# Shifting ocean carbonate chemistry during the Eocene-Oligocene climate transition: Implications for deep-ocean Mg/Ca paleothermometry

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[1] To date, no conclusive evidence has been identified for intermediate or deep water cooling associated with the >1‰ benthic $\delta^{18}O$ increase at the Eocene-Oligocene transition (EOT) when large permanent ice sheets first appeared on Antarctica. Interpretation of this isotopic shift as purely ice volume change necessitates bipolar glaciation in the early Oligocene approaching that of the Last Glacial Maximum. To test this hypothesis, it is necessary to have knowledge about deep water temperature, which previous studies have attempted to reconstruct using benthic foraminiferal Mg/Ca ratios. However, it appears likely that contemporaneous changes in ocean carbonate chemistry compromised the Mg/Ca temperature sensitivity of benthic foraminifera at deep sites. New geochemical proxy records from a relatively shallow core, ODP Site 1263 (estimated paleodepth of 2100 m on the Walvis Ridge), reveal that carbonate chemistry change across the EOT was not limited to deep sites but extended well above the lysocline, critically limiting our ability to obtain reliable estimates of deep-ocean cooling during that time. Benthic Li/Ca measurements, used as a proxy for $[CO_3^{2-}]$, suggest that $[CO_3^{2-}]$ increased by ~29 $\mu$mol/kg at Site 1263 across the EOT and likely impacted benthic foraminiferal Mg/Ca. A $[CO_3^{2-}]$–benthic Mg/Ca relationship is most apparent during the early EOT when the overall increase in $[CO_3^{2-}]$ is interrupted by an apparent dissolution event. Planktonic $\delta^{18}O$ and Mg/Ca records suggest no change in thermocline temperature and a $\delta^{18}O_{seawater}$ increase of up to 0.6‰ at this site across the EOT, consistent with previous estimates and supporting the absence of extensive bipolar glaciation in the early Oligocene.

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## 1. Introduction

[2] The >1‰ increase in deep-sea benthic $\delta^{18}O$ at the Eocene-Oligocene transition (EOT) represents the onset of a first permanent ice sheet on Antarctica [*Zachos et al.*, 2001]. Climate modeling [*DeConto and Pollard*, 2003] shows that the ensuing $\delta^{18}O$ shift likely reflects changes in both global ice volume and ambient bottom water temperature. Attempts to quantify the degree of deep-sea cooling across the EOT using benthic foraminiferal Mg/Ca records suggested a slight warming of bottom waters [*Lear et al.*, 2000; *Billups and Schrag*, 2003; *Lear et al.*, 2004] which in conjunction with a benthic $\delta^{18}O$ increase would imply a substantial bipolar glaciation on a scale comparable to the Last Glacial Maximum (LGM) [*Lear et al.*, 2004; *Coxall et al.*, 2005; *Eldrett et al.*, 2007]. However, sequence stratigraphy estimates a maximum sea level fall of ~70 m, limiting the ice volume component of the benthic $\delta^{18}O$ increase to ~0.7‰ [*Pekar et al.*, 2002; *Miller et al.*, 2008]. One possible explanation is that contemporaneous changes in carbonate chemistry compromised Mg/Ca temperature sensitivity, such as observed today in settings where ambient bottom water carbonate ion concentrations ($[CO_3^{2-}]$) change measurably on glacial-interglacial timescales [*Elderfield et al.*, 2006; *Yu and Elderfield*, 2008]. A deepening of the carbonate compensation depth (CCD) across the EOT observed in all deep-ocean basins [*Van Andel*, 1975] is diagnostic of such changes in carbonate chemistry.

[3] Benthic Mg/Ca records across the EOT to date come from sites that in the latest Eocene were at a similar depth as the CCD (ODP Site 1218 [*Lear et al.*, 2004]), or that were positioned within the lysocline where the first increases in $CaCO_3$ dissolution occur (DSSP Site 552 [*Lear et al.*, 2000]). *Lear et al.* [2004] hypothesize that increasing benthic Mg/Ca values across the EOT reflect a dramatic rise in $[CO_3^{2-}]$ at these deep sites, which is supported by increasing Li/Ca ratios [*Lear and Rosenthal*, 2006; *Lear et al.*, 2010] that serve as a proxy for $[CO_3^{2-}]$ as opposed to a secondary temperature influence [*Marriott et al.*, 2004]. Because these

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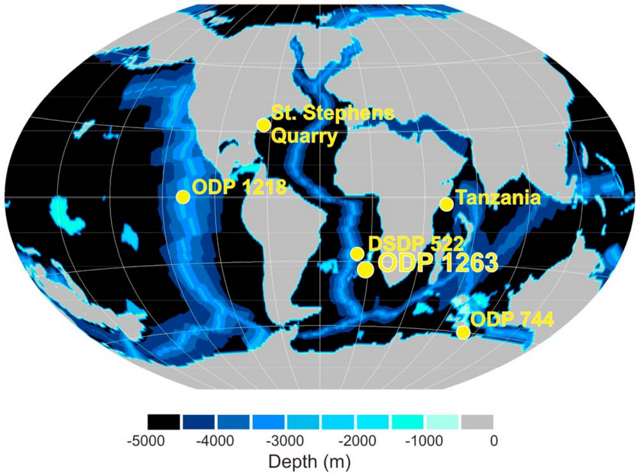


**Figure 1.** Paleolocations of ODP Site 1263 and other sites referred to in the discussion, plotted on a map of Eocene-Oligocene bathymetry and geography [*Müller et al.*, 2008].

