Foraminiferal Mg/Ca evidence for Southern Ocean cooling across the Eocene–Oligocene transition

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A B S T R A C T

Constraining the magnitude of high-latitude temperature change across the Eocene–Oligocene transition (EOT) is essential for quantifying the magnitude of Antarctic ice-sheet expansion and understanding regional climate response to this event. To this end, we constructed high-resolution stable oxygen isotope (δ 18O) and magnesium/calcium (Mg/Ca) records from planktic and benthic foraminifera at four Ocean Drilling Program (ODP) sites in the Southern Ocean. Planktic foraminiferal Mg/Ca records from the Kerguelen Plateau (ODP Sites 738, 744, and 748) show a consistent pattern of temperature change, indicating 2–3 °C cooling in direct conjunction with the first step of a two-step increase in benthic and planktic foraminiferal δ 18O values across the EOT. In contrast, benthic Mg/Ca records from Maud Rise (ODP Site 689) and the Kerguelen Plateau (ODP Site 748) do not exhibit significant temperature change. The contrasting temperature histories derived from the planktic and benthic Mg/Ca records are not reconcilable, since vertical δ 18O gradients remained nearly constant at all sites between 35.0 and 32.5 Ma. Based on the coherency of the planktic Mg/Ca records from the Kerguelen Plateau sites and complications with benthic Mg/Ca paleothermometry at low temperatures, the planktic Mg/Ca records are deemed the most reliable measure of Southern Ocean temperature change. We therefore interpret a uniform cooling of 2–3 °C in both deep surface (thermocline) waters and intermediate deep waters of the Southern Ocean across the EOT. Cooling of Southern Ocean surface waters across the EOT was likely propagated to the deep ocean, since deep waters were primarily sourced on the Antarctic margin throughout this time interval. Removal of the temperature component from the observed foraminiferal δ 18O shift indicates that seawater δ 18O values increased by 0.6 ± 0.15‰ across the EOT interval, corresponding to an increase in global ice volume to a level equivalent with 60–130% modern East Antarctic ice sheet volume.

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1. Introduction

Long-term cooling through the middle and late Eocene culminated in the rapid onset of continent-wide Antarctic glaciation at the Eocene–Oligocene transition (EOT), approximately 34 million years (Ma) ago (Miller et al., 1987, 1991; Zachos et al., 2001). In marine geochemical records, the primary evidence for paleoceanographic change across the EOT is an abrupt ~1.2–1.5‰ increase in δ 18O values of deep-sea benthic foraminifera (Coxall et al., 2005; Diester-Haass and Zahn, 1996, 2001; Miller et al., 1987; Riesselman et al., 2007; Zachos et al., 1992, 1996). The cause of the shift in marine carbonate δ 18O values has been the focus of much discussion and debate. Early studies that first documented this event in deep-sea cores (Kennett and Shackleton, 1976; Savin, 1977; Savin et al., 1975; Shackleton and Kennett, 1975) and outcrop sections (e.g. Devereux, 1967) attributed the δ 18O shift entirely to marine cooling (4–6 °C). Subsequent studies confirmed the isotope stratigraphy and dating of this event at multiple deep-sea sites, and interpreted a minor-to-moderate contribution of ice volume (e.g. Keigwin, 1980; Keigwin and Corliss, 1986; Miller and Curry, 1982; Murphy and Kennett, 1986; Shackleton, 1986; Shackleton et al., 1984; Wise et al., 1985) or significant ice accumulation in the early Oligocene (Matthews and Poore, 1980, 1981; Poore and Matthews, 1984; Prentice and Matthews, 1988). The discovery of proximal glaciomarine sediments in drill cores from shelf areas of the Ross Sea and Prydz Bay provided direct confirmation of widespread Antarctic glaciation during the early Oligocene (Hambrey and Barrett, 1993; Hambrey et al., 1991), but the extent of these early ice sheets, as well as the extent of glaciation in the Northern Hemisphere (Eldrett et al., 2007; Tripati et al., 2008), has remained in question.

Quantifying the timing and magnitude of global ice-volume and temperature change across the EOT is important for understanding this major climatic shift—the most significant step in the
progression from the early Cenozoic 'Greenhouse' to the late Cenozoic 'Icehouse'. Most critically, detailed knowledge of changes in these fundamental climatic parameters is required for assessing different possible causal mechanisms. One approach to deconvolving the ice-volume and temperature components embedded in the benthic foraminiferal $\delta^{18}O$ signal is to combine oxygen isotope analyses with an independent temperature proxy, such as Mg/Ca ratios. However, direct interpretation of changes in benthic foraminiferal Mg/Ca ratios across the EOT at pelagic, deep-sea sites has so far not provided evidence of cooling associated with the $\delta^{18}O$ shift (Billups and Schrag, 2003; Lear et al., 2000, 2004).

