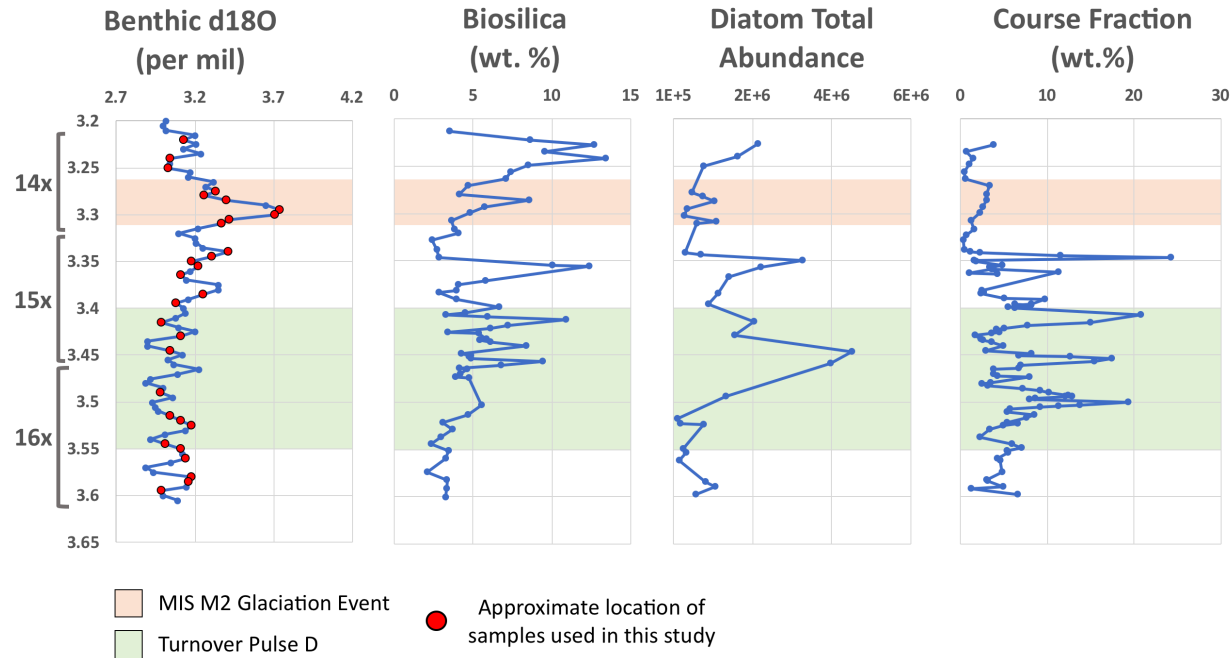


Figure 4.1. On the left, benthic foraminiferal $\delta^{18}\text{O}$ stack is plotted from ~ 3.6 to 3.2 Ma (sections 14x-16x in the core), which is an average of 57 globally distributed $\delta^{18}\text{O}$ records (Lisiecki and Raymo, 2005). MIS M2 glaciation (3.312 - 3.264 Ma) is highlighted by an orange box. The event produced a $\sim 0.5\%$ shift of benthic foraminiferal $\delta^{18}\text{O}$ (Tan et al., 2017). Turnover Pulse D is highlighted by a green box. The graph to the left of it is a plot of biosilica wt. % for sections 14x-16x, and serves as a proxy for productivity. The second to last graph contains the calculated diatom total abundance values for the quantitative samples used in this study. The last graph on the right is a plot of course fraction weight % for sections 14x-17x, and serves as a proxy for sea-ice retreat.