cores are from a depth range over which deep water [$CO_3^{2-}$] changes are likely to have had the greatest influence on foraminiferal Mg/Ca temperature sensitivity, our ability to constrain deep water temperature changes remains limited. We present a benthic Mg/Ca record from Site 1263, at Walvis Ridge, SE Atlantic, which was located at ~2100 m water depth in the latest Eocene and positioned ~1 km above the regional lysocline [*Zachos et al.*, 2004] prior to the abrupt lysocline/CCD deepening at the EOT. Complementary benthic stable isotope ($\delta^{18}$O) [*Riesselman et al.*, 2007] and elemental ratio (Sr/Ca, Li/Ca) records are used to constrain the carbonate chemistry of ambient bottom waters at Site 1263 and to test for the reliability of the benthic Mg/Ca record as an indicator of deep water temperature [*Lear and Rosenthal*, 2006; *Lear et al.*, 2010] at shallow water depths across the EOT.

## 2. Material and Methods

[4] Site 1263 (28° 31.98′S, 2° 46.77′E) was cored during ODP Leg 208 on Walvis Ridge in the SE Atlantic (Figure 1). The site is at a modern water depth of 2717 m, and represents the shallow drill site of the Leg 208 depth transect across Walvis Ridge. The age model for Site 1263 is based on sixty-two biostratigraphic and six magnetostratigraphic datums [*Zachos et al.*, 2004]. The seven age/depth points encompassing the latest Eocene and earliest Oligocene stratigraphy that was developed by the Leg 208 shipboard party represent calcareous nannofossil and planktonic foraminifer datums [*Bukry*, 1973, 1975; *Okada and Bukry*, 1980; *Berggren et al.*, 1995; *Zachos et al.*, 2004]; the C13n magnetochron is partially resolved [*Cande and Kent*, 1995]. We apply a second-order polynomial regression to these seven age/depth points to generate the age model used here [*Riesselman et al.*, 2007].

[5] A benthic $\delta^{18}$O record with ~6 kyr temporal resolution has been produced for Site 1263 using the infaunal foraminifera *Oridorsalis umbonatus* [*Riesselman et al.*, 2007]. The record displays a 1.1‰ increase in benthic $\delta^{18}$O across the EOT (Figure 2) and the structure of the $\delta^{18}$O record suggests the sediment sequence representing the EOT is intact and not disturbed by downslope transportation or reworking. We note that the age model for Site 1263 is not as robust as the orbitally tuned age model of ODP Site 1218 [*Coxall et al.*, 2005]; however, sedimentation rates of ~1.5 cm/kyr provide the highest-resolution Atlantic record for the EOT time interval [*Zachos et al.*, 2004].

[6] Optical lightness (L*) and magnetic susceptibility measurements of the suite of Leg 208 cores indicate the regional lysocline was positioned between Sites 1266 (3806 m water depth) and 1267 (4356 m water depth) in the latest Eocene [*Zachos et al.*, 2004]. Site 1263 was therefore positioned at least 1 km above the lysocline prior to CCD deepening. At Walvis Ridge the lysocline/CCD is determined to have deepened in excess of 1 km across the EOT [*Zachos et al.*, 2004], similar to other estimates from the Atlantic Ocean and intermediate between the Indian and Pacific Oceans, in which the CCD deepened by up to 700 m and ~1200 m, respectively [*Coxall and Pearson*, 2007, and references therein]. %$CaCO_3$ of core material collected from Site 1263 ranges from 88 to 96% (averaging 93%) through the interval 33.9–32.7 Ma [*Riesselman et al.*, 2007].

[7] For elemental ratio analysis, additional *O. umbonatus* specimens were picked from the 150–250 $\mu$m size fraction. For planktonic Mg/Ca and stable isotope analyses, surface dwelling *Turborotalia ampliapertura* and thermocline dwelling *Subbottina utilizindex* were picked from the 250–300 $\mu$m size fraction. Between 15 and 30 specimens of each species were collected from each sample. The specimens were placed between two glass plates and carefully cracked open. For planktonic samples containing more than 20 specimens the crushed tests were homogenized and aliquots were taken for elemental ratio and stable isotope analysis. Stable isotopes were measured on a PRISM mass spectrometer at Cambridge University with an analytical precision of ~0.08‰ for $\delta^{18}$O and 0.06‰ for $\delta^{13}$C.

[8] Samples were cleaned for elemental ratio analysis following cleaning protocols outlined by *Barker et al.* [2003], with no reductive step and five weak acid leaches [*Yu et al.*, 2007]. Complementary Sr/Ca and Li/Ca measurements were carried out on benthic samples that were large enough to provide ~300 $\mu$l of 100 ppm Ca solution. These measurements were made on a quadrupole ICP-MS according to the method described by *Yu et al.* [2005] and were intended to serve as additional indicators of possible change in ambient bottom water [$CO_3^{2-}$]. Samples containing fewer specimens were run at 60 ppm Ca on Varian Vista ICP-AES for Mg/Ca measurements only. Replicate measurements of standards indicate reproducibility of ±0.03 mmol/mol, ±0.01 mmol/mol, and ±0.32 $\mu$mol/mol for Mg/Ca, Sr/Ca, and Li/Ca, respectively.

