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Late Eocene to early Miocene ice sheet dynamics and the global carbon cycle

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[1] Paired benthic foraminiferal trace metal and stable isotope records have been constructed from equatorial Pacific Ocean Drilling Program Site 1218. The records include the two largest abrupt (<1 Myr) increases in the Cenozoic benthic oxygen isotope record: Oi-1 in the earliest Oligocene (∼34 Ma) and Mi-1 in the earliest Miocene (∼23 Ma). The paired Mg/Ca and oxygen isotope records are used to calculate seawater $\delta^{18}O$ (δw). Calculated δw suggests that a large Antarctic ice sheet formed during Oi-1 and subsequently fluctuated throughout the Oligocene on both short (<0.5 Myr) and long (2–3 Myr) timescales, between about 50 and 100% of its maximum earliest Oligocene size. The magnitudes of these fluctuations are consistent with estimates of sea level derived from sequence stratigraphy. The transient expansion of the Antarctic ice sheet at Mi-1 is marked in the benthic $\delta^{18}O$ record by two positive excursions between 23.7 and 22.9 Ma, each with a duration of 200–300 kyr. Bottom water temperatures decreased by ∼2°C over the 150 kyr immediately prior to both rapid $\delta^{18}O$ excursions. However, the onset of each of these phases of ice growth is synchronous, within the resolution of the records, with the onset of a 2°C warming over ∼150 kyr. We suggest that the warming during these glacial expansions reflect increased greenhouse forcing prompted by a sudden decrease in global chemical weathering rates as Antarctic basement silicate rocks became blanketed by an ice sheet. This represents a negative feedback process that might have operated during major abrupt growth phases of the Antarctic ice sheet. *INDEX TERMS:* 9604 Information Related to Geologic Time: Cenozoic; 4806 Oceanography: Biological and Chemical: Carbon cycling; 4870 Oceanography: Biological and Chemical: Stable isotopes; 4875 Oceanography: Biological and Chemical: Trace elements; 4885 Oceanography: Biological and Chemical: Weathering; *KEYWORDS:* Cenozoic paleoceanography, Antarctic ice sheet, silicate weathering Mg/Ca paleoceanography, sea level, Ocean Drilling Program, Site 1218

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1. Introduction

[2] Earth's transition from the warm, ice-free climate of the early Cenozoic to today's icehouse world is represented by a ∼4‰ increase in the benthic foraminiferal oxygen isotope record ($\delta^{18}O$) over a period of 50 million years [*Shackleton and Kennett*, 1975; *Miller et al.*, 1987; *Zachos et al.*, 2001a]. Of this ∼4‰ $\delta^{18}O$ increase, ∼1‰ can be accounted for by ice stored in present ice sheets [*Shackleton and Kennett*, 1975], while current understanding of oxygen isotope systematics and mass balance considerations of modern ice sheets suggests that the remainder reflects deep sea cooling on the order of 12°C. This long-term cooling trend is generally assumed to reflect, at least in part, reduced greenhouse-forcing accompanying declining levels in atmospheric carbon dioxide [*Berner et al.*, 1983; *Raymo*, 1991; *Pearson and Palmer*, 2000; *Zachos et al.*, 2001a]. Superimposed on the gradual increase in the Cenozoic oxygen isotope record are relatively abrupt increases that are associated temporally with phases of major ice sheet growth. The two largest abrupt (<1 Myr) $\delta^{18}O$ increases are in the earliest Oligocene (Oi-1, ∼34 Ma) and the earliest Miocene (Mi-1, ∼23 Ma). The forcing mechanisms behind the initiation and termination of these abrupt "climate aberrations" are unknown, and the role of ocean gateways, climate thresholds, declining greenhouse gases and orbital parameters have all been implicated in some way [*Kennett and Shackleton*, 1976; *Zachos et al.*, 1993, 2001b; *DeConto and Pollard*, 2003].

[3] Taken alone the oxygen isotope record, which reflects both temperature and ice volume, cannot be used to reconstruct accurately the history of global cooling and ice sheet dynamics through the Cenozoic: additional proxies are required to deconvolve the different components. Benthic foraminiferal Mg/Ca thermometry has shown promise in providing an independent temperature estimate from foraminiferal calcite and, therefore, in resolving the temperature and ice volume contribution to the oxygen isotope record [*Lear et al.*, 2000; *Martin et al.*, 2002; *Billups and Schrag*, 2002]. Previous work across the first major Cenozoic glaciation event at the Eocene-Oligocene boundary suggests

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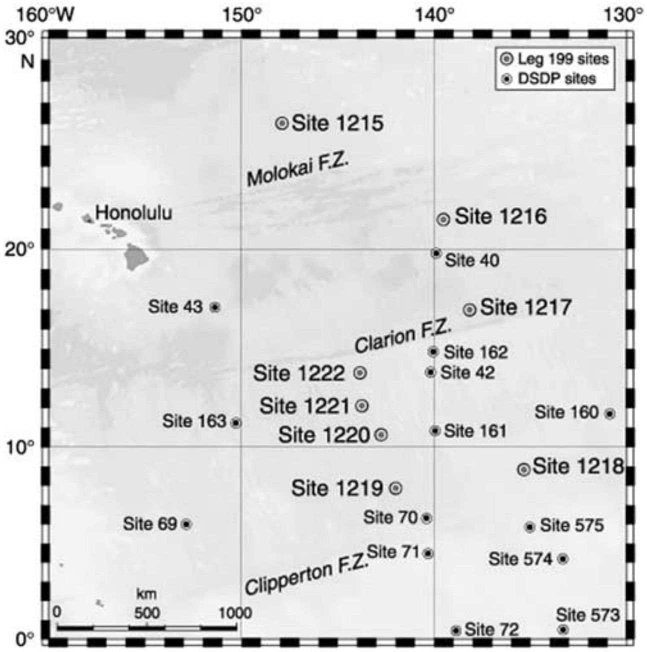

Figure 1. Location of ODP Leg 199 drilling sites.

that the entire oxygen isotope increase may be attributed to increased ice volume [*Lear et al.*, 2000; *Billups and Schrag*, 2003]. This finding has implications not only for the mechanisms of ice growth, but also for the subsequent stability of the Antarctic ice sheet, because mass balance considerations require that the ice sheet decayed substantially before the middle Miocene and Plio-Pleistocene ice growth events. While low-resolution Cenozoic records suggest that the Antarctic ice sheet did indeed undergo major fluctuations in size throughout the Oligocene and Miocene [*Lear et al.*, 2000; *Billups and Schrag*, 2002], a higher-resolution record is required to confirm and define these trends.

