Paleotemperatures and ice volume of the past 27 Myr revisited with paired Mg/Ca and ^{18}O/^{16}O measurements on benthic foraminifera

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[1]   We explore the applicability of paired Mg/Ca and ^{18}O/^{16}O measurements on benthic foraminifera from Southern Ocean site 747 to paleoceanographic reconstructions on pre-Pleistocene timescales. We focus on the late Oligocene through Pleistocene (27–0 Ma) history of paleotemperatures and the evolution of the δ^{18}O values of seawater (δ^{18}O$_{sw}$) at a temporal resolution of ~100–200 kyr. Absolute paleotemperature estimates depend on assumptions of how Mg/Ca ratios of seawater have changed over the past 27 Myr, but relative changes that occur on geologically brief timescales are robust. Results indicate that at the Oligocene to Miocene boundary (23.8 Ma), temperatures lag the increase in global ice-volume deduced from benthic foraminiferal δ^{18}O values, but the smaller-scale Miocene glaciations are accompanied by ocean cooling of ~1°C. During the mid-Miocene phase of Antarctic ice sheet growth (~15–13 Ma), water temperatures cool by ~3°C. Unlike the benthic foraminiferal δ^{18}O values, which remain relatively constant thereafter, temperatures vary (by 3°C) and reach maxima at ~12 and ~8.5 Ma. The onset of significant Northern Hemisphere glaciation during the late Pliocene is synchronous with an ~4°C cooling at site 747. A comparison of our δ^{18}O$_{sw}$ curve to the *Haq et al.* [1987] sea level curve yields excellent agreement between sequence boundaries and times of increasing seawater ^{18}O/^{16}O ratios. At ~12–11 Ma in particular, when benthic foraminiferal δ^{18}O values do not support a further increase in ice volume, the δ^{18}O$_{sw}$ curve comes to a maximum that corresponds to a major mid-Miocene sea level regression. The agreement between the character of our Mg/Ca-based δ^{18}O$_{sw}$ curve and sequence stratigraphy demonstrates that benthic foramaniferal Mg/Ca ratios can be used to trace the δ^{18}O$_{sw}$ on pre-Pleistocene timescales despite a number of uncertainties related to poorly constrained temperature calibrations and paleoseawater Mg/Ca ratios. The Mg/Ca record also highlights that deep ocean temperatures can vary independently and unexpectedly from ice volume changes, which can lead to misinterpretations of the δ^{18}O record.   INDEX TERMS: 4267 Oceanography: General: Paleoceanography, 4825 Oceanography: Biological and Chemical: Geochemistry, 4870 Oceanography: Biological and Chemical: Stable isotopes, 4875 Oceanography: Biological and Chemical: Trace elements KEYWORDS: paleoceanography, geochemistry, stable isotopes, trace elements

1.   Introduction

[2]   Mg/Ca ratios of foraminifera present a new geochemical proxy for seawater paleotemperatures [*Hastings et al.*, 1998; *Rosenthal et al.*, 1997; *Mashiotta et al.*, 1999; *Nuernberg et al.*, 2000; *Lear et al.*, 2000; *Elderfield and Ganssen*, 2000]. In conjunction with the oxygen isotopic composition of foraminifera this proxy has the potential to provide a means to trace the evolution of the oxygen isotopic composition of seawater (δ^{18}O$_{sw}$) and to infer the timing and stability of polar ice sheets and associated sea level changes. So far, most studies have focused on the application of Mg paleothermometry on relatively short, Pleistocene timescales [*Nuernberg*, 1995; *Nuernberg et al.*, 2000; *Mashiotta et al.*, 1999; *Hastings et al.*, 1998; *Elderfield and Ganssen*, 2000; *Lea et al.*, 2000] because the magnitude of changing seawater Mg/Ca ratios on longer, tectonic timescales is difficult to constrain. *Lear et al.* [2000] present a 70 million year long, low-resolution Mg/Ca record that roughly parallels a composite foraminiferal δ^{18}O record and suggests that water temperature might be the primary variable controlling the amount of Mg in a calcite test on timescales longer than the residence time of Mg in seawater (~13 Ma [*Broecker and Peng*,

1982]). Absolute paleotemperature reconstructions, however, are still limited by a lack of calibrations applicable to the cold temperatures (<5°C) of the deep ocean.

[3]   In this study we explore the potential of benthic foraminiferal Mg/Ca ratios to paleoceanographic reconstructions of the past 27 Myr. During the past 27 Myr the Earth's climate has cooled significantly via major expansions first on Antarctica and then in the Northern Hemisphere. Evidenced by benthic foraminiferal δ^{18}O values, the Oligocene to Miocene boundary ($\simeq$24 Ma) was accompanied by expansion of ice on Antarctica, followed by a period of relative global warmth during the early Miocene ($\simeq$22–16 Ma). A major phase of East Antarctic ice sheet growth took place during the early middle Miocene (between ~15 and 13 Ma), concurrent with a deep ocean cooling of ~3°C [*Shackleton and Kennett*, 1975; *Savin et al.*, 1985; *Miller et al.*, 1987; *Zachos et al.*, 2001]. Early Pliocene glaciation is still under debate; the foraminiferal δ^{18}O record does not support a major retreat of the Antarctic ice sheet and can accommodate an, at most, 2°C warming of the deep ocean [e.g., *Hodell and Venz*, 1992; *Shackleton et al.*, 1995]. Northern Hemisphere ice sheets grew large ~3 Myr ago and have grown and decayed in quasi-regular cycles since then [e.g., *Imbrie et al.*, 1984; *Raymo*, 1994]. These large-scale climatic changes lend themselves to investigate the applicability of benthic foraminiferal Mg/Ca ratios to paleoceanographic reconstructions on pre-Pleistocene timescales.
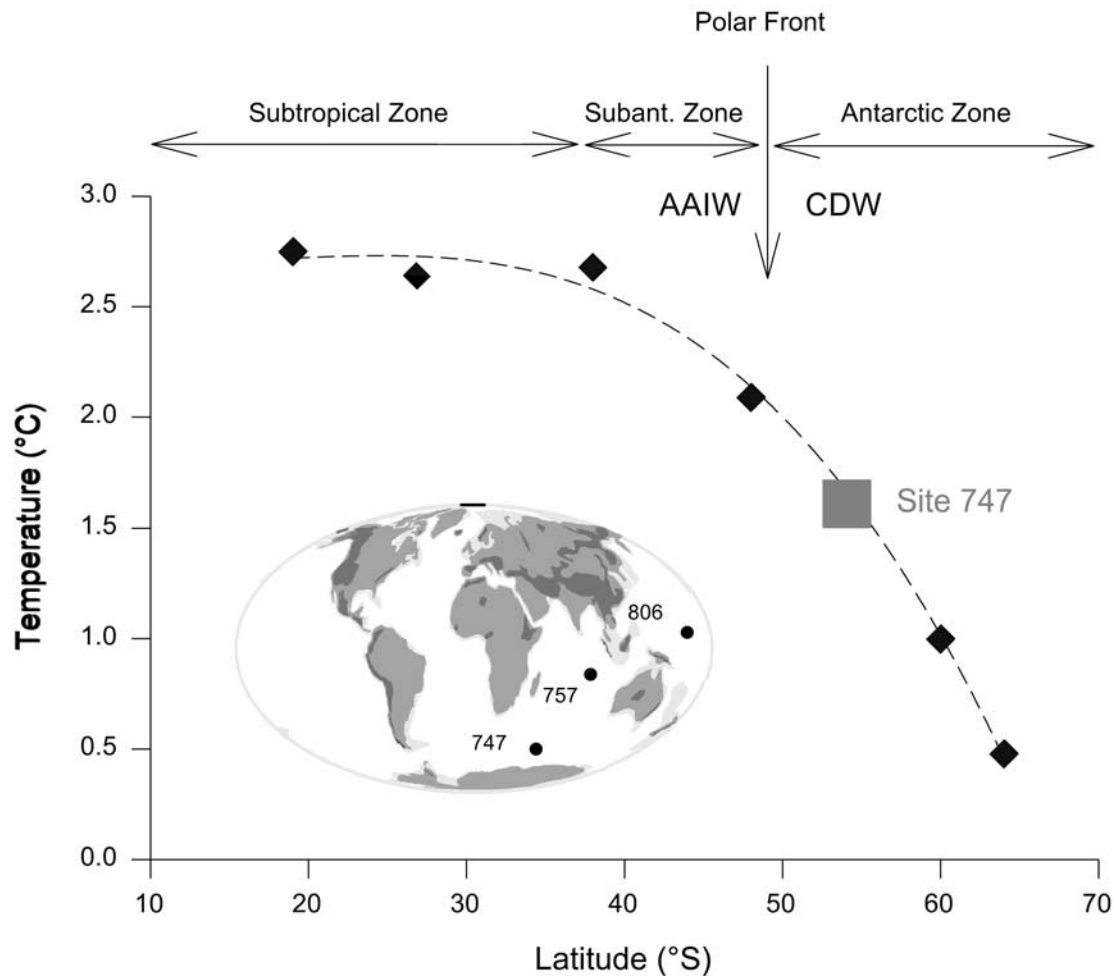
Figure 1. Meridional temperature profile at 60° east longitude based on GEOSECS stations 426–431 [*Ostlund et al.*, 1987] at 1700 m water depth. The dashed line represents a second-order polynomial fit. Division into zones is after *Pickard and Emery* [1990]. The Antarctic Polar Front separates regions of Circumpolar Deep Water (CDW) formation to the south from regions of Antarctic Intermediate Water (AAIW) formation to the north Site 747 (shaded box). The insert shows the locations of the three sites discussed in this study.

