A synthesis of Late Oligocene through Miocene deep sea temperatures as inferred from foraminiferal Mg/Ca ratios

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ABSTRACT

Published benthic foraminiferal Mg/Ca records have been compiled that span the latest Oligocene through Miocene, including new data for the South Atlantic. This synthesis, the first such of Mg/Ca data, necessitates consideration of uncertainties and limitations and provides a general perspective on the evolution of deep-sea temperatures over this period. Published Mg/Ca records show temperature patterns through the Miocene that are consistent with those first synthesized by Kennett (1985) utilizing isotope and other data. Accordingly, the early Miocene was an interval of relative warmth culminating in a climatic optimum at ~16 Ma that was characterized by the warmest (Mg-derived) temperatures of the past 20 million years. After the climatic optimum, palaeotemperatures dropped by 3–4 °C during the second major advance of Antarctic ice between ~15 Ma and 13 Ma. For the late Miocene, between 11 and 8.5 Ma, a distinct increase in benthic foraminiferal Mg/Ca ratios at two Atlantic sites provides evidence for deep to intermediate water circulation changes. Thereafter, temperatures close to modern are recorded at all sites. Assuming constant seawater Mg/Ca ratios through time, it can be concluded that the early Miocene climate was generally warmer than today and that by the late Miocene temperatures approached modern values.

Keywords Oligocene, Miocene, palaeotemperatures, palaeoclimate, palaeoceanography, foraminifera.

INTRODUCTION

The Miocene, a time of climatic extremes ranging from an early Miocene climatic optimum at about 16 Ma to the mid-Miocene period of ice growth on Antarctica between about 15 and 13 Ma, has long been of particular interest to palaeoceanographers. A volume synthesizing Miocene climate was published in 1985 in the context of the Cenozoic Paleooceanography Project (Kennett, 1985). Quantitative micropalaeontological data and stable-isotope records provided a view of the evolution of Miocene climate primarily based on results from the Deep Sea Drilling Project. Accordingly, multispecies planktonic oxygen-isotope records from throughout the world ocean suggested that during the early Miocene, surface-water temperatures were warm and meridional surface-water temperature gradients were small, with modern ocean conditions developing after the mid-Miocene expansion of the Antarctic ice sheet (Savin et al., 1985). Benthic foraminiferal faunal assemblages from the Pacific Ocean also indicated warm deep-waters and a less well-stratified water column, in comparison to the modern ocean (Woodruff et al., 1985). Many of the modern forms of benthic foraminifera first appeared during the mid-Miocene, indicative of deep water cooling (Woodruff et al., 1985). In short, these earlier studies documented a relatively warm early Miocene, followed by cooling of high-latitude surface and Pacific deep waters concurrent with mid-Miocene ice sheet expansion.

Much of what is known about past climate change (including the Miocene) comes from the oxygen-isotopic composition of benthic foraminifera. Although this proxy outlines large-scale climate change, the absolute magnitude and the relationship between ice growth and decay and ocean temperature changes cannot be determined uniquely. Foraminiferal δ18O values reflect the δ18O value of seawater due to global storage of ice at the poles and regional changes such as...
evaporation and precipitation at the sea surface, as well as the water temperature in which the organism calcifies. Thus, certain assumptions are required in order to interpret the records with respect to any of the palaeoenvironmental indicators (e.g. ice volume versus palaeotemperature). This inherently limits the degree to which past changes in temperature and ice-volume can be quantified.

The recent development of foraminiferal Mg/Ca ratios as a proxy for palaeotemperatures provides an opportunity to improve our understanding of past climate change. Several studies have explored the potential of this approach to resolve questions of longer term climate change. In particular, Lear et al. (2000) constructed a record of benthic foraminiferal Mg/Ca ratios to constrain first-order changes in Cenozoic deep-water temperature and, in conjunction with the foraminiferal δ¹⁸O values, the evolution of the isotopic composition of seawater. Billups & Schrag (2002) then developed higher-resolution records focused on the mid-Miocene and the Eocene, both periods of ice-sheet expansion. Other subsequent studies have further improved the temporal resolution of pre-Pleistocene Mg/Ca records, affording a more detailed view of Cenozoic climate change (Lear et al., 2003, 2004; Shevenell et al., 2004). These studies have elucidated the nature of the relationship between the temperature of seawater and its oxygen-isotopic composition, leading to new insights into the mechanisms of climate change.

The objective of this study is to compile published late Oligocene through Miocene Mg/Ca-derived palaeotemperature records. Collectively, these studies provide a continuous view of the evolution of Miocene palaeotemperatures in different parts of the world’s oceans (Fig. 1). For the late Miocene, sufficient published records now exist to constrain deep and intermediate water temperatures in the Atlantic, Southern Ocean, and Pacific. To augment this array of data, a new benthic foraminiferal Mg/Ca record from the South Atlantic is presented (Ocean Drilling Program Site 1088, Fig. 1). It will be shown that, taken together, these geochemical records provide a perspective on Miocene climate history that is not substantially different from those of earlier reconstructions presented in Kennett (1985).

