Deep water temperature, carbonate ion, and ice volume changes across the Eocene-Oligocene climate transition

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1. Introduction

[1] Paired benthic foraminiferal stable isotope and Mg/Ca data are used to estimate bottom water temperature (BWT) and ice volume changes associated with the Eocene-Oligocene Transition (EOT), the largest global climate event of the past 50 Myr. We utilized ODP Sites 1090 and 1265 in the South Atlantic to assess seawater δ¹⁸O (δ₁⁸o), Antarctic ice volume, and sea level changes across the EOT (~33.8–33.54 Ma). We also use benthic δ¹³C data to reconstruct the sources of the deep water masses in this region during the EOT. Our data, together with previously published records, indicate that a pulse of Northern Component Water influenced the South Atlantic immediately prior to and following the EOT. Benthic δ¹⁸O records show a 0.5‰ increase at ~33.8 Ma (EOT-1) that represents a ~2°C cooling and a small (~10 m) eustatic fall that is followed by a 1.0‰ increase associated with Oi-1. The expected cooling of deep waters at Oi-1 (~33.54 Ma) is not apparent in our Mg/Ca records. We suggest the cooling is masked by coeval changes in the carbonate saturation state (Δ[CO₃²⁻]) which affect the Mg/Ca data. To account for this, the BWT, ice volume, and δ₁⁸o estimates are corrected for a change in the Δ[CO₃²⁻] of deep waters on the basis of recently published work. Corrected BWT at Sites 1090 and 1265 show a ~1.5°C cooling coincident with Oi-1 and an average δ₁⁸o increase of ~0.75‰. The increase in ice volume during Oi-1 resulted in a ~70 m drop in global sea level and the development of an Antarctic ice sheet that was near modern size or slightly larger.


[2] Earth’s climate has experienced a long-term cooling over the past 50 million years as evidenced by a 5‰ increase in deep sea benthic foraminiferal δ¹⁸O during this period [Savin et al., 1975; Shackleton and Kennett, 1975; Miller et al., 1987, 2005; Zachos et al., 2001]. Resultant oxygen isotope temperature estimates [Miller et al., 1987, 2005; Zachos et al., 2001], along with benthic foraminiferal Mg/Ca paleotemperatures, suggest as much as a ~12°C cooling of deep waters over the past 50 Myr [Lear et al., 2000; Billups and Schrag, 2002, 2003]. The Cenozoic cooling trend has been attributed to changes in ocean-atmosphere circulation patterns associated with opening and closing of ocean gateways [Kennett, 1977; Schnitker, 1980; Woodruff and Savin, 1989; Wright et al., 1992; Raymo, 1994] and changes in atmospheric CO₂ levels [Vincent and Berger, 1985; Flower and Kennett, 1993; DeConto and Pollard, 2003; Pagani et al., 2005; Pearson et al., 2009].

[3] The Eocene-Oligocene transition (EOT) was the largest of several abrupt events that punctuated the overall Cenozoic cooling trend [Berger, 1982; Miller et al., 1987; Zachos et al., 2001]. In well-resolved records, the ~1.5‰ benthic foraminiferal δ¹⁸O increase at the EOT appears to be a two-step event with the first phase beginning at 33.8 Ma (0.5‰) followed by a second increase of 1.0‰, Oi-1 (“Oligocene isotope event 1”), at 33.54 Ma [Miller et al., 1991, 2008; Zachos et al., 1996; Coxall et al., 2005]. The δ¹⁸O shift across the EOT reflects both deep water cooling and the development of continental-size ice sheets on Antarctica [Miller et al., 1991, 2005; Zachos et al., 1996; Coxall et al., 2005; Lear et al., 2008]. Independent evidence for the onset of Antarctic glaciation associated with the EOT includes the presence of ice rafted detritus at high southern latitudes and changes in clay mineralogy in the Southern Ocean [Ehrmann, 1991; Ehrmann and Mackensen, 1992; Zachos et al., 1992; Robert et al., 2002].

[4] Mg/Ca ratios of benthic foraminiferal calcite can serve as an independent proxy for bottom water temperature [Nurnberg et al., 1996; Rosenthal et al., 1997; Lea et al., 1999; Elderfield and Ganssen, 2000]. However, the primary BWT component can be masked by changes in the carbonate ion concentration ([CO₃²⁻]) and saturation state (Δ[CO₃²⁻]) of deep waters [Elderfield et al., 2006; Rosenthal et al., 2006; Yu and Elderfield, 2008]. The [CO₃²⁻] ion effect is based on core top Mg/Ca calibrations that show

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higher temperature sensitivities in waters <3°C [Martin et al., 2002] attributed to the [CO$_3^{2-}$] and Δ[CO$_3^{2-}$] of seawater [Elderfield et al., 2006; Rosenthal et al., 2006; Healey et al., 2008; Yu and Elderfield, 2008]. A change in the [CO$_3^{2-}$] is important since there is a large-scale (>1 km) drop in the carbonate compensation depth (CCD) associated with the EOT [van Andel, 1975; Coxall et al., 2005]. Thus, paired benthic foraminiferal $\delta^{18}O$ and Mg/Ca ratios that are corrected for a change in the [CO$_3^{2-}$] of deep waters can, in principle, be used to differentiate the contributions of ice volume and temperature to the $\delta^{18}O$ increase at the EOT.

[5] Initial Mg/Ca studies of the past 50 million years at a low resolution indicated there was no major change in BWT across the EOT [Lear et al., 2000; Billups and Schrag, 2003], implying that the entire 1.5% $\delta^{18}O$ increase was due to an ice volume change. Subsequent work at a higher resolution by Lear et al. [2004] using South Atlantic Deep Sea Drilling Project (DSDP) Site 522 and equatorial Pacific Ocean Drilling Program (ODP) Site 1218 inferred a $\sim$2°C warming of deep water associated with Oi-1 (Figure 1). However, any increase in BWT poses a problem because it requires more growth of ice than can be accommodated on Antarctica today [Coxall et al., 2005; DeConto et al., 2008]. The issue of ice accommodation space led to the hypothesis that there were significant Northern Hemisphere ice sheets during the earliest Oligocene [Coxall et al., 2005; Tripati et al., 2005]. No definitive evidence of large-scale Eocene-Oligocene northern hemisphere glaciation exists, leaving only the current hypothesis of small valley glaciers and ephemeral ice caps to explain the presence of drop stones recently identified off the coast of Greenland [Eldrett et al., 2007].