B. Diatom Relative Abundance

Diatom Relative Abundance (%)

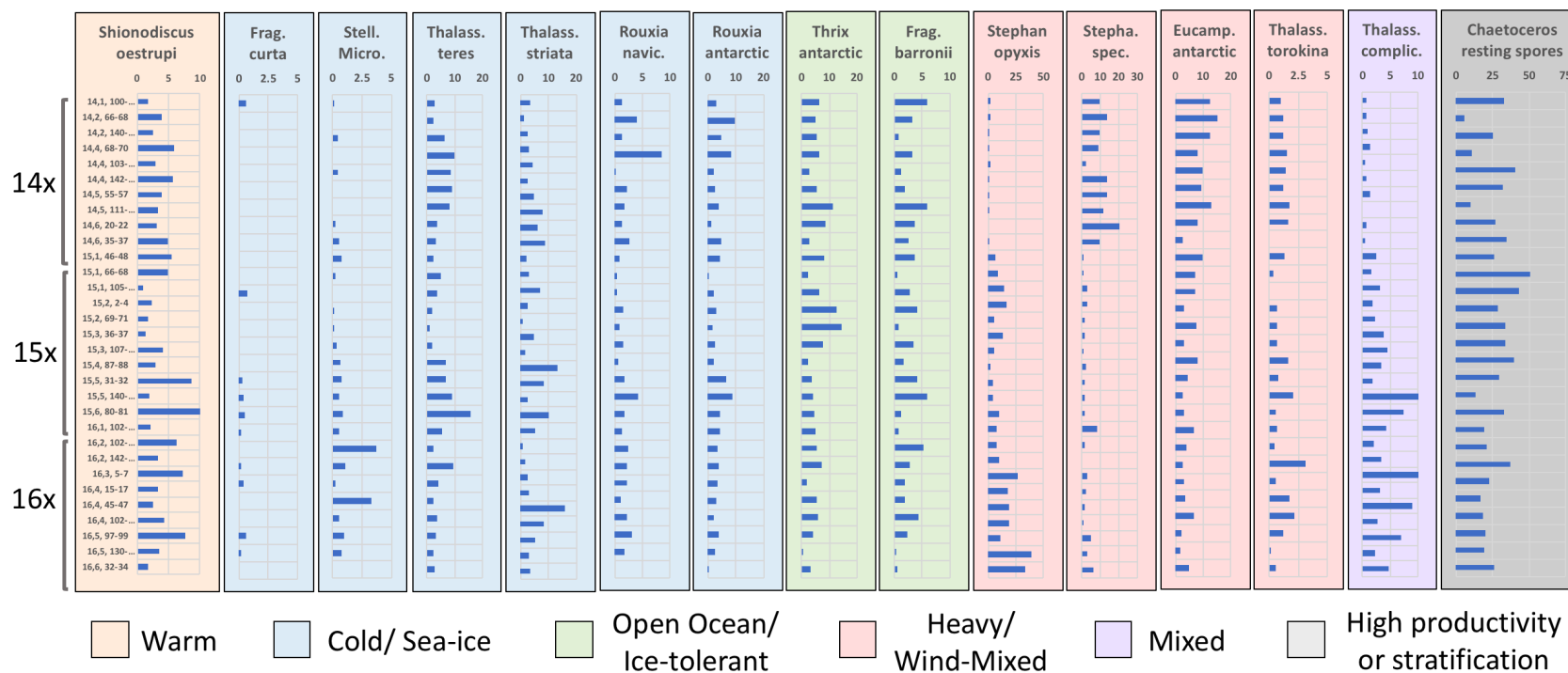


Figure 4.2. Relative abundance of select Site 697 diatom species. Environmental preferences were assigned using information from Crosta et al. (2005), Armand et al. (2005), Romero et al. (2005), Winter et al. (2010), and Barron (1996). Diatom species in the Warm category are highlighted in orange. Species inferred to be Open ocean/ ice tolerant species are highlighted in green. Diatom species in the Cold/Sea-ice group are highlighted in blue. Species in the Heavy/ Wind-Mixed category are highlighted in red, while the species in the Mixed category are highlighted in purple. Diatom species associated with high productivity or stratification are highlighted in grey. Additional information is provided in Table 5.1.

