Quaternary Science Reviews 29 (2010) 160–169

Contents lists available at ScienceDirect

Quaternary Science Reviews

journal homepage: www.elsevier.com/locate/quascirev

A record of bottom water temperature and seawater $\delta^{18}O$ for the Southern Ocean over the past 440 kyr based on Mg/Ca of benthic foraminiferal *Uvigerina* spp.

H. Elderfield [a,*], M. Greaves [a], S. Barker [b], I.R. Hall [b], A. Tripati [a], P. Ferretti [a], S. Crowhurst [a], L. Booth [a], C. Daunt [a]

[a] *Godwin Laboratory for Palaeoclimate Research, Dept. of Earth Sciences, University of Cambridge, Downing Street, CB23EQ Cambridge, UK*
[b] *School of Earth and Ocean Sciences, Cardiff University, Park Place, Cardiff, UK*

A R T I C L E I N F O

Article history:
Received 26 January 2009
Received in revised form
14 July 2009
Accepted 21 July 2009

A B S T R A C T

The sensitivity to temperature of Mg/Ca ratios in the shallow-infaunal benthic foraminifera *Uvigerina* spp. has been assessed. Core-top calibrations over ∼1–20 °C show a range in sensitivity of 0.065–0.084 mmol/mol/°C but few data are available spanning the temperature range anticipated in deep-sea records over glacial–interglacial cycles. In contrast to epibenthic foraminiferal species, carbonate ion saturation appears not to affect Mg/Ca significantly. A method based on estimating the ratio of the temperature sensitivity of foraminiferal Mg/Ca to that of $\delta^{18}O_{calcite}$ shows that sensitivity for Mg/Ca at the high end of the observed core-top range (∼0.1 mmol/mol/°C) is required for consistency with LGM–Holocene differences in each property as constrained by independent proxy data. This is supported by a Mg/Ca record for *Uvigerina* spp. generated for the Southern Ocean over the past 440,000 years from Ocean Drilling Program Site 1123 (Chatham Rise, New Zealand). The record shows variability that correlates with climate oscillations. The LGM deep ocean temperature derived from the Mg/Ca record is -1.1 ± 0.3 °C. Transformation to temperature allows estimates to be made of changes in bottom water temperature and seawater $\delta^{18}O$ and comparison made with literature records. Analysis reveals a ∼2.5-kyr lead in the record of temperature over calcite $\delta^{18}O$ and a longer lead over seawater $\delta^{18}O$. This is a reflection of larger phase offsets at eccentricity periods; phase offsets at tilt and precession are within error zero.

1. Introduction

Mg/Ca ratios of foraminifera have the potential to determine the temperature of the seawater in which they calcified and, in combination with foraminiferal $\delta^{18}O$, provide an estimation of seawater $\delta^{18}O$ ($\delta^{18}O_{seawater}$; Mashiotta et al., 1999; Elderfield and Ganssen, 2000). This proxy has been extensively applied to planktonic foraminifera (see Barker et al., 2005, for a review) but the application of Mg/Ca thermometry to investigate deep-sea temperature (and, with $\delta^{18}O$, global ice volume) using benthic foraminifera has been more limited (see Elderfield et al., 2006, and Bryan and Marchitto, 2008, for reviews).

Because Mg/Ca ratios of foraminifera are biologically mediated (Erez, 2003), empirical calibrations studies are essential to determine temperature sensitivity and the roles if any of other contributing factors. Unlike the situation for planktonic foraminifera where calibrations from culture experiments, sediment traps and core-top samples can be compared (most results define temperature sensitivities of 9–10% increase in Mg/Ca per °C), benthic Mg/Ca calibrations have relied almost exclusively on core-top studies. Recent reviews (Elderfield et al., 2006; Bryan and Marchitto, 2008) show a range in temperature sensitivities with values between about 6 and 15% per °C.