If deep waters did not cool across the EOT, the benthic foraminiferal $\delta^{18}O$ increase of ~1.2–1.5‰ requires a total global ice-volume equivalent to 1.5 to 3.0×the present volume of the East Antarctic Ice Sheet (EAIS) (Coxall et al., 2005). In the absence of evidence for significant ice accumulation in the Northern Hemisphere, some degree of marine cooling across the EOT must therefore have occurred to account for both the magnitude of the $\delta^{18}O$ shift and the limits of Antarctic ice storage. Indeed, several recent studies using paired $\delta^{18}O$–Mg/Ca analysis of foraminifera in shallow-water shelf sections (Katz et al., 2008; Lear et al., 2008) and organic-biomarker proxies (TEX86 and $U^37$) at multiple sites (Liu et al., 2009) have detected cooling in association with the $\delta^{18}O$ increase. It has also become evident that benthic foraminiferal Mg/Ca ratios are influenced by changes in deep-water carbonate ion concentration (Elderfield et al., 2006; Yu and Elderfield, 2008), and the combined application of benthic foraminiferal Mg/Ca and Li/Ca ratios has been used to re-interpret benthic foraminiferal Mg/Ca records at pelagic, deep-sea sites (Lear and Rosenthal, 2006; Lear et al., 2010). Although cooling is now documented across the EOT at several sites, there are large differences in the interpreted magnitude of the ice volume-driven change in seawater $\delta^{18}O$($\delta^{18}O_{SW}$) values, ranging from 0.2 to 1.2‰ (Katz et al., 2008, 2011; Lear et al., 2008, 2010; Liu et al., 2009; Peck et al., 2010; Pusz et al., 2011).

In order to address outstanding questions regarding the nature of the $\delta^{18}O$ shift across the EOT, we have developed high-resolution foraminiferal $\delta^{18}O$ and Mg/Ca temperature records for the time interval between ~35.0 and 32.5 Ma at four Southern Ocean drill sites. We employed a strategy of paired Mg/Ca and $\delta^{18}O$ analysis of both benthic and deep-dwelling planktonic foraminifera. The primary objective of this work was to constrain high-latitude temperature and global $\delta^{18}O_{SW}$ changes, and hence ice-volume variation, across the EOT.

## 2. Methods

### 2.1. Site locations

Foraminiferal $\delta^{18}O$ and Mg/Ca records were constructed across the EOT intervals of Ocean Drilling Program (ODP) Sites 689, 738, 744, and 748 (Supp. Fig. S1). Site 689 is located on Maud Rise (~64.5°S) in the Atlantic sector of the Southern Ocean. Sites 738, 744, and 748 are located on the southern Kerguelen Plateau in the Indian sector of the Southern Ocean (58–62°S) (Table 1). Using standard subsidence calculations described in Bohaty et al. (2009), relatively shallow paleodepths are estimated for all sites, spanning a range of bathyal water depths from ~800 to 1900 m (Table 1). Accordingly, paleoceanographic records derived from benthic foraminifera in these sections provide a history of changes in temperature and bottom-water chemistry for intermediate deep-water masses in the Southern Ocean.

### 2.2. Sample material

Samples for foraminiferal stable isotope and minor element analysis were obtained from ODP Holes 689B, 689D, 738B, 744A, and 748B at a sample spacing of 2 to 10 cm. New benthic stable isotope and minor element ratio (Mg/Ca and Mn/Ca) records were generated for Holes 748B and 689D (Figs. 1 and 2). For both analyses, 5–10 specimens of Cibicidoides praemundulus were used from each sample level, with a total sample mass of 250–700 μg. Specimens of C. praemundulus were picked from the 250–355 μm sieve fraction, and, in intervals where sufficient C. praemundulus specimens were not available, other undifferentiated Cibicidoides spp. were used in substitution.

Planktonic foraminiferal stable isotope and minor element ratio (Mg/Ca and Mn/Ca) records were generated for Holes 689B, 689D, 738B, 744A, and 748B using Subbotina angiporoides (Figs. 1 and 2). S. angiporoides is an extinct taxon that maintained a deep thermocline habitat, which we refer to here as 'deep surface' habitat since a well-developed thermocline may not have existed in the EOT interval at these high-latitude sites. In most intervals, specimens of S. angiporoides were picked from the 250–300 μm sieve fraction. In intervals where sufficient specimens were not present in the 250–300 μm range, specimens from the 212–250 μm fraction were used to supplement those from the larger fraction (bracketed intervals in Fig. 2). 10 to 15 specimens of S. angiporoides were used for stable isotope analysis, and 30 to 50 specimens were used for minor element analysis, with total sample masses of ~100 to 180 μg and ~300 to 600 μg, respectively, for each analysis. Additional notes

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concerning age models, carbonate preservation, and ecology of foraminiferal taxa used in this study are included in the supplementary materials.

2.3. Stable isotope and elemental analyses

Stable isotope analyses were performed using VG Prism and Optima dual-inlet isotope-ratio mass spectrometers at the University of California, Santa Cruz. Stable isotope ratio results are reported using standard delta notation (denoted $\delta$) in parts per mil (‰) relative to Vienna Pee Dee Belemnite (VPDB). NBS-19 was used as the primary reference standard, and an in-house standard prepared from Carrara marble was routinely analyzed in all runs. Long-term (inter-run) precision (1 s.d.) for $\delta^{18}O$ is estimated at 0.06‰. An equilibrium offset adjustment of +0.64‰ is applied to all Cibicidoides $\delta^{18}O$ values reported in this study.

Multi-specimen samples of planktic and benthic foraminifera were cleaned for minor element analysis using reductive, oxidative, and partial-dissolution steps, following the ‘Cd-cleaning’ procedure devised by Boyle and Keigwin (1985/86) and refined by Martin and Lea (2002). In order to evaluate the effect of the reductive cleaning step on the measured planktic Mg/Ca and Mn/Ca ratios, this step was omitted in a duplicate batch of 30 samples from Hole 744A (Suppl. Table S2).