[4] We use benthic foraminiferal Mg/Ca ratios as an independent paleotemperature proxy. Along with $\delta^{18}O$ values we attempt to distinguish deep-ocean cooling from ice buildup since the late Oligocene. The time interval we investigate is ∼27 Myr long, approximately twice the residence time of Mg in seawater, and various models suggest that the amount of Mg may have increased by as much as a factor of 2 [*Stanley and Hardie*, 1998] or as little as a factor of one fifth [*Wilkinson and Algeo*, 1989]. We evaluate these uncertainties in our paleotemperature reconstructions. As we shall show, in conjunction with paired stable isotopic analyses, Mg/Ca ratios provide a proxy for relative changes in the isotopic composition of seawater through time despite the number of uncertainties associated with the current lack of appropriate temperature calibrations and poorly constraint reservoir changes.

2. Methods

2.1. Site Selection

[5] We have chosen Ocean Drilling Program (ODP) Leg 120 Site 747 for this study because it meets a number of criteria that

we deem important for Mg/Ca-based paleoenvironmental reconstructions. Site 747 (54°48′S, 76°47′E) is located on the Kerguelen Plateau in the Indian Ocean sector of the Southern Ocean at a water depth of 1695 m. It lies south of the modern Polar Front within the Antarctic Zone and is bathed by Circumpolar Deep Water (CDW, Figure 1). The meridional temperature gradient is steep, and Site 747 should be sensitive to movements of the oceanic frontal systems associated with climate change and growth of ice on the Antarctic continent. Sedimentation rates are low (5 m/Myr), which is important for the Mg/Ca paleothermometer in order to avoid the possibility of recrystallization of primary calcite under high temperatures associated with heavy overburden in a thick sedimentary sequence, an effect similar to diagenetic effect on the $\delta^{18}O$ values of foraminifera [*Schrag et al.*, 1995]. Benthic foraminifera of the genus *Cibicidoides* are well preserved [*Wright and Miller*, 1992]. This aspect is crucial because the presence of impurities, such as Mg, Ba, and Sr in the calcite lattice increases its dissolution susceptibility [e.g., *Berner*, 1974; *Katz*, 1973], which may significantly alter the trace metal content in planktonic [*Rosenthal and Boyle*, 1993; *Russell et al.*, 1994; *Brown and Elder-*

Table 1. Duplicate Mg/Ca Measurements With and Without an Acid Leaching Step

Sample	Mg/Ca Without Acid Leach, mmol/mol	Mg/Ca With Acid Leach, mmol/mol	Difference
747A 4H-5 46 cm	2.19	1.95	0.24
747A 4H-6 46 cm	(1.98)[a]	(0.31)[a]	(1.67)[a]
747A 4H-7 46 cm	2.02	2.22	−0.2
747A 5H-6 44 cm	1.85	1.84	0.01
747A 5H-7 44 cm	2.32	2.46	−0.14
747A 6H-1 44 cm	2.00	2.00	0
747A 6H-2 44 cm	1.71	1.64	0.07
747A 6H-3 45 cm	1.82	1.93	−0.11
747A 6H-4 44 cm	1.56	1.95	−0.39
747A 6H-5 44 cm	1.76	2.17	−0.41
Average	1.91	2.02	−0.1
Standard deviation	0.24	0.24	0.21

[a] Values in parentheses were not used to calculate the averages.

field, 1996] and benthic foraminifera [*McCorkle et al.*, 1995], compromising their use as a paleothermometer.

2.2. Age Control

[6] At site 747 an almost complete Neogene sedimentary sequence was recovered with a chronology based on isotope correlation to the geomagnetic polarity timescale (GPTS) [*Wright and Miller*, 1992]. *Hodell and Woodruff* [1994] provide additional age control points with respect to *Cande and Kent* [1992], and we have converted the ages to the *Berggren et al.* [1995] timescale. There is a hiatus that spans a portion of the latest Miocene (~8−5 Ma) [*Shipboard Scientific Party*, 1989]. We extended the stable isotope record above the hiatus through the Pleistocene. Ages for the Plio/Pleistocene portion of the record are based on interpolation between biostratigraphic datums assuming linear sedimentation rates [*Shipboard Scientific Party*, 1989].

2.3. Analytical Methods

[7] About 40 cm^3 of material were requested from ODP Site 747 from intervals adjacent to the existing late Oligocene through early late Miocene record constructed by *Wright and Miller* [1992] and at a frequency of one sample per section for the Plio/Pleistocene, which needed to be completed. Bulk sediment samples were oven dried, weighed, soaked in a metahexaphosphate solution buffered to a pH of 7.5, and washed through a 63 μm sieve. Between 5 and 15 benthic foraminifera of the genus *Cibicidoides* (*wuellerstorfi* and *mundulus*) were picked from the sand size material (>63 μm), crushed between two glass plates, and split for trace metal and stable isotopic analyses.

[8] For the trace metal analyses, ~50−100 μg of crushed sample were repeatedly sonicated in deionized water and methanol to remove adhering sediment, sonicated in 1 *M* NH$_4$Cl to remove exchangeable ions, and boiled in alkaline peroxide solution (0.15% H$_2$O$_2$ in 0.1 *N* NaOH) for 10 min (sonicating once) to oxidize organic contaminants. Our methodology follows the procedures of *Brown and Elderfield* [1996], *Hastings et al.* [1998], *Nuernberg et al.* [2000], and *Lear et al.* [2000], who have determined that reductive cleaning is not necessary when analyzing for Mg. A number of duplicates (*n* = 10) were analyzed after subjecting them to a weak acid leach in 0.001 *M* HNO$_3$ [e.g., *Lear et al.*, 2000], but this additional step did not systematically change the Mg/Ca ratios (Table 1), and we omitted it from the protocol. Each cleaning step was followed by one rinse plus three sonication steps in deionized water to ensure complete removal of the waste solution. Depending on the amount of material, cleaned samples were dissolved in 0.4– 0.5 mL of 2% HNO$_3$ to obtain a solution of between 10 and 120 ppm Ca. Mg/Ca ratios were measured on an inductively coupled plasma atomic emissions spectrophotometer (ICP-AES) following methods outlined by *Schrag* [1999]. Analytical precision based on

analyses of a standard solution is better than 0.3%. External precision based on sample splits is difficult to assess because Mg is not homogeneously distributed throughout the test [*Nuernberg*, 1995; *Elderfield and Ganssen*, 2000]. This means that samples splits can differ in their Mg/Ca ratios but are usually within 5% for ratios below 2.5 mmol/mol.

[9] For stable isotope analyses, ~20−80 μg crushed samples were sonicated twice in deionized water, oven dried, and analyzed on a Finnigan Mat252 equipped with a Kiel device at Woods Hole Oceanographic Institution (WHOI). Oxygen isotope values are reported versus Vienna Peedee belemnite via in-house standards. The analytical precision is better than 0.07‰ for δ^{18}O [*Ostermann and Curry*, 2000]. We note that a constant offset exists between the late Oligocene to Miocene stable isotope record generated originally by *Wright and Miller* [1992] and our record measured at WHOI. We add 0.32‰ to the δ^{18}O record of *Wright and Miller* [1992] to account for this difference and then combine the isotope data. For the purpose of calculating the δ^{18}O$_{sw}$ we adjust *Cibicidoides* δ^{18}O values by +0.64‰ to bring them in line with equilibrium calcification at given temperature and δ^{18}O$_{sw}$ [*Shackleton*, 1974]. Between ~11 and 8 Ma we did not obtain stable isotope measurements from sample splits. Instead, we used interpolated stable isotope values from the record published by *Wright and Miller* [1992]. Between 11 and 27 Ma, there were a few intervals without sufficient material for isotopic analyses in addition to the Mg/Ca measurements. We filled these gaps (nine) with interpolated values based on adjacent data points generated in this study. Data are available electronically at the World Data Center-A for Paleoclimatology.[1]