[4] Composite stable isotope records are valuable in defining broad global trends in climate [*Zachos et al.*, 2001a] and in providing continuous stratigraphic coverage from otherwise discontinuous records. However, it is becoming increasingly apparent that large interbasin differences in Cenozoic stable isotope records exist, presumably reflecting multiple sources of deep water formation. It is important, therefore, to construct stratigraphically continuous records from single locations. Ocean Drilling Program (ODP) Leg 199 recovered new Paleogene to Neogene sedimentary records from the Pacific Ocean, the world's largest ocean basin, with more-or-less continuous sedimentation and excellent magnetostratigraphic and cyclostratigraphic control [*Lyle et al.*, 2002]. ODP Site 1218 provided the most extended section and, because it was situated just above the calcite compensation depth (CCD) for much of this time ($\sim$3700 m to $\sim$4300 m paleodepth), the most complete calcitic microfossil record. This site is ideally situated for capturing a globally averaged oceanographic signal from deep carbonate sediments, which should represent a true bottom water signal.

[5] Here we present paired benthic foraminiferal stable isotope and Mg/Ca records from the late Eocene to early Miocene. The records are used to assess the stability of the Antarctic ice sheet in a climate warmer than today's. The new record of Antarctic ice sheet growth and decay not only provides an independent record of eustasy in addition to that determined using sedimentary sequences from the New Jersey continental margin [*Kominz and Pekar*, 2001], but also offers new insights into possible feedbacks between the global carbon cycle and climate variability during periods of major glaciations.

2. Oceanographic Setting

[6] ODP Site 1218 is presently located north of the equator in the Pacific Ocean (8°53.378′N, 135°22.00′W) at a water depth of 4828 m, below the modern lysocline [*Lyle et al.*, 2002] (Figure 1). The site, which sits on $\sim$40 Ma crust, was situated on or near the equator from the middle Eocene through Oligocene but subsequently moved out of the high productivity equatorial zone and into the region of slow red clay accumulation in the early Miocene as the Pacific plate drifted north. Paleogene carbonate sediments at Site 1218 are therefore overlain by a relatively thin Neogene siliceous sequence, a condition that, other factors being equal, favors enhanced foraminiferal preservation for open ocean sediments of this age and water depth.

3. Methods

3.1. Core Lithology and Preservation

[7] The samples analyzed in this study are from between 50 and 300 m burial depth, primarily in nannofossil oozes and chalks. The predominant diagenetic process observed to have affected the foraminifera within the sediments is dissolution. In fact, most of the section witnessed such intense dissolution that planktonic foraminifers are only sporadically present, with preferential preservation of dissolution-resistant species (excepting Oligocene zones P20 and P21). There is no conclusive evidence that dissolution affects the stable isotopic composition or trace metal chemistry of benthic foraminifera, although the issue is still under debate [*McCorkle et al.*, 1995; *Martin et al.*, 2002]. Deeply buried (hundreds of meters) planktonic foraminifera from carbonate rich deep sea sites have been shown to be affected by diagenetic processes that involve precipitation of inorganic calcite onto test walls. Foraminifera preserved in hemipelagic clays may have "glassy" preservation, yet the proximity of such sediments to continents precludes the foraminifera from providing a deep ocean bottom water signal [*Norris and Wilson*, 1998; *Pearson et al.*, 2001; *Wilson et al.*, 2002]. Although benthic foraminifera from Site 1218 do not show this type of glassy preservation, the test walls are mostly free of inorganic secondary calcite coatings, perhaps as a result of the low carbonate saturation, and are considered to represent a predominantly primary isotopic signal. However, the sample preservation state deteriorates substantially below about 35 Ma. Indeed, in the deepest part of the record diagentic overprints are also suggested by inverse correlation between foraminiferal Mg/Ca and Sr/Ca, an indicator of post burial geochemical

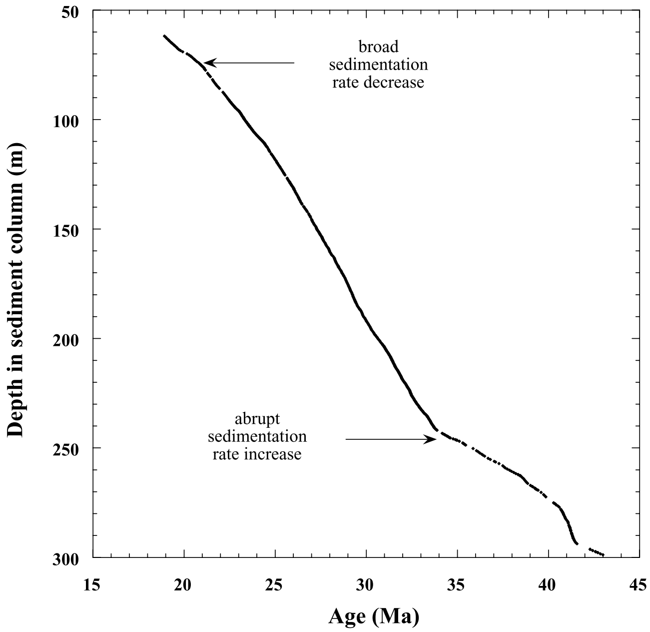

Figure 2. Tuned age (millions of years) versus composite depth in sediment (m) of the ODP Site 1218 samples used in this study. Continuous sample coverage was obtained by using the ODP Leg 199 shipboard composite splice. The small gaps in the record older than 33 Ma represent intervals that did not contain benthic foraminifera.

alteration [*Baker et al.*, 1982]. Furthermore, samples older than 41 Ma have been affected by dolomite contamination [*Lyle et al.*, 2002]. These samples have Mg/Ca around 6 mmol/mol, implying a 0.5% contribution of dolomite to the test calcite. Therefore we do not use the Mg/Ca data from samples older than 35 Ma in our discussion.