## 3. Results

### 3.1. $\delta^{18}$O and %$CaCO_3$

[9] Across the EOT, published benthic $\delta^{18}$O records from Site 1263 display an increase of ~1.1‰, from ~1.5‰ in the latest Eocene to ~2.6‰ in the earliest Oligocene (Figure 2c) [*Riesselman et al.*, 2007]. Although not as clearly defined as

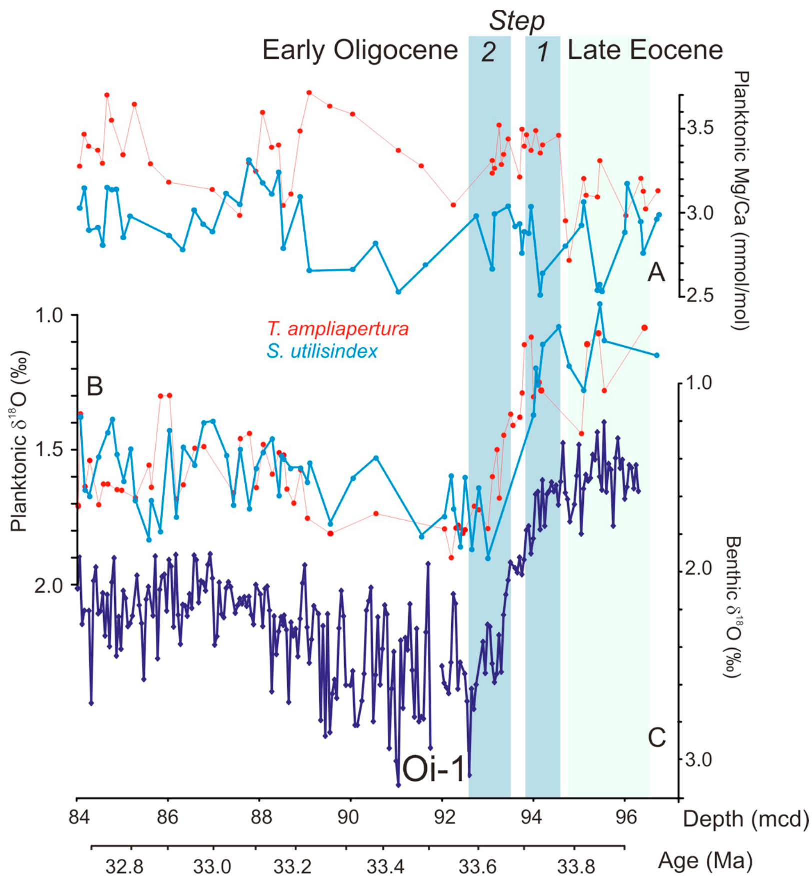


**Figure 2.** Planktonic foraminifera $\delta^{18}O$ and Mg/Ca records from ODP Site 1263. (a) Planktonic Mg/Ca, (b) planktonic $\delta^{18}O$ from surface-dwelling *T. ampliapertura* (red) and thermocline-dwelling *S. utilizindex* (blue), and (c) benthic foraminifera $\delta^{18}O$ (*O. umbonatus*) [*Riesselman et al.*, 2007]. Vertical bars indicate the latest Eocene and Steps 1 and 2 of the EOT.

at Site 1218 [*Coxall et al.*, 2005], Steps 1 and 2 of the $\delta^{18}O$ increase can be identified at Site 1263. Step 1 represents a 0.5‰ increase over ~80 kyr, while Step 2 represents a 0.6‰ increase over ~90 kyr [*Riesselman et al.*, 2007]. The $\delta^{18}O$ records of *T. ampliapertura* and *S. utilizindex* display a smaller shift, increasing by ~0.6‰, from ~1.2‰ to ~1.8‰ during the EOT (Figure 2b). Average %$CaCO_3$ values before and after the transition are similar, at 92% (n = 46) and 93% (n = 198), respectively (Figure 3a). At the onset of the $\delta^{18}O$ increase, %$CaCO_3$ values fall to a transient minimum of 88% (hereafter referred to as the dissolution event) early in Step 1. %$CaCO_3$ values progressively increase during the second half of Step 1 and reach latest Eocene values at the end of Step 2 (Figure 3a).

### 3.2. Elemental Ratio Records

[10] At the onset of Step 1, the average Mg/Ca ratio of surface-dwelling *T. ampliapertura* increases from ~3.1 mmol/mol in the latest Eocene to ~3.4 mmol/mol (Figure 2a) and these elevated values are maintained across Step 1. *S. utilizindex* Mg/Ca fluctuates between 2.5 to 3.1 mmol/mol across the EOT, but shows no change in average values across the EOT. In the early Oligocene, Mg/Ca records of both species fluctuate but display an overall increase of ~0.2 mmol/mol relative to the latest Eocene by the end of the studied interval.

[11] Benthic Mg/Ca increases across the EOT and into the early Oligocene, from an average value of 2.4 mmol/mol before the benthic $\delta^{18}O$ increase, to values approaching 2.8 mmol/mol after 33.0 Ma (Figure 3c). Lowest benthic Mg/Ca values precede the benthic $\delta^{18}O$ increase in the Latest Eocene, coincident with a %$CaCO_3$ maximum. As %$CaCO_3$ decreases in Step 1, Mg/Ca increases and then directly mimics the trend of the %$CaCO_3$ record through Steps 1 and 2 with Mg/Ca values increasing with rising %$CaCO_3$ (Figure 4).

[12] Benthic Sr/Ca (Figure 3d) varies within a range from 0.83 to 0.89 mmol/mol. In the latest Eocene, values average 0.86 mmol/mol, decreasing to ~0.84 mmol/mol across the EOT and then increase toward the end of the studied interval. Several Sr/Ca excursions during the latest Eocene and Step 1 are antiphased with Mg/Ca.