An important additional factor recognised in recent work is the influence of carbonate ion saturation ($\Delta[CO_3^{2-}] = [CO_3^{2-}]_{measured} - [CO_3^{2-}]_{saturation}$) on Mg incorporation into benthic foraminifera (Elderfield et al., 2006; Rosenthal et al., 2006) as inferred for other trace elements, Cd, Ba, Zn, Sr, Li and B (McCorkle et al., 1995; Elderfield et al., 1996; Marchitto et al., 2000, 2005; Rosenthal et al., 2006; Lear and Rosenthal, 2006; Yu and Elderfield, 2007). At present there are differences of opinion as to whether the carbonate ion effect is minor (Lear, 2007) or for some species dominates over temperature (Yu and Elderfield, 2008), or is limited to ocean waters near or below saturation or is more extensive (Elderfield et al., 2006; Bryan and Marchitto, 2008).

* Corresponding author. Tel.: +44 1223 333400.
E-mail address: he101@cam.ac.uk (H. Elderfield).

0277-3791/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.quascirev.2009.07.013

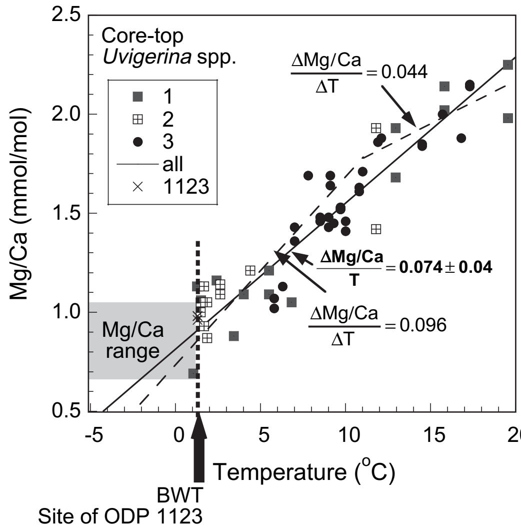


Fig. 1. Mg/Ca versus temperature for *Uvigerina* spp. from sources listed in Table 1 and Table S1. (1) = Yu and Elderfield (2008) and unpublished data, (2) = Elderfield et al. (2006), (3) = Bryan and Marchitto (2008), ("all") = single line showing linear regressions through all data: Mg/Ca = 0.81 ± 0.05 + 0.074 ± 0.004*T* (*r* = 0.96). Dashed lines distinguish slopes for <11 °C (0.096) and >11 °C (0.044). (1123) = core-top data from core CHAT 1K nearby ODP Site 1123. The shaded area shows ±2σ of the mean Mg/Ca measured in core ODP 1123 and the vertical dashed line shows the Bottom Water Temperature (BWT) at Site 1123. Note that all data obtained by oxidative cleaning adjusted by minus 0.2 mmol/mol.

One previous study has estimated bottom water temperature from benthic Mg/Ca for the past ~330 kyr (Martin et al., 2002), and highlighted the potential influence of dissolution (or saturation state) as an important secondary influence requiring further study. In the present study we have followed the approach of Martin et al. (2002) with the purpose of assessing how well bottom water temperature history may be derived from benthic foraminiferal Mg/Ca using *Uvigerina* spp. This genus has a shallow infaunal habitat and, as such, may show a weaker (or perhaps absent) sensitivity to carbonate ion than epifaunal species (Elderfield et al., 2006). Firstly, the approach taken has been to summarise new and literature core-top calibration results for *Uvigerina* spp. followed by two alternative methods of calibration, one of which provides a promising approach. Secondly, we present new benthic *Uvigerina* spp. Mg/Ca data from Ocean Drilling Program (ODP) Site 1123 located in the southwest Pacific sector of the Southern Ocean over the past 440 kyr and convert data into a bottom water temperature record. We assess the fidelity of the record through sensitivity analysis, comparison with other records, and via estimation of $\delta^{18}O_{seawater}$.