Foraminiferal Mg/Ca and Mn/Ca ratios were determined using a Perkin Elmer 4300 Optima DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) at the University of California, Santa Cruz. We followed the method described by Wara et al. (2003) in which two sets of working standard solutions are used to bracket a range of Mg/Ca and Mn/Ca ratios at two different Ca concentrations (~25 ppm and ~95 ppm). Intra-run drift, as well as long-term (inter-run) precision, was monitored using a liquid consistency standard. A foraminiferal consistency standard was also included in every sample rack (30 samples), composed of crushed specimens of the planktonic foraminifer Globigerinatheka index (250–300 µm) picked from a middle Eocene sample of Hole 748B. The long-term mean, standard deviation, and relative standard deviation for the liquid and foraminiferal consistency standards are given in Supplementary Table S1.

In order to evaluate and interpret the temporal trends in the $\delta^{18}O$ and Mg/Ca records, all of the datasets were smoothed with a Gaussian interpolation filter. These analyses were performed within Microsoft Excel using a Visual Basic for Applications macro. The filters were generated in the time domain using a time step of 20 kyr and a filter width of 150 kyr.

3. Results

3.1. Foraminiferal $\delta^{18}O$ records

New planktic and benthic foraminiferal $\delta^{18}O$ results from Sites 689, 738, 744, and 748 were combined with previously published benthic $\delta^{18}O$ records for Sites 689, 738, and 744 (Diester-Haass and Zahn, 1996; Scher et al., 2011; Zachos et al., 1996) for the time interval...
between 35.0 and 32.5 Ma. Despite differences in paleodepth and latitudinal position (Table 1), the benthic foraminiferal δ¹⁸O records (δ¹⁸O_Cib) at all study sites are characterized by similar values and temporal trends (Fig. 1). These records also mirror the high-resolution benthic δ¹⁸O record from equatorial Pacific Ocean ODP Site 1218 (Coxall and Wilson, 2011; Coxall et al., 2005). Most notably, the Southern Ocean sites exhibit a similar two-step increase in δ¹⁸O values across the EOT—here designated as ‘Step 1’ and ‘Step 2’ (Fig. 1). From a latest Eocene δ¹⁸O_Cib baseline of ~1.9–2.0‰, Step 1 at 34.0 Ma is marked by a ~0.4‰ increase, which is followed by a ~200 kyr interval characterized by relatively stable values. This transitional plateau is terminated by a second, larger increase of ~0.8–1.0‰ at ~33.7 Ma during Step 2. Neither a transient late Eocene δ¹⁸O excursion immediately prior to Step 1 (Coxall and Wilson, 2011; Katz et al., 2008) nor a prominent δ¹⁸O excursion within the plateau phase (Katz et al., 2008) is observed in these Southern Ocean records. Combining the two prominent δ¹⁸O steps, the total amplitude of the δ¹⁸O_Cib shift across the EOT interval is ~1.4‰ at Sites 738, 744, and 748 and ~1.2‰ at Site 689. Following this major shift, an extended interval of elevated δ¹⁸O_Cib values occurs between 33.7 and 33.2 Ma (Fig. 1). δ¹⁸O_Cib values then decrease at all sites to values of ~2.8‰ between 33.2 and 32.5 Ma (Fig. 1).

The planktic foraminiferal δ¹⁸O records derived from S. angiporoides (δ¹⁸O_subb) at Sites 689, 738, 744, and 748 display similar temporal patterns to those observed in the benthic foraminiferal records. At all sites, an average total increase in δ¹⁸O_subb Values of ~1.1‰ is observed across two steps between 34.0 and 33.7 Ma (Fig. 1). In contrast to the δ¹⁸O_Cib records, systematic offsets in δ¹⁸O_subb values are present between the study sites. The lowest δ¹⁸O_subb values are recorded at Site 748, and the highest δ¹⁸O_subb Values are recorded at Site 689 (Fig. 1).

### 3.2. Foraminiferal Mg/Ca records

At Site 748, S. angiporoides Mg/Ca ratios average 2.02 mmol/mol between 35.0 and 34.0 Ma (n = 70; 1 s.d. = 0.12 mmol/mol), decrease to a minimum of ~1.7 mmol/mol between 34.0 and 33.2 Ma, and then increase to ~2.0 mmol/mol at 33.2 Ma (Fig. 2a). In contrast with the S. angiporoides record, the benthic Mg/Ca record for C. praemundulus at Site 748 displays more inter-sample variability and does not exhibit a distinct temporal trend (Fig. 2a). Mg/Ca ratios for C. praemundulus range between ~1.2 and 1.9 mmol/mol and average ~1.53 mmol/mol (n = 140; 1 s.d. = 0.16 mmol/mol) through the entire study interval.

Sediments within the EOT interval of Sites 738 and 744 were deposited at similar paleodepths (~1750 to 1900 m), and the two sites are located in close proximity to one another on the southern tip of the Kerguelen Plateau (Supp. Fig. S1, Table 1). Therefore, the Mg/Ca data for S. angiporoides were combined for both sites (Fig. 2b). Relatively high Mg/Ca ratios (~2.0 and 2.4 mmol/mol) are observed between 35.0 and 34.0 Ma, followed by a broad interval of lower Mg/Ca ratios (~1.8 mmol/mol) between 34.0 and 33.2 Ma. A gradual increase in Mg/Ca ratios begins at 33.3 Ma and continues to 32.5 Ma, peaking in the youngest part of the record.