[6] A more likely scenario points toward a change in the Δ[CO$_3^{2-}$] of deep waters caused by a global CCD drop that influenced benthic foraminiferal Mg/Ca ratios across the EOT [van Andel, 1975; Lear et al., 2004; Coxall et al., 2005; Rea and Lyle, 2005]. Benthic foraminiferal Li/Ca ratios support the hypothesis that an increased [CO$_3^{2-}$] of deep waters is the primary influence on benthic foraminiferal Mg/Ca records across the EOT [Lear and Rosenthal, 2006; Lear et al., 2010; Peck et al., 2010]. Benthic foraminiferal Li/Ca ratios provide a way to estimate a change in deep water [CO$_3^{2-}$] because of a response to calcification rates that is influenced by the seawater [CO$_3^{2-}$] [Hall and Chan, 2004; Lear and Rosenthal, 2006].

[7] A recent study estimated a $\sim$29 μmol/kg [CO$_3^{2-}$] increase in South Atlantic deep waters coincident with Oi-1 based on benthic foraminiferal Li/Ca ratios [Peck et al., 2010]. Similarly, it is reported that there was a $\sim$37 μmol/kg [CO$_3^{2-}$] rise in equatorial Pacific deep waters associated with Oi-1 [Lear and Rosenthal, 2006; Lear et al., 2010]. We use published Li/Ca records from ODP Site 1263 on the Walvis Ridge [Peck et al., 2010] and ODP Site 1218 in the equatorial Pacific [Lear et al., 2010] to correct for benthic foraminiferal Mg/Ca overprinting due to [CO$_3^{2-}$] changes associated with Oi-1. Site 1218 Li/Ca data [Lear et al., 2010] was selected to correct our Site 1090 benthic foraminiferal Mg/Ca record because of its paleowater depth (≥3.7 km at $\sim$34 Ma). The Site 1263 Li/Ca record [Peck et al., 2010] was chosen to correct Site 1265 Mg/Ca ratios because it is in close proximity and has a similar paleowater depth at $\sim$34 Ma. The [CO$_3^{2-}$] correction factor used on our benthic foraminiferal Mg/Ca data is based on an empirical sensitivity of 0.0086 mmol/mol/μmol/kg [Elderfield et al., 2006].

[8] Two deep sea sediment records with complete sections across the EOT are utilized in the present study to investigate deep water temperature and global ice volume changes. We chose South Atlantic ODP Sites 1090 and 1265 (Figure 1) because of excellent core recovery, high carbonate content, and good foraminiferal preservation. Orbital-scale resolution (10 and 40 cm sampling) benthic foraminiferal (Cibicidoides spp.) $\delta^{18}O$, $\delta^{13}C$, and Mg/Ca records were generated across

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**Figure 1.** Paleoecographic reconstruction for 34 Ma showing the locations of Ocean Drilling Program (ODP) Sites 1090 and 1265 used in this study (red circles) and Deep Sea Drilling Project (DSDP) Site 522 and ODP Site 1218 (blue circles) from previous studies [Zachos et al., 1996; Coxall et al., 2005]. The map was created using the Ocean Drilling Stratigraphic Network (http://www.odsn.de/).
the EOT for both sites. As mentioned above, Sites 1090 and 1265 benthic foraminiferal Mg/Ca records are corrected for changes in the [CO$_3$]$^2$ based on recent Li/Ca data from Peck et al. [2010] and Lear et al. [2010].

[5] We assess the reliability of our benthic foraminiferal stable isotope records by placing them into a global context using the multisite isotopic compilation from Cramer et al. [2009]. Benthic foraminiferal $\delta^{13}$C data across the EOT from South Atlantic Sites 1090 and 1265 are compared to existing records from equatorial Pacific ODP Site 1218 [Coxall et al., 2005] and South Atlantic DSDP Site 522 [Zachos et al., 1996] to reconstruct source regions for deep water masses (Figure 1). Previous stable isotope work at Site 1265 [Liu et al., 2004] reported on the benthic foraminiferal species C. praemundulus at a low resolution (~50 kyr) from two separate holes across the EOT. Site 1265 stable isotope trace metal data from the present study is derived from a single hole (1265B) at a higher resolution (10 cm; equivalent to ~17 kyr) in efforts to gain complete coverage of changes in deep water across the EOT.

2. Methods

2.1. Site Selection and Age Control

[10] South Atlantic ODP Site 1090 hole B is located on the southern flank of the Agulhas Ridge ($42^\circ54.8'S$, $8^\circ53.9'E$) at a water depth of 3702 m, which is above the present-day lysocline depth (4300 m) [Milliman, 1993; Dittr and Henrich, 2000]. The paleoater depth for Site 1090 is estimated to have been ~3000–3300 m at ~34 Ma (using equations of Miller et al. [1986] and Stein and Stein [1992] and the following parameters: present water depth of 3702 m, sediment thickness of 800 m, basement age of 87 Ma, and pre-exponential empirical constant of ~3650). The CCD at ~34 Ma was positioned at ~3100 m in the South Atlantic [Peck et al., 2010]. Site 1090 was located at approximately 49°S, 2°E at ~34 Ma [Anderson and Delaney, 2005]. The Eocene-Oligocene boundary interval is located in sediments classified as nannofossil-diatom ooze with approximately 30 weight percent carbonate [Gersonde et al., 1999]. A total of one hundred and eighteen samples were taken at 40 cm intervals between 35 and 33.1 Ma (225–287 mcd), representing a sample spacing of ~10 kyr. ODP Site 1090 has excellent age control (Figures S1 and S2 in the auxiliary material) based on previously published magnetostratigraphy that is correlated to the geomagnetic polarity time scale (GPTS) [Channell et al., 2003]. Average sedimentation rates for the latest Eocene to earliest Oligocene section at Site 1090 are ~3.7 cm/kyr.