3. Results

3.1. Interspecies Calibration

[10] It is not possible to construct a Neogene benthic foraminiferal Mg/Ca record from only one species. *Cibicidoides wuellerstorfi*, which dominate the late Neogene and Pleistocene assemblages at Site 747, are not present in late Oligocene through mid-Miocene sediments. *Cibicidoides mundulus* are abundant during the earlier Neogene at this site, but they disappear during the Plio/Pleistocene. At Site 747, there are no intervals in which both species coexist for a direct assessment of species-specific Mg/Ca ratios. At ODP Site 757 in the Indian Ocean (Figure 1), on the other hand, we were able to measure 10 *C. wuellerstorfi* and *C.*
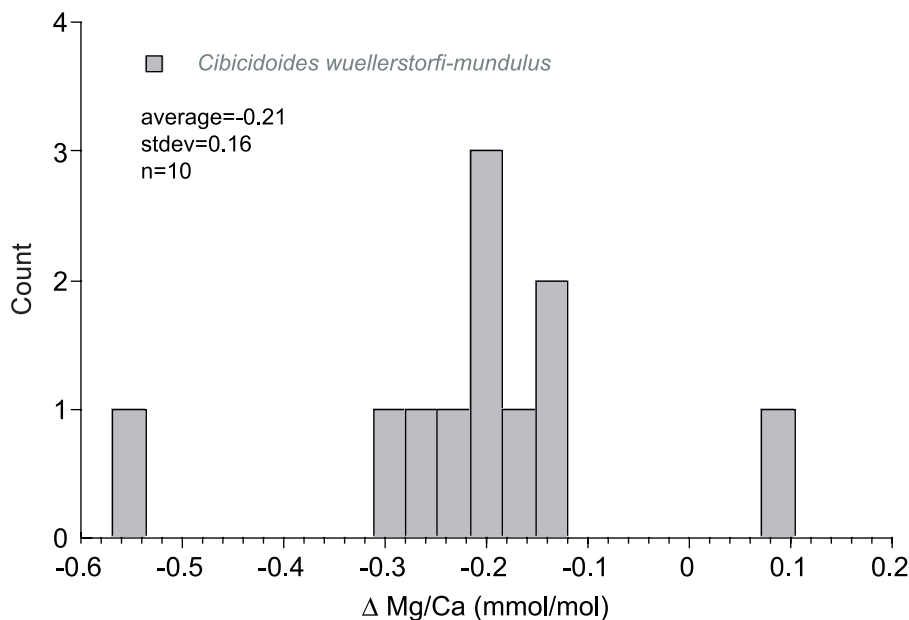
Figure 2. Distribution of the difference between Mg/Ca measurements of coexisting *Cibicidoides mundulus* and *Cibicidoides wuellerstorfi* at ODP Site 757 in the Indian Ocean. On the basis of 10 duplicates the average difference is −0.21 mmol/mol. We use this value to adjust *C. mundulus* to *C. wuellerstorfi* Mg/Ca ratios.

mundulus from the same interval. These data suggest that a species offset exists between Mg/Ca ratios of coexisting *C. wuellerstorfi* and *C. mundulus* of −0.21 ± 0.16 mmol/mol (Figure 2). For comparison, *Lear et al.* [2000] report a difference of 0.28 mmol/mol between these two species at ODP Site 926 and DSDP Site 573. These two estimates agree well, but we use the offset measured at Harvard University (Site 757) to adjust *C. mundulus* Mg/Ca ratios to those of *C. wuellerstorfi* at Site 747.

3.2. Mg/Ca Temperature Calibration

[11] A number of Mg/Ca temperature calibrations exist for planktonic foraminifera [e.g., *Nuernberg et al.*, 1996; *Mashiotta et al.*, 1999; *Elderfield and Ganssen*, 2000; *Lea et al.*, 1999], but reconstructions of absolute paleotemperatures from benthic foraminiferal Mg/Ca ratios are limited. *Rosenthal et al.* [1997] present one calibration based on relatively shallow dwelling species *Cibicidoides floridanus* along the Little Bahama Bank. Water temperatures in this region are warmer than ∼5°C, and extrapolations below the lowest temperature and the corresponding Mg/Ca ratio of ∼2.2 mmol/mol are questionable. For lack of a better means, we alleviate this problem by adding a low-temperature Mg/Ca calibration point from measurements of Mg/Ca ratios of six *C. wuellerstorfi* from core top sediments on the Ontong Java Plateau (ODP Site 806, Figure 1). The range in individual Mg/Ca ratios is small with only one outlying data point (Figure 3). We exclude the highest ratio from the average because it lies farther than one standard deviation from the mean and obtain an average of 1.37 mmol/mol. The modern temperature at 2500 m is ∼1.6°C (Geochemical Ocean Sections Study (GEOSECS) station 246 [*Ostlund et al.*, 1987]). Together with the two coldest temperature calibration points of *Rosenthal et al.* [1997] we obtain a linear approximation to the *Rosenthal et al.* [1997] relationship for low (<2.5 mmol/mol) Mg/Ca ratios (Figure 4). The difference in temperature between the two equations is 0.2°C at 2.2 mmol/mol and 0.5°C at 2.5 mmol/mol, with the Rosenthal et al. relationship yielding the warmer value. Even at its extreme, the temperature offset between the two calibration curves is no more than 0.5°C, which for comparison, is close to the analytical uncertainties associated with

δ^{18}O measurements (±0.07‰, or 0.3°C). Below 2.2 mmol/mol a comparison is not sensible because it would imply extrapolating a logarithmic function. All Site 747 Mg/Ca ratios (with the exceptions of a few outliers) are lower than 2.5 mmol/mol, and we use the linear fit to derive paleotemperatures.

3.3. Mg/Ca Ratios, δ^{18}O Records, and Paleotemperature Changes

[12] If deep water temperature changes accompany fluctuations in global ice volume, one would expect that the benthic foraminiferal Mg/Ca record parallels the δ^{18}O record. This is not the case
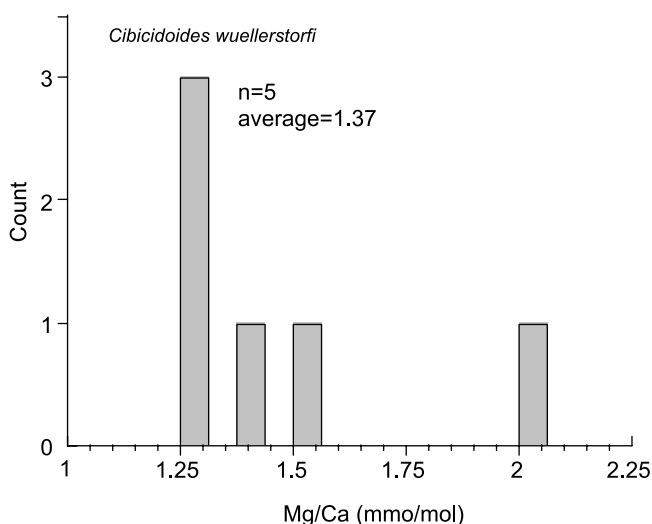

Figure 3. Mg/Ca ratios of six individual *Cibicidoides wuellerstorfi* in core top sediments from ODP Leg Site 806 on the Ontong Java Plateau in the western equatorial Pacific. Five of the measurements group between 1.3 and 1.5 mmol/mol. There is one outlier, and it has been excluded from the average.
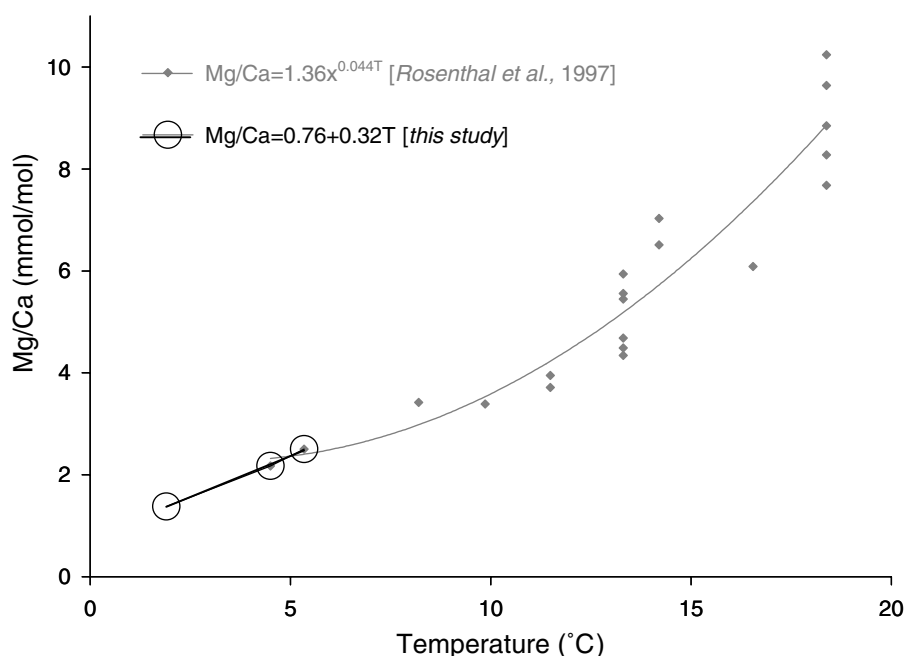
Figure 4. Mg/Ca-temperature calibration of *Rosenthal et al.* [1997] (shaded diamonds) together with the core top Mg/Ca measurement from site 806 (open circle). Deep water temperatures in the western equatorial Pacific at 2500 water depth are 1.6°C [*Ostlund et al.*, 1987], providing the lower temperature calibration point. Together with the two lowest Mg/Ca-temperature calibration points of *Rosenthal et al.* [1997] (circled shaded diamonds) we obtain a linear temperature calibration applicable to Mg/Ca ratios from the colder region of the ocean ($T = -2.33 + 3.10$ (Mg/Ca)). The difference in temperature between the two calibrations is 0.2°C at 2.2 mmol/mol and 0.5°C at 2.5 mmol/mol, with the Rosenthal et al. temperature calibration ($T = 22.7 \log$ (Mg/Ca) $- 3.05$) yielding the warmer value. Below 2.2 mmol/mol a comparison is not appropriate because it would imply extrapolating the logarithmic function to solve for temperature.