**Mg/Ca palaeothermometry**

Foraminiferal Mg/Ca ratios depend primarily on the temperature and the Mg/Ca ratio of the seawater in which the foraminifera calcify. Thus, if seawater Mg/Ca ratios can be constrained, or if it is assumed that these ratios are invariant on the time scale under consideration, then foraminiferal Mg/Ca ratios provide a quantitative proxy for water temperature. On the relatively short time scales of the Quaternary, when secular changes in seawater Mg and Ca concentrations are not significant because of the long residence times of these cations (~13 Myr and 1 Myr, respectively; e.g. Broecker & Peng, 1982), the tool has been widely used to reconstruct absolute sea-surface temperatures (e.g. Hastings et al., 1998; Elderfield & Ganssen, 2000; Lea et al., 2000; Stott et al., 2004). Currently, a number of temperature calibrations exist for planktonic (Nürnberg et al., 1996; Lea et al., 1999; Dekens et al., 2002; Rosenthal & Lohmann, 2004; Anand et al., 2003) and benthic (Lear et al., 2002; Martin et al., 2002) foraminiferal species, offering a multitude of opportunities for quantifying palaeoclimatic change.

General limitations associated with the Mg/Ca ratio proxy include calcite dissolution, diagenesis, insufficient removal of clays, and seawater carbon chemistry. Dissolution removes those portions of a foraminiferal shell that contain higher Mg/Ca ratios because Mg destabilizes the crystal lattice (Brown & Elderfield, 1996; Dekens et al., 2002; Fehrenbacher et al., 2006). Diagenesis adds inorganic calcite which, owing to a larger Mg distribution coefficient than biotic calcite, has comparatively higher Mg/Ca ratios than biogenic calcite (Morse & Bender, 1990; Carpenter & Lohmann, 1992).
Incomplete removal of high-Mg aluminosilicate clays from a test may yield abnormally high Mg/Ca ratios (Barker et al., 2003). In fact, the foraminiferal cleaning protocol may affect how effectively contaminants such as clays and manganese crusts are removed from the tests (e.g. Rosenthal et al., 2002). Lastly, recent studies have shown that at low seawater carbonate-ion concentrations there is a ‘carbonate-ion effect’ on benthic foraminiferal Mg/Ca ratios (Dekens et al., 2002; Martin et al., 2002; Elderfield et al., 2006).

It is possible to mitigate some of these factors. Sites can be chosen above a certain water depth to minimize carbonate-ion concentration effects on Mg incorporation into a test and post-depositional dissolution effects on Mg removal from a test. Scanning electron microscopy may show evidence of euhedral inorganic calcite crystals on a test. An inverse relationship between Mg/Ca and Sr/Ca ratios in a sample can be used as an identifier of diagenesis, because the Sr/Ca ratios of inorganic calcite are lower than in biogenic calcite (Baker et al., 1982; Morse & Bender, 1990; Carpenter & Lohmann, 1992). Clay contamination can be detected by measuring the Al content of samples (Barker et al., 2003).

With respect to the synthesis presented here, these uncertainties limit the comparison of absolute palaeotemperatures. Sites discussed here come from different water depths relative to the lysocline, and temporal changes in the lysocline differ among the sites. Thus post-depositional dissolution cannot be ruled out as having affected foraminiferal Mg/Ca ratios and palaeotemperature reconstructions. Furthermore, as detailed below, samples were cleaned and analyzed using different methods, which is now known to introduce differences in the Mg-derived temperature values (Rosenthal et al., 2002). In this regard, the temperature reconstructions presented below are intended to provide a general view of Miocene climate evolution.

Additionally, on long time scales, an important caveat arises from uncertainties in fluctuating Mg/Ca ratios of seawater through time. As recently collated by Tyrrell & Zeebe (2004), a variety of lines of evidence, including geochemical models (Hardie, 1996; Wilkinson & Algeo, 1998; Stanley & Hardie, 1998), measurements of fluid inclusions (e.g. Lowenstein et al., 2001) and porefluids (Fantle & DePaolo, 2006), have been used in an attempt to constrain changes in seawater Mg/Ca ratios through time. Mg/Ca ratios tend to increase toward the modern in all cases, but the rate of change differs (Fig. 2), illustrating the complexity of Mg$^{2+}$ and Ca$^{2+}$ cycling through carbonate and silica reservoirs. As noted above, the residence times of Mg$^{2+}$ and Ca$^{2+}$ in seawater are ~13 Myr and 1 Myr, respectively. Therefore, although absolute palaeotemperatures for the Oligocene and Miocene