[11] South Atlantic ODP Site 1265 hole B is located on the Walvis Ridge ($28^\circ50.1'S$, $2^\circ38.3'E$) at 3083 m water depth [Zachos et al., 2004]. The present-day position of the lysocline in the Cape Basin is 4000 m [Hodell et al., 2001; Volbers and Henrich, 2002; Henrich et al., 2003]. The paleoater depth for Site 1265 at ~34 Ma was ~2400 m [Zachos et al., 2004] and the CCD was at ~3100 m [Peck et al., 2010]. The paleolatitude for Site 1265 was ~34°S, 9°E during the latest Eocene [http://www.odsn.de/]. The EOT sediments at this location display a change in composition from uppermost Eocene clay bearing nannofossil ooze to lowermost Oligocene foraminiferal-dominated nannofossil ooze with carbonate content between 85% and 95% [Zachos et al., 2004]. A total of 121 samples were taken every 10 cm (equivalent to ~17 kyr) between 32.8 and 34.2 Ma (183–196 mcd). Age control for Site 1265 is based on the age-depth model determined from magnetostratigraphy and calcareous nannofossil stratigraphy [Zachos et al., 2004]. Sedimentation rates for the latest Eocene to earliest Oligocene interval average ~0.5 cm/kyr.

[12] The foraminiferal tests used are from burial depths of 180–200 m for Site 1265 and 200–300 m for Site 1090 and thus may have undergone some postdepositional dissolution of the primary calcite [Liu et al., 2004]. Postburial dissolution can alter the Mg/Ca ratios of foraminiferal tests by preferentially removing Mg-rich calcite causing artificially colder temperatures [e.g., Brown and Elderfield, 1996; Dekens et al., 2002; Regenberg et al., 2006; Rosenthal and Lohmann, 2002; Rosenthal et al., 2000]. Similarly, postburial accumulation of secondary calcite can modify the primary Mg/Ca ratio and yield spuriously colder temperatures estimates depending on the amount and composition of recrystalization [Baker et al., 1982; Delaney, 1989]. Scanning electron microscope (SEM) images of benthic foraminiferal tests from Sites 1090 and 1265 reveal excellent preservation, with no indication of secondary calcification (Figure 2). Furthermore, any potential BWT change resulting from minor dissolution/diagenesis would be less than the analytical (~0.9°C) or calibration (~1.3°C) error; major diagenesis is precluded based on the excellent preservation revealed by SEM micrographs. We conclude the original isotopic and geochemical signals incorporated in the foraminiferal tests are not altered by diagenesis or dissolution based on our SEM images for both sites (Figure 2).

[13] Oxygen and carbon isotope data for Sites 1090 and 1265 are plotted versus depth, core recovery, magnetochronology, biostratigraphic zones, and lithology to estimate sedimentation rates and develop age models (Figures S1 and S2 in the auxiliary material). Though both sites lack a precise orbital chronology, intersite correlations suggest that the magnetobiostratigraphic age models (Figure 3) have uncertainties of less than 0.1 Myr. Chronology for Site 1090 relies primarily on paleomagnetic age reversals [Channell et al., 2003] that are in good agreement with nannofossil datum levels [Marino and Flores, 2002]. The Site 1265 age model from 33 to 34 Ma is based primarily on nannofossil and paleomagnetic data [Zachos et al., 2004, chap. 6]. The oldest 200 kyr interval for Site 1265 (34–34.2 Ma) is correlated to the benthic foraminiferal $\delta^{13}$C record from Site 1090 to account for potential reworking.

2.2. Analytical Methods

[14] Sites 1090 and 1265 sediment samples were disaggregated in buffered water and washed through a 63 µm mesh sieve. Washed samples were dry sieved through a 150 µm sieve and five to ten benthic foraminiferal specimens of the epifaunal genus Cibicidoides were picked from each sample for stable isotope analysis. Approximately 100 µg of sample was dissolved in 100% phosphoric acid and analyzed for oxygen and carbon stable isotopes using a GV-IsoPrime stable isotope mass spectrometer. Isotope values are reported

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1Auxiliary materials are available in the HTML. doi:10.1029/2010PA001950.
relative to the VPDB (Vienna PeeDee belemnite) standard ($\delta^{18}O = -2.20^\circ$ and $\delta^{13}C = 1.95^\circ$; following Coplen et al. [1983]). Replicate analysis of our standard yields an analytical precision (1σ) of 0.06‰ for oxygen and 0.05‰ for carbon. A portion of the Site 1090 samples (35 to 33.4 Ma) were analyzed on a Micromass Optima mass spectrometer at Rutgers University using procedures similar to those described above. The laboratory standard was checked regularly against NBS-19, which has a $\delta^{18}O$ offset equal to 0.04‰ and a $\delta^{13}C$ offset of 0.10‰. The laboratory standard error (1σ) is equal to 0.08‰ for $\delta^{18}O$ and 0.05‰ for $\delta^{13}C$.

[15] Five to ten individual benthic foraminifera were cleaned for trace metal analysis with both the reductive and oxidative steps outlined by Boyle and Keigwin [1985]. Foraminiferal tests ($300-400 \mu g$) were crushed prior to cleaning to ensure homogenization. Each cleaned sample was dissolved in 500–800 µL of 5% HNO₃ to yield a calcium concentration of approximately 80 ppm. Magnesium and calcium were measured simultaneously on a Jobin Yvon Ultima Inductively Coupled Plasma Atomic Emission Spectrophotometer (ICP-AES). Replicate analyses of a standard solution produced an analytical precision of 0.4%. Duplicate trace metal analyses performed downcore on 10% of the benthic foraminiferal samples resulted in an average reproducibility of ±0.11 mmol/mol for Site 1265 and ±0.17 mmol/mol for Site 1090 (Figure S3 in the auxiliary material).