(Figure 5). During the late Oligocene the agreement is good; Mg/Ca ratios are relatively high and decrease at the Oligocene to Miocene boundary paralleling the trend in the δ^{18}O values. During the early Miocene, Mg/Ca ratios remain relatively constant until ~16 Ma, at which time they increase, while δ^{18}O values decrease gradually during this entire interval of time. In the middle Miocene at ~15 Ma, Mg/Ca ratios decrease, and δ^{18}O values increase. The δ^{18}O values reach a maximum at ~13 Ma and remain relatively constant thereafter. In contrast, Mg/Ca ratios reach a minimum at 12.5 Ma, increase to ratios characteristic of the middle Miocene, remain high for a period of ~1 Myr, decrease toward a minimum at ~11 Ma, and increase again toward ~8.5 Ma. During the Pliocene, Mg/Ca ratios decrease in a stepwise fashion, a trend that roughly parallels the δ^{18}O record. The Pleistocene sees a return to higher Mg/Ca ratios that is not apparent in the δ^{18}O record. There are four data points that differ from the longer-term average as well as from neighboring Mg/Ca ratios. We do not remove these outlying measurements from the data set, but we do not discuss them further.

[13] Paired analyses of Mg/Ca and stable isotope measurements highlight similarities and discrepancies between the foraminiferal Mg/Ca and δ^{18}O records (Figure 6a). Miocene glacial events Mi1a through Mi4 [*Miller et al.*, 1991] are accompanied by minima in the Mg/Ca ratios. However, Mi1, the glacial event that is associated with the Oligocene/Miocene boundary, is concurrent with a small Mg/Ca maximum, and minimum Mg/Ca ratios are not reached until ~200 kyr later. Mi5, which is a relatively small event in the benthic foraminiferal δ^{18}O record at the end of the mid-Miocene phase of Antarctic ice buildup, corresponds to marked maximum in the Mg/Ca record.

[14] Mg/Ca-derived paleotemperatures indicate a deep-ocean cooling of ~1.5°C lagging the δ^{18}O maximum at the base of Mi1 (Figure 6b). Mi1a through Mi2 are associated with cooling events of ~1°C. The increase in Mg/Ca ratios at ~16 Ma accommodates a ~2°C increase water temperature. Between 15 and 13 Ma, deep water cooled by ~3°C, in good agreement with the estimates inferred from foraminiferal δ^{18}O values. Between 12 and 11.5 Ma, temperatures increase by ~2.5°C, returning to almost "preglacial" levels. At 11 Ma, temperatures cool rapidly and then increase more gradually by ~3°C during the early late Miocene until reaching another maximum at ~8.5 Ma. During the Pliocene, temperatures dropped by ~4°C. In the Pleistocene, temperatures increase again, but our temporal resolution in the Mg/Ca as well as δ^{18}O record is too coarse to resolve glacial to interglacial-scale climate variability.

4. Discussion

4.1. Effect of Seawater Mg/Ca Ratios

[15] The absolute value of Mg/Ca-derived paleotemperatures depends on assumptions of the Mg composition of the seawater in which a foraminifer calcifies. Mg and Ca are supplied to the oceans by rivers; thus continental weathering rates and the types of source rocks being weathered (e.g., calcite versus dolomite) affect the amounts accumulating in the oceanic reservoir [e.g., *Berner et al.*, 1983; *Berner and Berner*, 1987; *Holland*, 1978, 1984; *Wilkinson and Algeo*, 1989]. Hydrothermal alteration of basalts at ocean ridges consumes almost all Mg supplied by rivers and releases an equivalent amount of Ca to the ocean [e.g., *Mottl and Wheat*, 1994; *Elderfield and Schultz*, 1996]. Carbonate
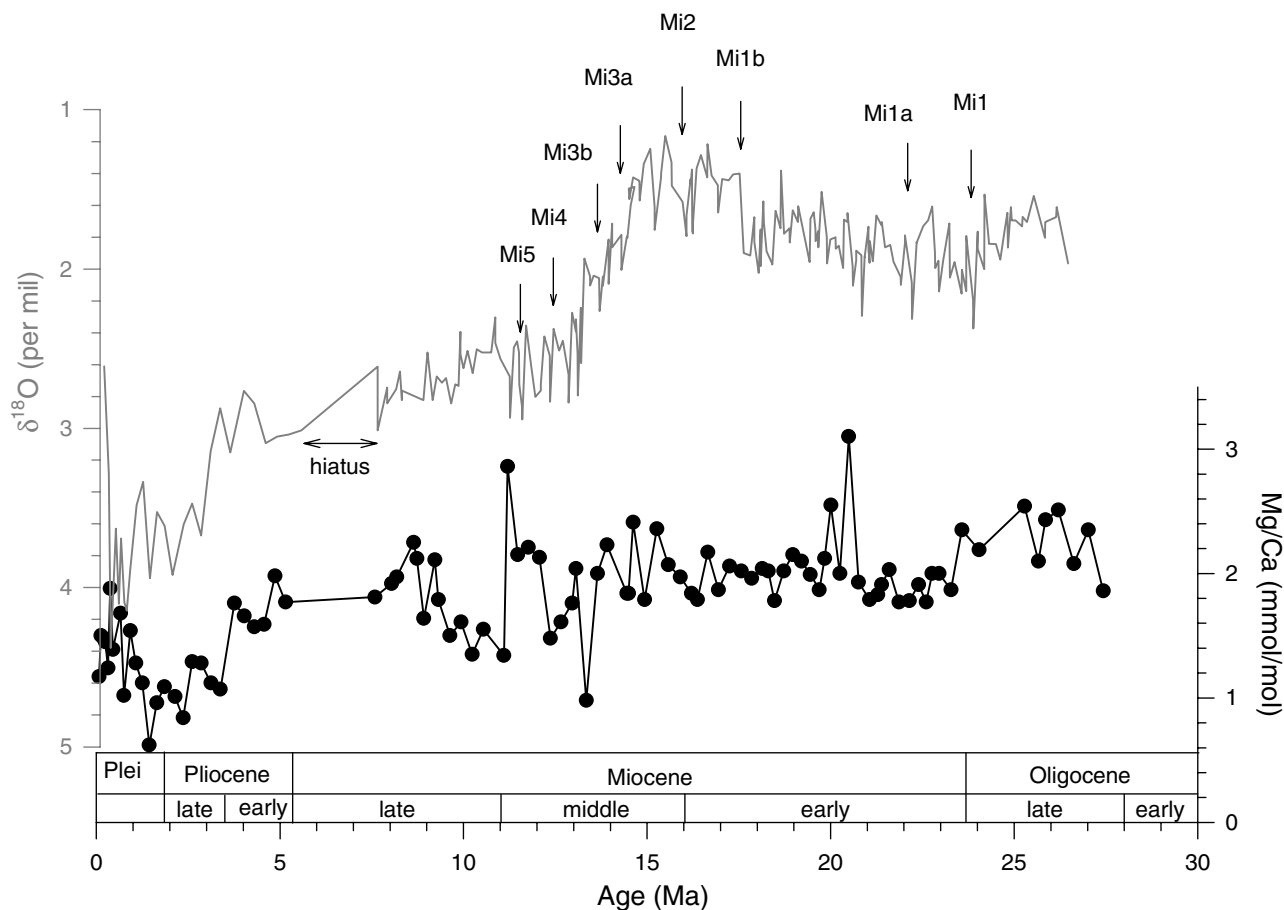
Figure 5. Site 747 *Cibicidoides* spp. δ^{18}O record and Mg/Ca ratios. The late Oligocene to late Miocene stable isotope data below the hiatus are from *Wright and Miller* [1992], augmented by stable isotope analyses from this study. Ages correspond to the *Berggren et al.* [1995] timescale. The Plio/Pleistocene portion of the record above the hiatus was generated in this study with ages based on interpolation between biostratigraphic datums. Nomenclature refers to Miocene glaciations (Mi events), which have been assigned to δ^{18}O maxima by *Miller et al.* [1991].

deposition removes relatively large amounts of Ca but provides only a small sink for Mg, at least during the more recent geologic past [*Drever*, 1974; *Wilkinson and Algeo*, 1989]. Additional, albeit small, sinks for Mg are ion exchange reactions with clays and low-temperature alteration of basalts [e.g., *Drever*, 1974; *Gieskes and Lawrence*, 1981].

[16] A number of studies have addressed the question of changing Mg/Ca ratios in seawater using mass balance relationships and box models [*Berner et al.*, 1983; *Wilkinson and Algeo*, 1989] or assumptions about seafloor spreading rates [*Hardie*, 1996; *Stanley and Hardie*, 1998] (Figure 7). Whether the Mg/Ca ratio of seawater has increased gently [*Wilkinson and Algeo*, 1989; *Stanley and Hardie*, 1998] or decreased dramatically [*Berner et al.*, 1983] over Cenozoic timescales depends on the choice of the relative magnitude of the sources and sinks. The Mg/Ca ratio of seawater may have increased since the early Cenozoic because seafloor spreading rates have decreased, allowing Mg to accumulate in the ocean [e.g., *Wilkinson and Algeo*, 1989; *Stanley and Hardie*, 1998]. This factor alone leads to the calculated seawater curve of *Stanley and Hardie* [1998], whose reconstruction suggests a doubling of Mg/Ca ratios since the early Neogene. *Wilkinson and Algeo* [1989], who provide a rigorous treatment of the individual processes that can change the seawater composition, suggest that oceanic Mg/Ca values may have increased by a factor of only one fifth over the past 25 Myr.