2. Mg/Ca calibration data for *Uvigerina* spp.

2.1. Core-top calibrations

In a recent study Bryan and Marchitto (2008) summarized their new and literature calibration data for *Uvigerina peregrina* and *Uvigerina* spp. Although not yet tested thoroughly, there appears not to be significant inter-species differences within the genus *Uvigerina*. Therefore, all literature data have been plotted together (Fig. 1; Table S1) and calibration equations resulting from individual data sets are listed in Table 1. As shown in Table 1 the calibration equations presented in the literature have been presented both in linear and exponential form. The core-top data from the various studies show, overall, an increase in Mg/Ca with increasing bottom water temperature and, when combined, the relationship between Mg/Ca and temperature shows a sensitivity using the linear format of about 0.071 ± 0.005 to 0.084 ± 0.005 mmol/mol/°C (Table 1). This sensitivity is weak compared with *Cibicidoides wuellerstorfi* for which the exponential constant is about 10% per °C; see the compilations of Elderfield et al. (2006) and Bryan and Marchitto (2008). As shown in Fig. 1, the core-top data show a variance equivalent to three or four degrees C which is similar to the expected glacial–interglacial temperature range in the bottom water. Thus, the precise estimation of sensitivity from the core-top summary is difficult.

Bryan and Marchitto (2008) suggest that the Mg/Ca-temperature sensitivity is greater at low temperatures (0.096 mmol/mol/°C < 11 °C) than at higher temperatures (0.044 mmol/mol/°C > 11 °C). This approach to calibration involving more than a factor of two change in slope is not statistically robust but, given the scatter in the data, would seem as valid as use of a single calibration equation.

Table 1
Uvigerina species foraminiferal Mg/Ca – temperature calibrations listed by temperature sensitivity.

Species	Location	Mg/Ca = *c* + *sT*		Temperature range (°C)	Reference
		c	*s*		
U. peregrina	Compilation[a]		0.096	<11	Bryan and Marchitto (2008)
U. peregrina	Compilation[a]	0.70 ± 0.05	0.084 ± 0.005	1.5–17.2	Bryan and Marchitto (2008)
U. peregrina	Florida Straits	0.77 ± 0.08	0.079 ± 0.077	5.8–17.2	Bryan and Marchitto (2008)
Uvigerina spp.	Arabian Sea	0.87 ± 0.21	0.075 ± 0.014	1.7–20	Elderfield et al. (2006)
U. peregrina	Off Somalia	0.91 ± 0.06	0.065 ± 0.011	1.5–11.8	Elderfield et al. (2006)
U. peregrina	Compilation	0.86 ± 0.04	0.071 ± 0.005	1.5–17.2	Bryan and Marchitto (2008)
Uvigerina spp.	Multiple areas	1.09 ± 0.09	0.066 ± 0.008	1.0–19.6	Yu and Elderfield (2008)
Uvigerina spp.	Multiple areas[a]	0.89 ± 0.08	0.067 ± 0.008	1.0–19.6	Yu and Elderfield (2008)
Uvigerina spp.	Compilation[a]	0.86 ± 005	0.070 ± 0.005	1.0–19.6	This study
Uvigerina spp.	Compilation	0.98 ± 006	0.065 ± 0.006	1.0–19.6	This study
U. peregrina	Compilation[a]		0.044	>11	Bryan and Marchitto (2008)
Species	**Location**	**Mg/Ca = *c* exp(*sT*)**		**Temperature range (°C)**	
		c	*s*		
U. peregrina	Florida Straits	0.98 ± 0.04	0.043 ± 0.003	5.8–17.2	Bryan and Marchitto (2008)
Uvigerina spp.	Compilation[a]	0.98 ± 0.05	0.045 ± 0.004	1.0–19.6	This study
Uvigerina spp.	Multiple areas	0.92	0.061	1.8–18.4	Lear et al. (2002)
Uvigerina spp.	Match to *C. wuellerstorfi*	0.76	0.15		Martin et al. (2002)

[a] Mg/Ca of samples without reductive cleaning lowered by 0.2 mmol/mol: see text. The constants have been named *c* and *s* for discussion when compared with the $\delta^{18}O$ paleotemperature Eq. Data in Table S1.