2.3. Mg-Temperature Calibration

[16] We utilized the Mg/Ca temperature calibration developed by Raitzsch et al. [2008] for the benthic foraminiferal species Cibicidoides mundulus,

$$\text{Mg/Ca} = 0.627 \exp(0.143 \times \text{BWT}),$$

Figure 2. SEM images of Ocean Drilling Program Sites 1090 and 1265 benthic foraminiferal specimens from the genus Cibicidoides at 228.24 and 186.58 m composite depth (mcd), respectively. (a) ODP Site 1090 Cibicidoides grimsdalei SEM image at 400 µms from 228.24 mcd with 30 weight percent CaCO₃ [Latimer and Filippelli, 2002]. (b) ODP Site 1090 Cibicidoides grimsdalei SEM image at 10 µms from 228.24 mcd with 30 weight percent CaCO₃ [Latimer and Filippelli, 2002]. (c) ODP Site 1265 Cibicidoides praemundulus SEM image at 400 µms showing spiral side of foraminifera from 186.58 mcd with 85 weight percent CaCO₃ [Kroon et al., 2006]. (d) ODP Site 1265 Cibicidoides praemundulus SEM image at 400 µms showing umbilical side of foraminifera from 186.58 mcd with 85 weight percent CaCO₃ [Kroon et al., 2006].
where Mg/Ca and BWT are the C. praemundulus Mg/Ca ratio and bottom water temperature (°C), respectively. Temperatures calculated with this equation have an uncertainty of ±1.27°C. While Yu and Elderfield [2008] found no correlation between the Mg/Ca ratios of C. mundulus and BWT, a few other studies have shown a significant correlation [Elderfield et al., 2006; Healey et al., 2008]. In addition, C. mundulus has been used successfully to reconstruct BWT changes across Neogene global climate transitions [Lear et al., 2003; Shevenell et al., 2008].

[17] The calibration from Raitzsch et al. [2008] was chosen for three reasons: (1) C. mundulus is considered to have evolved from C. praemundulus [van Morkhoven et al., 1986]; (2) the equation is based on present-day bottom water temperatures between 1° and 15°C; and (3) the absolute calculated BWT are comparable to previously published latest Eocene-earliest Oligocene deep water temperatures using stable oxygen isotopes [Savin et al., 1975; Zachos et al., 1994] and low-resolution benthic foraminiferal Mg/Ca records [Lear et al., 2000]. Our choice of temperature calibration should have a minimal effect on the relative temperature change because the published exponential equations that are based on both mixed species of Cibicidoides [Rosenthal et al., 1997; Martin et al., 2002; Lear et al., 2002; Elderfield et al., 2006] and C. mundulus [Lear et al., 2003; Raitzsch et al., 2008] have similar exponential constants (0.10 to 0.11 mmol/mol). Published linear calibrations for Cibicidoides spp. [Rathbun and De Deckker, 1997] and single species, C. mundulus [Healey et al., 2008], result in overall lower-amplitude temperature changes with the exception of the single species, C. mundulus, equation from Elderfield et al. [2006]. Furthermore, deep water temperatures during the Cenozoic are considered
to be fairly uniform throughout all of the ocean basins at any given time period [Savin et al., 1975].

[18] We assumed the seawater Mg/Ca ratio was 4.3 mmol/mol at ~34 Ma [Wilkinson and Algeo, 1989], compared to the present-day ratio of 5.1 mmol/mol [Broecker and Peng, 1982; Stanley and Hardie, 1998]. Although there is uncertainty in calculating Cenozoic paleotemperatures due to changes in seawater Mg/Ca over time [Lear et al., 2000; Billups and Schrag, 2002], we feel confident the relative temperature change across such a rapid event as the EOT remains unaffected by this issue because of the long residence times of Mg and Ca in the ocean [Broecker and Peng, 1982].

3. Results

3.1. Carbon Isotopes

[19] Site 1090 benthic foraminiferal (Cibicidoides spp.) δ13C values vary between 0.0 and 0.7‰ from the base of the record to ~33.9 Ma (Figure 3). A 0.5‰ increase occurs within ~100 kyr beginning at ~33.9 Ma and likely corresponds to EOT-1, although the data in this interval is sparse. A second increase in benthic foraminiferal δ13C of 1.0‰ begins at 33.52 Ma and is coincident with Oi-1. At the end of Oi-1, δ13C values reach a maximum of 1.7‰ at ~33.41 Ma. Subsequently, benthic foraminiferal δ13C decreases slightly to values between 1.0 and 1.5‰ for the youngest portion of the Site 1090 record.

[20] The Site 1265 benthic foraminiferal (Cibicidoides spp.) δ13C record shows little variability between 34.2 and 33.8 Ma, with values of 1.0–1.2‰ (Figure 3). Benthic foraminiferal δ13C values increase by ~1.2‰ over a 30 kyr period starting at ~33.65 Ma and including Oi-1 (Figure 3). As at Site 1265, benthic foraminiferal δ13C ratios decrease following Oi-1 from ~2.0‰ to 1.4‰ at 33.0 Ma.

3.2. Oxygen Isotopes

[21] Site 1090 benthic foraminiferal (Cibicidoides spp.) δ18O values from the oldest portion of the record (34–35 Ma) vary between 0.5 and 1.0‰, with no long-term trend over this one million year time interval (Figure 3). Between ~33.9–33.6 Ma, there is an increase in δ18O of ~0.5‰ (Figure 3). There are no obvious shifts associated with either EOT-1 or EOT-2, although the there are limited data across the first of these events. A rapid increase in benthic foraminiferal δ18O of 1.0‰ begins at 33.55 Ma and coincides with Oi-1. Following the increase during Oi-1, Site 1090 δ18O values decrease slightly to values centering near 2.2‰ for the remainder of the record (Figure 3).

[22] The Site 1265 benthic foraminiferal (Cibicidoides spp.) δ18O record is marked by relatively stable values (1.0–1.5‰) from 34.2 to 33.9 Ma (Figure 3). No apparent benthic foraminiferal δ18O change occurs during EOT-2 at Site 1265, though there appears to be a minor (<0.5‰) increase spanning EOT-1 (Figure 3). The benthic foraminiferal δ18O records from Sites 1265 and 1090 are offset prior to 33.8 Ma and convergence immediately above EOT-1. A rapid increase of 0.8‰ occurs at Site 1265 between 33.55 and 33.45 Ma and correlates with Oi-1. The Oi-1 shift is followed by a slight decrease between 33.45 and 33.35 Ma (Figure 3). Values range between 1.9 and 2.2‰ throughout the youngest part of the Site 1265 benthic foraminiferal δ18O record.