![Fig. 2. Examples of Cenozoic seawater Mg/Ca ratios. Curves from the geochemical box models of Wilkinson & Algeo (1998) are marked by filled and open circles; the curve using a two end-member mixing model of Stanley & Hardie (1998) is marked by diamonds. The vertical bars indicate seawater Mg/Ca ratios determined from halite fluid-inclusions (Lowenstein et al., 2001). In all cases, Mg/Ca ratios increase toward the present, but the rate of change differs.](image-url)
must be interpreted with caution, but the amplitude of change occurring over less than 1 Myr is robust. It should be noted that none of the Mg-derived palaeotemperature records reviewed here include a correction for temporal changes in seawater Mg/Ca ratios. The effects of this simplification on the interpretation of the data with respect to palaeotemperatures will be discussed.

**METHODS**

**Data compilation**

*Site 747*

Located on the Kerguelen Plateau in the Indian Ocean Sector of the Southern Ocean at 1695 m water depth, Ocean Drilling Program Site 747 is south of the modern Polar Frontal Zone and is bathed by the Antarctic Circumpolar Current (Table 1; Fig. 1). With a relatively low resolution (100 kyr), the geochemical record spans the past ~27 Myr (Billups & Schrag, 2002). Mg/Ca ratios (and δ18O values) were measured on *Cibicidoides mundulus* and *Cibicidoides wuellerstorfi*. A ~0.2 mmol mol⁻¹ Mg/Ca species offset was determined, and C. mundulus Mg/Ca ratios were adjusted (by ~0.2 mmol mol⁻¹) to those of C. wuellerstorfi.

Since the publication of the Site 747 study in 2002, a number of Mg/Ca temperature calibrations have become available. The genus-specific *Cibicidoides* calibration of Lear *et al.* (2002) may now be used to calculate palaeotemperatures from the Site 747 *Cibicidoides* Mg/Ca ratios. Analytical methods are described in detail by Billups & Schrag (2002) and followed the methodologies of Brown & Elderfield (1996), Hastings *et al.* (1998) and Lear *et al.* (2000), which involve repeated sonication in deionized water and methanol to remove clays as well as sonication in a hot alkaline peroxide solution to oxidize organic matter. Mg/Ca ratios were measured on an inductively coupled plasma - atomic emission spectrometer (ICP-AES) following the method outlined by Schrag (1999). Analytical precision of a standard solution was better than 0.3%. Stable isotope splits were analyzed on a Finnegan Mat252 equipped with a Kiel device at Woods Hole Oceanographic Institution with a precision of 0.07 per mille for δ18O.

*Site 1218*

Located in the northern tropical equatorial Pacific at 4828 m of water depth, Site 1218 is bathed by deep Pacific water (Lear *et al.*, 2004; Table 1; Fig. 1). Since the Eocene, the site has drifted north from its more equatorial position with a subsidence of over 1000 m (Lear *et al.*, 2004). During the Eocene through early Miocene, the site was located just above the calcium carbonate compensation depth, and dissolution has removed all but the most dissolution-resistant of the planktonic foraminiferal tests from the latest Oligocene through early Miocene assemblages (Lear *et al.*, 2004).

For the Oligocene/early Miocene interval (30–20 Ma) the temporal resolution of this record is ~40–50 kyr, while across the Oligocene/ Miocene boundary it is between 20–30 kyr. Lear *et al.* (2004) measured Mg/Ca ratios on *Oridorsalis umbonatus*, while *Cibicidoides* were used for the stable-isotope record. Palaeotemperatures were derived using the *O. umbonatus* calibration of Lear *et al.* (2002). The Mg/Ca cleaning procedure was detailed in Lear *et al.* (2004); it involved oxidative as well as reductive steps and analysis by a Finnegan MAT Element Sector Field Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) at Rutgers University, with a long-term precision of 1.2%. Stable-isotope ratios were measured at the Southampton Oceanography Centre using a Europa Geo 20-20 mass spectrometer with an analytical precision of better than 0.1 per mille for δ18O.