C. Extended IRD data

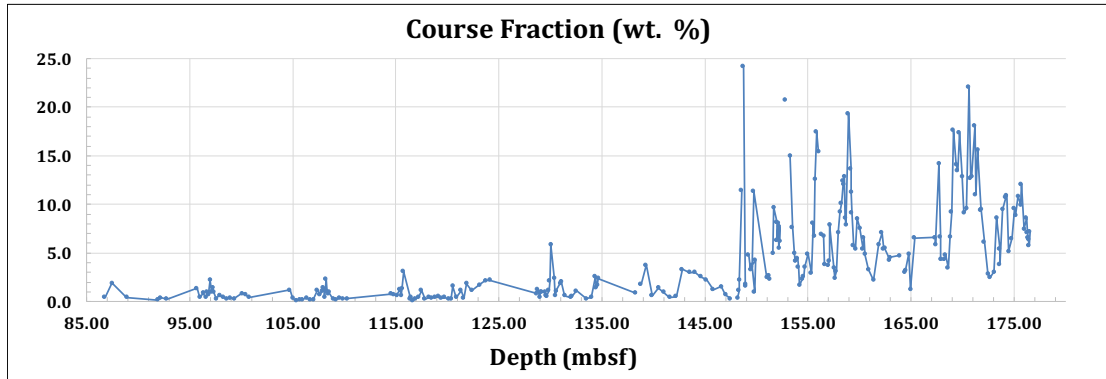


Figure 4.3. Extended course fraction record (wt.%) plotted against depth (mbsf).

D. Diatom PC Scores

	<i>Stephanopyxis</i> DA	<i>S. speculum</i> DA	<i>T. teres</i> DA	<i>T. striata</i> DA
Percentage of total variance explained	43.238	23.117	7.891	6.291
<i>Actinocyclus</i> spp.	-0.55	-0.37	-0.35	-0.55
<i>Actinocyclus actinochilus</i>	-0.48	-0.55	-0.45	-0.32
CRS Spine	-0.35	0.68	0.37	-2.14
<i>Eucampia antarctica</i>	0.04	2.41	1.64	-1.07
<i>Fragilariopsis barronii</i>	0.12	0.42	-0.86	0.81
<i>Odontella</i> sp.	-0.63	-0.56	-0.08	-0.48
<i>Rhizosolenia</i> spp.	-0.49	-0.61	-0.33	-0.41
<i>Rhizosolenia styloformis</i> (no wings)	-0.58	-0.56	-0.27	-0.40
<i>Rhizosolenia harwoodi</i>	-0.50	-0.01	-0.36	-0.81
<i>Rhizosolenia hebetata</i> group	-0.46	-0.60	-0.38	-0.41
<i>Rhizosolenia styliformis</i>	0.15	-0.49	-0.67	0.49
<i>Proboscia barboi</i>	-0.45	-0.32	-0.35	-0.82
<i>Rouxia antarctica</i>	-0.09	0.45	0.25	1.34
<i>Rouxia naviculoides</i>	-0.45	-0.23	-0.16	0.22
<i>Shionodiscus oestrupii</i>	-0.13	0.01	1.88	0.25
<i>Stellarima microtrias</i>	-0.30	-0.53	-0.62	-0.13
<i>Stephanopyxis</i> spp.	4.46	-1.04	0.50	-0.95
<i>Thalassiosira</i> spp.	-0.23	-0.44	-0.05	1.06
<i>Thalassiosira teres</i>	-0.71	0.25	3.31	1.34
<i>Thalassiosira complicata</i>	0.15	-0.79	0.34	1.31
<i>Thalassiosira inura</i>	0.79	-0.58	-0.96	0.68
<i>Thalassiosira oliverana</i>	-0.21	-0.67	0.08	-0.52
<i>Thalassiosira striata</i>	0.69	0.80	-0.78	2.84
<i>Thalassiosira torokina</i>	-0.52	-0.68	-0.12	-0.20
<i>Thalassiothrix antarctica</i>	1.11	1.42	0.46	-0.52
<i>Thalassionema Nitzeschiodes</i>	-0.49	-0.65	-0.05	-0.59
<i>Stephanocha speculum</i>	0.12	3.25	-2.00	-0.04

Table 4.1. PC scores for each species run through PC analysis is given for each DA. Important taxa for each DA are in bold.