3.3. Comparison to Global Stable Isotope Compilations

[23] A number of studies have compiled available δ18O and δ13C data in order to examine global trends during the late Eocene and early Oligocene [Miller et al., 1987; Zachos et al., 2001; Cramer et al., 2009]. To assess the reliability of the Sites 1090 and 1265 benthic foraminiferal δ18O and δ13C records across the EOT, we compare them to the most recent of these compilations (Figure 4) from Cramer et al. [2009]. Site 1090 δ18O values are lower than those of the entire ocean prior to EOT-1, suggesting it is bathed in a relatively warm or fresh water mass before 33.8 Ma (Figure 4). The Site 1090 benthic foraminiferal δ13C values also are at the lower end of those in the global record prior to EOT-1 but become more similar to those in the global compilation after this event. Our δ18O data from Site 1265 displays good agreement with the global compilation across the entire EOT (Figure 4). Conversely, the Site 1265 δ13C values are consistently at the higher end of the range of values seen in the global record (Figure 4). Based on this comparison, we are confident that the stable isotope records for Sites 1090 and 1265 are reliable indicators of past changes in water mass properties at these two locations.

3.4. Benthic Foraminiferal Mg/Ca Ratios

[24] Site 1090 benthic foraminiferal Mg/Ca ratios average 0.8 ± 0.4 mmol/mol (2 s.d.) throughout the entire record, ranging from a maximum value of 1.2 mmol/mol and minimum of 0.5 mmol/mol (Figure 5). The lowest benthic foraminiferal Mg/Ca values of 0.5 mmol/mol occur at ~33.8 Ma and subsequently increase by ~0.5 mmol/mol during Oi-1 (Figure 5). Following a 100 kyr period of relatively stable values (~0.8 mmol/mol) there is a second increase of ~0.3 mmol/mol beginning at 33.27 Ma (Figure 5). In the youngest portion of the Site 1090 record, from 33.27 to 33.1 Ma, Mg/Ca ratios average ~1.0 mmol/mol.

[25] For Site 1265, C. praemundulus Mg/Ca values vary between 1.1 and 2.1 mmol/mol over the entire length of the record, with the average being 1.7 ± 0.4 mmol/mol (2 s.d.) (Figure 5). The initial 500 kyr of the Site 1265 record (34.2 to 33.8 Ma) displays relatively large fluctuations that appear to track changes in the carbonate content (Figure 5). Site 1265 benthic foraminiferal Mg/Ca ratios show a brief decrease after EOT-1 from 1.6 mmol/mol at ~33.75 Ma to 1.1 mmol/mol at 33.65 Ma. Subsequently, the record displays a long-term (600 kyr) increase from 1.1 mmol/mol at 33.63 Ma to 2.1 mmol/mol at 33.21 Ma (Figure 5). The gradual Mg/Ca increase of 1.0 mmol/mol over 600 kyr encompasses the Oi-1 event identified in the δ18O records (Figure 5). The remaining portion of the Site 1265 benthic foraminiferal Mg/Ca record shows minimal variability with an average of 1.7 mmol/mol from 33.2 to 33.3 Ma.

4. Discussion

4.1. Secular Effects of Carbonate Ion and Carbon Cycle Variations

[26] Before assessing our benthic foraminiferal δ13C and Mg/Ca records from the perspective of past water mass variations, we evaluate the integrity of the data including
their use as ventilation and paleotemperature indicators. Variations in deep water δ¹³C values reflect changes in (1) the global carbon reservoir [Broecker, 1970, 1982; Shackleton, 1977], (2) deep water circulation patterns [Bender and Keigwin, 1979; Belanger et al., 1981; Curry and Lohmann, 1982, 1983; Boyle and Keigwin, 1982; Shackleton et al., 1983], and (3) regional surface water productivity [Sarnthein et al., 1982]. A global deep water δ¹³C increase coincident with Oi‐1 (Figure 3) is associated with a significant deepening of the CCD and rise in the [CO₃²⁻] of bottom waters [van Andel, 1975; Zachos et al., 1996; Salamy and Zachos, 1999; Coxall et al., 2005; Zachos and Kump, 2005; Merico et al., 2008]. The earliest Oligocene benthic foraminiferal δ¹³C increase coincides with changes in marine productivity and/or in the organic carbon to inorganic carbon burial rates in the high to middle southern latitudes [Diester‐Haass and Zahn, 1996, 2001; Salamy and Zachos, 1999; Diester‐Haass and Zachos, 2003; Anderson and Delaney, 2005]. Sites 1090 and 1265 benthic foraminiferal δ¹³C records show an increase (0.5–0.7‰) coeval with Oi‐1 (Figure 3) that is consistent with other deep sea records (Figure 6) [e.g., Miller et al., 1988; Miller and Thomas, 1985; Barrera and Huber, 1991; Zachos et al., 1992, 1996].

The proposed change in paleoproductivity and export of organic carbon relative to carbonate carbon associated with Oi‐1 can be attributed to more vigorous ocean mixing rates. Considerable debate exists concerning whether a stronger meridional temperature gradient, intensified wind stress and upwelling, or the opening of tectonic gateways in the Southern Ocean caused ocean mixing rates to increase at this time [Diester‐Haass, 1996; Salamy and Zachos, 1999; Diester‐Haass and Zahn, 2001; Diester‐Haass and Zachos, 2003; Hay et al., 2005; Latimer and Filippelli, 2002; Cramer et al., 2009].

### 4.2. Bottom Water Temperature and Water Mass Properties

Site 1090 BWT that are uncorrected for changes in the [CO₃²⁻] range between 1° and 3°C in the early portion of the record from 34.5 to 34 Ma (Figure 7). BWT eventually increases to as warm as 5°–6°C at the top of the Site 1090
In contrast, Site 1265 uncorrected BWT are uniformly warmer (6°–8°C) and marked by little change throughout (Figure 7). Currently, Site 1090 BWT (1.2°C) are only slightly colder than those at Site 1265 (2.4°C) [Levitus and Boyer, 1994]. A 2°C difference in uncorrected BWT between Sites 1090 and 1265 in the late Eocene and a 1–2°C contrast in the early Oligocene suggests the two sites were bathed in different water masses prior to and following the EOT. Colder BWT at Site 1090 compared to Site 1265 associated with the EOT are supported by recent work that found a substantial Δδ18O gradient between South and North Atlantic deep waters coincident with Oi-1 [Cramer et al., 2009]. Site 1090 shows a ~2°C BWT cooling from 34 to 33.8 Ma, the time period containing EOT-1. A 200 kyr gap in the Site 1090 BWT record, possibly due to dissolution (Figure 5), makes it impossible to constrain the timing and magnitude of change across EOT-1. At 33.8 Ma, Site 1265 BWT display a ~1°C cooling associated with EOT-1 (Figure 7).