<table>
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<th>Longitude</th>
<th>Latitude</th>
<th>Water depth (m)</th>
<th>Palaeodepth (m)</th>
<th>Time Slice</th>
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</table>

nd = not determined, Eo = Eocene, Mio = Miocene. References: 1, Billups & Schrag (2002); 2, Lear *et al.* (2004); 3, Shevenell *et al.* (2004); 4, Lear *et al.* (2003); 5, this study.
Site 1171

Although the major focus of this synthesis is on Miocene deep-water temperatures, the planktonic foraminiferal Mg/Ca record from Site 1171 offers a temperature record spanning the mid-Miocene interval of Antarctic ice sheet growth at orbital scale resolution (Shevenell et al., 2004); hence it is included here. Site 1171 is located at 2150 m water depth within the Antarctic Circumpolar Current, in the sub-Antarctic southwest Pacific (Table 1; Fig. 1). Mg/Ca ratios were measured on the mixed layer dweller *Globigerina bulloides*, for which a Mg/Ca-temperature calibration has been established (Mashiotta et al., 1999). Analytical methods were detailed in Shevenell et al. (2004) and involved oxidative as well as reductive cleaning steps and analysis via ICP-MS, with a precision of 0.7%. Stable-isotope analyses were conducted on separate picks of *G. bulloides* and measured on a Finnegan Mat 251 with a precision of 0.1 per mille for δ¹⁸O.

Sites 926 and 806

Sites 926 and 806 were the subjects of a study to trace deep water masses in the Atlantic since the late Miocene (Lear et al., 2003; Table 1; Fig. 1). Site 926 is located in the equatorial Atlantic on Ceara Rise at 3598 m water depth. It lies above the modern mixing zone of North Atlantic Deep Water and Antarctic Bottom Water. Conversely, Site 806 is located in the western equatorial Pacific at 2521 m water depth and should not be sensitive to changes in deep water masses. As detailed by Lear et al. (2003), Mg/Ca ratios were measured on *C. wuellerstorfi*, *C. mundulus* and *O. umbonatus* using species-specific calibrations to derive palaeotemperatures. Samples were cleaned using oxidative and reductive protocols and analyzed using ICP-MS with an analytical precision of 1.5–1.6%. Stable-isotope records were taken from the literature and augmented by additional analyses (*Cibicidoides*) conducted at Rutgers University using a VG Optima and at the University of Cambridge using a VG Prism with an analytical precision of better than 0.08 per mille for δ¹⁸O.

Site 1088

New benthic foraminiferal (*C. wuellerstorfi* and *C. mundulus*) Mg/Ca data were generated at intermediate water Site 1088 (Atlantic sector of the Southern Ocean; Fig. 1; Table 1). Site 1088, which is located on Agulhas Ridge at about 2000 m water depth, lies in the modern mixing zone of Upper Circumpolar Deep Water and North Atlantic Deep Water. Late Neogene benthic foraminiferal stable-isotope records have illustrated the sensitivity of this region to bottom-water circulation changes from the late Miocene through the early Pliocene (Billups, 2002). Thus, Mg/Ca records were generated with the aim of providing additional constrains on intermediate- and deep-water mass properties during this interval of time.

Geochemical cleaning procedures for the Site 1088 record include several sonication steps in deionized water and methanol to remove fine clays, sonication in NH₄Cl to remove exchangeable ions, sonication in hot, buffered peroxide to oxidize organic matter, and a weak acid leach. Samples were then dissolved in 2% nitric acid (trace metal grade) and analyzed by ICP-AES at the University of South Florida, St. Petersburg. Matrix effects were constrained using standards of varying Mg/Ca ratios; analytical precision (the relative standard deviation of repeat measurements of a reference solution) was better than 0.5 %. Palaeotemperatures were calculated using the genus-specific *Cibicidoides* calibration of Lear et al. (2002) after adjusting *C. mundulus* Mg/Ca ratios as noted above for Site 747. Stable isotope samples were analyzed at the University of California Santa Cruz using a VG Optima with a precision of better than 0.08 per mille for δ¹⁸O.

Age models

Comparison of the different geochemical records necessitates a common temporal reference framework. The Neogene time-scale has recently undergone significant revision with incorporation of orbitally tuned ages for biostratigraphic and magnetostratigraphic datums (Gradstein et al., 2004; Ogg et al., 2008). Two of the records presented here have orbitally tuned ages (Sites 1218 and 926) and are therefore already consistent with the Gradstein et al. (2004) time scale. No adjustments have been made to the originally published ages.

The published age model of the Site 1171 Mg/Ca record is based on biostratigraphic, magnetostratigraphic and stable-isotope control points reported on the Berggren et al. (1995) time scale (Shevenell et al., 2004). Orbitally tuned ages, however, were recently derived for a 1-Myr long mid-Miocene portion of Site 1171 (Holbourn et al., 2005), and...
this age model is adopted here. To derive ages outside the orbitally tuned section, constant sedimentation rates were assumed. It is noted that the ages outside of the 13.2 to 14.3 Ma tuned interval are likely to change as orbitally tuned ages become available for the entire record.