[13] The first-order trends in the lower-resolution Li/Ca record (Figure 3b) show some similarity with those of the higher-resolution %$CaCO_3$ record. Li/Ca values increase from ~14 mmol/mol to ~16 mmol/mol prior to Step 1, coincident with %$CaCO_3$ rise to a brief maximum of 96%. Li/Ca ratios and %CaCO3 decrease within Step 1, and from Step 2 onward Li/Ca stabilizes at ~15 mmol/mol,

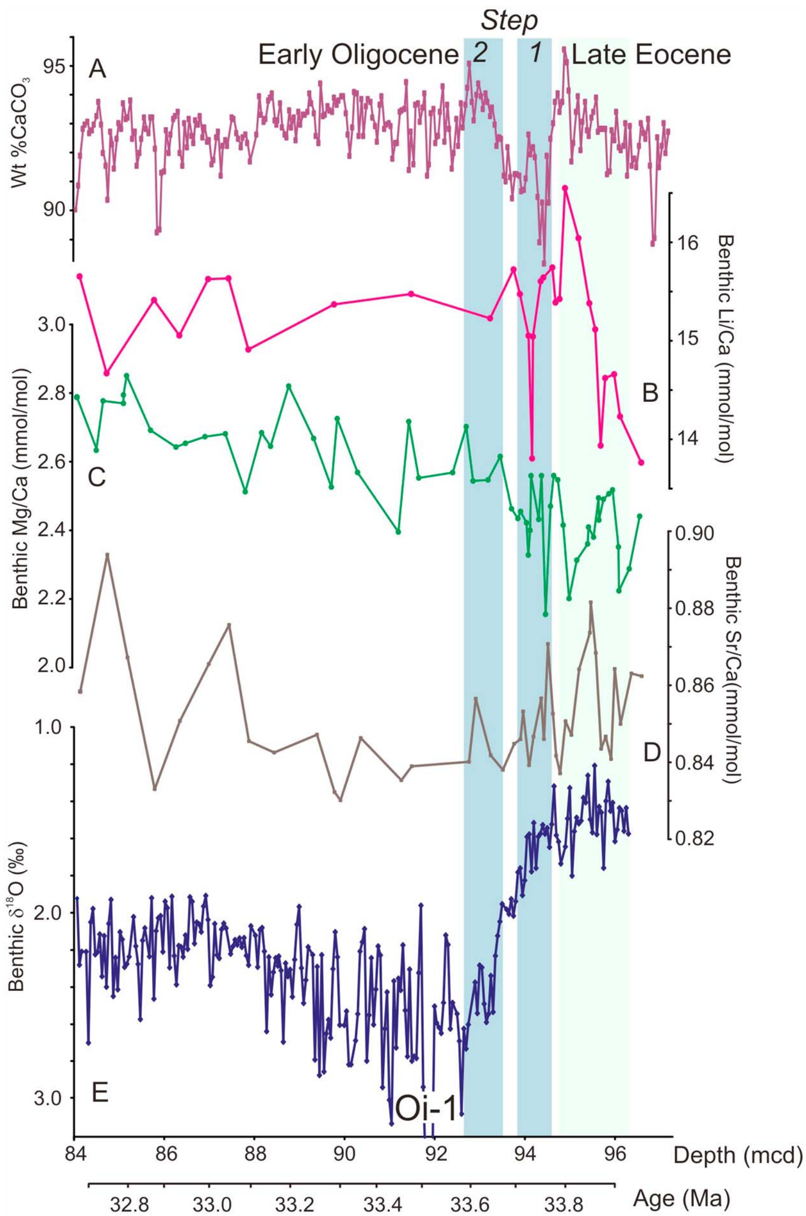


**Figure 3.** Records of $\%CaCO_3$, benthic foraminiferal $\delta^{18}O$ and elemental ratios from ODP Site 1263. (a) Weight $\%CaCO_3$ [*Riesselman et al.*, 2007], (b) Li/Ca, (c) Mg/Ca, (d) Sr/Ca, and (e) $\delta^{18}O$ [*Riesselman et al.*, 2007]. All from *O. umbonatus*. Vertical bars indicate the latest Eocene and Steps 1 and 2 of the EOT.

1 mmol/mol higher than values in the latest Eocene. The trend in Li/Ca indicates the influence of $[CO_3^{2-}]$ [*Marriott et al.*, 2004] in association with a deepening CCD across the EOT [*Van Andel*, 1975; *Lear and Rosenthal*, 2006]. The apparent increase in $[CO_3^{2-}]$ at this site has potential implications for carbonate preservation and benthic foraminiferal Mg/Ca, as will be discussed below.