3.2. Age Model and Sampling Strategy

[8] Lithological proxy measurements (bulk density, color reflectance and magnetic susceptibility) collected during ODP Leg 199 using the multisensor track (MST) core scanner were used to generate an aligned and stacked revised composite depth (rmcd) scale between ODP Sites 1218 and 1219 [*Lyle et al.*, 2002]. The tuned age model combines magnetostratigraphic, biostratigraphic and cyclostratigraphic data (Figure 2; H. Pälike, personal communication, 2004). Samples were taken from between 61.89 and 298.82 rmcd, the interval where benthic foraminifera are present. The linear sedimentation rate over this interval averages 9.8 m/Myr. Two noticeable changes in sedimentation rate occur in the record (Figure 2). The first is a sharp increase in sedimentation rates in the earliest Oligocene at around 34 Ma, corresponding to the dramatic (~1 km) deepening of the CCD (H. K. Coxall et al., Rapid stepwise onset of Antarctic glaciation and deeper calcite compensation in the Pacific Ocean, submitted to *Nature*, 2004, hereinafter referred to as Coxall et al., submitted manuscript, 2004). The second is a broader decrease in sedimentation rates associated with the gradual northward drift of Site 1218 out of the equatorial zone of high productivity in the early Miocene (approximately 21 Ma) (Figure 2). Samples (20 cc) were taken at ~50 cm intervals for most of the record, and at ~20 cm intervals across the Oligocene-Miocene boundary. This provides a temporal resolution of roughly 40–50 ka and 20–30 ka respectively. Sediments were disaggregated by shaking for 48 hours in deionized water and wet-sieved through 60 μm mesh. The coarse fraction was dry sieved and benthic foraminifera were picked out of the 250–355 μm size fraction. *Oridorsalis umbonatus* was used for trace metal analyses and a consistent mixture of *Cibicidoides* species was used for stable isotope analyses. *O. umbonatus* is a favored species for trace metal analysis owing to its wide geographic distribution, relatively high absolute Mg/Ca, (effectively enabling smaller temperature signals to be reconstructed) and long stratigraphic range (Cenozoic to Recent). *Cibicidoides* species are widely used in constructing stable isotope records because they appear to have consistent and predictable offsets from "equilibrium values" [*Shackleton and Hall*, 1997; *Katz et al.*, 2003]. Replicate stable isotope samples from ODP Site 1218 display little isotopic offset between *C. grimsdalei* and *C. havanensis* (~0.1‰ for $\delta^{18}O$ and $\delta^{13}C$). *C. subspiratus* from the same samples is isotopically lighter (by ~0.2‰ for $\delta^{18}O$ and $\delta^{13}C$). Species abundance varied considerably between samples, so two individuals of each species were used for each sample. The replicate samples showed that this produced a consistent record with values intermediate to all three *Cibicidoides* species. Further details of the species study are available from HKC upon request.

3.3. Analytical Methods

[9] The foraminiferal tests used for trace metal analyses were cleaned using a protocol to remove clays, organic matter and metal oxides [*Boyle and Keigwin*, 1985/1986]. The samples were analyzed at Rutgers University using Finnigan MAT Element Sector Field Inductively Coupled Plasma Mass Spectrometer (ICP-MS) operated in low resolution ($m/\Delta m$ = 300) following the method outlined in the work of *Rosenthal et al.* [1999]. Matrix effects, due to variations in the Ca content of the samples on measured Mg/Ca ratios were corrected for as described in the work of *Lear et al.* [2002]. To limit the variability in Ca concentrations among the samples, foraminifera shells were gradually dissolved in trace metal clean 0.065N HNO_3 (OPTIMA®) and 100 μl of this solution was diluted with 300 μl trace metal clean 0.5N HNO_3 to obtain a Ca concentration of 3 ± 1 mmol L^{-1}. A separate consistency standard with Mg/Ca of 1.25 mmol/mol was analyzed with every sample batch between May 2002 and September 2003, giving a long-term analytical precision (% r.s.d.) of 1.2%, which translates into a temperature uncertainty of approximately ±0.1°C. Stable isotope samples were cleaned ultrasonically in deionized water and analyzed at the Southampton Oceanography Centre using a Europa Geo 20-20 mass spectrometer equipped with a "CAPS" automatic carbonate preparation system. Results are reported relative to Vienna Peedee belemnite standard (VPDB). Standard external analytical precision, based on replicate analysis of

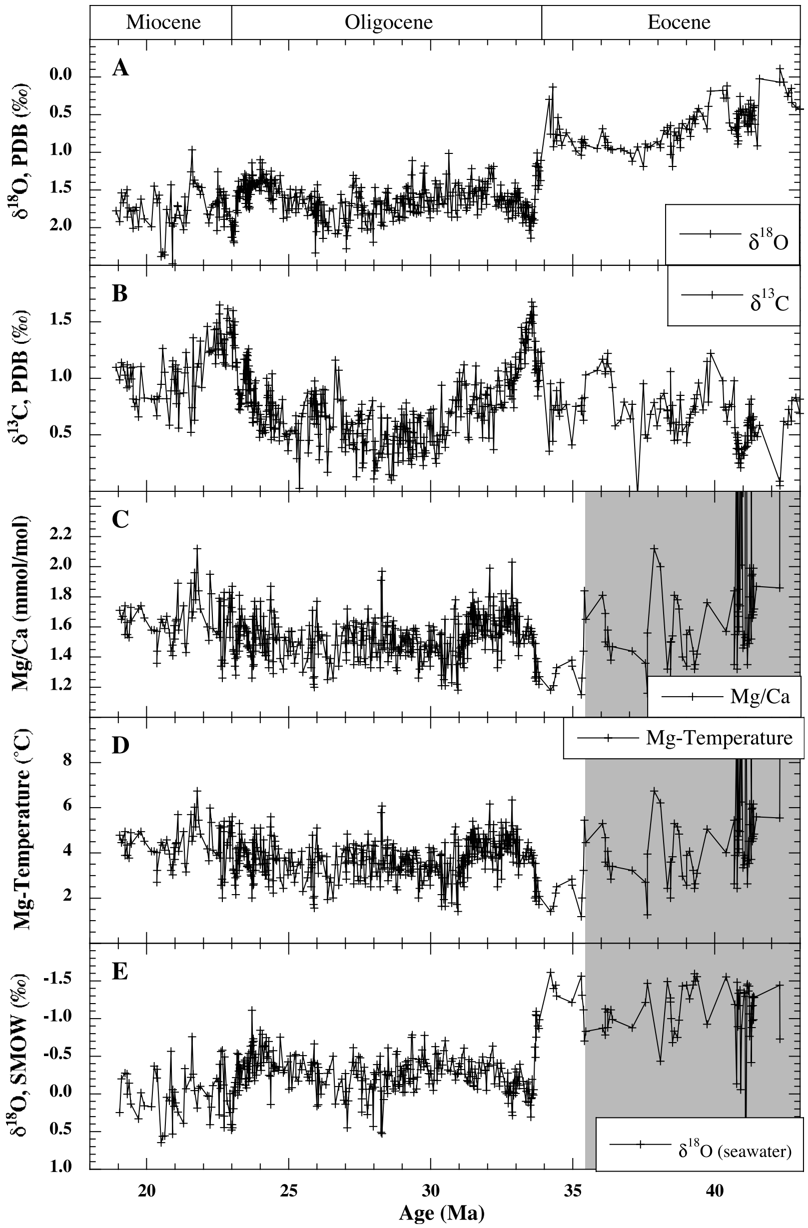

Figure 3. ODP Site 1218 benthic foraminiferal stable isotope and trace metal data versus astronomically tuned age. (a) Benthic foraminiferal $\delta^{18}O$ from *Cibicidoides* spp. (b) Benthic foraminiferal $\delta^{13}C$ from *Cibicidoides* spp. (c) Benthic foraminiferal Mg/Ca from *Oridorsalis umbonatus.* (d) Mg temperatures calculated from the data in Figure 3c using the *O. umbonatus* calibration of *Lear et al.* [2002] and assuming modern day seawater Mg/Ca. (e) Calculated seawater $\delta^{18}O$ using the data in Figures 3b and 3d. The *Cibicidoides* $\delta^{18}O$ data were first adjusted by adding 0.5‰ to obtain "equilibrium values" [*Shackleton and Hall*, 1997].

in-house standards calibrated to NBS-19, is better than 0.1‰ for $\delta^{18}O$ and $\delta^{13}C$.