On average, S. angiporoides samples prepared with both the oxidative and reductive steps have Mg/Ca ratios that are 0.085 mmol/mol (4.1%) lower than samples cleaned using only the oxidative step (n = 30; Suppl. Table S2). This result is in line with comparison studies of cleaning methods that show a systematic reduction in foraminiferal Mg/Ca ratios by up to ~10–15% when the reductive step is used (Barker et al., 2003; Yu et al., 2007). Despite slightly higher Mg/Ca ratios, the samples cleaned with only the oxidative step display a similar temporal pattern across the EOT as the samples cleaned with both oxidative and reductive steps (Fig. 2b, yellow squares), and the minor reduction in Mg/Ca ratios that results from the reductive step is small relative to the absolute change in Mg/Ca ratios observed across the EOT (Fig. 2b).

At Site 689, Subbotina angiporoides Mg/Ca ratios range between 1.2 and 2.2 mmol/mol, and C. praemundulus Mg/Ca ratios range between 1.3 and 2.1 mmol/mol. Both planktic and benthic Mg/Ca records exhibit considerable inter-sample variability at Site 689, but aside from a minimum in both records between 33.9 and 33.7 Ma, no distinct temporal patterns in Mg/Ca are evident (Fig. 2c).

### 4. Interpretation

#### 4.1. Latitudinal and vertical δ¹⁸O gradients

The high coherency of the planktic and benthic δ¹⁸O records from Sites 689, 738, 744, and 748 between 35.0 and 32.5 Ma (Fig. 1) is evident in the filtered records (Fig. 3a–b). The benthic foraminiferal δ¹⁸O records from the four sites are within ~0.35‰ of each other through the duration of the study interval. In contrast, the planktic foraminiferal δ¹⁸O records are offset according to site latitude (Fig. 3a). An average difference in δ¹⁸O_subb values of ~0.4‰ is calculated between the most southerly site (Site 689; 64.5‰) and the most northerly site (Site 748; 58.4‰) (Fig. 3d). If this gradient is assumed to be entirely a function of temperature, these differences indicate that the deep surface waters were ~2.0 °C warmer at Site 748 than at Site 689 throughout the EOT interval.

The difference between benthic and planktic foraminiferal δ¹⁸O values (δ¹⁸O_Cib–δ¹⁸O_subb) provides an indication of vertical temperature gradients between the deep surface layer and the seafloor. Site...
4.2. Mg/Ca temperature records

A common temporal pattern is observed in the S. angiporoides Mg/Ca records at Sites 738, 744, and 748 (Fig. 4a). At these three sites, a distinct decrease in S. angiporoides Mg/Ca ratios occurs in conjunction with Step 1 of the δ¹⁸O shift. Temperature anomalies calculated from the filtered records indicate a coherent pattern of temperature change in deep surface waters over the southern Kerguelen Plateau, with an average cooling of 2.6 ± 0.8 °C in the interval between 34.0 and 33.2 Ma (Fig. 4b). Following this cooling phase, a warming occurs in the youngest part of the records between 33.2 and 32.5 Ma (Fig. 4b). Mg/Ca ratios from S. angiporoides at Site 689 are generally comparable or lower than those obtained from S. angiporoides at the Kerguelen Plateau sites (Fig. 4a). In contrast to the Kerguelen sites, however, a consistent pattern of temperature change is not observed at Site 689 (Fig. 4b).

Benthic Mg/Ca records from Sites 689 and 748 exhibit significant variability and show no consistent pattern of change (Figs. 2 and 4c). Temperature anomalies calculated from these data indicate limited temperature variation (± 1.5 °C) with no distinct trends between 35.0 and 32.5 Ma (Fig. 4d). These data are in agreement with previously published benthic Mg/Ca temperature records at Site 689 and other deep-sea sites which indicate limited temperature change or warming in records that are not corrected for changes in carbonate ion saturation (Billups and Schrag, 2003; Lear et al., 2000, 2004). Even though Sites 748 and 689 were positioned at relatively shallow paleo-depths above the lysocline (≈800 and 1500 m, respectively; Table 1), it is likely that changes in carbonate ion saturation influenced the benthic Mg/Ca signals (Peck et al., 2010). Thus, it is unclear if temperature was the primary control on Mg/Ca records at these sites. This issue can be only assessed with additional proxy data that provide information on carbonate ion saturation state, such as benthic foraminiferal B/Ca and Li/Ca ratios (Lear and Rosenthal, 2006; Lear et al., 2010; Yu and Elderfield, 2007), which were not collected in this study.

The conflicting temperature histories interpreted from the benthic and planktic foraminiferal Mg/Ca records (Fig. 4) could be explained by cooling of deep surface waters with no concomitant temperature change in bottom waters at these sites. As discussed above, however, the relative stability of vertical δ¹⁸O gradients indicates a common temperature evolution for both the upper and lower levels of the water column. Therefore, the Mg/Ca paleotemperature estimates give contradictory indications that cannot be explained by invoking differential temperature changes between the upper water column and seafloor.