E. Diatom PC Loadings

Sample	<i>Stephanopyxis</i> DA	<i>S. speculum</i> DA	<i>T. teres</i> DA	<i>T. striata</i> DA
14x-1w, 100-102	0.107	0.888	0.070	0.112
14x-2w, 66-68	-0.044	0.858	0.103	-0.199
14x-2w, 140-142	-0.003	0.900	0.325	-0.134
14x-4w, 68-70	-0.058	0.734	0.407	0.167
14x-4w, 103-105	-0.054	0.583	0.653	0.016
14x-4w, 142-144	0.011	0.867	0.319	0.068
14x-5w, 55-57	0.054	0.934	0.214	0.060
14x-5w, 111-113	0.125	0.910	0.008	0.096
14x-6w, 20-22	0.040	0.821	-0.211	0.161
14x-6w, 35-37	0.132	0.913	0.120	0.149
15x-1w, 46-48	0.501	0.198	0.716	0.001
15x-1w, 66-68	0.657	0.380	0.555	-0.074
15x-1w, 105-106	0.921	0.229	0.032	0.125
15x-2w, 2-4	0.841	0.224	0.182	-0.187
15x-2w, 69-71	0.328	0.360	0.258	-0.472
15x-3w, 36-37	0.910	0.014	0.054	0.147
15x-3w, 107-109	0.311	0.261	0.820	-0.020
15x-4w, 87-88	0.250	0.395	0.251	0.738
15x-5w, 31-32	0.152	0.147	0.808	0.345
15x-5w, 140-141	0.240	0.099	0.352	0.700
15x-6w, 80-81	0.519	0.185	0.544	0.430
16x-1w, 102-104	0.664	0.403	-0.176	0.382
16x-2w, 102-104	0.505	0.090	0.649	0.175
16x-2w, 142-144	0.708	-0.033	0.401	0.137
16x-3w, 5-7	0.824	-0.069	0.290	-0.153
16x-4w, 15-17	0.875	-0.016	0.214	0.171
16x-4w, 45-47	0.843	0.022	0.046	0.301
16x-4w, 102-104	0.901	0.050	0.236	0.163
16x-5w, 97-99	0.711	0.073	0.171	0.358
16x-5w, 130-132	0.873	-0.167	0.149	-0.143
16x-6w, 32-34	0.930	-0.023	0.109	-0.089

Table 4.2. Diatom PC loadings show the similarities between assemblages from different samples. PC loadings exceeding a value of 0.4 are regarded as statistically significant and are in bold (Malmgren and Haq, 1982).

V. Discussion

Diatoms are the main biogenic tracer for past ocean surface water conditions and SST at Site 697. To assess paleoenvironmental conditions, knowledge of ecological preferences for the different species are required. The assemblages included in this study are dominated by extinct and newly described species. Therefore, we compare the assemblages in this study to analogs found in extant Antarctic diatom floras, extinct Antarctic floras, and extant floras found in other polar and sub-polar locations.

This study employs the ecological categories used by Winter et al. (2010), with the exception of a few changes, which serve to make the categories more applicable to the environment around Site 697. The ecological categories used to describe the changes in extant and extinct species are Cold/ Sea-Ice, Warm, Stratified, Heavy/ Wind Mixed, and Mixed (Table 5.1). Environmental preferences reflect both SST and habitat conditions, and are based on previously published environmental preferences of extant species, as well as inferred environmental preferences based on concurrent abundance changes.

