

Insights from the Paleogene tropical Pacific: Foraminiferal stable isotope and elemental results from Site 1209, Shatsky Rise

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[1] Stable isotope and elemental measurements were conducted on foraminifera from a sequence of calcareous pelagic ooze at Ocean Drilling Program Site 1209 to document the thermal evolution of the North Pacific water column over Shatsky Rise and to address long-standing questions about the nature of oceanic circulation in the early Paleogene. A major change in seasonality and water column structure in the early Eocene marks a change in tropical Pacific climate and circulation just prior to the early Eocene climatic optimum. Subsequent long-term cooling is interrupted by a transient positive $\delta^{18}\text{O}$ excursion identified in planktonic and benthic foraminifera during the late early Eocene that is interpreted as evidence for ephemeral formation of deep water from a low-latitude, saline source. Paired analysis of benthic Mg/Ca and $\delta^{18}\text{O}$ was undertaken to assess the relative contribution of temperature and seawater oxygen isotope composition to the benthic $\delta^{18}\text{O}$ record. Stratigraphic trends of benthic $\delta^{18}\text{O}$ and Mg/Ca decouple during two intervals in the early Eocene and early middle Eocene. Although variable seawater $\delta^{18}\text{O}$ is the most likely candidate to explain decoupling of benthic $\delta^{18}\text{O}$ and Mg/Ca, it is difficult to argue for substantial change in continental ice volume during a presumably ice-free interval of time.

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1. Introduction

[2] In the closing years of the Ocean Drilling Program (ODP), several locations were targeted in the Pacific and Atlantic Ocean basins (ODP Legs 198, 199, 207, and 208) to provide more complete records of extreme climates in the Cretaceous and Paleogene [Lyle *et al.*, 2002; Bralower *et al.*, 2003; Erbacher *et al.*, 2004; Zachos *et al.*, 2004]. The Paleogene is of particular interest to paleoclimatologists because it represents a transition between extreme climate states: from the “greenhouse” climate of the early Eocene climatic optimum (EECO) to the “icehouse” of the early Oligocene. The equable, warm climates of the early Paleogene were punctuated by at least one transient hyperthermal event at the Paleocene/Eocene boundary [e.g., Kennett and Stott, 1991; Thomas and Shackleton, 1996; Zachos *et al.*, 2003] and the occurrence of multiple hyperthermals in the early Eocene has been further postulated [Thomas *et al.*, 2001]. Thus the early Paleogene contains examples of extreme climates on both short (10^4 years) and long (10^6 years) timescales.

[3] Despite the identification of this climatically dynamic period of earth’s history, there are still several questions that persist about the driving mechanisms and feedbacks of Paleogene climate as well as the effects of climatic perturbations upon the biosphere. Paramount among these is the question of how low equator-to-pole temperature gradients can be maintained in the early Paleogene [Barron, 1987; Sloan *et al.*, 1995], particularly in light of evidence that oceanic and atmospheric circulation was sluggish, and therefore less capable of transporting heat to polar regions [Janecek and Rea, 1983; Rea, 1998]. A warm sluggish ocean with low vertical thermal gradients and no winter sea ice to facilitate downwelling of deep waters at high latitudes may have been prone to circulation reversals whereby warm, salty water sinks at lower latitudes. The viability of this hypothesis continues to be heavily debated in the literature [Bice *et al.*, 1997; Bice and Marotzke, 2001 and references therein], nearly a century after it was proposed by Chamberlain [1906]. Finally, the driving mechanisms of both long- and short-term climate changes in the Paleogene are still questioned, as well as the interaction and feedbacks between processes that operate on different timescales. Our collective ability to address these questions has been hampered in part by the coarseness of spatial and temporal

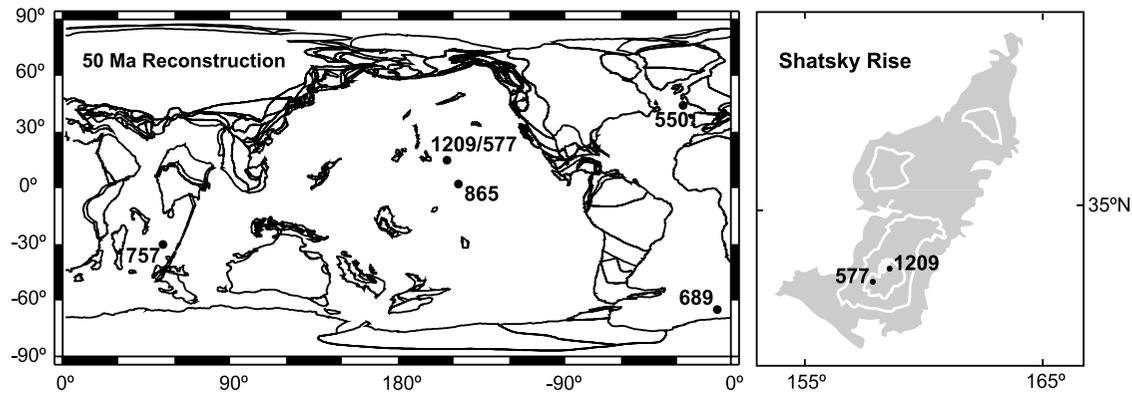


Figure 1. (left) Tectonic reconstruction (50 Ma) map [Hay *et al.*, 1999] with the location of Ocean Drilling Program (ODP) and Deep Sea Drilling Program (DSDP) sites referred to in this study. (right) Modern map of Shatsky Rise with locations of ODP Site 1209 and DSDP Site 577.

sampling of well-preserved Paleogene deep-sea sedimentary sections. To address this deficiency, this investigation was designed to provide a multiproxy documentation of long-term climatic and oceanographic history from a tropical site in the Pacific Ocean. The Pacific Ocean basin was much larger in the Paleogene (Figure 1), yet because of the relatively shallow depth of the carbonate compensation depth (CCD), particularly in the northern Pacific, recovery of well-preserved carbonate sediment from this region is rare.

[4] ODP Site 1209 (32°39.1081'N, 158°30.3564'E) was drilled on the Southern High of Shatsky Rise in a water depth of 2387 m. The sedimentary record recovered at Site 1209 contains an expanded Paleogene section consisting of unlithified calcareous ooze with moderately to well-preserved foraminifera. This site represents the shallowest in a depth transect of sites targeting Paleogene sediments cored during Leg 198, and was situated well above the CCD during most of the Paleocene and Eocene [Hancock and Dickens, 2005]. Stable isotope analyses were carried out on several planktonic taxa (*Acarinina*, *Morozovella*, *Globigerinatheka*, *Praemurica*, *Subbotina*) as well as several benthic taxa (*Nuttalides*, *Oridorsalis*, *Cibicidoides*, *Gavelinella*, *Lenticulina*). A record of Mg/Ca for benthic foraminifera has also been constructed to better evaluate the relative influence of temperature and oxygen isotope seawater composition upon the benthic oxygen isotope record.

2. Methods

2.1. Sample Preparation

[5] The samples studied are from the composite section of Site 1209, which splices together sections from three holes (A, B, and C) [Bralower *et al.*, 2003]. Approximately one 10-cm³ sample per section was selected for analysis; these were dried overnight in an oven at <50°C, disaggregated in buffered deionized water (pH ~10), washed through 63- and 125- μ m sieves, and oven dried again. The >125 μ m fraction was dry

sieved into four fractions: >125–250 μ m, >250–300 μ m, >300–355 μ m, and >355 μ m. Planktonic foraminifera were picked from a narrow size fraction (300–355 μ m) to minimize complicating factors of ontogenetic and other vital effects upon geochemical compositions [Shackleton *et al.*, 1985; Pearson *et al.*, 1993]. In seven samples planktonics were taken from the 250–300 μ m size fraction. Benthic foraminifera were picked from the >125 μ m size fraction.

2.2. Foraminiferal Taxa

[6] Species of *Acarinina* and *Morozovella* were selectively chosen from the surface-dwelling taxa present because they are abundant, morphologically distinctive, and frequently analyzed from other Paleogene deep-sea cores. In two samples, these taxa were not present and *Praemurica inconstans* and *Globigerinatheka* sp. were used instead. Because no single species of *Acarinina* or *Morozovella* spans the entire time interval studied, several different species were analyzed, including: *Morozovella conicotruncana*, *M. angulata*, *M. subbotinae* (including *M. gracilis*), *M. velascoensis*, *M. formosa*, *M. aragonensis*, *Acarinina soldadoensis*, and *A. bulbrooki*. Where possible, multiple taxa were examined for cross-calibration purposes. Species of *Subbotina* were grouped together for analysis, although most *Subbotina* samples consist of a single species. Each stable isotope analysis consists of four to seven individual planktonic foraminifera.

[7] Several benthic taxa were used for stable isotope analyses, including: *Gavelinella* spp., *Nuttalides* spp., *Oridorsalis* spp., *Lenticulina* spp., and *Cibicidoides* spp. Of these taxa, only *Nuttalides truempyi*, *Oridorsalis umbonatus*, and *Gavelinella beccariiformis* were used for elemental analyses. Multiple taxa were analyzed in several cases for both types of analyses to determine offsets in geochemical composition between species. Depending upon size and abundance, between one and five benthic specimens were used for stable isotope analysis and between 11 and 28 individual benthics were combined for elemental analysis.

Table 1. Relevant Geographic Information of Deep-Sea Sites Mentioned in the Text

Site	Location Name	Present Depth, m	Paleodepth, m	Paleodepth Zone	Latitude	Longitude	Paleolatitude
ODP 1209	Shatsky Rise	2387	2500 ^a	upper abyssal	33°N	159°E	15°–20°N
DSDP 577	Shatsky Rise	2675	2400 ^b	upper abyssal	32°N	158°E	15°–20°N
ODP 865	Allison Guyot	1518	1300–1500 ^c	lower bathyal	18°N	180°E	2°–6°N
ODP 689	Maud Rise	2080	1400–1650 ^d	lower bathyal	65°S	3°E	67°S
ODP 757	Ninetyeast Ridge	1652	1500 ^e	lower bathyal	17°S	88°E	45°S
DSDP 550	Goban Spur	4432	4000 ^f	lower abyssal	48°N	13°W	48°N

^aBralower *et al.* [2003].

^bZachos and Arthur [1986].