Figure 5. ODP Sites 1265 and 1090 benthic foraminiferal δ18O, Mg/Ca, and weight percent carbonate records verses age in millions of years. (a) Site 1265 benthic foraminiferal δ18O values (red circles; Cibicidoides spp.) verses age in millions of years. Isotope values are reported relative to the VPDB (Vienna PeeDee belemnite) standard. (b) Site 1265 benthic foraminiferal Mg/Ca ratios (red diamonds; C. praemundulus) in mmol/mol plotted with weight percent carbonate (black line) from Kroon et al. [2006]. (c) Site 1090 benthic foraminiferal δ18O values (blue circles; Cibicidoides spp.). (d) Site 1090 benthic foraminiferal Mg/Ca ratios (blue diamonds; Cibicidoides spp.) in mmol/mol plotted with weight percent carbonate (black line) from Latimer and Filippelli [2002]. Gray bars mark the EOT-1 (Eocene-Oligocene transition event 1), EOT-2 (Eocene-Oligocene transition event 2), and Oi-1 (Oligocene isotope event 1) events occurring at 33.8, 33.63, and 33.54 Ma, respectively [Miller et al., 1991, 2008; Lear et al., 2004; Coxall et al., 2005; Katz et al., 2008].
in the \([\Delta \text{CO}_2^\text{a}]\) of the oceans coincident with the EOT [Lear et al., 2004; Lear and Rosenthal, 2006; Peck et al., 2010; Lear et al., 2010]. An abrupt (<300 kyr) deepening (1.2 km) of the CCD occurred throughout the global ocean near the E-O boundary [van Andel, 1975; Rea and Lyle, 2005; Coxall et al., 2005]. A rise in bottom water \([\text{CO}_2^\text{a}]\) has been shown to cause an increase in benthic foraminiferal Mg/Ca ratios [Elderfield et al., 2006; Rosenthal et al., 2006; Healey et al., 2008; Yu and Elderfield, 2008], which in turn yield temperature estimates that are anomalously high.

A change in \([\Delta \text{CO}_2^\text{a}]\) may have affected the deeper of the two sites (Site 1090) more dramatically as evidenced by higher CaCO3 percentages at Site 1265 (85–95%) relative to those at Site 1090 (5–40%) across the entire EOT interval (Figure 5). Nearby ODP Site 1263 (28°31.9’S, 2°46.7’E) was determined to be above the lysocline at 2.1 km paleodepth at ~34 Ma [Peck et al., 2010]. Peck et al. [2010] estimated a ~29 μmol/kg \([\text{CO}_2^\text{a}]\) increase in bottom waters at Site 1263 associated with Oi-1. A ~29 μmol/kg \([\text{CO}_2^\text{a}]\) change is equivalent to a Mg/Ca ratio increase of ~0.25 mmol/mol using the relationship of 0.0086 mmol/mol per μmol/kg from Elderfield et al. [2006]. Correcting our Site 1265 Mg/Ca deep water record for a ~0.25 mmol/mol increase yields BWT estimates that show a ~1.5°C cooling beginning at ~33.6 Ma and culminating at Oi-1 (Figure 8).

Site 1090 Mg/Ca ratios are corrected for a larger change in the \([\text{CO}_2^\text{a}]\) because it is the deeper of the two sites located at 3.2 km paleodepth at ~34 Ma and the CaCO3 weight percent varies significantly more than Site 1265 (Figure 5). Site 1090 is adjusted for a 0.31 mmol/mol Mg/Ca increase [Elderfield et al., 2006] (Figure 8) based on a ~36 μmol/kg \([\text{CO}_2^\text{a}]\) change identified at equatorial Pacific ODP Site 1218 (4 km paleodepth at 34 Ma) across Oi-1[Lear et al., 2010]. Corrected Mg/Ca values for Site 1090 (Figure 8) yield a ~1.5°C BWT decrease associated with Oi-1, similar to that for Site 1265.

Our reconstructed Mg/Ca BWT records for Sites 1090 and 1265 can be used in conjunction with the benthic foraminiferal \(\delta^{13}C\) data to postulate the source regions for deep water masses at these two locations during the EOT [Bender and Keigwin, 1979; Curry and Lohmann, 1982, 1983; Boyle and Keigwin, 1982; Shackleton et al., 1983; Mix and Fairbanks, 1985; Oppo and Fairbanks, 1987]. At present, Site 1265 is bathed by nutrient-depleted North Atlantic Deep Water (NADW) with a \(\delta^{13}C\) value of ~1.0‰ [Kroopnick, 1985]. Likewise, Site 1090 is currently located in the mixing zone between NADW and lower Circumpolar Deep Water, with a \(\delta^{13}C\) value of ~0.4‰ [Kroopnick, 1985]. The principle region for deep water formation during the early Paleogene was the Southern Ocean [Miller and
Tucholke, 1983; Mountain and Miller, 1992; Pak and Miller, 1992; Thomas et al., 2003; Via and Thomas, 2006]. Some studies from the North Atlantic suggest a Northern Component Water mass (NCW; ancient analog to NADW [Wright et al., 1991]), probably originating in the Norwegian Sea, was produced in the early Oligocene and the latest Eocene [Miller and Tucholke, 1983; Miller, 1992; Wold, 1994].