## 4. Discussion

### 4.1. Planktonic Records and $\delta$w

[14] Before considering any implications of these data we must first assess the preservation of the planktonic foraminifera. In specimens selected from the high $\%CaCO_3$ interval at 94.89 mcd and the low $\%CaCO_3$ dissolution event at 94.44 mcd, scanning electron microscopy shows extensive recrystallization of the tests of both planktonic foraminiferal species (Figure 5). In addition, it was noted that specimens within the dissolution event were more susceptible to shattering (i.e., more fragile) during the cleaning process. Nonpristine or "frosty" planktonic foraminifera from deep-sea sites have been found to exhibit consistently heavier $\delta^{18}O$ values than pristine, or "glassy," foraminifera from similar latitude sites, due to the recrystallization of calcite in cold seafloor conditions [*Pearson*

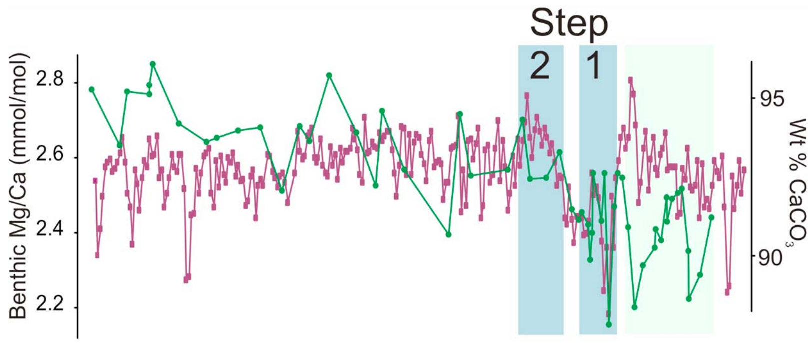


**Figure 4.** Expanded view of benthic Mg/Ca and weight %$CaCO_3$ records showing close correlation across Steps 1 and 2. Vertical bars as in Figures 2 and 3.

*et al.*, 2001; *Sexton et al.*, 2006]. Had there been bottom water cooling at this site across the EOT, the degree of diagenetic overprinting on the planktonic shells may have increased, biasing the planktonic $\delta^{18}O$ toward heavier values such that the similarity of the planktonic and benthic $\delta^{18}O$ records at Site 1263 may in part be attributed to a diagenetic component [*Pearson et al.*, 2001]. That is, the planktonic $\delta^{18}O$ increase may be an artifact stemming from post depositional alteration under colder ambient bottom waters during the EOT in addition to a global change in seawater $\delta^{18}O$ ($\delta$w) and/or surface water cooling. As we are unable to quantify the degree of diagenetic overprinting on the planktonic $\delta^{18}O$, we consider the 0.6‰ increase to represent the maximum shift caused by SST cooling and $\delta$w increase.

[15] The effect of diagenetic alteration on planktonic foraminiferal Mg/Ca is less well understood, but it has been observed that Mg/Ca in frosty specimens is only marginally higher than in glassy specimens of the same species [*Sexton et al.*, 2006]. The Mg/Ca values of surface-dwelling *T. ampliapertura* are consistently higher than subsurface-dwelling *S. utilizindex* which would be consistent with their depth habitats [*Pearson et al.*, 2006], assuming similar $Mg^{2+}$ incorporation for both species. *T. ampliapertura* displays an apparent warming at the onset of Step 1 as average Mg/Ca values increase from 3.1 to 3.4 mmol/mol. Assuming a ~1°C/9% sensitivity of Mg/Ca [e.g., *Anand et al.*, 2003], this change would represent a ~1°C warming, within the range of the ±1.2°C calibration uncertainty [*Anand et al.*, 2003]. However, as this increase in *T. ampliapertura* Mg/Ca is coincident with an increase in benthic Mg/Ca we consider the possibility of postdepositional alteration of planktonic Mg/Ca ratios under changing seafloor [$CO_3^{2-}$]. Further evidence in support of postdepositional alteration is the similarity of the planktonic $\delta^{18}O$ records, which unlike the Mg/Ca records do not display a temperature-related inter-species $\delta^{18}O$ offset. We propose that the thinner test of the surface-dwelling *T. ampliapertura* may have been more susceptible to diagenetic alteration than the more robust test of subsurface-dwelling *S. utilizindex* as may be interpreted by *T. ampliapertura*-Mg/Ca covariability with benthic Mg/Ca. We therefore consider that of the two planktonic Mg/Ca records it is possible that a primary temperature signal may be preserved in the *S. utilizindex* Mg/Ca record and propose that no significant change in thermocline temperature occurred across the EOT at this site. The apparent stability of upper ocean temperatures inferred from the planktonic Mg/Ca is consistent with nannofossil assemblage data from this same site. The relative abundances of warm and cold species do not change significantly across the benthic $\delta^{18}O$ increase, suggesting negligible change in SST (F. Tori, personal communication, 2008) and similarly, SSTs from the tropical Atlantic (ODP sites 925 and 929), reconstructed using $U^{K'}37$, also show little temperature change across the EOT [*Liu et al.*, 2009]. At higher latitudes, $U^{K'}37$ and $TEX_{86}$ records indicate cooling synchronous with the benthic $\delta^{18}O$ increase averaging 4.8°C [*Liu et al.*, 2009]. While independent SST estimators are not available for Site 1263, the planktonic Mg/Ca and nannofossil assemblage records at this midlatitude site suggest a stronger affiliation with tropical SST stability than with high-latitude SST cooling across the EOT.

[16] Assuming *S. utilizindex* Mg/Ca is predominantly documenting temperature, and that there was negligible change in thermocline temperature at this locality across the EOT, the planktonic $\delta^{18}O$ increase of 0.6‰ can be considered to represent changes in $\delta$w only. Taken at face value, this maximum value for $\delta$w change is in agreement with a similar $\delta$w increase across the EOT observed in exceptionally preserved planktonic foraminifera from Tanzania [*Lear et al.*, 2008], and also with an estimated sea level fall of about 60 m [*DeConto and Pollard*, 2003; *Miller et al.*, 2008]. In the case of a 0.6‰ change in $\delta$w, cooling of deep or intermediate waters in the range of 2°C is needed to account for the remaining ~0.5‰ increase in benthic $\delta^{18}O$ at Site 1263.