The Cold/ Sea-Ice category is comprised of species associated with modern environments near or within sea-ice, and extinct species whose changes are concurrent with extant sea-ice or cold-associated species. Species in the Warm category are suggested to reflect environments either close to or north of the modern Polar Frontal Zone. Species associated with the Stratified category are not attributed to specific temperature constraints, but with high productivity usually associated with stable upper water conditions caused by an increase in freshwater output. The Heavy/

Wind Mixed category is associated with increased numbers of larger and heavily-silicified species as well as silicoflagellates. The Heavy/ Wind Mixed group is interpreted to reflect increased bottom current winnowing and a somewhat size-sorted assemblage. Species in the Mixed category prefer non-stratified water column conditions, inferred from a co-occurrence with silicoflagellates and an inverse correlation with species indicating stratified water conditions. Figure 5.1 summarizes species present in greater abundance from this interval.

One third of the diatoms of the genus *Chaetoceros* are known to form resting spores within the vegetative cell. *Chaetoceros* rs have been associated with unfavorable conditions such as nitrogen deficiency and low light conditions (Hargraves and French, 1975, Leventer, 1991). Previous work has not detected a relationship between the abundance of *Chaetoceros* rs and SST (Zielinski and Gersonde, 1997). However, high productivity has been shown to be important to the distribution of *Chaetoceros* rs, and they are therefore part of the Stratified category (Donegan and Schrader, 1982, Leventer, 1991, Karpuz and Jansen, 1992, Zielinski and Gersonde, 1997).

i. Before Pulse D (~3.6-3.55)

This zone is characterized by the *Stephanopyxis* spp. DA (with accessory *Thalassiothrix antarctica*). In Shimada et al. (2008), layers of mixed *Thalassiothrix* and *Stephanopyxis* species correlate with high productivity intervals in the middle to late Pleistocene in the North Atlantic south of Greenland. High *Chaetoceros* rs values are also indicative of high productivity, but the relatively low *Chaetoceros* rs percentages throughout this interval (avg. 20%) suggest that perhaps this boost in

productivity is not related to a highly stratified water column, commonly associated with *Chaetoceros* spp. (Zielinski and Gersonde, 1997). However, the assumption that elevated *Stephanopyxis* and *Thalassiothrix antarctica* abundances infer a high productivity interval is also contradicted by the relatively low values in the biosilica wt.% and DTA values before Pulse D.

The low concentration of *Chaetoceros* spp. suggests decrease in size of ice sheet and outlet glaciers, which most likely terminate on land, thus decreasing freshwater input with little freshening and stabilization of surface water. This is in agreement with the low concentration of IRD in this first interval, and with the suggestion that less than 30% of *Chaetoceros* spp. are not associated with sea-ice (Armand et al., 2005).

Relatively high abundances of *S. oestrupii* and the highest values of *T. oliverana* during this interval indicate warmer conditions. In modern environments *T. oliverana* reaches a maximum relative abundance (MRA) of ~4% in temperatures between 2.5-3.5°C (Crosta et al., 2005). *T. oliverana* abundances exceeding this modern MRA (8.5 and 7.6% at 164.8 and 164.5 mbsf, respectively) provide support that this interval experienced warmer-than-present conditions.

This interval also records relatively high values of *T. complicata* and *T. inura*. Winter et al (2010) notes that during the mid-Pliocene in the McMurdo Ice Shelf, the extinct species *T. complicata* and *T. inura*, are at their highest abundances during warmer conditions with a wind-mixed, unstable water column (AND-1B; 426.50-403.10 mbsf). This is in agreement with the low *Chaetoceros* spp. abundance during this interval. This interval most likely correlates with the warmer-than-present

interval documented in the Ross Sea between 3.6 and 3.4 Ma described by Naish et al. (2009).

ii. Pulse D (3.55-3.4 Ma)

This dominance of the *Stephanopyxis* spp. DA extends into the first half of the Pulse D zone, and the low DTA values at the start of Pulse D represent a continuation of the warm and mixed environmental conditions seen in the preceding interval.