^cThomas and Shackleton [1996].

^dKennett and Stott [1990].

^ePierce *et al.* [1989].

^fMasson *et al.* [1985].

2.3. Stable Isotope Analyses

[8] Specimens were sonicated in deionized Milli-Q water and roasted in vacuo at 200°C prior to stable isotope analysis. Measurements were conducted at the Stable Isotope Laboratory at the University of Michigan using a Finnigan MAT 251 directly coupled to an automated Kiel device. All results are reported in permil (‰) relative to the Vienna Pee Dee belemnite (VPDB) standard. Analytical accuracy and precision were monitored by daily analysis of National Bureau of Standards (NBS)-19 in addition to various in-house standards. Precision was maintained at 0.06‰ for oxygen and 0.03‰ for carbon (1 σ). Precision of replicate measures of foraminiferal samples was consistently within 0.1‰ for both oxygen and carbon. To assess the isotopic variability between different specimens from the same sample, 11 individual foraminifera of the species *M. velascoensis* were analyzed for sample 1209C-12H-5, 40–42 cm. All geochemical data are compiled by Dutton *et al.* [2005].

[9] Paleotemperatures calculated from oxygen isotope data are accomplished using the equation of Erez and Luz [1983] with a $\delta^{18}\text{O}_{\text{SW}}$ value of -0.98‰ VSMOW [Zachos *et al.*, 1994] corrected relative to the Pee Dee belemnite standard by subtracting 0.27‰ [Gonfiantini *et al.*, 1995]. Sea surface temperatures (SST) are further corrected for surface water salinity as a function of paleolatitude [Zachos *et al.*, 1994] (Table 1). This surface salinity correction has the effect of increasing SSTs by 3.9°C relative to uncorrected temperatures at Shatsky Rise which was located between 15° and 20° north of the equator in the Paleogene [Bralower *et al.*, 2003].

2.4. Elemental Analyses

[10] Elemental analyses were conducted on benthic foraminifera cleaned following the protocol of Barker *et al.* [2003]. This treatment involves multiple rinses and sonications in Milli-Q water and methanol followed by bathing in a hot, buffered oxidizing solution, and a final weak acid leach that is performed after the specimens have been transferred into a new, acid-leached vial. We specifically chose not to include a reductive cleaning step on the basis of evidence that this treatment further reduces the Mg/Ca ratio [Martin and Lea, 2002; Barker *et al.*, 2003]. These studies are at odds in determining whether lower Mg/Ca values

associated with the reductive cleaning step are the result of further shell dissolution or the removal of contaminant phases (e.g., oxide coatings). Therefore we monitored Mn/Ca and Fe/Ca as proxies for the presence of oxide coatings and clays, respectively. All samples displayed Mn/Ca close to zero or below detection limits; only one sample (1209C-12H-3, 40–42 cm) displayed an elevated Fe/Ca ratio >0.1 mmol/mol, yet the Mg/Ca content of this sample is by no means anomalous. By omitting the reductive step, our results can be directly compared to existing benthic Mg/Ca records from the Paleogene [Lear *et al.*, 2000; Billups and Schrag, 2003], which also do not include a reductive step during sample preparation.

[11] Cleaned samples were dissolved in 0.075N HNO₃ roughly one hour prior to analysis. Measurements of Mg, Ca, Sr, Fe, and Mn were conducted on a Varian Vista axial ICP-AES at The Australian National University following the intensity ratio analytical method described by de Villiers *et al.* [2002]. More information on this procedure and the results of these geochemical analyses are detailed by Dutton *et al.* [2005]. Precision was assessed by repeated analysis of a check standard during the run and is reported here as 1 σ in mmol/mol and percent relative standard deviation (% rsd) for each element ratio examined: Mg/Ca, 0.019 and 0.37%; Sr/Ca, 0.006 and 0.32%; Mn/Ca, 0.005 and 0.32%; and Fe/Ca, 0.007 and 0.48%. For Mg/Ca, the intraspecies within sample variability average is ± 0.17 mmol/mol ($n = 3$) and the interspecies within sample variability average (using species-corrected Mg/Ca as described below) is ± 0.21 mmol/mol ($n = 8$). External accuracy of our standard stock solutions was assessed using a commercially available multielement standard as well as aliquots of gravimetrically prepared standards supplied by the laboratory at Cambridge University.

2.5. Age Model

[12] Age control is provided by nannofossil biostratigraphy of Site 1209 [Bralower, 2005] which indicates that the Paleocene and Eocene sequence of sediments is fairly complete aside from a hiatus within nannofossil Zone CP9, and another hiatus in the middle Eocene. An age datum for the Paleocene/Eocene boundary, which lies at the base of the carbon isotope excursion [Aubry, 2002], has been added to the nannofossil datums (211.21 mcd, 55.0 Ma). Accordingly, the last occurrence datum for

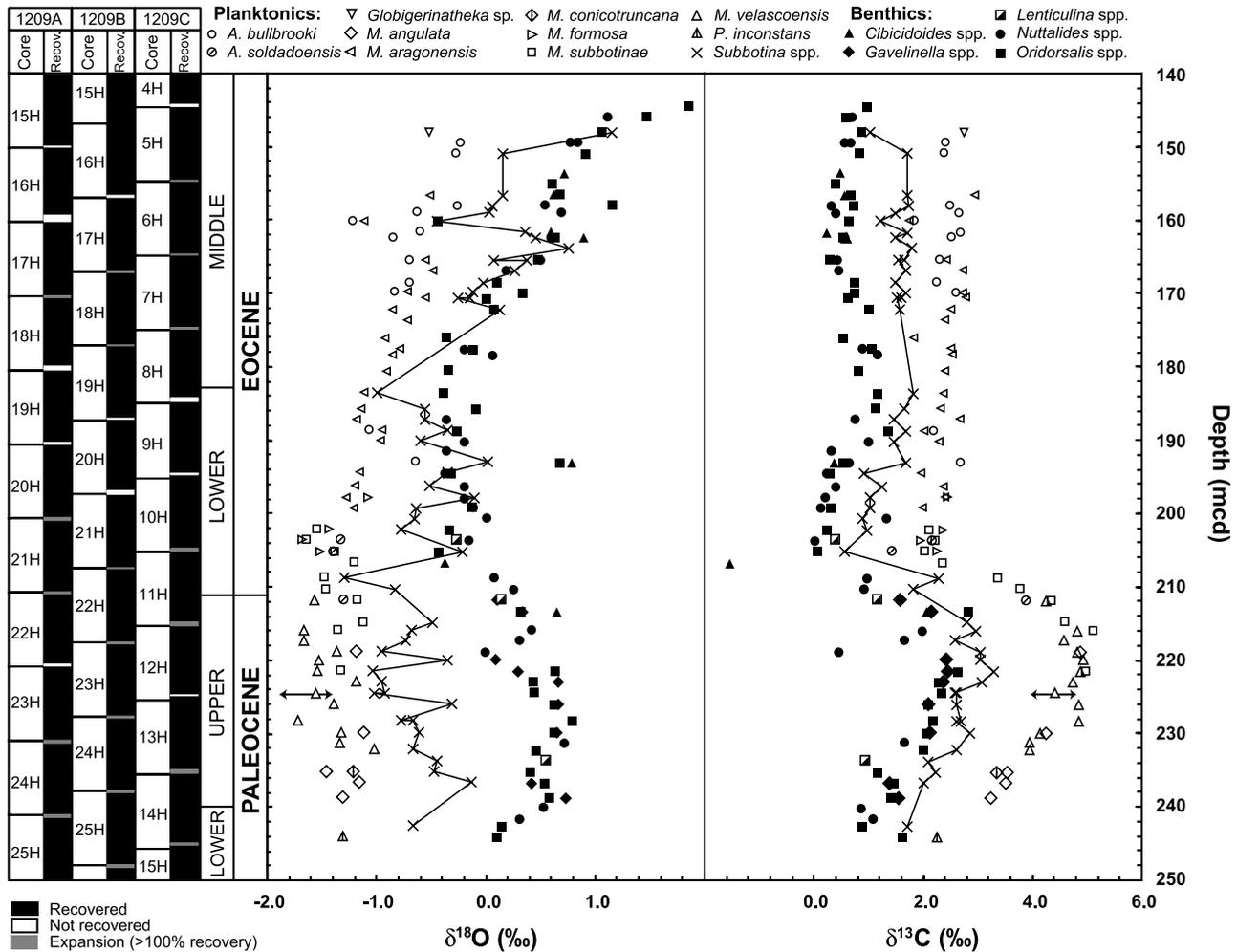


Figure 2. Foraminiferal (left) oxygen isotope and (right) carbon isotope data plotted relative to mean composite depth (mcd) for Site 1209. The double-headed arrows at ~ 225 mcd indicate the range in composition of 11 single specimen analyses from the same sample.

F. tympaniformis set at 55.0 Ma by Bralower [2005] was excluded. Magnetostratigraphic control for this sequence is not available.

3. Results

3.1. Stable Isotope Data

3.1.1. Surface-Dwelling Planktonics

[13] Oxygen isotope compositions of surface dwellers, species of *Acarinina* and *Morozovella*, maintain a relatively stable long-term stratigraphic trend centered on -1.4‰ throughout the Paleocene, but show substantial variability within this interval (Figure 2). Single specimen isotopic analyses of eleven *M. velascoensis* specimens from an upper Paleocene sample (224.5 mcd) display a range in compositions that is roughly an order of magnitude greater than the analytical precision of each analysis, spanning 0.5‰ in $\delta^{18}\text{O}$ and 0.9‰ in $\delta^{13}\text{C}$. The double-headed arrows in Figure 2 depict this range of intrasample variability, which is similar in magnitude to the variability between stratigraphically adjacent samples. Low $\delta^{18}\text{O}$ values reaching

-1.7‰ are recorded by lowermost Eocene *Acarinina* and *Morozovella*. These low values are followed by a positive shift of $\sim +0.3\text{‰}$ (199.3 mcd). From this point in the lower Eocene, $\delta^{18}\text{O}$ gradually increases into the upper middle Eocene where a maximum value of -0.2‰ is attained. The variability between stratigraphically adjacent samples is typically much smaller through the Eocene than in the Paleocene.