### 4.2. CCD Deepening and [$CO_3^{2-}$] Increase at ODP Site 1263 With Implications for Mg/Ca

[17] A dominant feature of the EOT is a deepening of the CCD by ~1 km, which has been attributed to a global shift in carbonate deposition from the shelf regions to the open ocean in response to significant sea level fall as ice accumulated on Antarctica [*Merico et al.*, 2008]. Site 1263 was situated well above the lysocline in the latest Eocene, and we observe no significant increase in average %$CaCO_3$ values from the Eocene to Oligocene, although we acknowledge that $CaCO_3$ accumulation rates would provide a

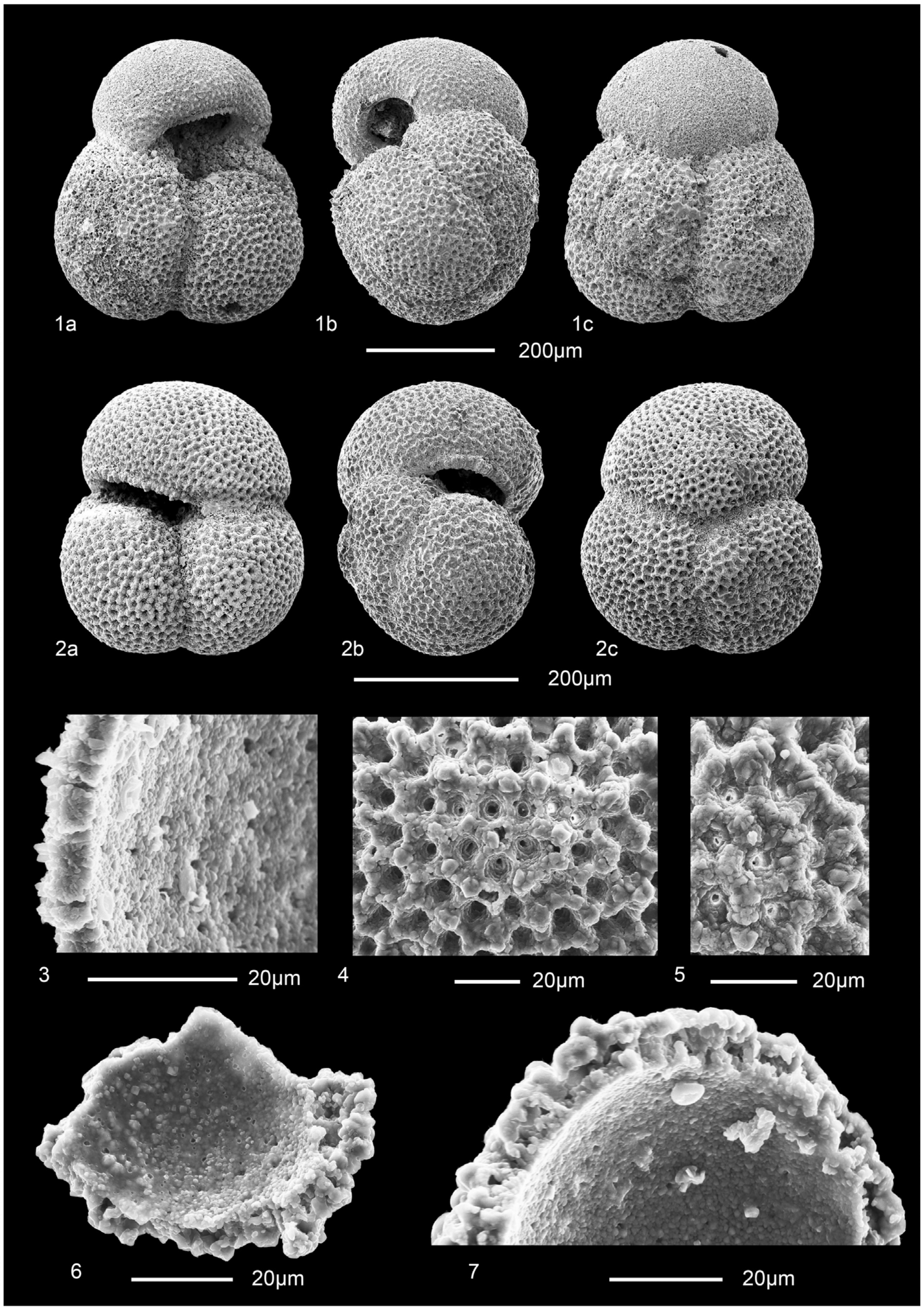


**Figure 5.** SEM images from planktonic foraminifera specimens from both a high %$CaCO_3$ interval (94.89 mcd) and the dissolution interval (94.44 mcd). Images 1a, 1b, and 1c, *Turborotalia ampliapertura*; images 2a, 2b, and 2c, *Subbotina utilizindex*; image 3, surface texture of *T. ampliapertura* from high %$CaCO_3$ interval; image 4, surface texture of *T. ampliapertura* from dissolution interval; image 5, surface texture of *S. utilizindex* from dissolution interval; image 6, wall texture of *S. utilizindex* from high %$CaCO_3$ interval; image 7, wall texture of *S. utilizindex* from dissolution interval.