Although there are several possible means by which either the planktic or benthic Mg/Ca temperature records from the Southern Ocean study sites may have been compromised, we interpret the S. angiporoides Mg/Ca temperature records from the Kerguelen Plateau (Sites 738, 744, 748) as providing the most reliable measure of Southern Ocean temperature change across the EOT. This assertion stems from evidence of a strong carbonate-ion influence on benthic foraminiferal Mg/Ca ratios (e.g., Elderfield et al., 2006; Lear and Rosenthal, 2006; Yu and Elderfield, 2008) and uncertain Mg/Ca-temperature sensitivity for Cibicidoides spp. at low temperatures (e.g., Yu and Broecker, 2010; Yu and Elderfield, 2008). Potential processes that may have compromised the primary planktic Mg/Ca signals at the study sites, such as seafloor dissolution or Mn-carbonate overgrowths, appear to be minimal (see supplementary materials). There are inconsistencies, however, with this interpretation, including (1) slightly higher S. angiporoides Mg/Ca ratios at Sites 738 and 744 than at the more northerly located Site 748 (Fig. 4a), and (2) the lack of a consistent pattern of temperature change in the S. angiporoides Mg/Ca record from Site 689 (Fig. 4b). Nevertheless, a consistent pattern and magnitude of temperature change throughout the study interval (35.0 to 32.5 Ma) is indicated by the planktic records at Sites 738, 744, and 748, giving reassurance that the signals are robust.

The relative magnitude of cooling interpreted from the S. angiporoides Mg/Ca records is directly dependent on the assumed temperature sensitivity (exponential constant) used to calculate temperature change. Exponential constants ranging from 0.070 to 0.113 have been determined for most modern planktic species (Anand et al., 2003; Cléroux et al., 2008; Dekens et al., 2002; Elderfield and Ganssen, 2000; Lea et al., 1999; Regenberg et al., 2008; Rosenthal and Lohmann, 2002), although a few taxa such as deep-dwelling, non-spinose species have a lower temperature response (Anand et al., 2003; Cléroux et al., 2008).
Subbotina is an extinct genus with a spinose morphology, and there are no direct modern relatives for comparison. Subbotina spp., however, show a similar magnitude of Mg/Ca-temperature change as other planktic taxa within older Eocene intervals (e.g., Tripati and Elderfield, 2004), and we use a range of exponential constant values between 0.08 and 0.10 for the temperature anomaly calculations (see supplementary text).

4.3. Southern Ocean change in δ18Osw

The planktic foraminiferal Mg/Ca results from Sites 738, 744, and 748 provide evidence that directly links the positive increase in δ18Osw, and δ18Osubb values across the EOT to a cooling of deep surface waters in the Southern Ocean that initiated during Step 1 of the δ18O shift. The interpreted magnitude of cooling (2.6 ± 0.8 °C) only accounts for −0.40 to 0.75‰ of the observed average −1.1‰ increase in δ18Osubb values. Therefore, the positive shift in δ18Osubb values must represent a mixed signal of cooling and increased δ18Osw values at Southern Ocean sites. Removal of the Mg/Ca-derived temperature component (Fig. 5b) from the δ18Osubb records (Fig. 5a) constructed at Sites 738/744 and 748 indicates that the average change in δ18Osw across the EOT interval is 0.6 ± 0.15‰ (Fig. 5c). This result is important as it allows further assessment of the magnitude of ice-volume change during the EOT—a primary goal of this study.

Although the long-term δ18Osw trends are consistent between Sites 738/744 and 748 (Fig. 5c), reconstruction of changes in δ18Osw in the transition interval ~34.0 and 33.75 Ma is problematic. In this interval, a negative change in δ18Osw is calculated in both records, resulting from a rapid decrease in Mg/Ca-based temperature that exceeds the equivalent δ18O increase during Step 1 of the transition (Fig. 5c). This negative δ18Osw excursion most likely does not represent a global signal, since a major deglaciation is not congruous with both Southern Ocean surface-water cooling and an increase in foraminiferal δ18O values. One possible explanation for the apparent decrease in δ18Osw between ~34.0 and 33.75 Ma is a transient local decrease in surface-water salinity over the Kerguelen Plateau, which would have acted to decrease the amplitude of the initial foraminiferal δ18O increase (Step 1) and, potentially, decrease planktic Mg/Ca ratios (e.g., Dueñas-Bohórquez et al., 2009; Mathien-Blard and Bassinot, 2009). The effects of a short-term salinity change may have also been combined with a decrease in Mg/Ca ratios due to dissolution within the IRD horizons at Sites 738, 744, and 748 (see supplementary text), thereby amplifying the Mg/Ca cooling signal within these discrete intervals. Regardless of the mechanism controlling the apparent transient negative shift in δ18Osw values, our results do not allow detailed assessment of global δ18Osw change within the ~250 kyr onset and transition interval of the EOT.

5. Discussion

5.1. Earliest Oligocene ice volume

At Sites 738, 744, and 748, an average increase in δ18Osw values of 0.6 ± 0.15‰ is calculated across the EOT (Fig. 5c), which is indicative of a global increase in δ18Osw due to continental glaciation if the local salinity increase was not substantially different than the global mean change. This value agrees well with the estimated −0.6‰ change in δ18Osw derived from paired δ18O–Mg/Ca analysis of planktic foraminifera in drill cores from the Tanzanian shelf (~200–500 m depth) (Leary et al., 2008) and at ODP Site 1263 on Walvis Ridge (~2100 m depth) (Peck et al., 2010). A slightly higher δ18Osw shift of −0.75‰ is interpreted from benthic foraminiferal Mg/Ca and δ18O records from Sites 1090 (Agulhas Ridge; ~3500 m paleo-depth) and 1265 (Walvis Rise; ~2400 m depth), after correction for an assumed carbonate influence on benthic Mg/Ca ratios (Pusz et al., 2011). An increase in δ18Osw of ~0.6‰ across the EOT is also in broad agreement the −0.25 to 0.75‰ increase in global δ18Osw inferred by Liu et al. (2009), who estimated 3.5–5°C cooling of deep waters in conjunction with ~5°C cooling of subantarctic SSTs interpreted from organic biomarker proxy (TEX86 and U13C) records.