[17] We evaluate the effect of changing seawater Mg/Ca ratios on temperature reconstructions (Figure 8). If, for example, 23.3 Myr ago, shortly after the Oligocene to Miocene boundary, Mg/Ca ratios of seawater were about half those of modern values as implied by *Stanley and Hardie* [1998], then the measured foraminiferal ratios at this time would yield a paleotemperature estimate 3 times higher than that derived assuming modern-day seawater Mg/Ca ratios (Figure 8a and Table 2). Using seawater ratios of *Wilkinson and Algeo* [1989], one obtains a temperature of ∼5°C. For comparison, using modern day ratios, this calculation yields paleotemperatures of ∼3°C, which is ∼1.5°C warmer than circumpolar deep water temperatures at Site 747 today. Similarly, 15 Myr ago, during the early Miocene climatic optimum, temperature reconstructions using this approach would be 10°, 7.5°, and 5°C for the three different seawater ratios, respectively (Figure 8b and Table 2). Given the Stanley and Hardie seawater curve, deep-ocean temperatures would have been the same during the early Miocene climatic optimum than during the glacial episode of the Oligocene/Miocene climate transition. According to the Wilkinson and Algeo curve, or using modern-day values, temperatures are higher during the early Miocene climatic optimum. Clearly, absolute temperature reconstructions are hampered by a lack of knowledge of how Mg/Ca ratios have changed in the oceanic reservoir. Furthermore, it is not possible to directly compare Miocene temperature reconstructions to modern measurements, but we are
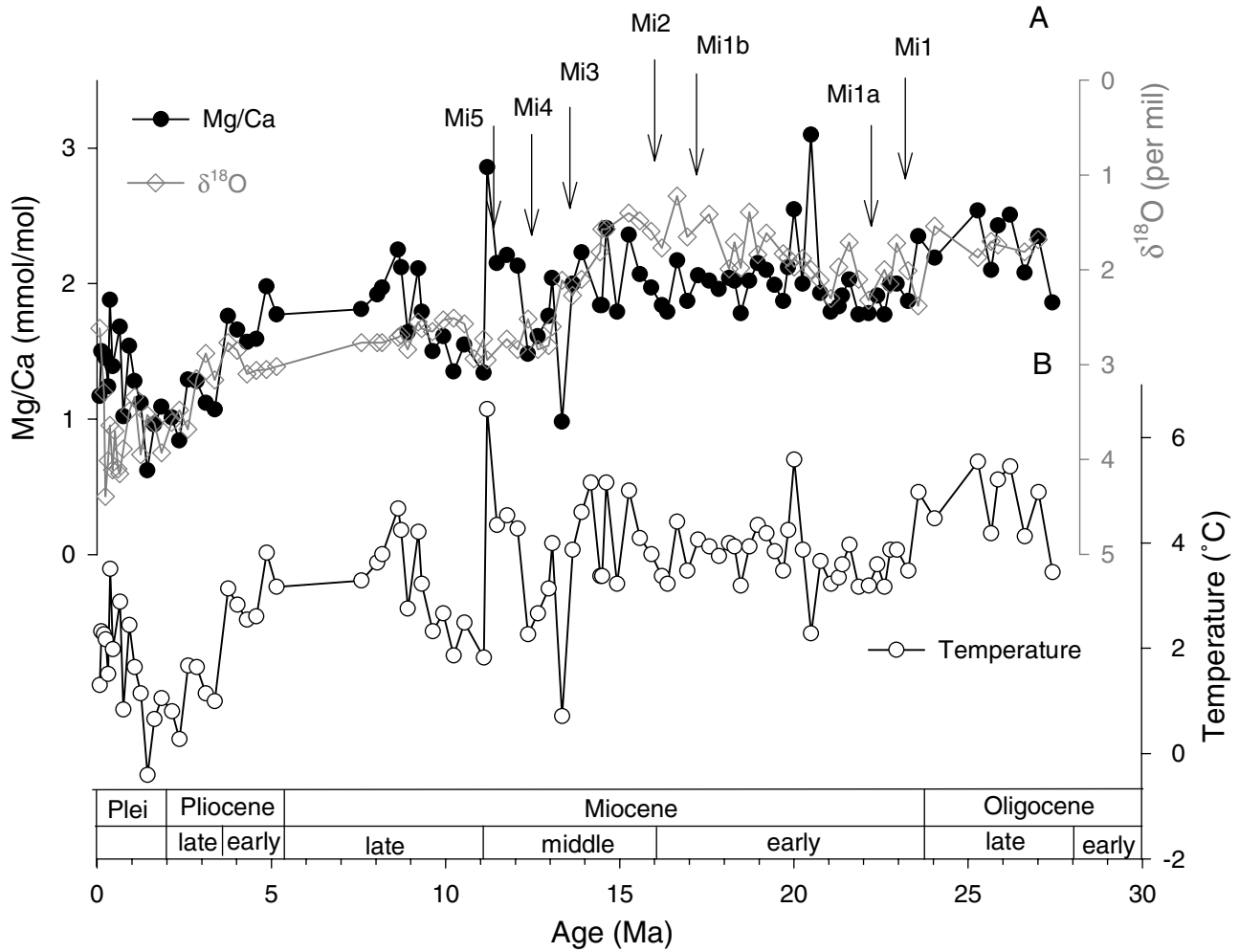
Figure 6. Paired analyses of Mg/Ca ratios and (a) $\delta^{18}O$ values and (b) temperature. Miocene glaciation events (Mi events) are as described in the legend to Figure 5. Temperature scale is derived from the linear calibration shown in Figure 4 and assuming modern Mg/Ca seawater ratios. Absolute temperature values are questionable, but temperature changes that occur within a relatively short interval of time are robust.

confident about the magnitude of those temperature changes that occurred during relatively short lived climate transitions such as the Oligocene/Miocene boundary and the mid-Miocene phase of Antarctic ice sheet expansion.

4.2. A 27 Myr History of the $\delta^{18}O$ of Seawater and Sea Level

[18] With the Mg/Ca record we constrain the temperature component embedded in the foraminiferal $\delta^{18}O$ record for a refined view of relative changes in the oxygen isotopic composition of seawater linked to sea level fluctuations. The $\delta^{18}O_{sw}$ is associated with ice growth/decay induced sea level changes and regional water mass salinity, the latter depending on surface water evaporation and precipitation patterns in the source region of a water mass. There is the additional caveat that $\delta^{18}O_{sw}$ and sea level changes may not be linked in a linear fashion over long periods of time. The $\delta^{18}O$ of polar ice is a function of high latitude climate, including temperature, humidity, and moisture transport [*Vimeux et al.*, 1999; *Jouzel et al.*, 2000; *Hendricks et al.*, 2000]. It has likely changed since the late Oligocene, and with it the $\delta^{18}O_{sw}$ has also likely changed [e.g., *Miller et al.*, 1987]. However, as a first step toward a revised view of sea level changes, we calculate the $\delta^{18}O_{sw}$ using the paleotemperature
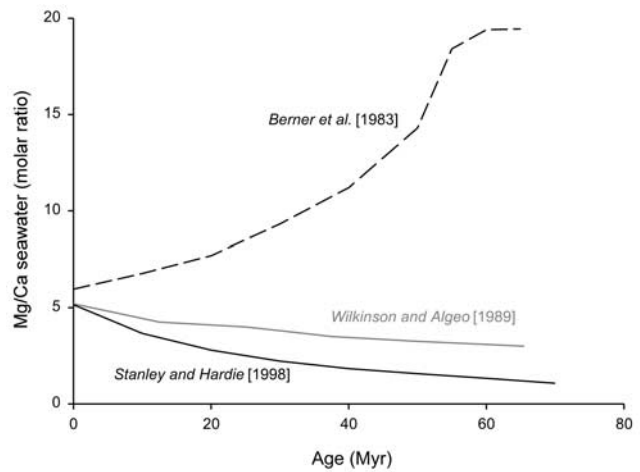

Figure 7. Illustration of how Mg/Ca ratios may have changed over the past 70 Myr according to three different numerical models. See text for details.
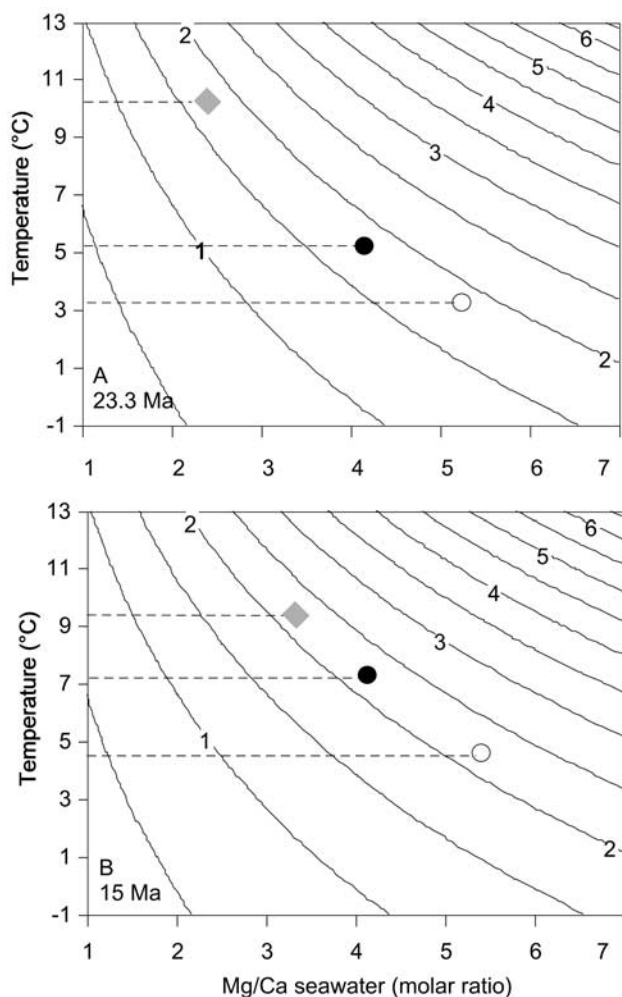
Figure 8. Relationship between temperature, Mg/Ca ratios of seawater, and predicted Mg/Ca ratios in calcium carbonates (contours) for two time slices (a) 23.3 Ma and (b) 15 Ma. The contours were derived using the temperature dependency of the distribution coefficient between Mg/Ca in calcite and seawater together with the temperature calibration of *Rosenthal et al.* [1997]. We use this temperature calibration instead of the linear approximation derived in Figure 4 because it is calibrated at higher temperatures, which might be more reflective of the Miocene ocean. The symbols are placed on the contour corresponding to the measured Mg/Ca ratio of benthic foraminiferal carbonate where it intersects the Mg/Ca ratio of seawater according to three different scenarios: shaded diamond, *Stanley and Hardie* [1998]; solid circle, *Wilkinson and Algeo* [1989]; open circle, modern seawater ratios. The y axis provides the corresponding temperature estimates, which are summarized in Table 2.