[10] The raw data contain some obvious "fliers." In the case of the trace metal records we attribute these to natural variability in the calcite test and contamination by secondary phases not removed during the vigorous cleaning procedure (e.g., inorganic calcite, dolomite and clays). In the stable isotope records we attribute fliers to a failing collector. In Figures 3–5 we do not plot data that are more than three standard deviations different from the mean of the four points bracketing the sample (a generous screening that only removes very obvious fliers).

4. Results

4.1. Stable Isotope Records

[11] The oldest benthic foraminifera analyzed in this study are of late Eocene age (42 Ma) and have $\delta^{18}O$ of

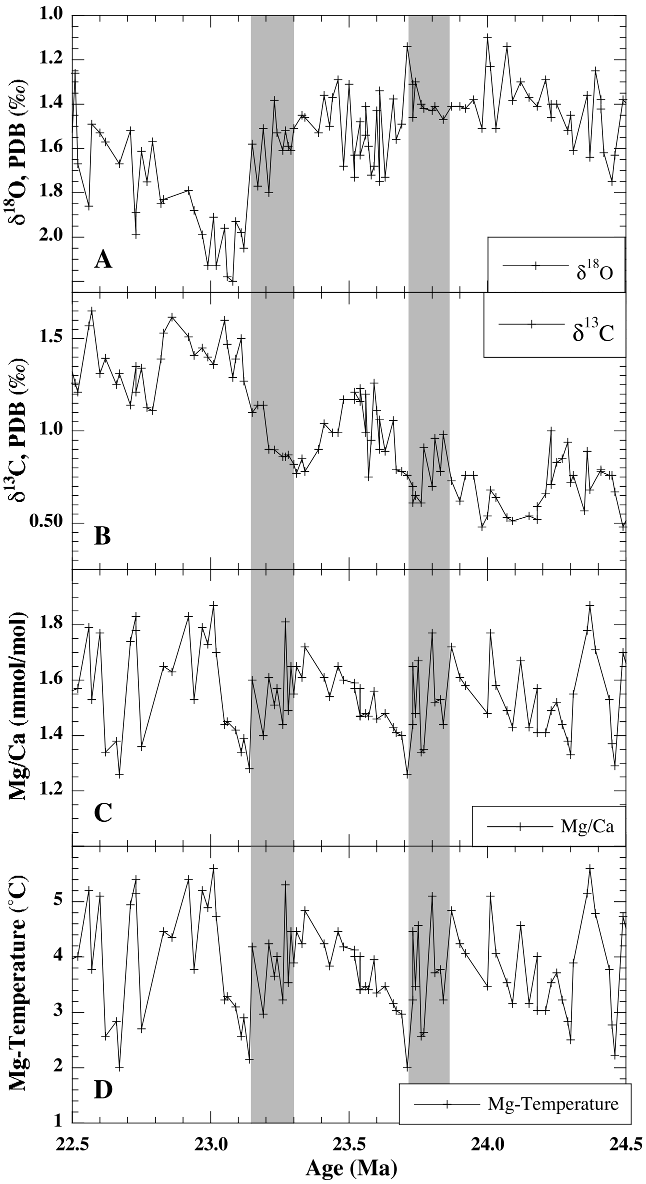

Figure 4. ODP Site 1218 benthic foraminiferal stable isotope and trace metal data versus tuned age highlighting the Mi-1 isotope event. (a) Benthic foraminiferal $\delta^{18}O$ from *Cibicidoides* spp. (b) Benthic foraminiferal $\delta^{13}C$ from *Cibicidoides* spp. (c) Benthic foraminiferal Mg/Ca from *Oridorsalis umbonatus.* (d) Mg temperatures calculated from the data in Figure 3c using the *O. umbonatus* calibration of *Lear et al.* [2002] and assuming modern day seawater Mg/Ca. The vertical shaded bars represent intervals of cooling inferred from the benthic foraminiferal Mg/Ca record.

around 0‰ (Figure 3). Benthic $\delta^{18}O$ increases gradually to around 1‰ by 35 Ma before a more rapid decrease of about 0.5‰ in the latest Eocene. The earliest Oligocene (34 to 33.5 Ma) displays a two-phase $\delta^{18}O$ increase totaling ~1.5‰, which is equivalent to "Oi-1" event using the terminology of *Miller et al.* [1991]. Following the rapid increase in the earliest Oligocene, $\delta^{18}O$ values remained relatively high (>1.0‰), decreasing to a broad early Oligocene minimum of ~1.5‰ at 31 Ma, before gradually returning to values similar to those at Oi-1 (~2‰) by 28 Ma. A brief (<1 Myr) excursion toward lighter values is centered at 27.3 Ma is superimposed on the longer-term trends. $\delta^{18}O$ subsequently decreases gradually to a minimum of ~1.3‰ at ~24 Ma, prior to a second abrupt positive excursion in the isotope record at the Oligocene-Miocene boundary. The excursion consists of a total increase of around 1‰ occurring in two phases, attaining maximum values of 2.2‰ at 23 Ma (Mi-1 using the terminology of *Miller et al.* [1991]). Following the Mi-1 event, the Neogene $\delta^{18}O$ record shows greater amplitude variations in $\delta^{18}O$, although we have not been able to further resolve these patterns with our data set because of slower sedimentation during this interval, and scarcity of foraminifera in the less carbonate-rich extra-equator sediments. The pre Oi-1 $\delta^{18}O$ record shows less 10^4-10^5 year variability than the post Oi-1 $\delta^{18}O$ record. This partly reflects the lower sample resolution, a result of the reduced sedimentation rates prior to the CCD deepening across Oi-1. However, we also attribute part of the increased variability post Oi-1 to the $\delta^{18}O$ record comprising variations in ice volume as well as temperature.