The pulsed nature of the IRD record mirrors the deposition of IRD in the Ross Embayment (AND-1B; ~430-370 mbsf) that has been interpreted to reflect glacial fluctuations linked to variations in Earth's orbital obliquity within the same time period (Naish et al., 2009). These lithologic markers of glacial cycles within Site 697 (>50 kyr apart) roughly match the well-documented ~40 kyr periodicity recorded in the polar and equatorial depositional environments (Shackleton et al., 1984; Hall et al., 2001; Crundwell et al., 2008; Dwyer et al., 1995; Ding et al., 2002; Naish, 2007). However, these changes in IRD are not correlated to changes in the diatom assemblages, except in the increase variability of *Chaetoceros* rs.

Samples from 148.95 mbsf record a dramatic increase in the total abundance of diatoms, which follows the sharp increase in the MAR of Opal in the Southern Ocean at ~3.45 Ma. This period of local and regional productivity is interpreted as the warmest within this study, wherein assemblages contain the highest abundance of *S. oestrupii* (10%). Today, the highest relative abundance of *S. oestrupii* (up to ~5%) only occurs north of the Subantarctic Front, and is also associated with warm currents in the North Atlantic (Jiang et al., 2001; Romero et al., 2005). Romero et al. (2005) observed that south of the Subantarctic Front, *S. oestrupii* abundances don't surpass

1% of the total assemblage. The increase in *T. teres* and *Chaetoceros* spp. at this time provide further indications of open-ocean conditions and high productivity.

The PCA data shows a clear change in the diatom community immediately following this peak in diatom productivity and, hence, indicates a step in environmental change. At 148.56 mbsf the *Stephanopyxis* spp. DA is replaced by mainly the *T. teres* (with accessory *S. oestrupii* and *E. antarctica*) and *T. striata* (with accessory *T. teres*, *R. antarctica*, *T. complicata*, and *Thalassiosira* spp.) DAs for the remainder of the interval.

Thalassiosira antarctica is a modern, morphologically similar species to *T. teres*, and is associated with summer productivity and a retreating sea-ice edge (Leventer et al., 2002; Taylor and Sjunneskog, 2002). A study by Winter et al. (2010) suggested *T. teres* prefers cool-open water conditions, since it is associated with decreasing abundances of *F. curta*.

Similarly, the same study also found that *T. striata* abundances are inversely proportional to abundances of *F. curta*, inferring that *T. striata* prefers cool, somewhat stable waters, with little sea-ice present (Winter et al., 2010). *T. teres* also appears to show an affinity for colder environments, but ones with lower amounts of sea-ice and decreasing water column stability. This is supported by the correlation between the *T. teres* DA and *S. oestrupii* (Winter et al., 2010).

Diatom mats are observed within the samples at 155.30 and 154.21 mbsf, which are associated with the abundance of *T. antarctica* despite relatively low abundance (4.2 and 4.5%, respectively). This interpretation of colder conditions agrees with the abundances of the mat-forming *T. antarctica*, as the species is also associated with

cold water masses in productive upwelling areas (Marlow et al., 2000; Pike and Kemp, 1999). Diatom mats composed of *Thalassiothrix* were also found in ODP Leg 177 Site 1093, in the late Pliocene and early Pleistocene (Zielinski and Gersonde, 2002).