equation of *Shackleton* [1974] with input temperatures and $\delta^{18}O$ values of calcite ($\delta^{18}O_c$) derived from the paired measurements of foraminiferal Mg/Ca and $^{18}O/^{16}O$ ratios (e.g., Figure 6). There are a number of errors associated with this approach, the primary source being the poorly constrained Mg/Ca temperature relationship and Mg/Ca reservoir changes. When subtracting values of similar magnitude, the errors are compounded. Analytical precision and calibration uncertainties affect all data points by the same magnitude, which means that interpretations of relative changes in the $\delta^{18}O_{sw}$ curve that occur during relatively brief geological time intervals are sound.

[19] A comparison of our $\delta^{18}O_{sw}$ curve to the *Haq et al.* [1987] sea level curve (recalibrated to the *Berggren et al.* [1995] timescale (K. G. Miller and J. V. Browning, personal communication, 2001) demonstrates agreement in the overall character of Mg/Ca-derived $\delta^{18}O_{sw}$ curve and the sequence stratigraphy (Figure 9). During the early Miocene, $\delta^{18}O_{sw}$ decreases until ~17 Ma, paralleling the general trend toward higher sea level (and lower foraminiferal $\delta^{18}O$ values). Between 15 and ~11 Ma the $\delta^{18}O_{sw}$ increases, and sea level drops. Maximum $\delta^{18}O_{sw}$ values occur between 12 and 11 Ma, while maximum sea level low stand has an age of 11 Ma, but this discrepancy is likely due to the relatively low temporal resolution in either record and associated age model discrepancies. During the late Pliocene and Pleistocene $\delta^{18}O_{sw}$ and sea level fluctuate about a long-term average until ~1 Ma when the $\delta^{18}O_{sw}$ reaches another maximum. A gap in the sea level record at this time precludes a more detailed comparison, but the return to lower $\delta^{18}O_{sw}$ values-corresponds to a sea level transgression at ~0.2 Ma.

[20] Individual Miocene through Pleistocene third-order sequence boundaries of *Haq et al.* [1987] (TB1.4 through TB3.9) correspond to increases in $\delta^{18}O_{sw}$ within the temporal resolution of our study (Figure 9). These results are in excellent agreement with the study of *Miller et al.* [1996], who compared an Oligocene through Miocene composite $\delta^{18}O$ record to New Jersey margin sequence stratigraphy and the *Haq et al.* [1987] sea level curve. They found that the majority of sequence boundaries correspond to times of increasing foraminiferal $\delta^{18}O$ values, consistent with the formation of sequence boundaries during intervals of rapid glacioeustatic fall. Mi5, the glacial event that corresponds to TB3.1, does not show a discrete foraminiferal ^{18}O maximum at Site 747 (Figure 9c). Our $\delta^{18}O_{sw}$ curve, however, does show a maximum at about this time (12–11 Ma) and brings into better agreement the geochemical approach to sea level reconstruction with the sequence stratigraphy (Figures 9a and 9b).

[21] It is not possible to estimate the absolute magnitude of sea level changes from the Mg/Ca-derived $\delta^{18}O_{sw}$ curve. While the temperature effect embedded in the foraminiferal $\delta^{18}O$ values has been removed, the residual, the $\delta^{18}O_{sw}$, contains the effects associated with changes in the isotopic composition of polar ice and/or ambient water mass salinity. The extreme $\delta^{18}O_{sw}$ maximum related to Mi5, for example, may reflect the presence of an ^{18}O-depleted ice sheet. The degree of ^{18}O depletion in an ice sheet is a function of the degree of $^{18}O/^{16}O$ fractionation during poleward water vapor transport, which in turn, is a function of the air temperature [*Dansgaard*, 1964]. As ice sheets grow larger and polar climates become colder, water vapor and hence snow become increasingly ^{18}O depleted. Thus an increase in the $^{18}O/^{16}O$ ratio in seawater associated with increase in ice volume will be augmented by the effect of larger $^{18}O/^{16}O$ fractionation during vapor transport. The issue begs for a numerical model that contains an oxygen isotope tracer and surface ocean paleotemperatures. Whether the high $\delta^{18}O$ ratios are related to an increase in

Table 2. Summary of Paleotemperature Estimates at 23.3 and 15 Ma

Time, Ma	Mg/Ca Shell, mmol/mol	Mg/Ca Seawater,[a] molar ratio	Temperature, °C
23.3	1.8	2.5 (1)	10
23.3	1.8	4.1 (2)	5
23.3	1.8	5.4 (modern)	3
15	2.3	3.5 (1)	10
15	2.3	4.2 (2)	7.5
15	2.3	5.4 (modern)	5

[a] Numbers in parenthesis refer to reference for Mg/Ca of seawater: 1, *Stanley and Hardie* [1998]; 2, *Wilkinson and Algeo* [1989].
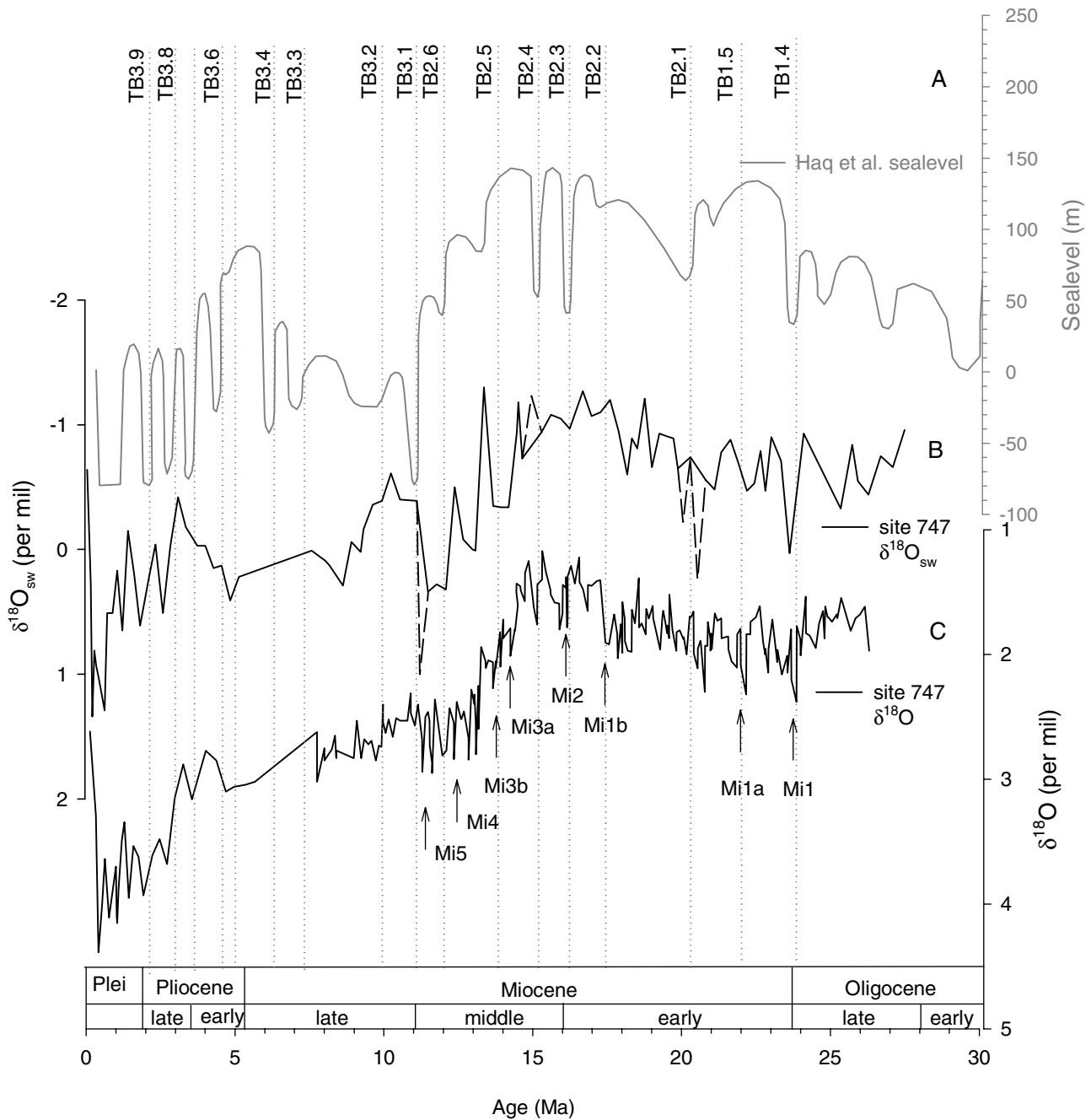
Figure 9. Comparison of (a) the *Haq et al.* [1987] sea level curve (recalibrated to the *Berggren et al.* [1995] timescale), (b) the $\delta^{18}O_{sw}$ derived from paired measurement of Mg/Ca ratios and benthic foraminiferal $\delta^{18}O$ values from paired measurements at Site 747 (see text for details), and (c) the Site 747 $\delta^{18}O$ record from *Wright and Miller* [1992]. The solid line in Figure 9b represents the $\delta^{18}O_{sw}$ curve calculated without using the four outlying Mg/Ca ratios apparent in Figure 5 (see text), and the dashed line is to illustrate $\delta^{18}O_{sw}$ values based on the outlying data points. Vertical dotted lines reflect the third-order sequence boundaries of *Haq et al.* (TB1.4 through TB3.9). Sequence boundaries coincide with times of increasing seawater $^{18}O/^{16}O$ ratios supporting the conclusions of *Miller et al.* [1996] that sequence boundaries are causally linked to sea level falls.