more meaningful measure of changes in deposition and preservation. However, the transient decrease in %$CaCO_3$ at Step 1 (Figure 3a), a feature common to several sites including the Southern and Pacific Oceans (Figure 6), suggests that the overall increase in $[CO_3^{2-}]$ across the EOT included an abrupt decrease in carbonate ion saturation state, or dissolution event, coincident with the onset of the benthic $\delta^{18}O$ increase. At Site 1263, Li/Ca values also fall in Step 1, but remain significantly higher than the latest Eocene average, suggesting that $[CO_3^{2-}]$ had increased and/or

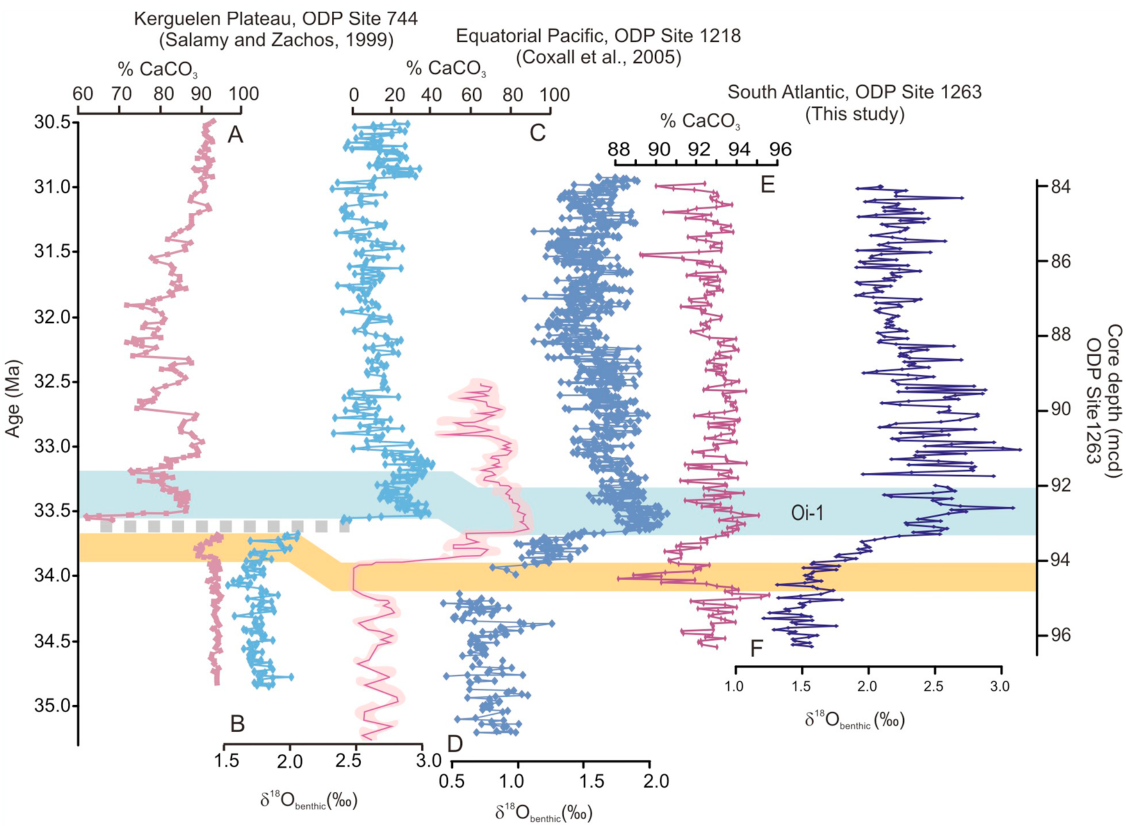


**Figure 6.** Evidence for dissolution horizon at the onset of the EOT in the South Atlantic, Southern, and Pacific oceans. (a) %$CaCO_3$ and (b) benthic $\delta^{18}$O from Site 744 [*Salamy and Zachos*, 1999]. Dashed gray line indicates coring disturbance. (c) %$CaCO_3$ and (d) benthic $\delta^{18}$O from Site 1218 [*Coxall et al.*, 2005]. (e) %$CaCO_3$ and (f) benthic $\delta^{18}$O from Site 1263 [*Riesselman et al.*, 2007]. Data from Sites 744 and 1218 are plotted on their published age models, while data from Site 1263 are plotted against depth. The blue horizontal bar indicates Oi-1, highlighting the correlation of the benthic $\delta^{18}$O maximum at each site. The orange horizontal bar locates the proposed dissolution horizon suggested at all three sites by minima in %$CaCO_3$. At Site 1218 a complete absence of carbonate accounts for the benthic $\delta^{18}$O data gap at this horizon.

bottom water temperatures had dropped relative to the latest Eocene. Higher $\Delta[CO_3^{2-}]$ relative to latest Eocene conditions may account for benthic Mg/Ca remaining above latest Eocene values even if bottom water temperatures did fall in Step 1. Furthermore, Mg/Ca tracks %$CaCO_3$ in fine detail during the transient %$CaCO_3$ minimum (Figure 4) which is suggestive of a mechanistic linking between the two records through varying $[CO_3^{2-}]$ in ambient bottom waters. This relationship is clearly different to the latest Eocene, prior to the benthic $\delta^{18}$O increase, when Mg/Ca displays a negative relationship with both %$CaCO_3$ and Li/Ca. The sensitivity of *O. umbonatus* Mg/Ca to changes in $\Delta[CO_3^{2-}]$ has not yet been determined, but based on our data profiles we hypothesize that changes in $[CO_3^{2-}]$ across the EOT have had a prominent influence on Mg/Ca.