Only two of the 57 samples shown in Fig. 1 had calcification temperature below 1.3 °C, the modern bottom water temperature at the Southern Ocean ODP Site 1123 on which we focus here. Thus, no *Uvigerina* spp. core-top calibration exists that covers the anticipated glacial–interglacial bottom water temperature range at this site.

A possible explanation for the range in temperature sensitivities is that *Uvigerina* spp. Mg/Ca is affected by bottom-water $\Delta[CO_3^{2-}]$ but this seems not to be a major influence. Core-top Mg/Ca versus $\Delta[CO_3^{2-}]$ where data are available shows a significant correlation (Fig. 2A; $r = 0.67$; $n = 46$; $p < 0.0001$) but of course the correlation of bottom water temperature and $\Delta[CO_3^{2-}]$ is also significant (Fig. 2B; $r = 0.87$; $n = 46$; $p < 0.0001$); see Elderfield et al. (2006) for a discussion. Multiple regression of associated Mg/Ca, temperature and $\Delta[CO_3^{2-}]$ data gives a temperature sensitivity of 0.078 ± 0.008 mmol/mol/°C, similar to that described earlier but a $\Delta[CO_3^{2-}]$ sensitivity of 0.002 ± 0.001 mmol/mol/μmol/kg.

The reason why *Uvigerina* spp. may be little affected by bottom-water $\Delta[CO_3^{2-}]$ is that it occupies a shallow infaunal habitat and may calcify from pore waters at 1–2 cm depth within the sediment (Tachikawa and Elderfield, 2002) in which $\Delta[CO_3^{2-}]$ tends to zero (Martin and Sayles, 1996). If correct, core-top calibrations such as Fig. 2A could be misleading for infaunal species where Mg/Ca (and other trace elements) are compared with bottom water $\Delta[CO_3^{2-}]$. Pore water would be expected to be offset from bottom water towards zero values such that changes in element/Ca ratios would reflect smaller changes in $\Delta[CO_3^{2-}]$ than implied from core-top calibration plots. However, the potential influence of respiration on organic matter in the sediments in $\Delta[CO_3^{2-}]$ may be more complex than described here.

2.2. Down-core calibrations

In order to obtain a calibration that would cover the anticipated glacial–interglacial bottom water temperature range at the Southern Ocean site, and help distinguish between the ranges in core-top calibrations at higher temperatures we also estimated temperature sensitivity using approaches based on down-core data. We used benthic foraminiferal Mg/Ca data from ODP Site 1123 and a short core, CHAT 1K which was taken nearby, for the Holocene and Last Glacial Maximum (LGM) (for sampling and analytical details see Section 3).

Our first approach is similar to Martin et al. (2002) who "bootstrapped" down-core *Uvigerina* spp. Mg/Ca to coincide with *C. wuellerstorfi* Mg/Ca data for which they had derived

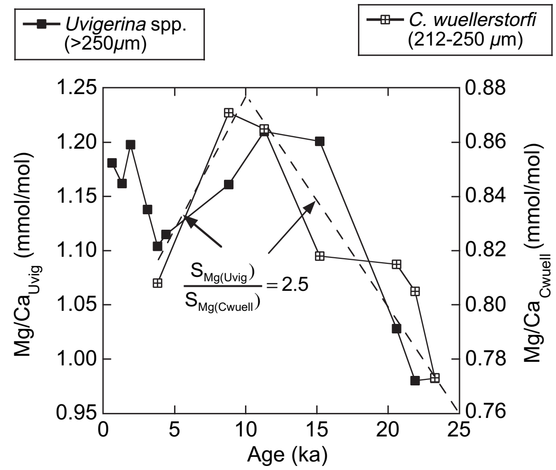


Fig. 3. Mg/Ca of *Uvigerina* spp. and *C. wuellerstorfi* from core CHAT 1K. The data (Table S2) were scaled and the dashed lines show the relationships between data for 3.8–10 kyr and 10–25 kyr, each giving $S_{Uvig}/S_{Cwuell} = 2.5$. Data obtained without reductive cleaning.