global ocean ^{18}O content due to ice (volume and composition) or the result of an increase in the salinity of the water mass at Site 747 awaits the construction of additional records from sites representing different hydrographic regimes (K. Scheiderich and K. Billups, work in progress, 2001). Most importantly, however, our results demonstrate that benthic foraminiferal Mg/Ca ratios are sensitive to ocean temperature changes over long periods of time. In conjunction with paired stable isotopic analyses, Mg/Ca ratios provide a proxy for relative changes of $\delta^{18}O_{sw}$ through time despite the number of uncertainties associated with the current lack of appropriate temperature calibrations and poorly constrained reservoir changes.

4.3. Implications for Reconstructing Temperature and Ice Volume History

[22] Assumptions about past ocean temperature changes necessary to interpret benthic foraminiferal $\delta^{18}O$ values with respect to ice volume fluctuations can be misleading, as demonstrated by the results from Site 747. During the early Miocene the $\delta^{18}O$ decrease between 23 and 17 Ma is an ice volume signal, as indicated by the lack of long-term trend in the Mg/Ca ratios. During the Pliocene, on the other hand, a 4°C cooling concurrent with a $\delta^{18}O$ increase does not leave a large residual to signal large-scale Northern Hemisphere glaciation beginning at ~3 Ma, but perhaps the most unexpected result from the site 747 Mg/Ca analyses is a late middle Miocene (12–11 Ma) and an early late Miocene (~10–8.5 Ma) return to relatively high Mg/Ca ratios, indicating deep water warming at Site 747. The first temperature anomaly follows a major phase in Antarctic ice sheet growth, which according to foraminiferal $\delta^{18}O$ values from a number of locations, reached maximum extent at ~13 Ma [e.g., *Shackleton and Kennett*, 1975; *Miller et al.*, 1987, 1991; *Flower and Kennett*, 1993]. The Site 747 warming beginning at 12 Ma appears to have dampened the foraminiferal $\delta^{18}O$ signal, leading to an underestimate of the ice volume component embedded in the foraminiferal $\delta^{18}O$ record. Because none of the published benthic foraminiferal $\delta^{18}O$ records display a maximum at this time [e.g., *Zachos et al.*, 2001], the warming event may have been of extra regional importance. The global significance and the source of the warming remain elusive until additional records become available that span this interval of time (K. Scheiderich and K. Billups, work in progress, 2001). The second temperature excursion (~8.5 Ma), however, coincides with an increase in foraminiferal Mg/Ca ratios equivalent to a 3°–4°C warming of deep waters in the tropical Atlantic [*Lear*, 2001]. Lear ascribes the temperature increase to an increase in the relative flux of Northern Component Deep Water (NCW). If the tropical Atlantic and Southern Ocean temperature anomalies are related via ocean circulation changes, they imply that the relative flux of NCW was strong enough for its temperature signature to be preserved within the Antarctic Circumpolar Current, which should be of global climatic significance.

5. Conclusion

[23] Mg/Ca ratios of benthic foraminifera at ODP Leg 120 Site 747 provide a sensitive proxy for relative changes in paleotemperatures and the $\delta^{18}O_{sw}$ during the past 27 Ma. The results validate the applicability of this proxy to pre-Pleistocene timescales despite the uncertainties related to the lack of a well-constrained, species-specific low-temperature calibration and changes in the global ocean Mg reservoir. Benthic foraminiferal Mg/Ca data show that many of the smaller-scale Miocene glaciations are accompanied by cooling of deep ocean temperatures of ~1°C and that temperatures lag ice volume at the Oligocene to Miocene boundary. The mid-Miocene phase of Antarctic ice buildup is accompanied by deep ocean cooling of ~3°C in agreement with inferences from foraminiferal $\delta^{18}O$ values. Between 12 and 11 Ma and again at ~8.5 Ma, when $\delta^{18}O$ values have reached maximum Miocene extent, Mg/Ca ratios increase to levels similar to those of the Miocene climatic optimum, suggesting that an increase in local deep ocean temperatures took place. Calculating the $\delta^{18}O_{sw}$ using the paired trace metal and stable isotopic measurements shows very good agreement between times of increasing seawater $^{18}O/^{16}O$ ratios and the sequence boundaries of *Haq et al.* [1987]. Particularly, at 12–11 Ma, the $\delta^{18}O_{sw}$ illustrates excellent agreement with a major mid-Miocene sea level regression (TB3.1) that is not evident in the foraminiferal $\delta^{18}O$ values. This observation reconciles the geochemical approach to sea level reconstruction with sequence stratigraphy. Further work will determine the global extent of the middle to late Miocene temperature anomalies, which will then allow a more detailed investigation into Miocene climate change.

References

Berggren, W. A., D. V. Kent, C. C. Swisher, and M.-P. Aubry, in *Geochronology, Time Scales and Stratigraphic Correlation: Framework for an Historical Geology*, edited by W. A. Berggren et al., *Spec. Publ. SEPM Soc. Sediment. Geol.*, *54*, 138–144, 1995.

Berner, R. A., The role of magnesium in crystal growth of calcite and aragonite from sea water, *Am. J. Sci.*, *274*, 489–504, 1974.

Berner, R. A., A. C. Lasaga, and R. M. Garrels, The carbonate-silicate geochemical cycle and its effect on atmospheric carbon dioxide over the past 100 million years, *Am. J. Sci.*, *283*, 641–683, 1983.

Berner, E. K., and R. A. Berner, *The Global Water Cycle-Geochemistry and Environment*, 398 pp., Prentice-Hall, Old Tappan, N. J., 1987.

Broecker, W. S., and T.-H. Peng, *Tracers in the Sea*, Lamont-Doherty Earth Obs., Palisades, N. Y., 1982.

Brown, S. J., and H. Elderfield, Variations in Mg/Ca and Sr/Ca ratios of planktonic foraminifera caused by postdepositional dissolution: Evidence of shallow Mg-dependent dissolution, *Paleoceanography*, *11*, 543–551, 1996.

Cande, S. C., and D. V. Kent, A new geomagnetic polarity time scale for the late Cretaceous and Cenozoic, *J. Geophys. Res.*, *97*, 13,917–13,951, 1992.

Dansgaard, W., Stable isotopes in precipitation, *Tellus*, *16*, 436–468, 1964.

Drever, J. I., The magnesium problem, in *The Sea*, vol. 5, edited by E. D. Goldberg, pp. 1334–1336, Wiley Interscience, New York, 1974.

Elderfield, H., and G. Ganssen, Past temperature and $\delta^{18}O$ of surface ocean waters inferred from foraminiferal Mg/Ca ratios, *Nature*, *405*, 442–445, 2000.

Elderfield, H., and A. Schultz, Mid-ocean ridge hydrothermal fluxes and the chemical composition of the ocean, *Annu. Rev. Earth Planet. Sci.*, *24*, 191–224, 1996.

Flower, B. P., and J. Kennett, Middle Miocene ocean-climate transition: High resolution oxygen and carbon isotopic records from Deep Sea Drilling Project Site 599A, southwest Pacific, *Paleoceanography*, *8*, 811–843, 1993.

Gieskes, J. M., and J. R. Lawrence, Alteration of volcanic matter in deep sea sediments-evidence from the chemical composition of inter-stitial waters from deep sea drilling cores, *Geochim. Cosmochim. Acta*, *45*, 1687–1703, 1981.

Haq, B. U., J. Hardenbol, and P. R. Vail, Chronology of fluctuating sea levels since the Triassic, *Science*, *235*, 1156–1167, 1987.

Hardie, L. A., Secular variations in seawater chemistry: An explanation for coupled secular variation in the mineralogies of marine limestones and potash evaporites over the past 600 m.y., *Geology*, *24*, 279–283, 1996.