[18] Site 1218 in the Equatorial Pacific was close to the CCD in the latest Eocene and %$CaCO_3$ increased from ~10% to >80% across the EOT (Figure 6) [*Coxall et al.*, 2005] thus reflecting a substantial increase in ambient bottom water $[CO_3^{2-}]$. *Lear and Rosenthal* [2006] record a 17% increase in Li/Ca across the EOT at Site 1218, occurring mostly within Step 1. A change of this magnitude would represent an approximately 37 $\mu$mol/kg increase in $[CO_3^{2-}]$ at this site as the CCD deepened, although some of the Li/Ca increase plausibly reflects deep water cooling [*Marriott et al.*, 2004]. Applying the Li/Ca-$\Delta[CO_3^{2-}]$ calibration of *Lear and Rosenthal* [2006] to Site 1263 suggests the ~8% increase of Li/Ca ratios was equivalent to a ~29 $\mu$mol/kg $[CO_3^{2-}]$ increase across the EOT, with the absolute $[CO_3^{2-}]$ concentrations about 48 $\mu$mol/kg higher at Site 1263 than at the deep Pacific Site 1218.

[19] Recent studies have also demonstrated an inverse relationship between bottom water $[CO_3^{2-}]$ and benthic foraminifera Sr/Ca; for example, *Rathmann and Kuhnert* [2008] found that a 0.05 mmol/mol decrease in Sr/Ca corresponded to a 10 $\mu$mol/kg increase in $[CO_3^{2-}]$ in a depth transect off Namibia. At Site 1263 we observe a Sr/Ca decrease of ~0.02 mmol/mol which is small compared to an expected decrease of 0.15 mmol/mol if one uses the Sr/Ca-$[CO_3^{2-}]$ correlation of *Rathmann and Kuhnert* [2008]

and a $[CO_3^{2-}]$ increase of 29 $\mu$mol/kg indicated by the coeval Li/Ca increase. This small change in Sr/Ca may reflect a coeval increase in seawater Sr/Ca. As sea level fell across the EOT, an increase in Sr/Ca may be expected due to erosion of high-Sr/Ca shelf carbonates [*Stoll and Schrag*, 1998], however, an accelerated increase in seawater Sr/Ca has not yet been observed across the EOT [*Billups et al.*, 2004].

[20] Although we cannot unambiguously resolve the issue of absolute changes in ambient deep water $[CO_3^{2-}]$ at Site 1263 across the EOT, any change in deep water carbonate chemistry would impact benthic Mg/Ca ratios. An increase in deep water $[CO_3^{2-}]$ would elevate Mg/Ca in benthic foraminiferal shells [*Elderfield et al.*, 2006; *Yu and Elderfield*, 2008]. Had we ascribed the observed increase in benthic Mg/Ca across the EOT entirely to temperature changes and applied the calibration for *Cibicidoides* from *Lear et al.* [2002], the resulting temperature change of approximately 1°C would be within the range of calibration error and therefore insignificant. Conversely, a 29 $\mu$mol/kg increase in $[CO_3^{2-}]$ as indicated by Li/Ca would result in a Mg/Ca increase of about 0.25 mmol/mol, similar to the observed change in our record (Figure 3c). Therefore, even at this relatively shallow site, the increase in $[CO_3^{2-}]$ that is associated with a deepening of CCD and increase in benthic foraminiferal Li/Ca could readily account for the rising Mg/Ca and simulate an apparent warming during the EOT.

## 5. Conclusions

[21] Although positioned ~1 km above the lysocline in the latest Eocene, benthic foraminiferal Mg/Ca from Site 1263 appears to have recorded changes in $[CO_3^{2-}]$ rather than temperature across the EOT. A Li/Ca record from this intermediate water site suggests that $[CO_3^{2-}]$ increased by ~29 $\mu$mol/kg across the EOT. Together with the close coupling of the benthic Mg/Ca and %CaCO$_3$ records across the benthic $\delta^{18}$O increase, we consider the Li/Ca evidence to indicate that Mg/Ca was predominantly controlled by $\Delta[CO_3^{2-}]$, rather than temperature, across the EOT, as has previously been observed at deep sites. In the latest Eocene, Mg/Ca may have been more sensitive to temperature based on the stronger correlation of Mg/Ca with benthic $\delta^{18}$O and its anticorrelation with %CaCO$_3$ or with Li/Ca. We propose that the Mg/Ca sensitivity of *O. umbonatus* switched from a temperature influence to a $[CO_3^{2-}]$ control at the onset of the benthic $\delta^{18}$O increase due to a significant increase in intermediate water $[CO_3^{2-}]$. Without a correction method, the sensitivity of benthic Mg/Ca to $[CO_3^{2-}]$ prevents this proxy from quantifying deep or intermediate water cooling across the EOT. Coupled $\delta^{18}$O and Mg/Ca for thermocline-dwelling *S. utilizindex* suggest no change in thermocline temperature and therefore a 0.6‰ increase in $\delta$w at the EOT, similar to *Lear et al.* [2008], negating the necessity for extensive bipolar glaciation [*Coxall et al.*, 2005]. Deep or intermediate water cooling of at least 2°C would account for the remainder of the benthic $\delta^{18}$O increase.

[22] A dissolution event, identified by an interval of low %CaCO$_3$ and Li/Ca ratio, is observed at the onset of the benthic $\delta^{18}$O increase and is also recognized in a number of other sites. Further investigation of this time interval is essential to understanding what caused the apparent transient shoaling of the CCD and what influence it may have had on the dramatic changes in global climate that followed.

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