a temperature sensitivity based on the exponential format of a 10.9% change in Mg/Ca per °C. From this comparison, they obtained a 15% change in Mg/Ca per °C for *Uvigerina* spp. (that is, a 1.36 times higher sensitivity). In our study, Mg/Ca was determined for coexisting *Uvigerina* spp. and *C. wuellerstorfi* in core CHAT 1K (Fig. 3; Table S2). *C. wuellerstorfi* was extremely sparse in the core and it was necessary to sample smaller sized individuals than for *Uvigerina* spp. Mg/Ca shows similar trends in each species with a significant correlation between values (Fig. 3). Using the linear form of the Mg/Ca-temperature calibration, the ratio of changes in Mg/Ca for each species, is equal to the corresponding ratio in temperature sensitivity (the constant *S*):

$$\frac{S_{(\mathrm{Uvig})}}{S_{(\mathrm{Cwuel})}} = \frac{\Delta \mathrm{Mg/Ca_{Uvig}}}{\Delta \mathrm{Mg/Ca_{Cwuell}}} = 2.5 \quad (1)$$

For an exponential formulation of the calibration this ratio is 1.85, a broadly similar sensitivity to that determined by Martin et al. (2002).

Thus, both Martin et al. (2002) and this study (each based on a down-core record from a single site) show a higher sensitivity of Mg/Ca to temperature for *Uvigerina* spp. than *C. wuellerstorfi.*

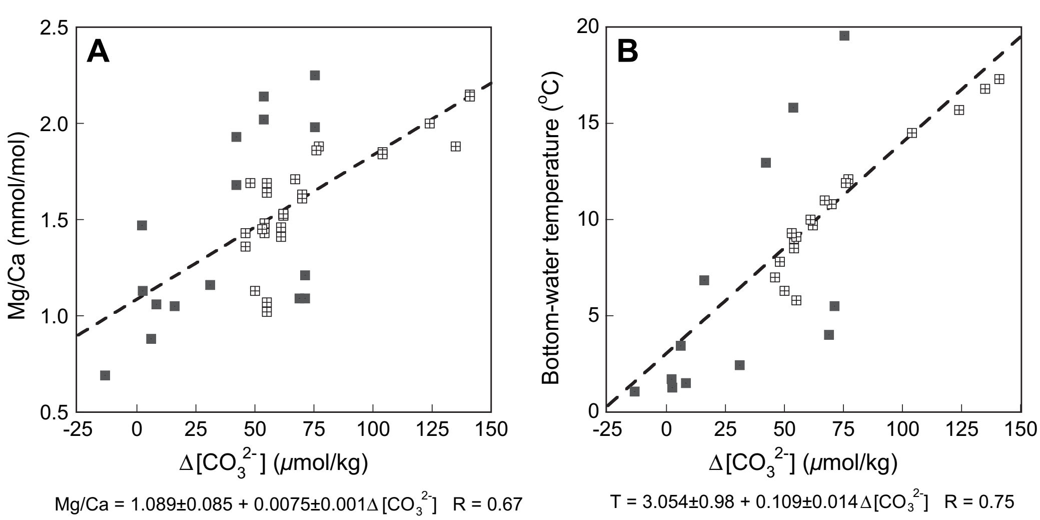


Fig. 2. A. Mg/Ca versus bottom water $\Delta[CO_3^{2-}]$. B. Bottom water temperature versus $\Delta[CO_3^{2-}]$. Symbols as in Fig. 1.