Hastings, D. W., A. D. Russell, and S. R. Emerson, Foraminiferal magnesium in Globigerinoides sacculifer as a paleotemperature proxy, *Paleoceanography*, *13*, 161–169, 1998.

Hendricks, M. B., D. J. DePalolo, and R. C. Cohen, Space and time variations of $\delta^{18}O$ and δD in precipitation: Can paleotemperatures be estimated from ice cores?, *Global Biogeochem. Cycles*, *3*, 851–862, 2000.

Hodell, D. A., and K. Venz, Towards a high-resolution stable isotopic record of the Southern Ocean during the Pliocene-Pleistocene (4.8-0.8 Ma), in *The Antarctic Paleoenvironment: A Perspective on Global Change, Antarct. Res. Ser.*, vol. 56, edited by J. P. Kennett

and D. A. Warnke, pp. 265–310, AGU, Washington, D. C., 1992.

Hodell, D. A., and F. Woodruff, Variations in the strontium isotopic ratio of seawater during the Miocene: Stratigraphic and geochemical implications, *Paleoceanography*, 9, 405–426, 1994.

Holland, H. D., *The Chemistry of the Atmosphere and Oceans*, 351 pp., John Wiley, New York, 1978.

Holland, H. D., *The Chemical Evolution of the Atmosphere and Oceans*, 584 pp., Princeton Univ. Press, Princeton, N. J., 1984.

Imbrie, J., D. Hays, D. G. Martinson, A. McIntyre, A. C. Mix, J. J. Morely, N. G. Pisias, W. L. Prell, and N. J. Shackleton, The orbital theory of Pleistocene climate: Support from a revised chronology of the marine δ^{18}O record, in *Milankovitch and Climate*, edited by A. L. Berger et al., pp. 269–306, D. Reidel, Norwell, Mass., 1984.

Jouzel, J., G. Hoffmann, R. G. Koster, and V. Masson, Water isotopes in precipitation: Data/model comparison for present-day and past climates, *Quat. Sci. Rev.*, 19, 363–379, 2000.

Katz, A., The interaction of magnesium with calcite during crystal growth at 25–90°C and one atmosphere, *Geochim. Cosmochim. Acta*, 37, 1563–1586, 1973.

Lea, D. W., T. A. Mashiotta, and H. J. Spero, Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing, *Geochim. Cosmochim. Acta*, 63, 2369–2379, 1999.

Lea, D. W., D. K. Pak, and H. J. Spero, Climate impact of late Quaternary equatorial Pacific sea surface temperatures variations, *Science*, 289, 1719–1724, 2000.

Lear, C., Middle to late Miocene benthic foraminiferal Mg/Ca, a new tracer for NADW?, *Eos Trans. AGU*, 82, Spring Meet. Suppl., OS82A-09, 2001.

Lear, C. H., H. Elderfield, and P. A. Wilson, Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite, *Science*, 287, 269–272, 2000.

Mashiotta, T. A., D. W. Lea, and H. J. Spero, Glacial-interglacial changes in subantarctic sea surface temperature and the ^{18}O-water using foraminiferal Mg, *Earth Planet. Sci. Lett.*, 170, 417–432, 1999.

McCorkle, D. C., P. A. Martin, D. W. Lea, and G. P. Klinkhammer, Evidence of a dissolution effect on benthic foraminiferal shell chemistry: δ^{13}C, Cd/Ca, Ba/Ca, and Sr/Ca, results from the Ontong Java Plateau, *Paleoceanography*, 10, 699–714, 1995.

Miller, K. G., R. G. Fairbanks, and G. S. Mountain, Tertiary oxygen isotope synthesis, sea level history, and continental margin erosion, *Paleoceanography*, 2, 1–19, 1987.

Miller, K. G., J. D. Wright, and R. G. Fairbanks, Unlocking the ice house: Oligocene-Miocene oxygen isotopes, eustacy and margin ero-

sion, *J. Geophys. Res.*, 96, 6829–6848, 1991.

Miller, K. G., and G. S. Mountain, the Leg 150 Shipboard Party, and Members of the New Jersey Coastal Plain Drilling Projects, Drilling and dating New Jersey Oligocene-Miocene sequences: Ice volume, global sea level, and Exxon records, *Science*, 271, 1092–1095, 1996.

Mottl, M. J., and G. Wheat, Hydrothermal circulation through mid-ocean ridge flanks: Fluxes of heat and magnesium, *Geochim. Cosmochim. Acta*, 58, 2225–2237, 1994.

Nuernberg, D., Magnesium in tests of *Neogloboquadrina pachyderma* sinistral from high northern and southern latitudes, *J. Foraminiferal Res.*, 25, 350–368, 1995.

Nuernberg, D., J. Bijma, and C. Hemleben, Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperature, *Geochim. Cosmochim. Acta*, 60, 803–814, 1996.

Nuernberg, D., A. Muller, and R. R. Schneider, Paleo-sea surface temperature calculations in the equatorial east Atlantic from Mg/Ca ratios in planktonic foraminifera: A comparison to sea surface temperature estimates from $U^{k'}_{37}$, oxygen isotopes, and foraminiferal transfer functions, *Paleoceanography*, 15, 124–134, 2000.

Ostermann, D. R., and W. B. Curry, Calibration of stable isotopic data: An enriched δ^{18}O standard used for gas mixing detection, *Paleoceanography*, 15, 353–360, 2000.

Ostlund, H. S., H. Craig, W. S. Broecker, and D. Spencer, *GEOSECS Atlantic, Pacific, and Indian Ocean Expedition*, vol. 7, *Shorebased Data and Graphics*, Natl. Sci. Found., Washington, D. C., 1987.

Pickard, G. L., and W. J. Emery, *Descriptive Physical Oceanography: An Introduction*, 320 pp., Pergamon, New York, 1990.

Raymo, M. E., The initiation of Northern Hemisphere glaciation, *Annu. Rev. Earth Planet. Sci.*, 22, 353–383, 1994.

Rosenthal, Y., and E. Boyle, Factors controlling the fluoride content of planktonic foraminifera: An evaluation of its paleoceanographic applicability, *Geochim. Cosmochim. Acta*, 57, 335–346, 1993.

Rosenthal, Y., E. A. Boyle, and N. Slowey, Temperature control on the incorporation of magnesium, strontium, fluorine, and cadmium into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline paleoceanography, *Geochim. Cosmochim. Acta*, 61, 3633–3643, 1997.

Russell, A. D., S. Emerson, B. K. Nelson, J. Erez, and D. W. Lea, Uranium in foraminiferal calcite as a recorder of seawater uranium concentrations, *Geochim. Cosmochim. Acta*, 58, 671–681, 1994.

Savin, S. M., L. Abel, E. Barrera, D. Hodell, J. P. Kennett, M. Murphy, G. Keller, J. Killingly, and E. Vincent, The evolution of Miocene sur-

face and near surface temperatures: Oxygen isotope evidence, in *The Miocene Ocean: Paleoceanography and Biogeography*, edited by J. P. Kennett, *Mem. Geol. Soc. Am.*, 163, 49–82, 1985.

Schrag, D. P., Rapid analysis of high-precision Sr/Ca ratios in corals and other marine carbonates, *Paleoceanography*, 14, 97–102, 1999.

Schrag, D. P., D. J. dePaolo, and F. M. Richter, Reconstructing past sea surface temperatures: Correcting for diagenesis of bulk marine carbonate, *Geochim. Cosmochim. Acta*, 59, 2265–2278, 1995.

Shackleton, N. J., Attainment of isotopic equilibrium between ocean water and the benthonic foraminifera genus *Uvigerina*: Isotopic changes in the ocean during the last glacial, *Cent. Nat. Sci. Colloq. Int.*, 219, 203–209, 1974.

Shackleton, N. J., and J. P. Kennett, Paleotemperature history of the Cenozoic and the initiation of Antarctic glaciation: Oxygen and carbon isotopic analyses in DSDP Sites 277, 279, and 281, *Initial Rep. Deep Sea Drill. Proj.*, 29, 743–755, 1975.

Shackleton, N. J., M. A. Hall, and D. Pate, Pliocene stable isotope stratigraphy of Site 846, *Proc. Ocean Drill. Program Sci. Results*, 138, 337–353, 1995.

Shipboard Scientific Party, Site 747, *Proc. Ocean Drill. Program Initial Rep.*, 120, 36–156, 1989.

Stanley, S. M., and L. A. Hardie, Secular oscillations in the carbonate mineralogy or reef-building and sediment producing organisms driven by tectonically forced shifts in seawater chemistry, *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 144, 3–19, 1998.

Vimeux, F., V. Masson, J. Jouzel, M. Stievenard, and J. R. Petit, Glacial-interglacial changes in ocean surface conditions in the Southern Hemisphere, *Nature*, 398, 410–413, 1999.

Wilkinson, B. H., and T. J. Algeo, Sedimentary carbonate record of calcium-magnesium cycling, *Am. J. Sci.*, 289, 1158–1194, 1989.

Wright, J. D., and K. G. Miller, Miocene stable isotope stratigraphy, Site 747, Kerguelen Plateau, *Proc. Ocean Drill. Program Sci. Results*, 120, 855–866, 1992.

Zachos, J. C., M. Pagani, L. Sloan, E. Thomas, and K. Billups, Trends, rhythms and aberrations in global climate 65 Ma to present, *Science*, 292, 686–693, 2001.

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