In order to make an accurate estimate of the change in ice volume responsible for the shift in δ18Osw across the EOT, an assumption regarding the average isotopic composition of the early Oligocene ice sheets (δ18Oice) is required. If a constant δ18Oice value is assumed, then a linear relationship exists between changes in δ18Osw and ice volume (Fig. 6a). On the other hand, if average δ18Osw values evolved through different stages of glaciation (see discussion in Sima et al., 2006), then a non-linear relationship exists between changes in δ18Osw and ice volume (Fig. 6b). Global climate–ice sheet model simulations with an oxygen-isotope tracer component suggest that the initial small ice caps on Antarctica may have had δ18O values as high as −20 to −25‰ (VSMOW) and that the average δ18Oice value of the expanding ice sheets decreased as air temperatures cooled and ice-sheet elevation increased (DeConto et al., 2008). These model results highlight the need to account for evolving δ18Oice trajectories when interpreting ice volume changes from deep-sea proxy records, particularly during intermediary phases of glaciation. However, in order to calculate peak ice volumes during the earliest Oligocene, only an estimate of δ18Oice for the fully expanded ice sheet(s) is required.

The estimated average δ18Oice value for the modern EAIS is −56.5‰ (Lhomme, 2004; Lhomme et al., 2005) (Suppl. Table S4), but this value is most likely too low for a large Antarctic ice sheet formed in the early Oligocene when high-latitude air temperatures were warmer than present. Model results indicate that the average δ18Oice value of initial large Antarctic ice sheets was ~42‰ or higher (DeConto et al., 2008). We therefore assume that the initial early Oligocene Antarctic ice sheet(s) had an isotopic composition between −45‰ and −35‰. This range takes into account the model results of DeConto et al. (2008) and brackets the modern average δ18Oice.
value of the West Antarctic Ice Sheet (−41%) (Lhomme et al., 2005). It is also close to the modern value of the Greenland Ice Sheet (−34%) (Lhomme et al., 2005).

5.2. Ice volume scenarios

Assuming average δ18Oice values between −45‰ and −35‰ for the early Oligocene Antarctic ice sheet(s), relatively well-constrained ice volume estimates can be made for different scenarios of δ18Osw change across the EOT. Three different scenarios are considered here (Table 2; Fig. 7). Scenario #1 assumes no change in Southern Ocean intermediate deep-water temperatures across the EOT, as suggested by benthic foraminiferal Mg/Ca results from Site 748. In other words, this scenario assumes that the Southern Ocean benthic foraminiferal δ18O signal is entirely a function of ice-volume changes. Scenario #2 utilizes the Δδ18Osw record derived from planktic foraminiferal δ18O and Mg/Ca records at Sites 738, 744, and 748, including the uncertainty associated with the range of assumed Mg/Ca—temperature sensitivities and differences between sites (Fig. 5c). Scenario #3 assumes that the total magnitude of cooling is underestimated from planktic foraminiferal Mg/Ca records, in accordance with the average magnitude of deep-water cooling (−4 °C) inferred by Liu et al. (2009). In this scenario, a cooling step of 4 °C is imposed between 34.0 and 33.6 Ma and sustained between 33.6 and 32.5 Ma; the temperature component, equivalent to a 1.0‰ increase in δ18O (Shackleton, 1974; Eq. D), is subtracted from the filter of the Southern Ocean δ18Osw compilation to generate a residual Δδ18Osw record. The ice-volume estimates for all three scenarios assume ice-free conditions in the latest Eocene, with a pre-glacial baseline δ18Osw value of −1.1‰ (Supp. Table 54; Fig. 7b). The time interval between ~34.0 and 33.7 Ma is not considered in Scenario #2 because of the issues discussed above.

Ice volumes computed with near constant temperature across the EOT (Scenario #1) are unrealistically high, averaging ~4.2 × 107 km3 to ~5.3 × 107 km3 within the ‘Earliest Oligocene Glacial Maximum’ (EOGM) interval (Liu et al., 2004; 33.1 to 33.6 Ma)—equivalent to 165–215% modern EAIS volume (Table 2; Fig. 7c). As discussed in previous studies, limited or no cooling across the EOT is incompatible with independent evidence of ice-sheet activity and extent, requiring the build-up of large ice sheets in both the Antarctic and Northern Hemisphere (Billups and Schrag, 2003; Coxall et al., 2005; Lear et al., 2004). Although ice-rafting records indicate some Eocene glacial activity on Greenland (Eldrett et al., 2007; Tripati et al., 2008), no unequivocal evidence (e.g., well-dated proximal glacial till deposits) exists for large Oligocene ice sheets in the Arctic. Additionally, model simulations by DeConto et al. (2008) suggest that extensive Northern Hemisphere glaciation is only possible at low atmospheric pCO2 levels (<280 ppm), which were likely not reached until the late Oligocene (Pagani et al., 2005, 2011).