Sites 747, 806 and 1088 do not have orbitally tuned age models. For Site 747, ages were updated to the Berggren et al. (1995) time scale by Billups & Schrag (2002). This age model was revised further by using orbitally tuned ages of Miocene glacial events Mi 1 (23.0 Ma), Mi 3 (13.9 Ma), and Mi 4 (13.2 Ma), which are readily identifiable in the Site 747 $\delta^{18}O$ record, as depth-age control points (Shackleton et al., 2000; Holbourn et al., 2005, Westernhold et al., 2005 respectively) to bring the ages in line with the Gradstein et al. (2004) time scale. Regarding Site 806, Lear et al. (2003) assigned orbitally tuned ages to the original shipboard biostratigraphic datums, so this record is consistent with Gradstein et al. (2004). In the case of Site 1088, Billups (2002) revised the age model using the benthic foraminiferal $\delta^{13}C$ record and tuned ages for the onset (7.6 Ma) and termination (6.6 Ma) of the late Miocene carbon-isotope shift (from Hodell et al., 2001). As additional control points, the depth of the epoch boundaries are correlated with the corresponding ages on the Gradstein et al. (2004) time scale.

Although the geochemical records compiled here are consistent with Gradstein et al. (2004), uncertainties remain that are related to the relatively coarse temporal resolution of the records (e.g. Sites 926, 747, 806, 1088). Therefore, to minimize the impact of age model uncertainties on data interpretations, the discussion of temporal changes in deep-sea temperatures through time is limited to averages within individual Epochs (e.g. early, middle, late Miocene).

RESULTS

Neogene overview

A benthic foraminiferal Mg-derived palaeotemperature record that spans the Neogene, albeit at low temporal resolution, was published in 2002 by Billups & Schrag (Fig. 3). The $\delta^{18}O$ record (Fig. 3A)

Fig. 3. (A) Benthic foraminiferal $\delta^{18}O$ and (B) Mg/Ca-derived palaeotemperature records from Southern Ocean Site 747 (Billups & Schrag, 2002). Note that the left hand y-axis in (B) indicates the Mg/Ca ratios employed to calculate the palaeotemperatures using the Cibicidoides equation of Lear et al. (2002). So-called Miocene glaciation events (Mi events after Miller et al., 1991) are labelled.
A synthesis of Late Oligocene through Miocene deep sea temperatures

During the mid-Miocene, which is equivalent to the Oligocene/Miocene boundary (the Mi1 Miocene glacial event defined in 1991 by Miller et al.), a general decrease toward the late early Miocene climatic optimum, and a step-wise increase during the mid-Miocene, signifying the second major ice growth phase on Antarctica.

Mg-derived palaeotemperatures (Fig. 3B) are relatively warm during the late Oligocene, cool at the Oligocene/Miocene boundary, increase by ~2 °C toward the late early Miocene climatic optimum, and then drop by 3–4 °C during the mid-Miocene, contemporaneously with increasing δ18O values. These palaeotemperature changes are consistent with the conclusions of Shackleton & Kennett (1975), drawn from co-varying planktonic and benthic foraminiferal δ18O records.

At the smaller scale, it becomes apparent that at the Oligocene/Miocene boundary, minimum temperatures are not reached until after the δ18O maximum (Fig. 3B and A respectively). In fact, the δ18O maximum is accompanied by relatively warm temperatures. The smaller-scale early Miocene glaciations (Mi1a and Mi1b), however, are concurrent with cooling events of ~1 °C. At the end of the middle Miocene, there is a brief but pronounced return to warm temperatures, and temperatures increase again during the late Miocene. As discussed by Billups & Schrag (2002), when the δ18O of seawater is derived from these temperatures and the corresponding foraminiferal δ18O values, excellent agreement is observed between increases in the δ18O of seawater and sequence stratigraphic boundaries in the Haq et al. (1987) sea-level curve.

Oligocene/Miocene boundary

The benthic foraminiferal Mg/Ca record of Lear et al. (2004) from the eastern equatorial Pacific Site 1218 provides a highly resolved palaeotemperature history across the Oligocene/Miocene boundary (Fig. 4). As at Site 747 (discussed above), here too, δ18O values are relatively low during the late Oligocene and increase rapidly at the Oligocene/Miocene boundary (Fig. 4A). However, Mg/Ca-derived palaeotemperatures do not show a longer-term increase toward the Oligocene/Miocene boundary; rather, the boundary event is marked by a decrease in Mg/Ca ratios. This appears to be part of a series of warming/cooling cycles that distinguish the late Oligocene (Fig. 4B). Temperatures cool by ~2 °C, which is equivalent to the magnitude of the temperature change observed at Site 747.

Lear et al. (2004) highlighted that in the deep eastern equatorial Pacific, minimum temperatures are reached prior to the δ18O maximum, and that temperatures were already increasing when δ18O values reached a maximum (Fig. 4C provides an expanded view of the boundary). These particular findings are opposite of those recorded at Site 747, where the δ18O maximum precedes the temperature minimum (Fig. 3). It may well be that regional water-mass effects are important in determining the specific relationship between bottom-water temperatures and the δ18O of the benthic foraminifera. For example, Site 747 lies at intermediate water depths in the Southern Ocean, whereas Site 1218 is a deep water site in the eastern Pacific. Alternatively, the true δ18O-temperature relationship may not have been captured by the relatively low temporal resolution record from Site 747.