[14] Carbon isotope compositions of surface-dwelling planktonics steadily increase from the lower Paleocene to the upper Paleocene where they peak at maximum values of 4.9 to 5.1‰ . After reaching this apex, $\delta^{13}\text{C}$ rapidly decreases by $\sim 3.5\text{‰}$ through the uppermost Paleocene and lowermost Eocene. $\delta^{13}\text{C}$ values stabilize in the lower Eocene and display gradual enrichment in ^{13}C from lower to middle Eocene, increasing from roughly 2.0 to 2.7‰ .

3.1.2. Deeper-Dwelling Planktonics

[15] *Subbotina* displays rather large amplitudes of $\delta^{18}\text{O}$ variability on the order of roughly 0.6‰ throughout the section, punctuated by occasional larger excursions. $\delta^{18}\text{O}$ data display decreasing values for *Subbotina* through the

upper Paleocene, reaching a minimum of -1.3‰ in the lowermost Eocene (208.8 mcd). This minimum is immediately followed by a 1.0‰ increase to higher $\delta^{18}\text{O}$ values that prevail for most of the lower Eocene. A return to low $\delta^{18}\text{O}$ values occurs in one *Subbotina* sample (183.6 mcd) near the lower to middle Eocene boundary, but a dearth of well-preserved *Subbotina* immediately above this sample precludes us from establishing whether low values are maintained or if this one sample is anomalously low relative to its stratigraphic neighbors. The middle Eocene exhibits high $\delta^{18}\text{O}$ values from -0.4 to $+1.2\text{‰}$ that generally increase up section with the exception of a notable excursion to lower values in the upper middle Eocene (160.1 mcd).

[16] Carbon isotope compositions of *Subbotina* display oscillatory values in the Paleocene, and steadily increase from 1.7‰ in the lower Paleocene to 3.3‰ in the upper Paleocene. Maximum values are attained during the same stratigraphic interval that records the highest values for the surface-dwelling planktonics. These high $\delta^{13}\text{C}$ values decay rapidly through the uppermost Paleocene and lowermost Eocene, reaching a minimum of 0.6‰ that is coincident with the minimum attained in the surface planktonic $\delta^{13}\text{C}$ record (205.2 mcd). After reaching this minimum, *Subbotina* displays gradually increasing $\delta^{13}\text{C}$ values during the lower Eocene that lead into a sharp increase of 0.8‰ (193.0 mcd). After this point, *Subbotina* $\delta^{13}\text{C}$ values remain steady at about 1.7‰ from the lower into the middle Eocene.

3.1.3. Benthic Foraminifera

[17] Benthic oxygen isotope values shown in Figure 2 have been adjusted for interspecies offsets. We used the corrections calculated for *Nuttalides*, *Cibicidoides*, and *Oridorsalis* by Katz *et al.* [2003] who carried out a rigorous assessment of intertaxa offsets for Paleogene specimens. Corrections for *Nuttalides* and *Cibicidoides* have been applied to this data set as well as to all benthic oxygen isotope data from other deep-sea cores cited herein. We chose to use these corrections because they yield better coherency between values recorded by multiple taxa from the same sample and/or within the same stratigraphic interval both in our data set and for Paleogene data in the global compilation of Zachos *et al.* [2001]. Similar adjustments were made for the carbon isotope data using offsets from Katz *et al.* [2003], in part because of the combination of infaunal (*Oridorsalis*, *Lenticulina*) and epifaunal taxa (*Nuttalides*, *Cibicidoides*, *Gavelinella*) in this study. These taxa display significant offsets in $\delta^{13}\text{C}$ because the infaunal taxa are exposed to ^{12}C -enriched pore waters. We note that species-adjusted $\delta^{13}\text{C}$ also reduces the apparent scatter in the Site 1209 data as well as in the Zachos *et al.* [2001] Paleogene data set. *Lenticulina* and *Gavelinella* were not included in the Katz *et al.* [2003] study; therefore additive correction factors were calculated for these taxa based on average offsets observed in the Shatsky Rise data set ($\delta^{18}\text{O}$, $+0.33\text{‰}$ for both species; $\delta^{13}\text{C}$, $+1.24\text{‰}$ for *Lenticulina* and $+0.36\text{‰}$ for *Gavelinella*).

[18] Paleocene benthic foraminifera display gradual oscillations in $\delta^{18}\text{O}$ that range from 0.1 to 0.8‰ . A rapid decrease occurs in $\delta^{18}\text{O}$ values from about 0.5 to -0.4‰ in the uppermost Paleocene and lowermost Eocene (213.3 to 206.7 mcd). Benthic $\delta^{18}\text{O}$ stabilizes at low values

between -0.4 and 0.0‰ for the duration of the lower Eocene and the lower middle Eocene with the exception of one sample (1209B-20H-4, 51–53 cm; 193.0 mcd), represented by three different benthic species, that records exceptionally high $\delta^{18}\text{O}$ values of 0.7 to 0.8‰ . This positive $\delta^{18}\text{O}$ excursion of $\sim 1.0\text{‰}$ is accompanied by positive excursions in *Acarinina* and *Subbotina* that are both 0.5‰ in magnitude. Low $\delta^{18}\text{O}$ values that characterize most of the lower and lower middle Eocene rapidly increase from -0.4 to 0.9‰ in the middle Eocene (176.0 to 162.4 mcd). A second anomalous sample (1209C-6H-4, 40–42 cm; 160.1 mcd) is observed in the middle Eocene which displays a negative $\delta^{18}\text{O}$ excursion of $\sim 1.1\text{‰}$, and again is accompanied by an excursion in *Acarinina*, *Morozovella*, and *Subbotina*. The surface dwellers only decrease by $\sim 0.5\text{‰}$ in this horizon while *Subbotina* $\delta^{18}\text{O}$ diminishes by 0.8‰ .

[19] Trends in carbon isotope values of benthic foraminifera at Shatsky Rise are remarkably similar to trends recorded in *Subbotina* $\delta^{13}\text{C}$. Benthic $\delta^{13}\text{C}$ increases from the lower to upper Paleocene attaining a maximum value of 2.1‰ that is largely coincident with peak values recorded in planktonic foraminifera. These high $\delta^{13}\text{C}$ values rapidly decrease across the Paleocene/Eocene boundary and reach minimum values in the lowermost Eocene. The $\delta^{13}\text{C}$ then gradually recovers to higher values through the lower Eocene and is marked by a distinctive positive step of 0.7‰ in the upper lower Eocene, similar in timing and magnitude to the stepwise increase observed in *Subbotina* specimens. The $\delta^{13}\text{C}$ slowly decreases back to values averaging 0.5‰ that remain relatively constant through the remainder of the middle Eocene.

3.2. Elemental Data

[20] Mg/Ca values for all taxa were normalized to *Oridorsalis umbonatus* by determining the difference between pairs of species for several samples. Additive corrections using fixed values cannot be used to normalize Mg/Ca data in the way that benthic foraminiferal $\delta^{18}\text{O}$ data is typically treated because the relationship between Mg/Ca and temperature is exponential. This temperature dependence can be described in a general manner by the following equation:

$$\text{Mg/Ca} = B \exp(A \times T)$$

where *Mg/Ca* is in mmol/mol, *T* is in $^{\circ}\text{C}$, *A* is the exponential constant that represents temperature sensitivity and *B* is the preexponential constant. Thus, the difference in Mg/Ca between two species is a function of the temperature of calcification (Figure 3). As such, it is imperative to derive an exponential function for the relation between Mg/Ca and temperature for each extinct species. This procedure is illustrated for *Nuttalides truempyi* in Figure 3. In this diagram, the temperature for seven paired analyses of *N. truempyi* and *O. umbonatus* Mg/Ca measurements was determined using the Mg/Ca-temperature equation for *O. umbonatus* from the core top calibration of Lear *et al.* [2002]. Additional paired analyses of these two species from the study of Lear *et al.* [2000] are also included. This exercise demonstrates that a number of exponential functions encompassing the range of temperature sensitiv-

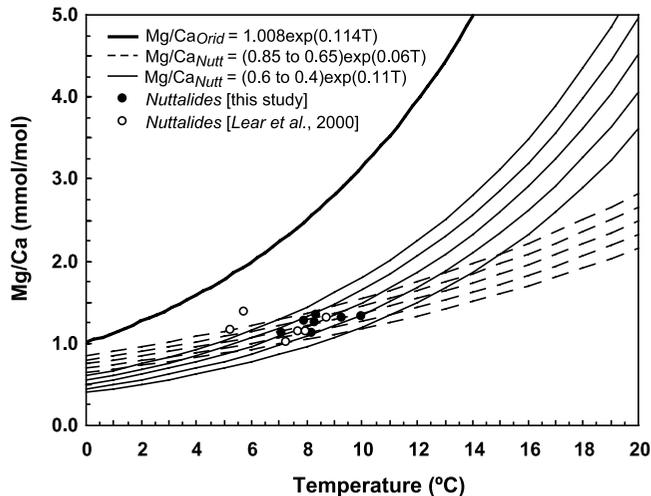


Figure 3. Mg/Ca composition of *Nuttallides* versus temperature computed from Mg/Ca values of *Oridorsalis* in the same sample. Thin solid lines represent a temperature sensitivity of 11.6% ($0.11/^{\circ}\text{C}$) for preexponential constants between 0.6 and 0.4, shown in increments of 0.05. Dashed lines represent a temperature sensitivity of 7.6% ($0.6/^{\circ}\text{C}$) for preexponential constants ranging from 0.85 to 0.65, shown in increments of 0.05. Thick solid line represents core top calibration of *O. umbonatus* [Lear et al., 2002].

ities observed in core top calibrations of extant benthic taxa [Lear et al., 2002] could provide reasonable fits to the data (Figure 3). Unfortunately, the Mg/Ca-temperature relation for *N. truempyi* is poorly constrained due in part to the lack of data points at higher temperatures. We chose to apply an exponential constant of $0.11/^{\circ}\text{C}$ for *N. truempyi* using two criteria. First, modern benthic taxa exhibit a bimodal distribution in temperature sensitivities with typical values near 0.11 or $0.06/^{\circ}\text{C}$ [Lear et al., 2002]. Secondly, comparison of amplitudes of variation in paired Mg/Ca and $\delta^{18}\text{O}$ measurements through the section display the best agreement during periods assumed to be ice free using a value of $0.11/^{\circ}\text{C}$ for the exponential constant whereas lower values of A produce large differences in temperature for very small changes in Mg/Ca resulting in unreasonably large amplitudes of variability relative to those recorded in $\delta^{18}\text{O}$. The corresponding preexponential constant was chosen to best fit the data ($B = 0.5$). We emphasize that this derivation is provisional; however, manipulation of these constants for *N. truempyi* does not alter the fundamental patterns in Mg/Ca relative to $\delta^{18}\text{O}$ that are discussed in this manuscript, and therefore does not modify our conclusions.