[32] Sites 1090 and 1265 benthic foraminiferal δ^{13}C records are compared with two high-resolution EOT δ^{13}C records (Figure 6) from equatorial Pacific Site 1218 (4 km paleodepth) [Coxall et al., 2005] and South Atlantic Site 522 (3 km paleodepth) [Zachos et al., 1996] (Figure 1). Throughout the entire study interval, Site 1265 benthic δ^{13}C values are higher than those at both Site 1090 and Site 1218, but often similar to those for Site 522 (Figure 6). Site 1090 is marked by relatively low (0.4‰) benthic δ^{13}C values prior to EOT-1 that are comparable to the modern-day Circumpolar Deep Waters [Kroopnick, 1985]. In contrast, Site 1265 benthic δ^{13}C values are consistently 1.0‰ or higher, which would be indicative of a more nutrient-depleted water mass, most likely from a northern source region. In Figure 6, Site 1090 is considered to represent the Southern Ocean end-member, with Site 1218 [Coxall et al., 2005] serving as the Pacific end-member for deep water during the latest Eocene-earliest Oligocene. Sites 522

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**Figure 7.** ODP Sites 1090 and 1265 benthic foraminiferal δ^{18}O, uncorrected Mg/Ca, and uncorrected bottom water temperature (BWT) records verses age in millions of years. (a) Benthic foraminiferal (Cibicidoides spp.) δ^{18}O records from Sites 1090 (blue circles) and 1265 (red circles). Isotope values are reported relative to the VPDB (Vienna PeeDee belemnite) standard. (b) Sites 1090 (blue diamonds; Cibicidoides spp.) and 1265 (red diamonds; C. praemundulus) benthic foraminiferal Mg/Ca ratios in mmol/mol uncorrected for changes in the deep water carbonate ion concentration associated with Oi-1 [Peck et al., 2010; Lear et al., 2010]; black lines show three-point running average. (c) Unadjusted bottom water temperatures (Site 1090, blue triangles; Site 1265, red triangles) calculated from uncorrected benthic foraminiferal Mg/Ca data in Figure 7b using the benthic foraminiferal calibration of Raitzsch et al. [2008] with the modern-day Mg/Ca seawater value (5.1 mmol/mol) and assuming Mg/Ca = 4.3 mmol/mol at 34 Ma; black lines display three-point running average. Gray bars mark the EOT-1 (Eocene-Oligocene transition event 1), EOT-2 (Eocene-Oligocene transition event 2) and Oi-1 (Oligocene isotope event 1), events occurring at 33.8, 33.63, and 33.54 Ma, respectively [Miller et al., 1991, 2008; Lear et al., 2004; Coxall et al., 2005; Katz et al., 2008].
and 1265 have similar δ13C values prior to EOT-1 and following Oi-1 (Figure 6), likely indicating the presence of northern sourced waters at these two locations prior to EOT-1 and in the earliest Oligocene (Figure 6).

A late Eocene to early Oligocene age for deep water formation in the North Atlantic is considerably older than most previous estimates from benthic foraminiferal δ13C and faunal studies [e.g., Schnitker, 1980; Wright et al., 1992; Wright and Miller, 1996]. Our benthic δ13C record for Site 1265 is consistent with the presence of nutrient-depleted northern sourced water at 2400 m depth in the South Atlantic in the earliest Oligocene (Figure 6). Neodymium isotope records support an early Oligocene age for NCW export production [Scher and Martin, 2004; Via and Thomas, 2006]. Likewise, recent seismic stratigraphic studies from the Southeast Faeroes drift and the northwestern Rockall Trough report an age of 35 Ma in late Eocene for the presence of NCW [Davies et al., 2001; Howe et al., 2001], consistent with prior studies from the northern North Atlantic that noted an erosional pulse associated with reflector R4 spanning the Eocene/Oligocene boundary.

**Figure 8.** ODP Sites 1090 and 1265 benthic foraminiferal δ18O, corrected Mg/Ca, corrected bottom water temperature (BWT), and corrected seawater δ18O records verses age in millions of years. (a) Benthic foraminiferal (Cibicidoides spp.) δ18O records from Sites 1090 (blue circles) and 1265 (red circles). Isotope values are reported relative to the VPDB (Vienna PeeDee belemnite) standard. (b) Sites 1090 (blue diamonds; Cibicidoides spp.) and 1265 (red diamonds; C. praemundulus) benthic foraminiferal Mg/Ca ratios in mmol/mol corrected for changes in the deep water carbonate ion concentration associated with Oi-1 [Peck et al., 2010; Lear et al., 2010]; black lines show three-point running average. (c) Adjusted bottom water temperatures (BWT) corrected for changes in the carbonate ion concentration from Sites 1090 (blue triangles) and Site 1265 (red triangles) calculated from adjusted benthic foraminiferal Mg/Ca data in Figure 8b using the benthic foraminiferal calibration of Raitzsch et al. [2008] with the modern-day Mg/Ca seawater value (5.1 mmol/mol) and assuming Mg/Ca = 4.3 mmol/mol at 34 Ma; black lines display three-point running average. (d) Corrected bottom water δ18O (δw) calculated from benthic foraminiferal δ18O data in Figure 8a and adjusted BWT in Figure 8c using the equation of Shackleton [1974]. Gray bars mark the EOT-1 (Eocene-Oligocene transition event 1), EOT-2 (Eocene-Oligocene transition event 2), and Oi-1 (Oligocene isotope event 1) events occurring at 33.8, 33.63, and 33.54 Ma, respectively [Miller et al., 1991, 2008; Lear et al., 2004; Coxall et al., 2005; Katz et al., 2008].
4.3. Seawater $\delta^{18}O$, Sea Level, and Global Ice Volume

[34] Utilizing the Mg/Ca BWT estimates corrected for changes in the [CO$_2$]$_w$, we attempt to partition the benthic foraminiferal $\delta^{18}O$ records into their temperature and ice volume components. The $\delta^{18}O$ of bottom water ($\delta_{bw}$) for Sites 1090 and 1265 is estimated using the equation below from Shackleton [1974]:

$$\delta_{bw} = \delta_c - [(16.9 - T)/4],$$

where $T$ and $\delta_c$ are the C. praemundulus corrected Mg/Ca temperature and $\delta^{18}O$, respectively.

[35] While the Site 1090 $\delta_{bw}$ record lacks data across EOT-1, Site 1265 displays a small $\delta_{bw}$ increase of $\sim0.5\%$ (Figure 8). The estimated 2°C BWT cooling during EOT-1 in the Site 1090 corrected Mg/Ca record would be equivalent to a benthic foraminiferal $\delta^{18}O$ shift of $\sim0.5\%$, which is virtually the entire measured change. Thus, we conclude that EOT-1 is primarily a cooling event accompanied by minimal ice growth.