Middle Miocene

Shevenell et al. (2004) published a high-resolution planktonic foraminiferal Mg/Ca-derived palaeotemperature record from sub-Antarctic Pacific Site 1171 that details the mid-Miocene transition of surface ocean cooling and ice growth on orbital time scales (Fig. 5). Although this record reflects surface-water changes, and the main focus of the present study is the evolution of bottom waters, it is included here because to-date, it is the only temperature record that shows this important climatic transition in any detail. Accordingly, during the interval of ice growth, surface waters cooled in a stepwise fashion by 6–7 °C (Fig. 5A and B). The overall magnitude is larger than in the intermediate waters at the more southwesterly Site 747, which is consistent with generally higher temperature sensitivity of the surface versus the deeper ocean. As Shevenell et al. (2004) discussed, this sea-surface temperature record reveals orbitally (eccentricity) forced temperature variations preceding benthic foraminiferal δ18O values, and hence Antarctic ice-volume change. An expanded view focusing on the mid-Miocene interval of ice growth (Fig. 5C) illustrates how temperatures reached minimum values approximately 100 kyr before δ18O values reached their maximum. Shevenell et al. (2004) proposed that ocean circulation changes played a major role in mid-Miocene global climate cooling, rather than greenhouse gas forcing.
Late Miocene

At South Atlantic Site 1088 (Fig. 1; Table 1), results from Mg/Ca analyses presented here indicate an increase in ratios beginning at about 10 Ma, with a maximum at ~9 Ma and a decrease thereafter until ~7 Ma, whilst foraminiferal $\delta^{18}O$ values remain relatively constant (Fig. 6B and A, respectively). Mg/Ca ratios then fluctuate about a relatively constant mean during the latest Miocene through Pliocene. The increase in foraminiferal $\delta^{18}O$ values during the late Pliocene, signifying growth of ice in the Northern Hemisphere (Fig. 6A), is not accompanied by a decrease in Mg/Ca ratios that would indicate concomitant cooling of the intermediate water mass with the Northern Hemisphere (Fig. 6B).

Continuous Mg-derived palaeotemperature records for late Miocene through Pliocene sections in the western tropical Atlantic (Ocean Drilling Program Site 926) and western tropical Pacific
Site 1171

Fig. 5. (A) Planktonic foraminiferal $\delta^{18}\text{O}$ and (B) Mg/Ca-derived surface-water temperature record from Subantarctic Pacific Site 1171 [Shevenell et al., 2004]. (C) An expanded view of the middle Miocene climate transition. Note that the left hand y-axis in (B) indicates the *Globigerina bulloides* Mg/Ca ratios used to calculate the palaeotemperatures. Records were smoothed using a weighted (10% sampling portion) Gaussian fit (heavy lines). Grey shading highlights the interval of $\delta^{18}\text{O}$ increase and temperature decrease.

In the interim, Atlantic temperatures first increased by 4°C, and then decreased by the same amount with maxima slightly warmer than Pacific deep waters. The Mg/Ca data from the South Atlantic (Site 1088) agrees with the findings from Site 926: a warming of ~4°C is apparent between 10 Ma and 7 Ma. Benthic foraminiferal $\delta^{18}\text{O}$ records from each site (Fig. 7A, B and C, respectively) do not indicate any major climatic changes during this interval of time.
DISCUSSION

Uncertainties in palaeotemperature reconstructions

Changes in seawater geochemistry

On the long time scale of interest in this review, consideration of seawater Mg/Ca ratios becomes important. Although there are large discrepancies, the available data suggest that seawater ratios may have been as much as 2.5 mol mol$^{-1}$ lower than modern during the early Neogene (Fig. 2). Assuming that the partitioning of Mg into foraminiferal calcite from variable seawater ratios is a linear function, Mg-derived temperatures using modern seawater ratios may underestimate palaeotemperatures by a factor of 2 (e.g. equation 1, Lear et al., 2000). Thus, allowing for lower seawater Mg/Ca ratios in the past results in warmer palaeotemperature estimates with the magnitude of the discrepancy decreasing toward the modern. However, these uncertainties do not call into question the direction of change; the early Miocene remains an interval of warmth in comparison to today, although how much warmer than the modern is equivocal. In the late Miocene time slice, on the other hand, the site-to-site comparison of averaged palaeotemperatures is robust, as all sites would be equally affected by changes in seawater Mg/Ca ratios.