F. curta, the most extensively used sea-ice indicator, appears in low but consistent abundance throughout Pulse D. An abundance of 3% or greater of *F. curta* is used to interpret the northern limit of winter sea-ice in the Southern Ocean (Gersonde and Zielinski, 2000). *F. curta* abundances in this interval (0-0.6%) suggest that the winter sea-ice edge likely never extended out to Site 697. However, trace occurrences of *F. curta* north of this limit are believed to be associated with drifting icebergs, indicating that ice was present event in the warmest interval of this study (Zielinski and Gersonde, 1997; Armand et al., 2005).

iii. Between (3.4-3.312 Ma)

The peak in biosilica wt.%, DTA, and IRD (~149 mbsf; ~3.35 Ma) during the interval between Pulse D and MIS M2 is characterized by the *Stephanopyxis* DA (with accessory *T. antarctica*). A diatom mat is found within this same period of time, most likely caused by the peak abundance of *T. antarctica*. The dominance of *Stephanopyxis* spp. and *T. antarctica*, along with rising abundance of *S. oestrupii*, suggests a warm period marked by high productivity, similar to the conditions in the first interval, Before Pulse D.

The dramatic decrease in IRD, biosilica wt.%, and DTA shortly after results in an increase in *Chaetoceros* rs, likely indicating a stratified water column caused by an

increase in fresh meltwater. The prolonged low values in the Site 697 IRD record, which extends into the Holocene, remains unclear.

iv. M2 (3.312-3.264 Ma)

Samples from the M2 interval are marked by an increase in the silicoflagellate *S. speculum* to the overall assemblage; made evident by the dominance of the *S. speculum* DA (with accessory *E. antarctica* and *Thalassiothrix antarctica*). In modern conditions, *S. speculum* has been observed to be the most abundant in the upwelling dominated areas near the Polar Front (Olguin et al., 2006). Areas of upwelling are associated with an increased supply of nutrients and an unstable water column, for which modern silicoflagellates show an affinity (McCartney, 1993).

Stephanopyxis spp., associated with wind mixing and increased bottom current activity, abruptly disappears at the start of this interval for the rest of the samples (Esparza-Alvarez et al., 2007). Sea-ice species remain low, and increasing values of *S. oestrupii* and *T. teres* indicate that cold open-ocean conditions continue through the 50 kyr glaciation event.

Relatively high values of *T. antarctica* correlate with the increase in DTA and biosilica during the coldest interval in the M2 glaciation event. This species has been shown to be concentrated near frontal zones, and thus might indicate further migration of the Polar Front at this time period. *Chaetoceros* rs experiences a slight resurgence after this small peak in productivity, potentially indicating a variability in winter sea-ice (Cremer et al., 2003).

The last two samples in this interval are also characterized by the *T. teres* DA (with accessory *S. oestrupii* and *E. antarctica*), marking a transition to cold-open

ocean conditions during the late stages of this glaciation event. Pliocene cooling in the AND-1B record began at ca. 3.3 Ma (McKay et al., 2012), and continued through the late Pliocene. Consistently low abundances of *F. curta* and other important sea-ice related species through this interval show little evidence of dramatic cooling at Site 697.

v. After M2 (3.312-3.264 Ma)

Increasing temperatures after M2 result in the increase in productivity we see in the biosilica record. This interval is characterized by the *S. speculum* DA (with accessory *E. antarctica* and *T. antarctica*), likely indicating a wind mixed water column, increased bottom current winnowing, and a somewhat size sorted assemblage. Low abundances of *T. teres* and *F. barronii* also indicate open-ocean conditions persist throughout the entire studied interval. *Chaetoceros* rs values during this interval vary and suggest unstable water column condition