However, this contrasts with core-top studies that produce higher temperature sensitivities of Mg/Ca for *Cibicidoides* than *Uvigerina* species (Section 2.1). The likely reason for this discrepancy lies in the assumption that Mg/Ca ratios in both species are controlled only by bottom water temperature. Observations suggest that Mg/Ca in the epibenthic foraminifer *C. wuellerstorfi* is strongly affected by $\Delta[CO_3^{2-}]$ and that its sensitivity to temperature is weak as shown below (Elderfield et al., 2006). Therefore, it seems that the proportional Mg/Ca sensitivity on temperature and carbonate ion saturation is different for these two species with a weaker $\Delta[CO_3^{2-}]$ control for the infaunal species. On that basis, we have estimated temperature sensitivity of *Uvigerina* spp. from this ratio method using the "$\Delta[CO_3^{2-}]$ corrected" temperature sensitivity for *C. wuellerstorfi*. This is given as 0.056 ± 0.011 mmol/mol/°C by Elderfield et al. (2006) and translated using Eq. (1) to a sensitivity for *Uvigerina* spp. of 0.14 ± 0.03 mmol/mol/°C. However, a much smaller estimate of Mg/Ca-temperature sensitivity, <0.03 mmol/mol/°C, was obtained for *C. wuellerstorfi* by Yu and Elderfield (2008) giving <0.075 mmol/mol/°C for *Uvigerina* spp. using Eq. (1). This uncertainty in apportioning *C. wuellerstorfi* data between a temperature and $\Delta[CO_3^{2-}]$ influence allows us to conclude only (as seen from Fig. 3) that the temperature sensitivity for *Uvigerina* spp. is greater than that for *C. wuellerstorfi*.

The temperature sensitivity for $\delta^{18}O$ in calcite is much better characterised than for Mg, and, therefore, it can be used as a constraint on the Mg sensitivity given measured glacial–interglacial differences and the pore-water derived bottom-water $\delta^{18}O$ change from the same site. (Adkins et al., 2002). Although the LGM bottom water temperature was also estimated by Adkins et al. (2002), it is itself a derived quantity (from $\delta^{18}O_{seawater}$ and measured $\delta^{18}O_{calcite}$) and a better constraint on temperature sensitivity is that LGM temperature derived from Mg/Ca when combined with $\delta^{18}O_{calcite}$ should match the value of $\delta^{18}O_{seawater}$. Although the advantage of ODP Site 1123 is that $\delta^{18}O_{seawater}$ has been independently estimated, this approach could be adopted more generally using $\delta^{18}O_{calcite}$ at any site and estimates of regional variations from the global mean LGM $\delta^{18}O_{seawater}$ (see McCave et al., 2008, for a discussion).

Given the narrow range in bottom water temperatures, linear versions of the paleotemperature equations for Mg/Ca and $\delta^{18}O_{calcite}$ should be adequate for this treatment and rewriting them gives

$$T = \frac{(\mathrm{Mg/Ca}) - C_{\mathrm{Mg}}}{S_{\mathrm{Mg}}} = C_{\mathrm{O}} - \frac{1}{S_{\mathrm{O}}}\left(\delta^{18}\mathrm{O}_{\mathrm{calcite}} - \delta^{18}\mathrm{O}_{\mathrm{seawater}}\right) \quad (2)$$

where S_{Mg} and S_O are sensitivities of Mg/Ca and $\delta^{18}O_{calcite} - \delta^{18}O_{seawater}$ to temperature (C_{Mg} and C_O are constants). It follows that, for a change in Mg/Ca and $\delta^{18}O_{calcite}$, such as between LGM and Holocene,

$$\frac{S_{\mathrm{Mg}}}{S_{\mathrm{O}}} = -\frac{\Delta(\mathrm{Mg/Ca})}{\Delta\delta^{18}\mathrm{O}_{\mathrm{calcite}} - \Delta\delta^{18}\mathrm{O}_{\mathrm{seawater}}} \quad (3)$$