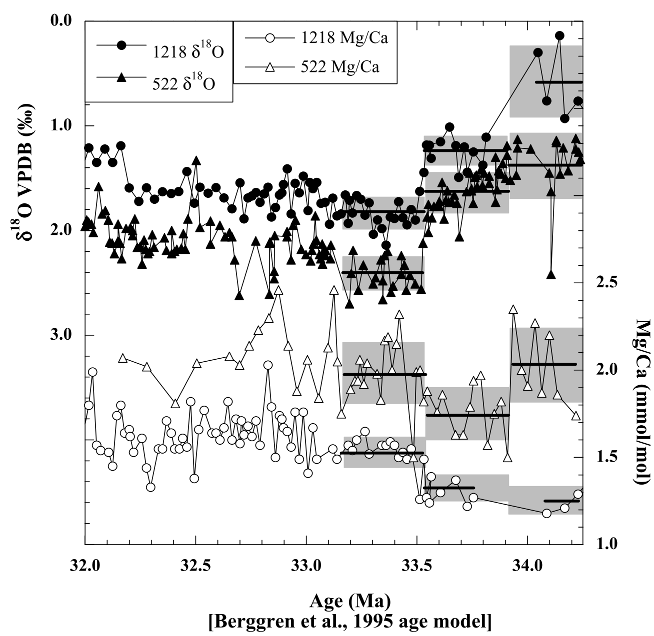

Figure 5. Benthic foraminiferal $\delta^{18}O$ (open symbols) and Mg/Ca (closed symbols) records across Oi-1 from Deep Sea Drilling Project Site 522 [*Zachos et al.*, 1996; *Lear et al.*, 2000] and Ocean Drilling Program Site 1218. Site 522 data are represented by triangles, Site 1218 data are represented by circles. The shaded boxes represent the two standard deviations of benthic foraminiferal Mg/Ca and $\delta^{18}O$ within three time intervals: immediately prior to the first isotope step, across and immediately following the first isotope step, and across and immediately following the second isotope step (see text).

[12] The benthic carbon isotope record varies between about 0 and 1.5‰, with a mean value of 0.77‰ (Figure 3). Values are low in the late Eocene and rise gradually from about 0‰ to 1‰ between 42 and 35 Ma. There is a general decrease in $\delta^{13}C$ in the early Oligocene, from about 1‰ to $\sim$0.5‰ between 33 and 30 Ma and another phase of $\delta^{13}C$ increase between 28 and 23 Ma. Superimposed on these broad trends are two intervals of rapid increase in $\delta^{13}C$. The first coincides with the early Oligocene Oi-1 event, and the second with the early Miocene Mi-1 event. Both excursions comprise an increase of around 1‰, and both are transient features in the record.

4.2. Mg/Ca and Mg-Temperature Records

[13] Mg/Ca ratios in benthic foraminifera (*O. umbonatus*) show relatively low variability through the Oligocene (between 23.03 and 33.95 Ma), averaging 1.53 ± 0.272 mmol/mol (2 s.d.), and are bracketed by two Mg/Ca maxima centered at about 32.5 Ma ($\sim$1.7 mmol/mol) and 21.5 Ma ($\sim$1.8 mmol/mol). As discussed above, Mg/Ca ratios in samples older than about 35 Ma may be diagenetically altered. Bottom water temperatures are calculated from the Mg/Ca data using the calibration equation determined from a core-top study of the same species used in this study, *Oridorsalis umbonatus* [*Lear et al.*, 2002]. In order to do this, it is necessary to estimate seawater Mg/Ca at the time the foraminifera was calcifying its shell. Seawater Mg/Ca may have changed over the interval studied [*Wilkinson and Algeo*, 1989; *Stanley and Hardie*, 1998], although a recent reevaluation of seafloor spreading and oceanic crustal generation rates, one of the primary influences on seawater Mg/Ca over geological timescales, suggests little variation throughout the Cenozoic [*Rowley*, 2002]. Additional evidence comes from examination of parallel benthic foraminiferal Sr/Ca records. Calcium has a residence time about ten times shorter than that of magnesium, and variations in seawater Mg/Ca driven solely by changes in calcium concentration should be similar to variations in seawater Sr/Ca (although unlike Mg/Ca, seawater Sr/Ca would not be affected by variations in dolomite formation). Benthic foraminiferal Sr/Ca may be used to estimate seawater Sr/Ca if the appropriate partition coefficient is known [*Graham et al.*, 1982; *Delaney et al.*, 1985; *Lear et al.*, 2003]. Our ODP Site 1218 Sr/Ca record from *Oridorsalis umbonatus* averages 0.78 mmol/mol between 19 and 35 Ma, with up to 10% variability around the mean on timescales of $\ll$1 Myr, but little systematic long-term trend. Therefore we assume that seawater Mg/Ca remained more or less constant over the study interval, and use the modern day seawater value to calculate Mg temperatures. BWT calculated using the modeled seawater Mg/Ca values of *Wilkinson and Algeo* [1989] would have the effect of increasing our absolute temperatures by $\sim$1°C in the youngest part of our record (19 Ma) and by $\sim$2°C in the oldest part of our record, but short-term variations in temperature throughout the record would be unaffected by the choice of seawater Mg/Ca.

[14] We estimate that through the Oligocene, bottom water temperatures at Site 1218 averaged 3.7°C with variations of about ±1.5°C on less than 0.5 Myr timescales (Figure 3). In addition there are well-defined trends in benthic foraminiferal Mg/Ca associated with major climatic transitions. The first trend is an increase from 1.2 mmol/mol to 1.6 mmol/mol that corresponds to a warming of 2°C across the Oi-1 event. Subsequently, Mg/Ca decreases to 1.4 mmol/mol between 31.5 and 30.5 Ma, equivalent to a 2°C cooling. A $\sim$1°C warming is observed between 30 and 28 Ma, followed by a 1°C cooling between 28 and 26 Ma, as Mg/Ca again decreases back to 1.4 mmol/mol. The Mg/Ca record also exhibits some intriguing features across the Mi-1 event (Figure 4). Mg/Ca initially decreases from 1.6 to 1.3 mmol/mol between 23.8 and 23.7 Ma, suggesting a relatively rapid cooling of 2°C. Subsequently, Mg/Ca displays a well-defined though slightly more gradual increase back to 1.6 mmol/mol between 23.7 and 23.3 Ma, presumably reflecting a warming of 2°C. This cycle is repeated with a second abrupt cooling of 2°C between 23.3 and 23.1 Ma associated with the second isotope step, followed by a 2.5°C warming reaching a maximum temperature of $\sim$5°C at 23.0 Ma.

5. Discussion

5.1. Intersite Variations

[15] Benthic foraminiferal Mg/Ca at Site 1218 are lower than Mg/Ca of the same age from shallower paleowater depths. For example, Oligocene mean Mg/Ca at ODP Site 1218 (paleowater depth > 3500 m) is 1.53 mmol/mol (n = 372). Oligocene mean Mg/Ca at Deep Sea Drilling Project (DSDP) Site 573 (paleowater depth $\sim$3000 m) is 1.80 mmol/mol (n = 16) [*Lear et al.*, 2000]. This Mg/Ca offsets implies that Site 1218 was 1.4°C cooler than Site 573, yet the benthic oxygen isotope records from DSDP Site 77 (similar location and water depth to DSDP Site 573) are similar to those of ODP Site 1218 [*Keigwin and Keller*, 1984]. These observations may be reconciled by invoking a deeper water mass at ODP Site 1218 that is 1.4°C colder, and has 0.6‰ lower salinity (assuming a 1.0‰ salinity change corresponds to a $\sim$0.5‰ change in $\delta^{18}O$ of seawater [*Broecker*, 1989]). However, we note that additional factors may have influenced the Mg/Ca and/or $\delta^{18}O$ records (e.g., species offsets, interlaboratory offsets, precipitation effects, diagenesis [*McCorkle et al.*, 1995; *Pearson et al.*, 2001; *Martin et al.*, 2002]).