[21] For *Gavelinella beccariiiformis*, there are only three Mg/Ca measurements ranging from 2.53–2.64 mmol/mol; two of these samples are paired with Mg/Ca data of *N. truempyi*. Owing to the limited number of analyses and restricted range of Mg/Ca in this data set, we use an additive correction of +1.05 mmol/mol to normalize *G. beccariiiformis* Mg/Ca data to those of *O. umbonatus*.

[22] In all diagrams displaying Mg/Ca data, species-corrected Mg/Ca data have been converted to temperature using the core top calibration for *O. umbonatus* [Lear et al., 2002] to facilitate comparison with oxygen isotope data that are linearly related to temperature. Absolute temperatures calculated from Mg/Ca data depend on the assumed Mg/Ca composition of Paleogene seawater, yet relative change in temperature is insensitive to this parameter. Mg/Ca displays variability that corresponds to $\sim 2^{\circ}\text{C}$ in temperature during the Paleocene, although the long-term trend is relatively constant during this interval and in the early Eocene (Figure 4). Mg/Ca values, and their corresponding inferred temperatures, decrease gradually from late early to middle Eocene. This cooling trend begins at ~ 50 Ma and continues through the remainder of the section studied (to ~ 40 Ma). Fluctuations in benthic Mg/Ca mimic patterns observed in benthic $\delta^{18}\text{O}$ throughout much of the section except for the earliest Eocene and the early middle Eocene where Mg/Ca and $\delta^{18}\text{O}$ decouple. These intervals are both marked by relatively rapid change in $\delta^{18}\text{O}$ relative to the Mg/Ca record.

4. Discussion

4.1. Foraminiferal Preservation

[23] Paleocene and Eocene foraminifera at Site 1209 are generally moderately to well preserved with increasing effects of dissolution upward toward the upper Eocene [Hancock and Dickens, 2005; Petrizzo et al., 2005]. A minor component of secondary calcite was evident in some SEM images [Dutton et al., 2005]. The volume of recrystallized calcite in the best preserved specimens is less than 5% and ranges up to $\sim 10\%$ for the more poorly preserved specimens. Individuals that were strongly recrystallized and samples dominated by fragments and corroded calcite were not selected for geochemical analysis, including all samples from the upper Eocene. Objective evidence such as maintenance of intertaxa offsets and similarity to other deep-sea data sets combined with a more subjective visual assessment of shell textures suggests that the geochemical signatures of these foraminifera are largely unaffected by diagenesis. Nonetheless, diagenesis can be subtle and can elude standard procedures aimed at elucidating its effects. Therefore we cannot completely rule out the possibility that postdepositional alteration has had some effect on the geochemical data generated from Site 1209.

4.2. Intertaxa Offsets in Stable Isotope Composition

4.2.1. Planktonic Foraminifera

[24] Systematic differences between $\delta^{18}\text{O}$ and/or $\delta^{13}\text{C}$ of planktonic taxa can indicate the influence of different depth habitats, vital effects, or season of calcification. *Acarinina* and *Morozovella* are both considered to have lived in the surface mixed layer [e.g., Pearson et al., 1993] but their relative depth habitats are debatable. Offsets reported for *Acarinina* and *Morozovella* from several different Paleogene deep-sea cores are inconsistent from site to site and sometimes show different patterns through time [Oberhänsli and Toumarkine, 1985; D'Hondt et al., 1994; Bralower et al., 1995a]. Paired measurements of these taxa at other sites

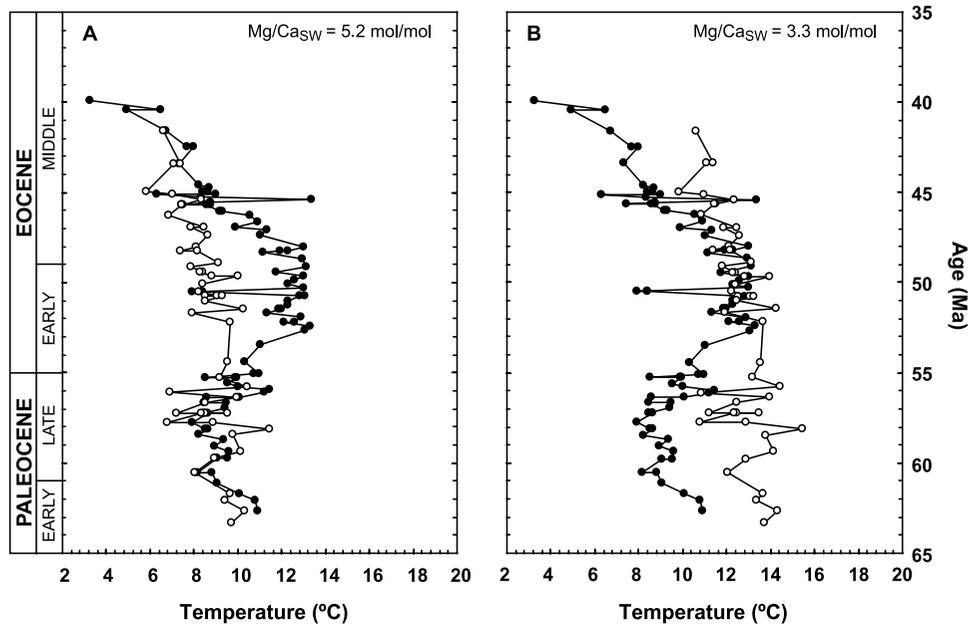


Figure 4. Benthic paleotemperature reconstruction based on Mg/Ca values (open circles) and $\delta^{18}\text{O}$ (solid circles) plotted relative to age. (a) Modern seawater Mg/Ca value (5.2 mol/mol) is assumed. (b) Paleoseawater Mg/Ca composition is estimated at 3.3 mol/mol assuming an ice-free world from 48 to 53 Ma, when the most negative benthic $\delta^{18}\text{O}$ values are recorded. Oxygen isotope paleotemperatures are calculated using the equation of Erez and Luz [1983] with $\delta_w = -0.98\text{‰}$.

do not always display systematic offsets [Pearson *et al.*, 1993]. At Site 1209, early Eocene *A. soldaoensis* does not show systematic differences in comparison to *M. subbotinae*. Early to middle Eocene *A. bulbrooki* is 0.1‰ lower in $\delta^{18}\text{O}$ than *M. aragonensis* in four different samples, but no consistent offset is observed in $\delta^{13}\text{C}$.

[25] The relation between these surface dwellers and deeper dweller *Subbotina* is much clearer. *Subbotina* consistently records more positive $\delta^{18}\text{O}$ values and more negative $\delta^{13}\text{C}$ than any of the surface-dwelling taxa throughout the section at Site 1209. This systematic pattern of offsets in both isotope records has been inferred as an indicator of a depth habitat within or below the thermocline [Stott *et al.*, 1990; Pearson *et al.*, 1993; D'Hondt *et al.*, 1994]. Interestingly, *Subbotina* records from Shatsky Rise are similar to those at Allison Guyot [Bralower *et al.*, 1995b] in that more short-term variability is observed for this taxon than for the other planktonic taxa. This variability could be attributed to mobility in depth habitat, temporal fluctuations in environmental conditions of deep surface waters, or may result from the combination of multiple species used to generate this record. Of these possibilities, we suggest that fluctuating temperatures in thermocline waters is the most likely explanation. This idea is consistent with predictions of a coupled ocean atmosphere climate model, which describes an El Niño-like oscillation in the tropical and subtropical Pacific during the early Paleogene [Huber, 2002].

4.2.2. Benthic Foraminifera

[26] We measured stable isotope compositions of both *Nuttalides* and *Oridorsalis* in eight samples. Removing one outlier from this group, we observe an excellent correlation

between their $\delta^{18}\text{O}$ values ($r^2 = 0.97$): $\delta^{18}\text{O}_{\text{NUTT}} = (\delta^{18}\text{O}_{\text{ORID}} - 0.44)/0.89$. This relation is very similar to that determined by Katz *et al.* [2003] which is derived from a larger data set compiled from several cores. Carbon isotope values of epifaunal benthic taxa (*Cibicidoides*, *Gavelinella*, *Nuttalides*) are more positive than *Oridorsalis* $\delta^{13}\text{C}$ values in 15 out of 17 cases. This result agrees with the findings of other studies that suggest a shallow infaunal habitat for *Oridorsalis* [e.g., Rathburn and Corliss, 1994]. Although we have applied the correction of Katz *et al.* [2003] to normalize $\delta^{13}\text{C}$ of *Oridorsalis* to *Cibicidoides*, we note that this produces values that are somewhat high relative to the other taxa throughout the section (Figure 2). This result indicates that the $\delta^{13}\text{C}$ adjustment for *Oridorsalis* may be slightly overcorrecting $\delta^{13}\text{C}$ values relative to compositions that are in equilibrium with dissolved organic carbon of ambient seawater.