Therefore, the derivation of temperature from Mg/Ca data (S_{Mg}) must be consistent with the derivation of temperature from $\delta^{18}O_{calcite} - \delta^{18}O_{seawater}$ (S_O). The conversion of Mg/Ca to temperature is constrained by the ratio of sensitivities (S_{Mg}/S_O) and, thus, by the temperature sensitivity of the $\delta^{18}O$ paleotemperature equation. The LGM–Holocene difference $\Delta\delta^{18}O_{seawater}$ at ODP Site 1123 is $+1.1 \pm 0.1‰$ (Adkins et al., 2002) with which ΔMg/Ca and $\Delta\delta^{18}O_{calcite}$ data (Fig. 4) can be compared. Using Holocene values of Mg/Ca (1.25 mmol/mol; an average of core-top values for cores ODP 1123 and CHAT 1 K) and $\delta^{18}O_{calcite}$ (3.1‰) and the range in 5 kyr Gaussian interpolated LGM values of 0.96–1.06 mmol/mol and 4.7–4.9‰, respectively, gives S_{Mg}/S_O of 0.4 ± 0.05.

The slope of the $\delta^{18}O$ paleotemperature equation invariably used for benthic foraminifera is −4.0 °C/‰ (a sensitivity, $S_O = 0.25‰$/°C) modified from O'Neil et al. (1969), see also Kim and O'Neill (1997), and calibrated against *Uvigerina* spp. (Shackleton, 1974). The slope of the O'Neil et al. (1969) curve at near freezing temperatures is closer to 0.27‰/°C but because our data are from *Uvigerina* spp. we have used the value of 0.25‰/°C. Consistency with this value of S_O requires a sensitivity of Mg/Ca to temperature, S_{Mg}, of 0.1 ± 0.013 mmol/mol/°C. Using this estimate of S_{Mg} with ΔMg/Ca data (0.24 mmol/mol) gives a LGM minus Holocene temperature difference of -2.4 ± 0.3 °C.

2.3. Discussion

Summarising the results of Section 2.2, it can be concluded that core-top calibrations of *Uvigerina* spp. mostly rely on data from warmer temperatures and give too wide a range of temperature sensitivities to define bottom-water temperatures accurately in the past. The difference in reconstructed temperature between the use of the >11 °C (0.044 mmol/mol/°C) and <11 °C (0.096 mmol/mol/°C) sensitivities is more than a factor of two. The range in sensitivities from Table 1 of 0.065–0.084 mmol/mol/°C is equivalent to a 30% difference in temperature range. The "bootstrapping" approach of Martin et al. (2002) was found to be unsuccessful, possibly because of the strong $\Delta[CO_3^{2-}]$ influence on the epibenthic species with which *Uvigerina* spp. data were compared.

The recognition that the partition of $\delta^{18}O_{calcite}$ between temperature and seawater is defined by the ratio of the sensitivities

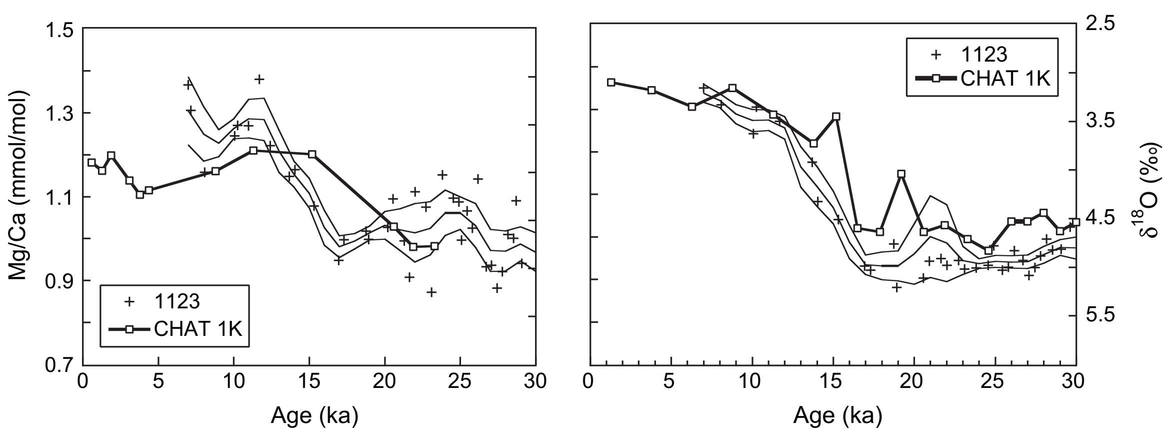


Fig. 4. A. Mg/Ca and B. $\delta^{18}O$ versus age for Uvigerina spp from CHAT 1K (open squares) and ODP 1123 (crosses and Gaussian interpolations $\pm 1\sigma$ of data). Data oxidatively cleaned ("uncorrected").