[16] Composite stable isotope records provide valuable continuous stratigraphic coverage from otherwise discontinuous records [e.g., *Miller et al.*, 1987; *Zachos et al.*, 2001a]. However, as discussed above, there is increasing evidence for significant interbasin differences in both water temperature and salinity, suggesting that there may be instances where splicing together records from different sites may lead to an aliased climate signal. An example of this could be the late Oligocene warming that is shown in the composite $\delta^{18}O$ record but not in our continuous Site 1218 $\delta^{18}O$ record [*Zachos et al.*, 2001a]. This warming is therefore likely an artifact of the switch from Southern Ocean to Pacific and North Atlantic sites in the composite record. While there remains some measure of uncertainty in comparing absolute Mg/Ca

and $\delta^{18}O$ records at present, there are interesting similarities and differences in the temperature trends between sites.

5.2. Benthic Foraminiferal Mg/Ca Across the Oi-1 Event

[17] The positive oxygen isotope shift across Oi-1 occurs in two distinct phases (Coxall et al., submitted manuscript, 2004). Although the first phase at Site 1218 is interrupted by a data gap, DSDP Site 522 Mg/Ca records are continuous and show this phase to be associated with a 2°C cooling of intermediate depth waters (Figure 5). The second phase is associated with an apparent warming in the benthic Mg/Ca records at both Site 522 and Site 1218. This apparent warming leads to little overall temperature change at Site 522 [*Lear et al.*, 2000] and an overall 2°C warming of deep waters at 1218 associated with Oi-1. The timing of the two Mg/Ca trends leads us to hypothesize that the Mg/Ca decrease at Site 522 reflects a ~2°C cooling of intermediate waters that was somehow associated with the underlying cause of the Antarctic glaciation, while the Mg/Ca increase observed at both sites reflects a response to the glaciation event. Clearly additional high-resolution records are required to reconstruct the changing paleoceanography at this time.

[18] We consider two possible causes of the Mg/Ca increase coinciding with the second phase of the isotope shift. The first possibility is that it reflects a temperature increase caused directly by Antarctic glaciation. The temperature increase may reflect a $p\mathrm{CO_2}$ induced greenhouse effect, resulting from glacial blanketing of the vast expanse of Antarctic silicate bedrock, previously an enormous sink for atmospheric CO_2 via chemical weathering. Eventually the increased $p\mathrm{CO_2}$ would cause chemical weathering rates elsewhere to increase, until global chemical weathering rates readjusted to the new conditions. Thus the Mg temperature record reflects a transient negative feedback response of the climate system to the expanding Antarctic ice sheet. This mechanism has been proposed for the late Ordovician glaciation [*Kump et al.*, 1999]. The switch from rapid clastic sedimentation to slow carbonate sedimentation in the Tasmanian Seaway in the earliest Oligocene provides support for this hypothesis [*Shipboard Scientific Party*, 2001].

[19] The second possibility is that a dramatic increase in deep water carbonate saturation has influenced the Mg/Ca data. The Eocene-Oligocene transition has been associated with a ~1 km deepening of the CCD [*van Andel*, 1975; Coxall et al., submitted manuscript, 2004]. Core-top Mg/Ca data from deep ocean bathymetric transects have hinted at a secondary control on benthic foraminiferal Mg/Ca other than temperature [*Russell et al.*, 1996; *Martin et al.*, 2002]. Specifically, Mg/Ca from core-top depth transects appears to decrease faster than expected when temperature alone is considered. No systematic difference in Mg/Ca between "live" and "dead" benthic foraminifera has been found, suggesting that the depth-dependent secondary control on Mg/Ca is more likely to be a precipitation effect rather than a dissolution effect [*Marchitto et al.*, 2000; *Lear et al.*, 2002]. The current Mg/Ca–temperature calibration predicts a ~10% decrease in benthic foraminiferal Mg/Ca associated with the 1°C temperature decrease between 3200 m and 4700 m water depth on Ceara Rise. However, Mg/Ca decreases from 1.2 mmol/mol to 0.7 mmol/mol over the 1.5 km depth transect (Figure 6). Therefore, if the dramatic 1 km deepening of the CCD across the Eocene-Oligocene transition is equivalent to moving 1 km up the Ceara Rise depth transect, we might expect the increased carbonate saturation to have caused a 20% increase in benthic foraminiferal Mg/Ca, roughly equivalent to an apparent 2°C warming. This is the magnitude of the Mg/Ca increase observed across the second phase of the isotope shift, yet the 1 km CCD deepening, revealed by bulk sediment $\%\mathrm{CaCO_3}$ measurements, occurred across both phases of the isotope shift (Coxall et al., submitted manuscript, 2004). In the latest Eocene, the paleowater depth of ODP Site 1218 was similar to that of the CCD [*Lyle et al.*, 2002]. In these undersaturated waters, benthic foraminiferal Mg/Ca may have been sensitive to the initial increase in carbonate saturation across the Eocene-Oligocene transition. Benthic foraminiferal Mg/Ca was likely less sensitive to the second incremental phase of increasing carbonate saturation. This could explain why the contrast between the deep ODP Site 1218 Mg/Ca record and the intermediate depth DSDP Site 522 Mg/Ca record is greater across the first phase than the second phase of the isotope shift.

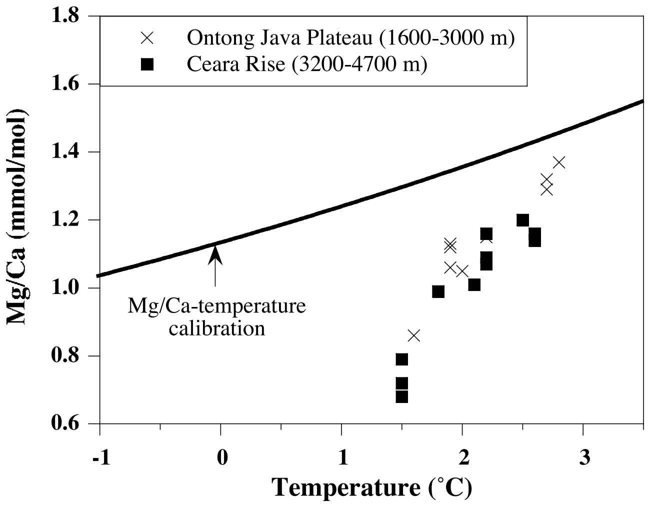

Figure 6. Published core-top benthic foraminiferal Mg/Ca from two water depth transects show a steeper decrease in Mg/Ca relative to temperature than expected relative to the temperature calibration [*Martin et al.*, 2002; *Lear et al.*, 2002].