Recent studies have demonstrated that benthic foraminiferal Mg/Ca ratios are offset from temperature calibrations when tests precipitate in waters with low carbonate-ion concentration (Dekens et al., 2002; Martin et al., 2002; Fehrenbacher et al., 2006). This effect is different from post-depositional carbonate dissolution (Martin et al., 2002; Lear et al., 2004; Elderfield et al., 2006). It poses an additional uncertainty to temperature reconstructions, in particular if the regional deep-water carbonate-ion concentration changed through time. At ~3700–4300 m palaeodepth, benthic foraminiferal Mg/Ca ratios from Pacific Site 1218 may be the most severely affected by contemporaneous CO$_3^-$ undersaturation (and post-depositional dissolution).

Furthermore, benthic foraminiferal Mg/Ca ratios from the Atlantic sites (926 and 1088) spanning the late Miocene may have been influenced by temporal changes in the carbonate-ion concentration. The late Miocene is known as a period of intense changes in carbonate preservation (King et al., 1997). Specifically, the end of the carbonate crash in the Pacific at about 10.5 Ma (Lyle et al., 1995) corresponds to an increase in carbonate preservation in the Atlantic, which can be explained by enhanced flow of relatively nutrient-depleted (CO$_3^-$ enriched) northern-sourced deep water in the Atlantic (Nisancioglu et al., 2003). Thus an increase in the Mg/Ca ratios, as observed in the
two Atlantic sites at around 11 Ma, may partially reflect an increase in the CO$_3^{2-}$/CO$_2$ concentration associated with new deep-water circulation patterns. Although studies are emerging that seek to quantify the effect of carbonate-ion concentration on foraminiferal Mg/Ca ratios and palaeotemperatures (Dekens et al., 2002; Elderfield et al., 2006), little is known about the changing carbonate-ion concentrations in deep water through time (e.g. Tyrrell & Zeebe, 2004). Hence, at the magnitude of the uncertainty on the temperature reconstructions cannot be estimated.

**Analytical limitations**

The records compiled in this study were constructed using different cleaning methods (e.g. oxidative only, oxidative and reductive, with or without acid leaching) and analyzed using different techniques (ICP-AES versus ICP-MS). Recent

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**Fig. 7.** Comparison of late Miocene palaeotemperature (black symbols) and corresponding $\delta^{18}$O (grey symbols) records from the: (A) North Atlantic; (B) South Atlantic; and (C) Pacific. Records were smoothed using a weighted (10% sampling portion) Gaussian fit (heavy lines). Grey shading highlights an apparent warming of deep waters in the Atlantic between 11 Ma and 8 Ma.
studies have elucidated that Mg/Ca ratios of tests cleaned with a reductive step are lower than those cleaned using only the oxidative step (Rosenthal et al., 2002; Elderfield et al., 2006). Methodological differences among laboratories may introduce an uncertainty of about 2–3 °C (e.g. Rosenthal et al., 2002). Consequently, only a more general discussion of similarities and differences in long-term trends among the sites will be presented here.

**Palaeotemperatures through time**

Modern ocean temperatures at each of the deep and intermediate water sites (Fig. 8A) reflect the relatively warm (2.2 °C) North Atlantic Deep Water bathing tropical Atlantic Site 926, relatively warm intermediate water at South Atlantic Site 1088 (2.6 °C), relatively cold circumpolar waters at Site 747 (1.6 °C), and colder waters filling the deep western (2 °C) and eastern Pacific (1 °C). In the sub-Antarctic southwest Pacific at Site 1171, surface-water temperatures have a relatively large seasonal range (8–12 °C), reflecting the position of the sub-Antarctic frontal zone (Shevenell et al., 2004; Fig. 8A).

At all sites, the reconstructed late Oligocene through Miocene palaeotemperatures are higher than the temperatures in the modern ocean,
regardless of the specific time slice (Fig. 8B I – IV). The least deviation, with respect to the modern, is recorded in the deep eastern Pacific where late Oligocene and early Miocene temperatures are at most 4°C warmer than today, assuming no temporal change in seawater Mg/Ca ratios. In contrast, Southern Ocean (Site 747) water temperatures are up to 8°C warmer than today during these intervals of time (Fig. 8B). The mid-Miocene climatic optimum, which is recorded at Sites 747 and 1171, shows warmer temperatures by 7–10°C. The magnitude of the subsequent cooling, about 6°C at Site 747 and 7–8°C at Site 1171, is also comparable (not shown).