More modest ice volumes are estimated in Scenarios #2 and #3. Average ice volumes calculated in Scenario #2 using a range of Δδ18Osw and δ18Oice assumptions (Table 2) vary between ~1.55 × 107 km3 and 3.30 × 107 km3, equivalent to ~60–130% modern EAIS volume (Fig. 7c; Table 2). In the case of more extreme cooling (Scenario #3), average computed ice volumes are smaller, ranging between ~7.9 × 106 km3 and ~1.0 × 107 km3 (~30–40% modern EAIS volume), followed by a return to near ice-free conditions between 33.1 and 32.5 Ma (Fig. 7c). Extensive ice build-up outside of Antarctica is not required in either of these scenarios. At peak ice volume, several small ice sheets may have coalesced to form a single large ice sheet covering East Antarctica (DeConto and Pollard, 2003b) and perhaps even a larger area, if parts of West Antarctica were sub-aerially exposed (Wilson et al., in press). Although sedimentological data from around the Antarctic margin indicate significant glacial activity in the early Oligocene (Hambrey and Barrett, 1993; Hambrey et al., 1991), proximal geological evidence does not provide a clear picture of the maximum size of ice sheet(s) at peak glaciation. Therefore, Scenarios #2 and #3 cannot currently be distinguished on the basis of proximal evidence of

Table 2

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>No temperature change in Southern Ocean deep waters</th>
<th>Pre-glacial δ18O of seawater (‰, VSMOW)</th>
<th>Earliest Oligocene δ18O of seawater (‰, VSMOW)</th>
<th>δ18O of Early Oligocene ice sheets (‰, VSMOW)</th>
<th>% Modern EAIS volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario #1: No temperature change in Southern Ocean deep waters</td>
<td>1.23b</td>
<td>−1.10</td>
<td>0.13b</td>
<td>−45</td>
<td>4.15</td>
</tr>
<tr>
<td>Scenario #2: δ18Osw record from Subbotina δ18O and Mg/Ca</td>
<td>0.45b</td>
<td>−1.10</td>
<td>−0.65b</td>
<td>−45</td>
<td>1.55</td>
</tr>
<tr>
<td>Scenario #3: ~4 °C cooling of Southern Ocean and deep waters across the EOT</td>
<td>0.23b</td>
<td>−1.10</td>
<td>−0.87b</td>
<td>−45</td>
<td>0.79</td>
</tr>
<tr>
<td>0.23b</td>
<td>−1.10</td>
<td>−0.87b</td>
<td>−35</td>
<td>1.02</td>
<td>41</td>
</tr>
</tbody>
</table>

a See Supplementary Table S4.
b Average increase between 33.6 and 33.1 Ma, relative to the late Eocene baseline.
c Lower bound for the increase between 33.6 and 32.5 Ma, relative to the late Eocene baseline.
d Average increase between 33.6 and 32.5 Ma, relative to the late Eocene baseline.
e Upper bound for the increase between 33.6 and 32.5 Ma, relative to the late Eocene baseline.

Fig. 6. Relationship between changes in δ18Osw and global ice volume, calculated using different assumptions for the average bulk δ18O value of the ice sheets (δ18Oice). (A) Ice-volume estimates assuming fixed δ18Osw values between −60‰ and −25‰. (B) Ice-volume estimates assuming evolving δ18Osw values. All calculations assume an initial ice-free state. The vertical gray bar denotes the average early Oligocene increase in δ18Osw (−0.6‰) interpreted from S. angiporoides Mg/Ca and δ18O records at Sites 738, 744, and 748. An additional gray bar in Panel B denotes partitioning of the total 0.6‰ increase in δ18Osw between Step 1 (0.2‰) and Step 2 (0.4‰) of benthic foraminiferal δ18O shift interpreted by Lear et al. (2008).

### Table 2: Ice volume calculations for the early Oligocene.

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e Upper bound for the increase between 33.6 and 32.5 Ma, relative to the late Eocene baseline.
The apparent uncertainties in $\delta^{18}O_{sw}$ calculations in the transition interval, the relative ice-volume contribution to ‘Step 1’ and ‘Step 2’ of the foraminiferal $\delta^{18}O$ signal cannot be assessed using the Southern Ocean Mg/Ca records presented here. Lear et al. (2008) interpret a 0.2‰ change in $\delta^{18}O_{sw}$ during Step 1 and a 0.4‰ change during Step 2. If average $\delta^{18}O_{ice}$ values decreased during initial ice-sheet expansion (DeConto et al., 2008), the 0.2‰ increase in $\delta^{18}O_{sw}$ during Step 1 may reflect the build-up of a moderate-scale ice sheet (~35–50% modern EAI volume in scenarios with $\delta^{18}O_{ice}$ evolving from ~35 to ~45% and ~25 to ~35%). (Fig. 6b). The progressive build-up of East Antarctic ice sheets across the EOT interval is supported by high-resolution fish-tooth neodymium isotope data from Site 738, which suggest increased Antarctic weathering in conjunction with ice expansion during both Step 1 and Step 2 of the $\delta^{18}O$ shift (Scher et al., 2011), as well as far-field records of glacioeustasy during the EOT (Houben et al., in press).