[36] The Site 1265 $\delta_{bw}$ record adjusted for changes in the [CO$_2$]$_w$ shows a larger shift ($\sim1.0\%$) than for Site 1090 ($\sim0.5\%$) across Oi-1 (Figure 8). The average $\delta_{bw}$ shift across Oi-1 for Sites 1090 and 1265 is $\sim0.75\%$, which equates to an average $\sim70$ m drop in sea level, using either the Pleistocene sea level $\delta_{sw}$ calibration of 0.11%/$10$ m [Fairbanks and Matthews, 1978] or the Oligocene calibrations of 0.10%/10 m [Pekar et al., 2002; DeConto and Pollard, 2003; Katz et al., 2008]. A 0.5 to 1.0% $\delta_{bw}$ shift at Sites 1090 and 1265 equates to a minimum 45 m and maximum 90 m eustatic fall coincident with Oi-1. An average global sea level fall of $\sim70$ m is comparable to earlier independent estimates of a 55–70 m drop associated with Oi-1 determined at other locations using different techniques [Pekar et al., 2002; Miller et al., 2005; Katz et al., 2008].

[37] We estimate an average ice volume increase of $21 \times 10^6$ km$^3$ associated with Oi-1 based on a value of $\sim50\%$ for the Antarctic ice sheet $\delta^{18}O$ [Shackleton and Kennett, 1975] and a 0.75% change in the $\delta_{bw}$ of the oceans. Our ice volume calculation assumes an ice-free world with an average oceanic $\delta^{18}O$ composition of $\sim1.2\%$ and total water volume of $1.39 \times 10^3$ km$^3$ [Shackleton and Kennett, 1975]. Using the $\delta_{bw}$ changes at Sites 1090 and 1265, we estimate the volume of ice on Antarctic coincident with Oi-1 ranged from 14 to $10^3$ km$^3$ to 28 to $10^3$ km$^3$, which is equivalent to $\sim55$ to 115% of the present-day ice sheet [Lythe et al., 2001] with $\sim85\%$ being the average change. Alternately, a less depleted $\delta^{18}O$ value ($\sim45\%$) has been proposed for the earliest Oligocene ice sheet based on evidence for lower $\delta^{18}O$ precipitation values during late Early Cretaceous caused by an intensified hydrologic cycle [White et al., 2001]. A lower ice sheet $\delta^{18}O$ value of $\sim45\%$ yields an average ice volume of $23 \times 10^6$ km$^3$ that is equivalent to nearly 95% of today’s Antarctic ice sheet. We find an earliest Oligocene Antarctic ice sheet of $55$–$115\%$ of its present-day size plausible based on the recent work from Wilson and Layendyk [2009] that suggests the West Antarctic landmass was $10$–$20\%$ larger in area during the latest Eocene.

5. Conclusions

[38] While it has long been recognized that major climate reorganization occurred at the EOT, it has been difficult to differentiate temperature and ice volume changes associated with this event. Our results from ODP Sites 1090 and 1265 show a $0.5\%$ $\delta^{18}O$ increase associated with EOT-1 (33.8 Ma) that reflects a 2°C global cooling event based on benthic foraminiferal Mg/Ca data, with little if any ice growth and sea level change at this time. Our uncorrected Mg/Ca records yield a 3°C warming of bottom water temperatures that are concurrent with Oi-1. The absence of bottom water cooling coincident with Oi-1 is consistent with other deep sea records (i.e., Sites 522 and 1218) [Lear et al., 2000, 2004], but is most likely an artifact of a deepening of the CCD at this time [van Andel, 1975; Rea and Lyle, 2005; Coxall et al., 2005]. Sites 1090 and 1265 BWT and benthic $\delta^{13}C$ records provide evidence for a pulse of Northern Component Water prior to and following the EOT. Reconstructed BWT and seawater $\delta_{bw}$ records corrected for a change in the [CO$_2$]$_w$ show a $\sim1.5$°C cooling and simultaneous $0.75\%$ $\delta_{bw}$ average increase coincident with Oi-1. The $0.75\%$ $\delta_{bw}$ increase during Oi-1 is equivalent to a $\sim70$ m mean eustatic lowering and an ice volume change that is $85$–$95\%$ of the modern Antarctic ice sheet.

Acknowledgments. We thank Eric Tappa for sample analyses and data processing and Mimi Katz, Howie Scher, and Ben Cramer for their insightful discussions and suggestions. We graciously thank Vicky Peck and Carrie Lear for access to their manuscripts recently accepted to Paleoceanography. We thank Rainer Zahn and two anonymous reviewers for editorial reviews and helpful advice to improve our manuscript. Samples for this work were obtained from the Ocean Drilling Program (ODP), which is supported by the U.S. National Science Foundation (NSF) and by Joint Oceanographic Institutions. This research was funded by NSF grants ANT-0732995 (Thunell) and OCE0623256 (Miller).

References


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Martin and colleagues (2008) present a comprehensive review of the paleoceanography of the North Atlantic during the last 500,000 years, emphasizing the role of the Atlantic Meridional overturning circulation (AMOC). They conclude that the AMOC has varied significantly over the past 500,000 years, with important implications for climate change and sea level.

Peck and colleagues (2008) discuss the role of the North Atlantic's deep water formation in regulating global climate and ice volume. They highlight the importance of understanding the processes that control deep water formation and how these processes have varied over time.

Boyer et al. (2002) provide a detailed analysis of the 3D circulation of the Atlantic Ocean using satellite data and ocean models. They conclude that the circulation patterns have changed dramatically over the past century, with significant implications for ocean heat transport and climate regulation.

The study by Miller et al. (2002) provides evidence for changes in ocean chemistry and biogeochemistry during the late Pleistocene, with implications for understanding past climate change and the role of the oceans in the carbon cycle.

The work by Lipps et al. (2002) offers new insights into the role of the North Atlantic Deep Water in regulating global climate, with implications for understanding future climate change.

Overall, these studies demonstrate the importance of understanding the paleoceanography of the North Atlantic, with implications for understanding past climate change and its effects on the global carbon cycle.