For the late Miocene (Fig. 8B IV), the spatial representation of deep- and intermediate-water temperatures is reasonably good. In contrast to the modern Atlantic-to-Pacific temperature gradient defined by a colder Pacific, during the late Miocene, the western Pacific appears to have remained relatively warm. Only during the late Miocene temperature maximum do the Atlantic and Southern Ocean sites approach, or exceed, temperatures recorded in the Pacific. Lear et al. (2003) proposed that the relatively cool temperatures in the Atlantic flanking the 11–8 Ma warm excursion reflect the formation of cool North Atlantic Deep Water before the closure of the Central American Seaway diverted warmer and more saline waters to the source regions of deep water formation. The authors discussed that this interpretation reconciles benthic foraminiferal carbon-isotope records (a proxy for changes in the relative nutrient content of a water mass) and geophysical evidence (a seismic reflector indicating sediment erosion), which both suggest enhanced North Atlantic Deep Water formation before and after the temperature maximum of 11–8.5 Ma.

An alternate view emerges if it is assumed that this late Miocene Mg/Ca maximum at the Atlantic sites reflects a temporary incursion of warm waters, rather than a relatively high flux of cooler water before and after the event. The begin of the warming event at about 11 Ma is consistent with the timing of the closure of the eastern Mediterranean, which would result in an increase in relatively warm and saline deep- to intermediate-water flowing westward into the North Atlantic (Woodruff & Savin, 1989, 1991), where it may have contributed to Northern Component Deep Water formation (Wright et al., 1992). In the modern ocean, Mediterranean overflow contributes significantly to the temperature and salinity of the North Atlantic Deep Water (e.g. Schmitz & McCartney, 1993). It may be that with continued constriction of the Straits of Gibraltar, the overflow of warm intermediate water lessened and allowed Northern Component Deep Water to cool after ~8 Ma. Temperature proxy records from the higher latitudes of the North Atlantic may help to clarify the mechanisms (e.g. warmer source water or enhanced relative flux) responsible for the late Miocene deep-water warming event in the tropical Atlantic Ocean.

A scenario of increased relative flux of North Atlantic Deep Water between ~11 Ma and 8.5 Ma (as oppose to assuming a temperature change only) would appear to conflict with the benthic foraminiferal δ13C evidence for deep water circulation changes. The difference between Atlantic and Pacific δ13C records is commonly used to infer the relative flux of nutrient-depleted North Atlantic Deep Water in the Atlantic, but this approach assumes that the δ13C value of the source water remained constant through time (for a recent review see Hodell et al., 2006). If the reduced Atlantic-to-Pacific δ13C gradient between ~11 Ma and 8.5 Ma, which was originally interpreted to indicated enhanced North Atlantic Deep Water flux (e.g. Wright et al., 1991 and discussed by Lear et al., 2003, see above) were brought about by an increase in the δ13C value of the Pacific deep water, then the relative flux of North Atlantic Deep Water in the Atlantic cannot be resolved using this approach. Other proxies for deep water flow, such as neodymium isotopes (e.g. Frank et al., 2002), are needed to constrain deep water circulation changes better during this interval of time.

Lastly, as noted above, the beginning of increasing Mg/Ca-derived temperatures in the Atlantic at ~11 Ma is close in timing with the beginning of enhanced carbonate preservation in the Atlantic (King et al., 1997). Recent modelling experiments by Nisancioglu et al. (2003) illustrate that the change in carbonate preservation can be explained by an increase in the southward flux of North Atlantic Deep Water in the Atlantic Ocean, once the Central American Seaway shoals to a depth that obstructs deeper water outflow to the Pacific. Younger, relatively nutrient-depleted North Atlantic Deep Water is characterized by a higher carbonate-ion concentration than older, nutrient-rich southern-sourced deep waters, at least in the modern ocean, so it cannot be ruled out that a portion of the apparent late Miocene warming may indeed
reflect enhanced Mg incorporation in response to an increase in the carbonate-ion concentration of bottom water. If correct, this factor would not change the interpretation of the geochemical records with respect to ocean circulation changes, but it would affect the absolute magnitude of the warming associated with the northern-sourced water mass.

CONCLUSION

This Late Oligocene through Miocene Mg/Ca synthesis provides a first order view of the evolution through time of deep, intermediate, and for the middle Miocene, surface-water temperatures. The Mg-derived palaeotemperatures support the Miocene climate framework provided by the earlier, δ18O and faunal-based reconstructions of Savin et al. (1985) and Woodruff et al. (1985). The early Miocene was a time of relatively warmth, and it is well after the mid-Miocene that deep and intermediate water temperatures approached a modern distribution.

Although potentially increasing seawater Mg/Ca ratios cannot be accounted for, it is noted that if they were lower, as proposed in some studies, palaeotemperature reconstructions would be even warmer with respect to today. For the late Miocene, Mg-derived palaeotemperatures trace deep and intermediate water circulation changes. However, whether the increase in late Miocene Mg/Ca ratios reflects a warming, enhanced Mg incorporation associated with higher bottom water CO$_3^{2-}$ levels, or a combination of both, cannot currently be resolved.

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