4.3. Stable Isotope Paleoclimate Reconstruction

[27] During the Paleocene and Eocene, trends in planktonic $\delta^{18}\text{O}$ at Site 1209 are largely similar to those at other sites [Boersma *et al.*, 1987; Stott *et al.*, 1990; Barrera and Huber, 1991, 1993; Zachos *et al.*, 1994; Bralower *et al.*, 1995b]. Surface water foraminifera record low but relatively stable $\delta^{18}\text{O}$ values during the Paleocene and earliest Eocene that correspond to a temperature of $\sim 22^\circ\text{C}$ (Figure 2). Considerable intrasample and intersample variability in $\delta^{18}\text{O}$ during this time interval is interpreted as the result of a seasonal climate. This pattern is contrasted by low intersample variability during the late early and middle Eocene that may reflect a substantial decrease in the seasonal amplitude of SST. Planktonic oxygen isotope

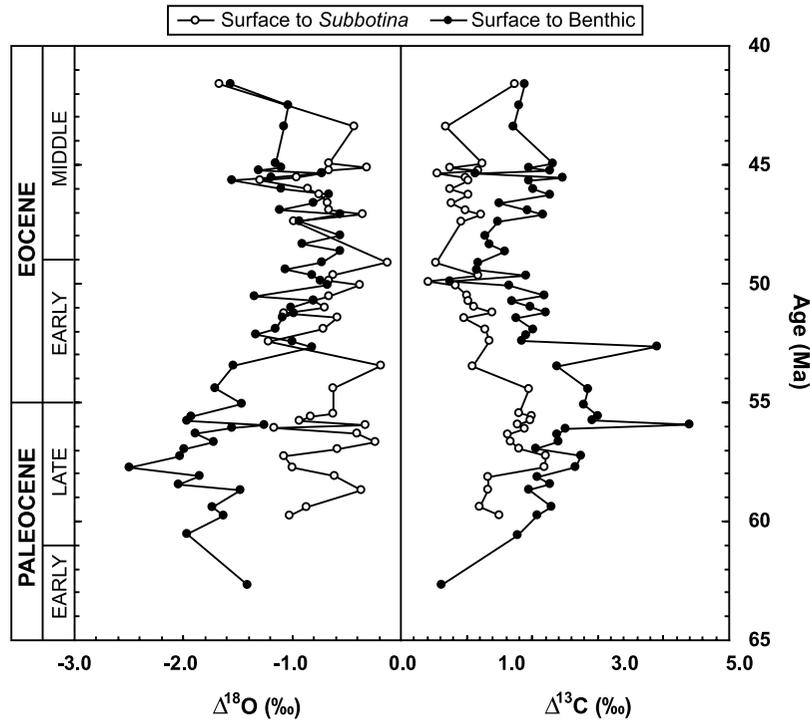


Figure 5. Vertical oxygen and carbon isotope gradients in the water column over Shatsky Rise plotted relative to age for Site 1209. Gradients were calculated using average values of surface planktonics, deeper dwelling planktonics (*Subbotina*), and benthics for each sample.

values steadily increase from the early Eocene through the middle Eocene, signifying the initiation of a long-term cooling trend. Temperatures drop from 22° to 17°C in surface waters from ~52 to 45 Ma (202.2 mcd to 156.6 mcd). This surface cooling trend precedes cooling in the benthic record, which attains minimum $\delta^{18}\text{O}$ values (maximum warmth) at roughly 52 Ma yet does not begin to increase (cool) until after 48 Ma (176.1 mcd). The significance of anomalously negative planktonic and benthic $\delta^{18}\text{O}$ values at 45.4 Ma (160.1 mcd) is not clear, but may correlate to a transient negative excursion seen in the planktonic isotope record from Site 865 in the equatorial Pacific [Bralower et al., 1995b].

[28] *Subbotina* $\delta^{18}\text{O}$ shows substantial variability throughout the section, and in this sense is very similar to the *Subbotina* $\delta^{18}\text{O}$ record at Site 865 [Bralower et al., 1995b]. High variability of water temperature at the depth of the thermocline in the equatorial and tropical Pacific may be the result of a dynamic thermocline due to an El Niño-like oscillation [Huber, 2002]. Benthic $\delta^{18}\text{O}$ values are relatively stable during the Paleocene, recording temperatures between 9° and 11°C, but decrease substantially in the latest Paleocene and early Eocene reflecting warming to 13°C. Benthic temperatures stabilize during maximum Cenozoic warmth of the EECO and then decay rapidly in the early middle Eocene by ~3.5°C.

[29] There is a notable association of strong surface-to-benthic $\delta^{18}\text{O}$ gradients over Shatsky Rise with more positive values of benthic $\delta^{18}\text{O}$ (Figure 5). The collapse of the $\delta^{18}\text{O}$ gradient in the early Eocene is accomplished primarily by a

substantial decrease in benthic $\delta^{18}\text{O}$ and is accompanied by a positive shift in *Subbotina* $\delta^{18}\text{O}$ (Figure 2). The shift observed in *Subbotina* is similar in timing, magnitude, and direction to the shift in *Subbotina* at DSDP Site 550 in the abyssal North Atlantic [Charisi and Schmitz, 1996]. The near elimination of a gradient between thermocline and deep waters seen at Site 1209 (~53 Ma) is also recorded at Site 550. This reduction in the vertical $\delta^{18}\text{O}$ gradient precedes initiation of long-term cooling of both surface (after 52 Ma) and deep waters (after 48 Ma), but is coincident with minimum $\delta^{13}\text{C}$ values recorded by benthic and planktonic foraminifera at Site 1209 and is also coincident with the change from high seasonality in the surface waters to low seasonality (as demonstrated by the inter-sample variability of *Acarinina* and *Morozovella* values). This point (52.7 Ma, 206.7 mcd) marks the termination of a long-term decrease in benthic $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in the late Paleocene and earliest Eocene and may signify a change in ocean circulation at this time. The surface-to-thermocline (*Subbotina*) $\delta^{18}\text{O}$ gradient remains relatively stable in comparison to the surface-to-benthic gradient. A strong vertical gradient in $\delta^{18}\text{O}$ is reestablished as benthic $\delta^{18}\text{O}$ begins to increase in the upper middle Eocene.

[30] Surface-to-benthic carbon isotope gradients reach a maximum in the late Paleocene, similar to observations at other deep-sea sites [Corfield and Cartlidge, 1992]. The vertical $\delta^{13}\text{C}$ gradient reaches a minimum in the late early Eocene but increases thereafter. In this case, the surface-to-thermocline and surface-to-benthic gradients parallel each other throughout the section (Figure 5). Differences be-

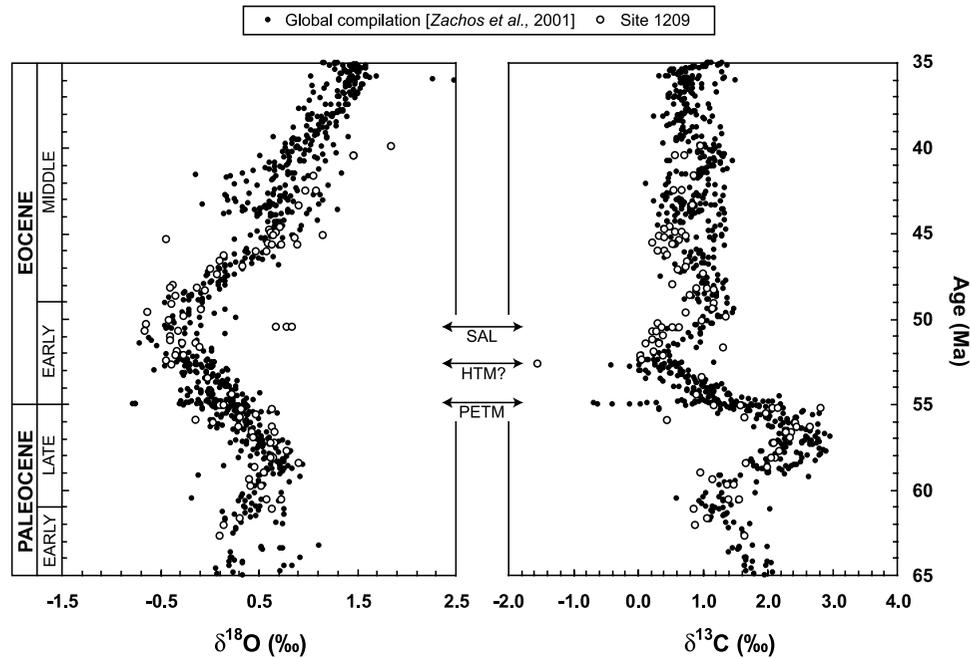


Figure 6. Benthic $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of Site 1209 (open circles) and of all *Nuttalides* and *Cibicidoides* taxa included in the global compilation of Zachos *et al.* [2001] (solid circles). Arrows denote position of the salinity event (SAL) (see section 4.4), the Paleocene-Eocene thermal maximum (PETM), and a hyperthermal (HTM) event.

tween surface and benthic $\delta^{13}\text{C}$ result from the preferential uptake of ^{12}C by photosynthesis in the surface ocean, thus changes in the magnitude of this gradient should be a reflection of the amount of organic carbon exported to the deep ocean. If the partitioning of ^{12}C between surface and deep water over Shatsky Rise is interpreted in this way, we infer peak productivity in the late Paleocene is associated with a thermally well-stratified but highly seasonal upper water column, while minimum productivity is recorded in the early Eocene near the apex of $\delta^{18}\text{O}$ (warmth) in the benthic record and reduced seasonality in the surface record.

[31] There are a number of isotopic studies of Paleogene foraminifera from DSDP Site 577 on Shatsky Rise [Shackleton *et al.*, 1985; Zachos and Arthur, 1986; Miller *et al.*, 1987; Corfield and Cartlidge, 1992; Pak and Miller, 1992; Lu and Keller, 1996]. The Paleogene section recovered at ODP Site 1209 is more complete than the section recovered at Site 577, thus a major goal of this study was to temporally extend this isotopic record and to pair benthic $\delta^{18}\text{O}$ data with Mg/Ca to evaluate the relative influence of temperature and water composition on the oxygen isotope record. Where our data set overlaps with temporally equivalent data from Site 577, agreement between absolute values and trends of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ is excellent with the exception of the *Subbotina* data. Site 1209 *Subbotina* isotopic values agree well with those of Shackleton *et al.* [1985], but these data are offset from compositions reported by Corfield and Cartlidge [1992]. To some extent this discrepancy may be attributed to differences between taxa, but because all of these studies used multiple species of *Subbotina* this is

unlikely to account for systematic offset between these different data sets. Differences between size fractions cannot explain this observation as Shackleton *et al.* [1985] found no significant ontogenetic trend in stable isotope compositions of *Subbotina*. The more likely, yet unsettling interpretation is that *Subbotina* measurements on samples taken several years after core collection have experienced alteration. *Subbotina* may be more susceptible to alteration after core recovery than other planktonic or benthic taxa because of its coarsely perforate shell. We emphasize that this interpretation is tentative but may call for further investigation into this type of phenomenon.