[20] We therefore consider the possibility that the initial increase in carbonate saturation at ODP Site 1218 caused a Mg/Ca increase that was offset by a cooling of deep waters, while the Mg/Ca increase associated with the second phase of the transition reflects a warming, perhaps also with some small influence from increasing carbonate saturation levels. Taking this uncertainty into account, the underlying cause

of the early Oligocene ice sheet growth (i.e., polar cooling versus increased precipitation) remains unresolved. For example, a polar warming prompting ice growth through a "snow-gun hypothesis" has been proposed [*Prentice and Matthews*, 1991]. In addition, we note that a higher-resolution study is required to determine the lead-lag relationship between the $\delta^{18}O$ and the Mg/Ca records across each phase of Oi-1. We emphasize that the Eocene-Oligocene CCD deepening was an extreme and unique event; we do not believe that carbonate saturation was a significant control on benthic foraminiferal Mg/Ca at other specific times in the record.

5.3. Benthic Foraminiferal Mg/Ca Across the Mi-1 Event

[21] The Mi-1 event is the first significant, transient isotope excursion in the Miocene and is marked by two positive steps in benthic oxygen isotope records [*Miller et al.*, 1991; *Paul et al.*, 2000]. The Mg/Ca temperature record suggests that deep waters cooled by around 2°C at the inception of Mi-1 (23.8–23.7 Ma), which may have been the trigger for expansion of the Antarctic ice sheet at this time (Figure 4). However, following the initial stages of ice buildup, Mg temperatures gradually warmed by 2°C between 23.7 and 23.3 Ma. We propose that the warming represents a negative feedback in the climate system, which we attribute to a greenhouse effect caused by the reduction in global chemical weathering rates resulting from the blanketing of Antarctic bedrock by the newly formed ice sheet, similar to the scenario hypothesized in the early Oligocene. The warming led to partial melting of the ice sheet, and by 23.3 Ma, both deep-sea temperatures and the extent of the ice sheet had recovered to pre-Mi-1 values. The cooling of Mg/Ca temperatures by about 2°C between 23.3 and 23.1 Ma is associated with the second advance of the Antarctic ice sheet as indicated in the $\delta^{18}O$ record. Once again, blanketing of the Antarctic continent is followed by a ~2.5°C warming of deep and therefore possibly polar surface waters. The benthic Mg/Ca temperature record contains shorter term warming and cooling cycles. A higher-resolution study is needed to determine whether these temperature cycles might be related to orbital forcing.

[22] The hypothesized increase in pCO_2 would have caused changes in the isotopic fractionation of carbon by photosynthetic organisms, leading to an increase in whole ocean $\delta^{13}C$. An increase in pCO_2 from 230 to 460 ppmV could account for the positive 1‰ shift observed across the Mi-1 event. Owing to the nonlinear response of carbon fractionation to pCO_2 shown by phytoplankton, this scenario requires an initially low paleoatmospheric pCO_2 (e.g., 230 ppmV), in agreement with published estimates [*Pagani et al.*, 1999]. An alternative mechanism to cause the increase in whole ocean $\delta^{13}C$ is to increase the burial fraction of organic carbon to carbonate carbon at this time [*Kump*, 1991], yet there is little evidence of organic carbon rich sediments deposited at this time. Likewise, a regional reduction in carbonate mass accumulation rates has been found between Mi-1 and Mi-2, but not associated with the Mi-1 event itself [*Lyle*, 2003].

5.4. Seawater $\delta^{18}O$ and a Sequence Stratigraphic Record of Eustasy

[23] The benthic Mg/Ca temperature record is combined with the oxygen isotope record to calculate variations in seawater $\delta^{18}O$ (δw) (Figure 3). We use the equation: $\delta w = (T\text{-}16.5 + 4.8{*}\delta^{18}O)/4.8 + 0.27$ [*Bemis et al.*, 1998]. Using the equation of *Shackleton* [1974] produces a record that is similar in form, but is offset to lighter vales by an average of 0.6‰ ± 0.1‰ (2 s.d.). Calculated δw increases by about 1.5‰ across Oi-1, although the magnitude of this shift (and therefore all post-Oi-1 absolute values) could be artificially high if part of the Mg/Ca increase across Oi-1 is a response to the 1 km deepening of the CCD at this time. Following Oi-1, the measured $\delta^{18}O$ and calculated δw records display variations on the order of 0.4–0.6‰, on short (around 100 kyr) timescales. Superimposed on these variations are longer-term trends. Between 33 and 31 Ma, δw decreases by about 0.5‰, which we interpret as reflecting a gradual halving in the mass of the Antarctic ice sheet over the two million year interval. The ice sheet subsequently increased in mass, reaching its former size at ~28 Ma. Calculated δw values are generally relatively high between 27 and 28 Ma, although there is a brief "interstadial-like" event, lasting ~0.5 Myr, centered at 27.3 Ma during which the ice sheet was abruptly reduced to half of its previous size before returning to background values. A second long-term trend of decreasing ice volume started around 27 Ma, with the size of the ice sheet again reaching about half of its former mass at ~24 Ma. Between 24 and 23 Ma, two rapid pulses of ice sheet growth culminate in "Mi-1" at 23 Ma, with the ice sheet again reaching the size of its Oi-1 counterpart.

[24] A record of eustasy determined from backstripping sedimentary sequences from the New Jersey coastal margin has recently been published for the Oligocene [*Kominz and Pekar*, 2001]. The eustasy record is multiplied by 1.48 to convert to apparent sea level [*Pekar et al.*, 2002]. This published record uses the *Berggren et al.* [1995] timescale, so we have plotted our record of seawater $\delta^{18}O$ on this timescale (Figure 7) and use these ages in the following discussion. The dramatic increase in carbonate saturation may have caused the apparent 2°C warming across the Eocene-Oligocene transition (section 5.2). Therefore the post-Oi-1 δw estimates may be biased by ~0.44‰ toward heavier values, equivalent to a sea level drop of ~40 m using the Pleistocene calibration of *Fairbanks and Matthews* [1978] of 0.11‰ per 10 m sea level change. We compare the backstripping derived sea level curve to both uncorrected and corrected δw records. The δw record that is corrected by −0.44‰ agrees more closely with the backstripping derived sea level curve, lending support to the idea that the overall Mg/Ca increase across Oi-1 at Site 1218 is at least in part a response to the dramatic increase in the carbonate saturation state (Figure 7).