5.3. Global deep-water cooling?

An important question regarding EOT climate change is what component of the benthic foraminiferal $\delta^{18}O$ shift at low and mid-latitude deep-sea sites can be attributed to cooling. Although the processes of deep-water formation most likely differed from those of the modern ocean in the Paleogene, the Southern Ocean is interpreted to have been a primary source of deep water to the world’s ocean basins throughout the middle Eocene–early Oligocene interval (Thomas et al., 2003; Wright and Miller, 1993). Beginning in the late Eocene, however, there is evidence for an additional source of deep water in the North Atlantic region (Davies et al., 2001; Pusz et al., 2011; Via and Thomas, 2006; Wright and Miller, 1993). This raises the possibility that deep-sea sites areas outside the Southern Ocean do not share a similar temperature history, particularly if these sites were influenced by deep waters not sourced from the Antarctic region (Cramer et al., 2009; Ravizza and Zachos, 2003). One approach to evaluate possible differential temperature histories is to examine the gradients between benthic foraminiferal $\delta^{18}O$ records. Since the effects of changes in $\delta^{18}O_{sw}$ due to ice volume changes are globally synchronous, observed offsets in well-correlated records are due to local salinity, temperature, or diageneric differences between different locations. For this exercise, we compare the filtered composite benthic foraminiferal $\delta^{18}O$ record from the Southern Ocean with records from mid-latitude South Atlantic Site 522 (Zachos et al., 1996), subantarctic Atlantic Site 1090 (Pusz et al., 2011), and equatorial Pacific Site 1218 (Coxall and Wilson, 2011; Coxall et al., 2005) (Fig. 8a; Supp. Fig. S1). This comparison shows relatively constant offsets between 35.0 and 32.5 Ma (Fig. 8b), with only a slight decrease in the Southern Ocean–Site 1090 gradient (~0.2‰) across the EOT. These calculations contrast with previous interpretation of an earliest Oligocene increase in the Southern Ocean–Pacific $\delta^{18}O$ gradient (Cramer et al., 2009). Our calculations suggest that deep-water temperature gradients between basins remained relatively constant across the EOT. These observations imply that the interpreted 2–3°C cooling in the Southern Ocean in the earliest Oligocene was matched by synchronous deep-water cooling of similar magnitude at low and mid-latitude sites in both the Pacific and Atlantic basins. Global deep-ocean cooling across the EOT is supported by the model simulations of Liu et al. (2009), which indicate an average deep-ocean cooling of ~4°C in response to high-latitude SST cooling.

There was most likely not a singular causal mechanism for high-latitude and deep-ocean cooling at the EOT, since both long-term tectonic changes influencing Southern Ocean circulation and short-term changes in global carbon cycling occurred in the late Eocene–early Oligocene interval. Progressive deepening of the Tasman Gateway (Stickley et al., 2004) and initiation of proto-Antarctic Circumpolar Current circulation likely cooled both Southern Ocean surface waters
and the deep ocean through the late Eocene (Sipp et al., 2011). Although the opening of Southern Ocean gateways may have also acted to increase in EOT, a range of possible ice volumes between \(\sim 1.55 \times 10^7 \text{ km}^3\) and \(\sim 1.3 \times 10^7 \text{ km}^3\) is slightly lower than the average \(\sim 5^\circ C\) sea surface cooling inferred from foraminiferal Mg/Ca records, however, high-latitude cooling in the earliest Oligocene. The magnitude of cooling at intermediate deep waters of the Southern Ocean. These results suggest that there was a direct link between glaciation and high-latitude cooling in the earliest Oligocene. The magnitude of deep surface cooling interpreted from the Mg/Ca records, however, is slightly lower than the average \(-5^\circ C\) sea surface cooling inferred by Liu et al. (2009) at subantarctic sites. This difference may not be problematic, since subantarctic surface waters may have cooled to a greater degree than deep surface waters further to the south. Alternatively, organic SST proxies at subantarctic sites may have been influenced by changes in thermocline structure, seasonality, and/or vertical mixing of nutrients coincident with the EOT.

Removal of the cooling signal embedded in planktic foraminiferal \(\delta^{18}O\) from Kerguelen Plateau sites results in a calculated average \(\Delta \delta^{18}O_{sw}\) increase of \(0.6 \pm 0.15\%\) across the EOT. This estimate agrees well with the increase in \(\delta^{18}O_{sw}\) interpreted from foraminiferal Mg/Ca and \(\delta^{18}O\) records from the Tanzanian margin (Lear et al., 2008) and Kerguelen Plateau (Peck et al., 2010), suggesting that the global increase in \(\delta^{18}O_{sw}\) was \(-0.6\%\). Assuming ice-free conditions prior to the EOT, a range of possible ice volumes between \(-1.55 \times 10^7 \text{ km}^3\) and \(-3.3 \times 10^7 \text{ km}^3\), equivalent to \(-60\%\) of modern EAS, is calculated for the interval between \(-33.6\) and \(-32.5 \text{ Ma}\). Although there may have been significant short-term fluctuations in ice volume through this early Oligocene interval, we interpret a prolonged period of glaciation that subsequently followed the rapid establishment of a continental-scale Antarctic ice sheet at \(33.7 \text{ Ma}\).

The two-step shift in benthic foraminiferal \(\delta^{18}O\) values across the EOT originally observed at ODP Site 1218 in the equatorial Pacific (Coxall et al., 2005) is confirmed in this study in both planktic and benthic \(\delta^{18}O\) records from multiple Southern Ocean sites. Comparison of the Southern Ocean composite benthic \(\delta^{18}O\) record with lower latitude sites (Sites 522 and 1218) reveals that uniform \(\delta^{18}O\) gradients persisted between \(-35.0\) and \(-32.5 \text{ Ma}\). This demonstrates synchronous cooling of the Southern Ocean and the global deep ocean across the EOT.

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Appendix A. Supplementary data

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References


Cramer, B.S., Toggweiler, J.R., Wright, J.D., Katz, M.E., Miller, K.G., 2009. Ocean overturning and the opening of Southern Ocean gateways may have also acted to...