4.4. Evidence for Saline Deep Water

[32] Evaluation of deep water isotopic signals is an important step toward constraining the evolution of circulation patterns and thermal history of the Paleogene. Modern ocean circulation is driven by thermohaline processes whereby dense surface waters in the Southern Ocean and the North Atlantic sink to form deep water. The globally warm climate of the early Cenozoic may have further affected ocean circulation patterns by lowering the density of high-latitude surface waters and causing low-latitude gradients in SST. This may have allowed for the production of warm, saline bottom water (WSBW) derived from low latitudes [Chamberlain, 1906; Brass *et al.*, 1982; Kennett and Stott, 1990]. Though many investigators have sought direct evidence for such a reversal in ocean circulation, indisputable evidence of such an event has remained elusive. In addition to differences in thermal gradients, the

connectivity of ocean basins in the Paleogene was also quite different than the modern configuration. Continental rearrangements during this time frame affected several oceanic gateways, including the opening of the northern North Atlantic, Tasman Sea, and the Drake Passage, as well as the closing of the Tethys [Scotese *et al.*, 1988]. These changes may well be associated with concomitant change in climatic regime and ocean circulation.

[33] To place the results of our study in the context of global climate and oceanic circulation, we first compare Site 1209 benthic isotope data to the compilation of Zachos *et al.* [2001] (Figure 6). For comparative purposes, isotopic values from these records have been normalized as described in section 3.1.3. Long-term trends in both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ at Site 1209 are quite similar to those at other sites, but some differences exist.

[34] In the modern ocean, the oldest deep waters are in the North Pacific Ocean where ^{12}C -enriched waters result from the contribution of increasing amounts of oxidized organic matter on the seafloor. This results in a $\delta^{13}\text{C}$ gradient between the Pacific Ocean and the Southern, Atlantic, and Indian Ocean basins that have younger deep waters. During the early Paleogene, carbon isotope values of Pacific sites, including Site 1209, are generally more negative than those from other ocean basins except during a brief interval of the Eocene from ~ 50 to 48 Ma when the interbasinal gradient is minimal and all ocean basins display a positive shift in $\delta^{13}\text{C}$ (Figure 6). It has been argued that amplified basinal gradients in $\delta^{13}\text{C}$ during the Paleocene and Eocene reflect a stronger influence of Southern Ocean-derived deep water whereas diminished basinal gradients result from possible downwelling of warm saline bottom water derived from the Tethys or the tropical/subtropical Pacific [Corfield and Carlidge, 1992; Pak and Miller, 1992]. This interpretation would lead us to speculate that during the interval from ~ 50 to 48 Ma there may be a component of WSBW. This notion is substantiated by a fully coupled model of early Eocene (~ 50 Ma) climate that indicated the presence of relatively warm, salty deep water that formed primarily in the Tethys and the North Atlantic Oceans [Huber and Sloan, 2001].

[35] At 50.5 Ma, an anomalously positive $\delta^{18}\text{O}$ value is recorded in foraminifera at all depths in the water column over Shatsky Rise (Figures 2 and 7). Both surface and deeper dwelling planktonics increase in $\delta^{18}\text{O}$ by 0.5‰ whereas all three benthic taxa analyzed increase by roughly 1‰. Although only one sample shows this shift, we believe that it represents a significant change in ocean circulation caused by a rapid switch to more saline deep water that resulted in high values of $\delta^{18}\text{O}$. Although the planktonic foraminifera for this sample show slightly more secondary calcite than samples taken from the sections immediately above and below, the benthics appear well preserved under binocular and scanning electron microscope examination. If the aberrant values were entirely a product of diagenesis, mixing between primary calcite and a positive diagenetic end-member should induce more of a shift in the composition of the planktonic taxa, yet the positive shift observed is actually larger in magnitude for the benthics. We therefore

interpret that the benthic taxa grew in equilibrium with saline bottom waters and that the planktonic taxa either (1) grew in somewhat saline surface waters that were less saline than the source of deep water or, (2) having settled out on the sediment-water interface, were subject to early diagenesis that produced secondary calcite and shifted their overall $\delta^{18}\text{O}$ to higher values.

[36] Additional evidence for production of deep water from a saline source in the early Eocene is provided by comparison of data from Site 1209 in the subtropical Pacific and Site 865, which was located in the equatorial Pacific during the Paleogene (Figure 7). The inferred switch in circulation is associated with a global shift toward more positive $\delta^{13}\text{C}$ as well as a collapse in the vertical carbon isotope gradient at Site 865 (Figures 6 and 7). These patterns suggest that ^{13}C -enriched surface water in the tropical Pacific may have been the source of saline deep water. This downwelling may have had more impact on intermediate water formation than on true deep-water formation depending on the depth to which these waters penetrated. Our sampling resolution constrains this downwelling to less than 0.5 m.y. in duration. Interestingly, during this time interval surface planktonic foraminifera at Site 865 record high temperatures and high salinities on the basis of a Mg/Ca-based temperature reconstruction [Tripathi *et al.*, 2003] (Figure 7). These Mg/Ca data require a positive shift of $\sim 1.0\text{‰}$ in surface water $\delta^{18}\text{O}$ over Allison Guyot because of salinity; this is the same amount of change in benthic $\delta^{18}\text{O}$ at Shatsky Rise that we have attributed to salinity. The coincidence of a brief hiatus at Site 865 [Bralower and Mutterlose, 1995] during this circulation reversal event lends further support for a change in deep-water currents at this time, although the question of why saline deep waters should form in the tropical Pacific rather than in the subtropical belt is a question that needs to be addressed.

[37] Model-predicted locations of deep water convection at ~ 50 Ma appear to be controlled by salinity gradients suggesting a circulation pattern that is “quasi-halothermal” [Huber and Sloan, 2001]. Such an ocean circulation regime would be susceptible to alteration by sudden changes net evaporative patterns and would be expected to produce deep water masses that are more salty, but not necessarily colder than overlying intermediate water. Another model of the early Paleogene ocean predicts that subduction of low-latitude, saline surface waters would have been ephemeral, and may result in the delivery of saline intermediate waters to high latitudes that could lead to a reintensification of high-latitude deep water formation [Bice and Marotzke, 2001]. This progression from weak low-latitude sinking of saline water to intensification of convection at middle and high latitudes is referred to as “flushing” [Weaver and Sarachik, 1991] and is predicted to lead to cooling of the deep ocean. It is possible that a brief period of subduction of saline surface water in the late early Eocene led to deep ocean cooling; this hypothesis is supported by benthic Mg/Ca and $\delta^{18}\text{O}$ records at Site 1209 which both show the initiation of cooling following the inferred switch in circulation (Figure 4).

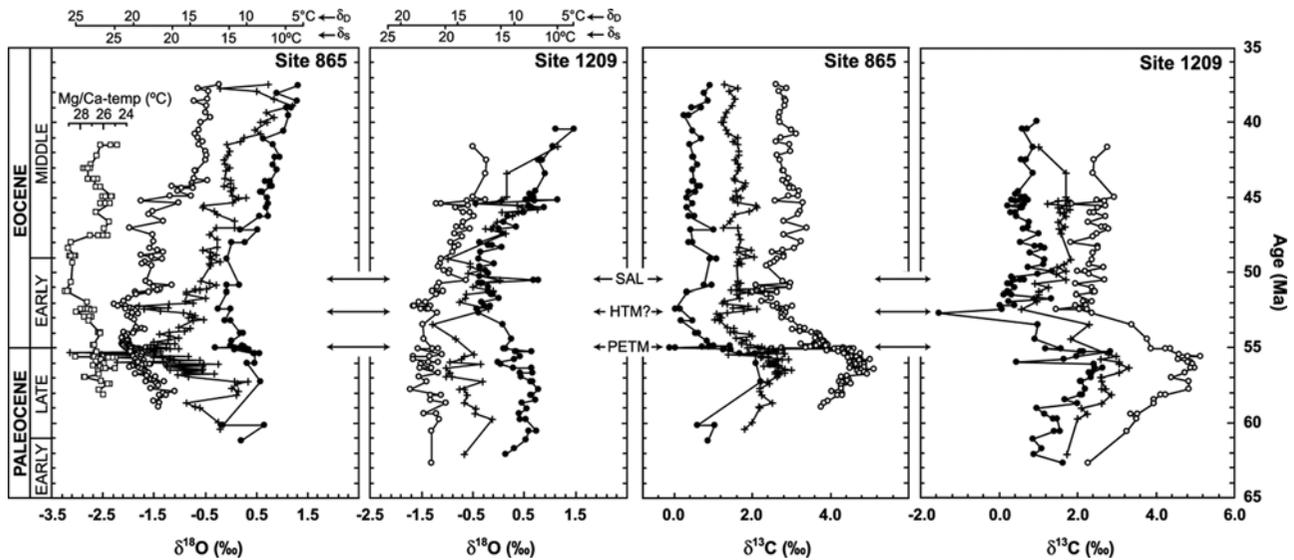


Figure 7. Stable isotope results for foraminifera from Site 1209 in the subtropical Pacific (this study) and Site 865 in the equatorial Pacific [Bralower *et al.*, 1995b] plotted relative to age using the nannofossil stratigraphies of Bralower [2005] and Bralower and Mutterlose [1995], respectively, relative to the Berggren *et al.* [1995] timescale. Symbols indicate as follows: squares, surface planktonic Mg/Ca data at Site 865 [Tripathi *et al.*, 2003]; open circles, surface planktonics; crosses, *Subbotina* spp.; solid circles, benthics. Paleotemperature scales calculated using the equation of Erez and Luz [1983] with δ_w of deep water = $\delta_D = -0.98\text{‰}$ and δ_w of surface water = $\delta_S = -0.14\text{‰}$.