[25] There is a broad coherence between our seawater $\delta^{18}O$ record and the independent record of sea level change [*Kominz and Pekar*, 2001]. Both records indicate a large sea level fall in the earliest Oligocene, associated with Oi-1. Our

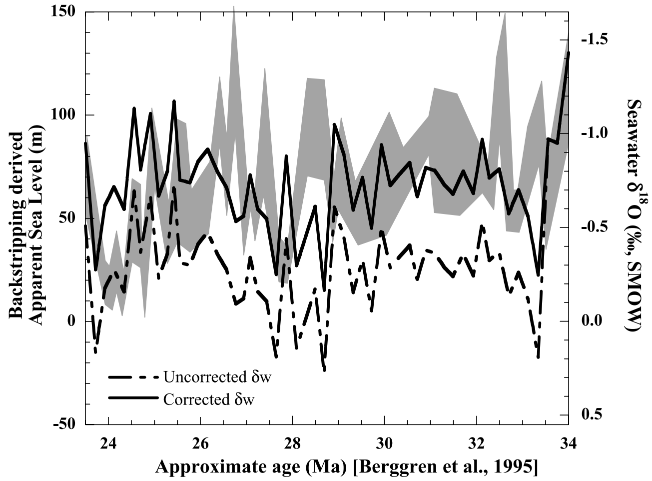

Figure 7. Seawater δ^{18}O calculated from ODP Site 1218 benthic foraminiferal δ^{18}O and Mg-temperatures (dashed heavy line). The solid heavy line represents calculated seawater δ^{18}O that has been "corrected" by -0.44‰ (see text). Both lines represent a Kaleidagraph® weighted fit (1%) which uses the locally least squared error method to fit the best smooth curve through the compiled seawater δ^{18}O data. The shaded gray area represents the *Kominz and Pekar* [2001] record of "apparent sea level" determined from New Jersey coastal margin sediments. Both records are plotted on the *Berggren et al.* [1995] timescale.

estimate derived from the "corrected" δw curve is on the order of 90 m, compared to backstripping estimates of 80 ± 15 m. Without the -0.44‰ correction, our sea level fall increases to around 130 m, which is outside the range of the backstripping estimates. The Oi-1 sea level fall is followed by a general rise in sea level and a subsequent fall to a lowstand at ~28 Ma. Both records suggest a sea level rise after 28 Ma, followed by a further sea level drop culminating at the Mi-1 event, at ~24 Ma (on the *Berggren et al.* [1995] timescale). The timing of some of the variations is slightly offset between the records, however, and we attribute this to poorer age control in the New Jersey sequence stratigraphy records. For example, the younger portion of the eustasy record (23.9–25.5 Ma) is dated using strontium isotope stratigraphy with absolute age uncertainties of ±0.6–1.0 Myr [*Kominz and Pekar*, 2001], and appears offset toward older ages relative to the δw record. Despite the broad coherence between the two records, the sequence stratigraphy derived sea level record also contains two significant highstands (at 26.7 Ma and 32.6 Ma) that are not supported by the δw record, and whose duration appears too short to be explained by changes in tectonoeustasy. Nevertheless, if the Pleistocene calibration of 0.11‰ per 10 m sea level change [*Fairbanks and Matthews*, 1978] is assumed for this interval, then both techniques suggest that sea level varied on the order of 50 to 100 m throughout the Oligocene, and that the Antarctic ice sheet varied between about 100 and 50% of its earliest Oligocene mass (Figure 7). As pointed out by *Pekar et al.* [2002], the general agreement between the magnitudes of the eustasy record and the sea level estimates using the Pleistocene calibration suggests that the oxygen isotopic composition of Oligocene snow was not substantially different to Pleistocene snow, despite the warmer climate.

6. Conclusions

[26] Significant intersite differences in both Mg/Ca and δ^{18}O records suggest that global compilations of paleoceanographic records may misrepresent certain features of the climate record. Although they complicate global compilations, intersite offsets in Mg/Ca and δ^{18}O records are extremely informative if they reflect the physical properties of different water masses. A caveat is that such differences may also reflect interlaboratory analytical offsets, species effects or diagenetic processes, but the general coherence of δ^{18}O records from a particular water depth and region suggests that they record a paleoceanographic signal. It seems that with additional records we will be able to start reconstructing the paleo-ocean general hydrography and circulation.

[27] This paper, as previous ones, raises a concern about the accuracy of bottom water temperature estimates derived from benthic foraminiferal Mg/Ca in deep ocean sediments. Specifically, the increase in benthic foraminiferal Mg/Ca coincident with the ~1 km deepening of the CCD across Oi-1 leads us to reassess the possibility of a carbonate saturation effect on benthic foraminiferal Mg/Ca. Carbonate saturation has been shown to affect the partitioning of other trace metals into calcite at low levels of saturation (e.g., Zn/Ca; *Marchitto et al.* [2000]). Plotted versus bottom water temperature, modern benthic foraminiferal Mg/Ca from waters above 4°C lie on a single exponential curve regardless of carbonate saturation state [*Lear et al.*, 2002], whereas at lower temperatures there is evidence for the influence of the calcite saturation state on the Mg/Ca ratio of benthic foraminifera. It is unknown, however, whether this change in trend is due to postburial dissolution or a carbonate ion effect during the shell calcification. Clearly, if we are to use Mg/Ca paleothermometry for reconstructing deep ocean temperatures, an effort should be made to resolve these fundamental questions.

[28] The isotope events in the earliest Oligocene and earliest Miocene (Oi-1 and Mi-1 respectively) are both associated with increased continental ice volume and, surprisingly, increased deep-sea temperature. A high-resolution record of δ^{18}O and Mg/Ca across Mi-1 at Site 1218 shows that the inception of Mi-1 was in fact associated with a 2°C cooling, and that the subsequent deep sea warming lagged the ice growth. We propose a "missing sink" mechanism whereby the rapid glacial blanketing of the vast Antarctic continent shut down an enormous chemical weathering sink for atmospheric CO_2. Until global chemical weathering rates achieved a new steady state, this would cause atmospheric pCO_2 to increase, thus causing global warming via a greenhouse effect. Under higher pCO_2, the δ^{13}C of organic carbon decreases, resulting in increased mean oceanic δ^{13}C. A spectral analysis study suggests that the δ^{18}O increases lead slightly (0–28 kyr) the foraminiferal

$\delta^{13}C$ increases during Mi-1 [*Paul et al.*, 2000]. An increased pCO_2 scenario provides a negative feedback to the glaciation, whereas the alternative explanation proposed for the oceanic $\delta^{13}C$ increase (increased organic carbon burial) provides a positive feedback [*Paul et al.*, 2000]. Therefore an advantage of our "missing sink" mechanism is that it can also account for the transient nature of the Mi-1 event.

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