vi. Chapter V Figures

A. Diatom environmental preferences

Species	Maximum Relative Abundance (MRA) (%)	Temperature at MRA (°C)	Environmental Preference	Sources
<i>Chaetoceros</i> resting spores	91.8 ¹	-0.5-1.5 ¹	Require stable, warm upper water column ²	Armand et al. (2005) ¹ ; Crosta et al. (1997) ²
<i>Thalassiosira oestrupii</i>	21	12-19	Warm water, pelagic	Romero et al. (2005)
<i>Fragilariopsis curta</i>	64.6	0.5-1	Confined southward from the maximum winter sea ice extent. Trace excursions are potentially linked to iceberg pathways.	Armand et al. (2005)
<i>Stellarima microtrias</i>	3.2 ³	-0.5-0.5 ³	Open water with sea ice ⁴	Armand et al. (2005) ³ ; Whitehead et al. (2001) ⁴
<i>Rouxia</i> spp.			Inferred Cold/ Sea-ice preference	Winter et al. (2010)
<i>T. teres</i>			Inferred cold but not sea-ice associated, also present in warm, mixed intervals -perhaps indicates neritic with ~colder SST preference	Winter et al. (2010)
<i>T. striata</i>			Similar to <i>T. teres</i>	Winter et al. 2010
<i>Thalassiosira oliverana</i>	4.2	2.5-3.5	Open-Ocean preference, between maximum winter sea-ice edge and PFZ	Crosta et al. (2005)
<i>Thalassiothrix</i> spp. group	3.1	2-14	Open-Ocean preference	Crosta et al. (2005)
<i>Fragilariopsis barronii</i>			Open-Ocean preference, south of the PFZ	Barron (1996)
Silicoflagellate spp.			Preference for areas of upwelling	Olguin et al. (2006)
<i>E. antarctica</i>		-2-12	No clear correlation of distribution to environmental preference	Zielinski and Gersonde (1997)

<i>Stephanopyxis</i> spp.	Late winter to early spring winds and upwelling, prefer cool waters that are nutrient-rich	Esparza-Alvarez et al. (2007)
<i>T. torokina</i>	Inferred association with Cold and Heavy/Wind-mixed species	Winter et al. (2005)
<i>T. complicata</i>	Inferred mixed, warm species	Winter et al. (2005)

Table 5.1. Environmental preference of abundant or environmentally significant species. Diatom species in the Warm category are highlighted in orange. Species inferred to be Open ocean/ ice tolerant species are highlighted in green. Diatom species in the Cold/Sea-ice group are highlighted in blue. Species in the Heavy/ Wind-Mixed category are highlighted in red, while the species in the Mixed category are highlighted in purple. Diatom species associated with high productivity or stratification are highlighted in grey

VI. Conclusion

This study of the ~3.6-3.2 Ma diatom record of Site 697 is consistently characterized by open-ocean conditions and records a period of decreasing warmth. Even through the M2 glaciation event, Cold/ Sea-Ice species comprise only a small portion of the diatom assemblages, and glacial cycles were minimally reflected in the diatom assemblages.

The base of this interval documents warm, wind mixed conditions associated with low levels of productivity. During Pulse D at 158.52 mbsf, a major increase in diatom productivity, which is interpreted to represent the warmest conditions of the study, marks a significant change in environmental conditions. Temperatures are interpreted to have decreased through the second half of Pulse D. The end of Pulse D records a change back to the warm, wind mixed conditions with increased productivity and stability of the water column. Bottom current activity appears to increase at the start of the M2 glaciation event which persists throughout the top portion of the interval.

The most striking features of the diatom assemblages throughout this interval is the regularly high abundance of *S. oestrupii*. This Warm species is characterized as a tropical/ subtropical species by Romero et al. (2005), and only exceeds a relative abundance over 1% north of the SAF. The high abundances of *S. oestrupii* demonstrate that the modern cold conditions attributed to the Weddell Sea were not yet established by the mid-Pliocene, which is consistent with the greater circum-Antarctic record (e.g., Naish et al., 2009). Consistently low values of modern sea-ice assemblages indicate that the interval between 3.6-3.2 Ma remain largely ice free.

The paleoenvironmental information provided by this mid-Pliocene diatom record will help further constrain the paleo-latitudinal position of the major fronts within the Southern Ocean (e.g., Taylor-Silva and Riesselman, 2018). Future studies should focus on further characterizing other major diatom turnover events of the last 15 Ma as they record major climatic changes specific to the Antarctic.

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