[38] Instability of the water column at low latitudes during the early Paleogene may have resulted in episodic downwelling that is difficult to resolve without intense sampling resolution. If WSBW penetrated the depths of the Paleogene ocean, we would expect to see this effect upon a number of chemical, sedimentary and biological systems. In fact, the sulfur isotope record from marine barite displays a dramatic shift which begins at the Paleocene-Eocene boundary, but accelerates rapidly at ~ 50 Ma [Paytan *et al.*, 1998]. This shift is interpreted by Kurtz *et al.* [2003] to represent a peak in pyrite burial flux at 50 Ma as a consequence of warmer source waters for the deep ocean. Evidence for warm, euxinic deep water at this time is further supported by Kaiho [1991], who calculated an oxygen index through faunal analysis of benthic foraminifera and found that oxygenation of the deep ocean drops to a minimum at the Paleocene/Eocene boundary and remains low until the benthic $\delta^{18}\text{O}$ signal rapidly increases at ~ 50 Ma. Both of these records indicate that warm water began to penetrate to depth in the oceans at the Paleocene-Eocene boundary, and that an abrupt return to more oxygenated deep water occurs near the end of the early Eocene. These data complement our hypothesis of an oceanic circulation reversal in the late early Eocene and suggest that weak, downward advection of warm water, possibly only to intermediate water depths, began in the early Eocene. The strength in our hypothesis of WSBW formation during the EECO lies in the temporal alignment of perturbations in several proxies from multiple sites including carbon isotopes, oxygen isotopes, Mg/Ca ratios, sulfur isotopes, and a faunal proxy for deep-water oxygenation. We expect that future high-resolution studies

during this time interval should help to clarify the interpretation put forth here.

4.5. Early Eocene Hyperthermal Events

[39] The Paleocene-Eocene thermal maximum at Shatsky Rise is recognized by a shoaling of the CCD and lysocline along the depth transect of cores recovered, and it is characterized by a dramatic drop in carbonate content, a temperature spike of 5°C in surface waters, and a sea surface salinity anomaly of $+0.5\text{‰}$ [Bralower *et al.*, 2003; Zachos *et al.*, 2003; Colosimo *et al.*, 2005]. Although the existence of multiple such hyperthermal events in the early Paleogene has been postulated [Thomas *et al.*, 2001], direct evidence for this hypothesis was lacking until multiple conspicuous clay layers associated with peaks in the magnetic susceptibility record were identified at both Shatsky Rise and Walvis Ridge [Bralower *et al.*, 2003; Zachos *et al.*, 2004]. We observe a very negative benthic $\delta^{13}\text{C}$ value at 52.7 Ma (206.7 mcd), which may be correlative to the “Chron 24n event” clay layer observed at Walvis Ridge [Zachos *et al.*, 2004] (Figure 7). Further high-resolution study of these hyperthermal events should help to better constrain their timing, duration, and magnitude.

4.6. Benthic Mg/Ca Record at Shatsky Rise

[40] To this point, we have made preliminary inferences of $\delta^{18}\text{O}$ data assuming that this proxy primarily records temperature of the ambient water. However, it is well known that foraminiferal oxygen isotope data are subject to the influence of temperature as well as the oxygen isotope

composition of seawater (δ_w) [Miller *et al.*, 1987; Zachos *et al.*, 1994; Lear *et al.*, 2000; Zachos *et al.*, 2001]. The δ_w is affected by changes in salinity, and over long timescales it is sensitive to change in continental ice volume. To investigate the relative influence of temperature and water composition on the benthic $\delta^{18}\text{O}$ record at Shatsky Rise, these measurements were paired with an independent paleothermometer relying on the Mg/Ca ratio of foraminiferal calcite.

[41] As with the $\delta^{18}\text{O}$ proxy, foraminiferal Mg/Ca is a function of seawater composition as well as temperature. The residence time of Mg in the oceans is roughly 13 m.y. whereas the residence time of Ca is ~ 1 m.y. [Broecker and Peng, 1982]; therefore over the interval of time studied here the Mg/Ca ratio of seawater ($\text{Mg}/\text{Ca}_{\text{SW}}$) may be variable. Constraints on Paleogene $\text{Mg}/\text{Ca}_{\text{SW}}$ are provided by fluid inclusion data from halite [Lowenstam *et al.*, 2001], Mg/Ca values of echinoderm calcite [Dickson, 2002], and by two models [Wilkinson and Algeo, 1989; Stanley and Hardie, 1998]. The error associated with each of these techniques is quite large and therefore uncertainty in the Mg/Ca of Paleogene seawater is significant (see summary given by Billups and Schrag [2003]). Nonetheless, all of these attempts to reconstruct the evolution of $\text{Mg}/\text{Ca}_{\text{SW}}$ agree that Mg/Ca of seawater was lower in the Paleogene.

[42] As the appropriate value of $\text{Mg}/\text{Ca}_{\text{SW}}$ to apply to our data is debatable, the Mg/Ca data are shown relative to the benthic $\delta^{18}\text{O}$ record using two estimates of seawater composition (Figure 4). Assuming that the world was ice-free at ~ 50 Ma, when minimum benthic $\delta^{18}\text{O}$ values are recorded globally, measured values of Mg/Ca at Site 1209 imply a $\text{Mg}/\text{Ca}_{\text{SW}}$ of 3.3 mol/mol. This estimate is in agreement with the Wilkinson and Algeo [1989] model, which predicts $\text{Mg}/\text{Ca}_{\text{SW}}$ values of 3 to 4 mol/mol for this period of time. Regardless of the absolute value of $\text{Mg}/\text{Ca}_{\text{SW}}$ that we apply, our data display a distinct decoupling between Mg/Ca and $\delta^{18}\text{O}$ during two intervals in the early (~ 55 – 53 Ma) and early middle Eocene (~ 48 – 45 Ma). Both of these time intervals are characterized by rapid change in $\delta^{18}\text{O}$ and relatively little change in Mg/Ca. The long-term trend in benthic water temperature according to Mg/Ca-derived estimates is quite different than that for $\delta^{18}\text{O}$ -derived paleotemperatures. The Mg/Ca record indicates little change in average temperature from ~ 63 to 50 Ma, and displays a gradual decline in temperature beginning at ~ 50 Ma. This long-term trend may be punctuated by short-term pulses in temperature that are not captured by this relatively coarse resolution record.

[43] If we assume that Mg/Ca is a reliable paleothermometer then we must conclude that the classic trough in benthic $\delta^{18}\text{O}$ of the early Eocene that is taken to represent peak Cenozoic warmth (i.e., the EECO) is not a product of increased warmth and requires another explanation. This idea seems unlikely at first glance for several reasons, the most apparent of which is that the most likely candidate for change in $\delta^{18}\text{O}$ apart from temperature is ice volume, and these data would require melting and subsequent accumulation of ~ 50 – 80% of modern ice volume in a climate considered to be entirely ice-free! Given these considerations, we present several scenarios that could explain the observation of decoupling between

Mg/Ca and $\delta^{18}\text{O}$ of benthic foraminifera from Shatsky Rise.

4.6.1. Hypothesis 1: Diagenesis

[44] Diagenesis of carbonate sediment in the deep-sea occurs as dissolution of primary calcite and/or precipitation of secondary calcite (also termed recrystallization). Dissolution has the effect of lowering the Mg/Ca ratio of foraminiferal calcite [Brown and Elderfield, 1996; Rosenthal *et al.*, 2000] whereas recrystallization should increase the Mg/Ca ratio because the distribution coefficient of Mg in abiotic calcite is greater than that of biotic calcite [e.g., Mucci and Morse, 1983]. In either case, diagenesis should induce convergence of Mg/Ca toward a diagenetic calcite end-member. Yet, Mg/Ca and $\delta^{18}\text{O}$ vary sympathetically through much of the section, with the exception of the two intervals of decoupling described earlier (Figure 4). This indicates that relative temperature changes were responsible for the patterns observed and that these signals have not been diagenetically homogenized. Moreover, Mg/Ca and $\delta^{18}\text{O}$ are altered proportionately during dissolution of foraminiferal calcite, which preserves their relationship to temperature [Rosenthal *et al.*, 2000]. Hence paired measurements of Mg/Ca and $\delta^{18}\text{O}$ can still be used to reconstruct δ_w even in partially dissolved specimens but even more importantly, dissolution is not a mechanism that can explain decoupling of these two proxies.

4.6.2. Hypothesis 2: Variable Seawater Mg/Ca

[45] Our initial comparison of relative change in Mg/Ca and $\delta^{18}\text{O}$ at Site 1209 was made with the tacit assumption that $\text{Mg}/\text{Ca}_{\text{SW}}$ was invariant. Yet, the residence times of Mg and particularly Ca in the ocean require that we entertain the possibility that secular variation in $\text{Mg}/\text{Ca}_{\text{SW}}$ can explain decoupling of the benthic Mg/Ca and $\delta^{18}\text{O}$ records. This argument has several weaknesses: (1) The data would require extremely rapid (1–2 m.y.) changes in seawater composition separated by a protracted period of invariant $\text{Mg}/\text{Ca}_{\text{SW}}$ and these rapid changes must be coupled with rapid temperature change to produce foraminiferal calcite that has approximately the same value before and after both of these rapid changes. (2) Amplified hydrothermal activity in the early Eocene [Leinen, 1987] would have the effect of lowering $\text{Mg}/\text{Ca}_{\text{SW}}$ to produce the first decoupling, but would require a large change in $\text{Mg}/\text{Ca}_{\text{SW}}$ (from 5.2 to 3.3 mol/mol) and available data on seafloor spreading rates imply declining rates of hydrothermal activity at this time [e.g., Kominz, 1984; Gaffin, 1987]. (3) The trend in benthic Mg/Ca parallels that of planktonic $\delta^{18}\text{O}$ and records the same temperature as subthermocline waters for $\text{Mg}/\text{Ca}_{\text{SW}} = 3.3$ mol/mol (Figure 8). This conformity of long-term temperature trends at several depths in the water column suggests that the benthic Mg/Ca temperature reconstruction is genuine, and unaffected by substantial change in $\text{Mg}/\text{Ca}_{\text{SW}}$ during this interval. This observation is particularly interesting and turns our attention to the fidelity of the benthic oxygen isotope record as a proxy for temperature.

4.6.3. Hypothesis 3: Ice Volume

[46] It seems likely that perturbations to the $\delta^{18}\text{O}$ signal should explain the decoupling observed between Mg/Ca

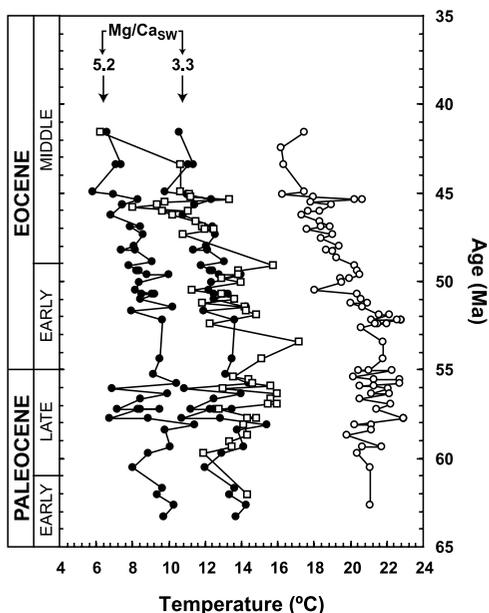


Figure 8. Reconstructed paleotemperatures for benthic foraminifera (solid circles), deep-dwelling planktonics (i.e., *Subbotina*, squares), and surface-dwelling planktonics (open circles). Benthic paleotemperatures are calculated using Mg/Ca compositions; planktonic paleotemperatures are calculated using $\delta^{18}\text{O}$ data and $\delta_w = -0.98\text{‰}$ (*Subbotina*) and -0.14‰ (surface dwellers).

and $\delta^{18}\text{O}$ because benthic $\delta^{18}\text{O}$ changes rapidly during these intervals while Mg/Ca remains relatively stable through the Paleocene and changes gradually through part of the Eocene record. Although the decay and subsequent regrowth of a large ice sheet in the Eocene is the mostly likely mechanism to drive the change in benthic $\delta^{18}\text{O}$, such a large volume of ice (50–80% of modern ice volume) in the globally warm early Paleogene world is not very plausible. Not only is there a lack of geological and paleontological evidence for an ice sheet of this size in the early Paleogene, climate studies from this time interval indicate a very warm, equable climate characterized by low gradients in pole-to-equator surface temperatures [e.g., Zachos *et al.*, 1994]. Unless direct evidence of such ice is discovered we must acknowledge that the scenario for significant ice volume in the late Paleocene and early middle Eocene is difficult to prove independently.

4.6.4. Hypothesis 4: pH

[47] In addition to temperature and seawater oxygen isotope composition, the $\delta^{18}\text{O}$ proxy is also sensitive to pH [Spero *et al.*, 1997]. To induce a negative shift of 0.8‰ in $\delta^{18}\text{O}$ would require an increase in carbonate ion concentration, $[\text{CO}_3^{2-}]$, of 400 mmol/kg and a concomitant decrease in $\delta^{13}\text{C}$ of 2.4‰ according to the modern calibration of planktonic foraminifera [Spero *et al.*, 1997]. Although $\delta^{13}\text{C}$ does decrease by roughly this amount, the proposed change in pH is well beyond the range of $[\text{CO}_3^{2-}]$ in the modern ocean as well as the range proposed for the last glacial maximum [Broecker and

Peng, 1982; Sanyal *et al.*, 1995]. Moreover, there is not evidence for a significant deepening of the carbonate compensation depth in the early Eocene Pacific basin, though there are few records that span this time period [Van Andel, 1975; Lyle *et al.*, 2002; Hancock and Dickens, 2005]. One further weakness of this hypothesis is that change in pH has been demonstrated to decrease planktonic Mg/Ca by 6% per 0.1 pH unit [Lea *et al.*, 1999]. If a similar relationship exists for benthic Mg/Ca and pH, then variable pH in the deep ocean cannot explain decoupling of Mg/Ca and $\delta^{18}\text{O}$.

4.6.5. Hypothesis 5: Opening of an Oceanic Gateway

[48] We submit one final hypothesis for a mechanism capable of altering δ_w by 0.8‰ in the early Paleogene that calls upon the dynamic rearrangement of the global ocean during this time interval. The opening of several major oceanic gateways mentioned earlier might have established a deep-water connection to a large, restricted basin of significantly different oxygen isotope composition. Such a scenario could account for an influx of water depleted in ^{18}O that would be capable of affecting the benthic $\delta^{18}\text{O}$ signal in all ocean basins. This explanation is appealing because the opening northern North Atlantic would have established a connection to the Arctic Ocean basin, which likely would have had a much lower δ_w , due in part to the entrapment of ^{18}O -depleted, high-latitude meteoric water. Whether there was a large enough volume of water and whether it was depleted enough to induce a large negative shift in benthic $\delta^{18}\text{O}$ of all ocean basins is debatable.

4.6.6. Comparison to Other Paleogene Mg/Ca Records

[49] To this point, we have focused on comparison of Mg/Ca and $\delta^{18}\text{O}$ of benthic foraminifera at Site 1209 without consideration for other benthic Mg/Ca records from this time interval. Only two other studies have been conducted representing two somewhat shallower sites in the Southern Ocean (ODP Site 689) and the Indian Ocean (ODP Site 757) (Table 1 and Figure 1) [Lear *et al.*, 2000; Billups and Schrag, 2003]. For purposes of comparison, data from these studies have been converted to temperature using modern core top calibrations of Lear *et al.* [2002] and assuming a modern $\text{Mg}/\text{Ca}_{\text{SW}}$ of 5.2 mol/mol (Figure 9).

[50] If we assume that ODP Sites 689, 757, and 1209 all represent an intermediate to deep water signal then their benthic Mg/Ca records should be comparable. Site 1209 shows excellent agreement with the Lear *et al.* [2000] Mg/Ca data where these records overlap. In contrast, both records generated by Billups and Schrag [2003] display dramatic increase in Mg/Ca (and hence in reconstructed temperatures) down core. This is somewhat paradoxical because the Lear *et al.* [2000] data during this time interval is entirely based upon ODP Site 689, the same site investigated by Billups and Schrag [2003]. The difference in these records is presumably due to (1) potential differences in cleaning protocols; (2) accuracy of interlaboratory Mg/Ca data; (3) unrecognized size and/or ontogenetic differences in Mg/Ca of benthic foraminifera; or (4) inappropriate application of modern core top calibrations to extinct taxa. Unfortunately, it is difficult to discuss comparisons between

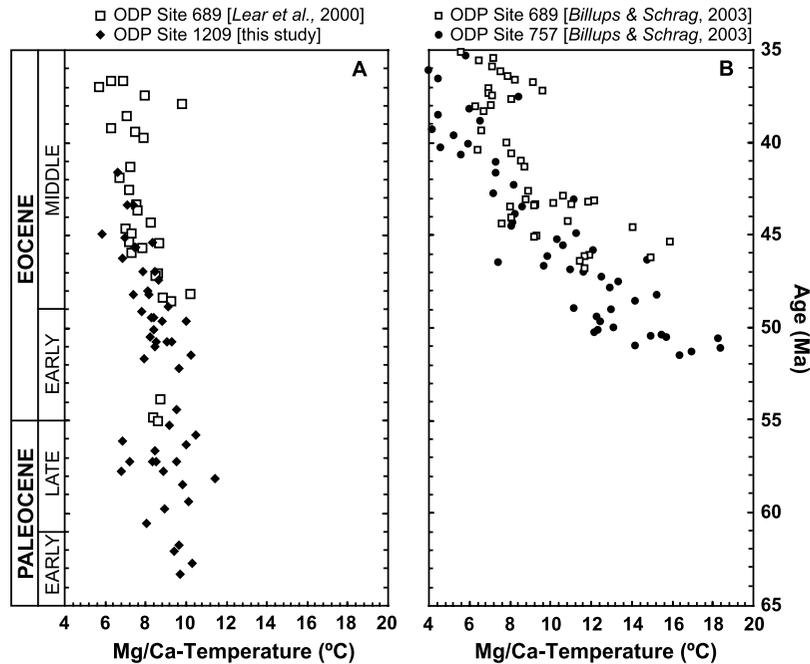


Figure 9. Benthic Mg/Ca records for the Paleocene and Eocene are plotted relative to the *Berggren et al.* [1995] timescale. (a) Data from *Lear et al.* [2000] and this study. (b) Data from *Billups and Schrag* [2003]. Mg/Ca values have been converted to temperatures using core top calibrations of extant taxa [*Lear et al.*, 2002] to facilitate comparison between Mg/Ca data that have been normalized to different taxa.

the Site 1209 benthic Mg/Ca record and these other two studies until an adequate explanation can be provided for the differences between two records generated from the same sediment core.

5. Summary and Conclusions

[51] Foraminiferal geochemistry results from Site 1209 highlight a number of critical intervals of change in oceanic circulation and climate during the Paleocene and Eocene. An important positive $\delta^{18}\text{O}$ excursion (50.5 Ma) has been identified during the EECO that we interpret to represent an ephemeral switch in oceanic circulation patterns to a deep-water source derived from saline surface waters in the tropical Pacific. The data presented here also highlight the transition at 52.7 Ma as an important change from high- to low-temperature seasonality in surface waters, coincident with a collapse in the thermocline-to-benthic $\delta^{18}\text{O}$ gradient that persisted until ~ 45 Ma, and marked by an extremely negative benthic $\delta^{13}\text{C}$ value that we tentatively correlate to the “Chron 24n event” clay layer observed at Walvis Ridge [*Zachos et al.*, 2004]. This juncture also represents the attainment of the Cenozoic minimum in benthic $\delta^{18}\text{O}$ referred to as the EECO. Increasing *Subbotina* $\delta^{18}\text{O}$ values at Sites 1209, 865, and 550 may be an indication that saline waters began to penetrate thermocline depths at this time, which preconditioned the ocean for an abrupt reversal in oceanic circulation at ~ 50.5 Ma.

[52] The most important lesson from this investigation is that this multiproxy reconstruction of deep ocean temperatures in the early Paleogene provides two very different scenarios of the thermal history of the ocean. The generation of additional benthic Mg/Ca records from other sites will undoubtedly help to support or refute the interpretations put forth here with respect to the thermal evolution of deep-water masses during the early Paleogene. Intriguingly, benthic Mg/Ca from ODP Site 1209 on Shatsky Rise predicts upper abyssal water temperatures of 8° – 10°C (using modern $\text{Mg}/\text{Ca}_{\text{SW}}$) in the early Eocene which is a good match to temperatures predicted by climate models [*Huber*, 2002]. While this agreement between models and data does not necessarily validate the Mg/Ca proxy, this comparison highlights the critical need to generate multiproxy records for Paleogene climate in order to better interpret the $\delta^{18}\text{O}$ signal and to discern key modes of oceanic circulation of this ancient greenhouse climate.

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