of Mg/Ca and of $\delta^{18}O_{calcite}$ to temperature (S_{Mg} and S_O) provides a useful way of estimating S_{Mg}. Relative to the commonly used S_O of 0.25‰/°C, the S_{Mg} of *Uvigerina* spp. is estimated to be 0.1 ± 0.013 mmol/mol/°C. This method attributes all the Holocene to LGM change in Mg/Ca to temperature and thus ignores $\Delta[CO_3^{2-}]$. The use of the multiple regression, with $\Delta[CO_3^{2-}]$ included, on core-top data provides a similar sensitivity of 0.078 ± 0.008 mmol/mol/°C, although its effect in the regression is insignificant.

3. A 440 kyr record of *Uvigerina* spp. Mg/Ca from ODP Site 1123

3.1. Samples, methods and results

ODP Leg 181 Site 1123 at 41°47.15′S, 171°29.94′W is located on the northeast slope of Chatham Rise, east of New Zealand at 3290 m water depth (Carter et al., 1999). The site (Fig. 5) lies beneath the southwest Pacific deep western boundary current within Lower Circumpolar Deep Water (Hall et al., 2001; McCave et al., 2008). Nearby core CHAT 1K (41°35′S, 171°30′W, 3556 m water depth) a 3.57-m Kasten core located close to ODP Site 1123 (Weaver et al., 1998; Lean and McCave, 1998) provided core-top samples not recovered by the ODP core as well as samples down to the LGM.

Two hundred samples covering the past 440 kyr were obtained for Mg/Ca analysis from the upper 18.2 m of core ODP Site 1123. CHAT 1K was sampled at 1 cm intervals to a depth of 10 cm and at 4 cm intervals deeper in the core. *Uvigerina* spp. were picked from the >250 μm size fraction of the washed sediment. A total of 470 samples were analysed for $\delta^{18}O$. Most measurements of *Uvigerina* spp. $\delta^{18}O$ were made earlier (Hall et al., 2001) and supplemented where necessary on a Micromass multicarb sample preparation system attached to a PRISM mass spectrometer. Measurements of $\delta^{18}O$ were determined relative to the Vienna Peedee Belemnite (VPDP) Standard with an analytical precision of ±0.08‰. Mg/Ca analyses were carried out following the cleaning procedure described by Barker et al. (2003) and element ratios determined by ICP–OES (de Villiers et al., 2002). Long-term instrumental precision of element ratio data, determined by replicate analyses of a standard solution containing Mg/Ca = 1.3 mmol/mol, was ± 0.46%. Accuracy of Mg/Ca determinations was confirmed by an interlaboratory study of carbonate reference materials (Greaves et al., 2008).

The age model for core ODP Site 1123 used here was obtained by tuning the *Uvigerina* spp. $\delta^{18}O$ data to the Lisiecki and Raymo (2005) $\delta^{18}O$ stack. The model is for the most part similar to the age model constructed by Hall et al. (2001). Conversion of Mg/Ca to temperature was made using a sensitivity of 0.1 mmol/mol/°C, in effect fixing the calibration to the glacial–interglacial temperature and $\delta^{18}O_{water}$ differences derived for ODP Site 1123 from modelling the $\delta^{18}O$ gradient in the sediment pore waters (Adkins et al., 2002): $Mg/Ca = 1 + 0.1T$ (Fig. 6A; Table S3). Seawater $\delta^{18}O$ was estimated using $\delta^{18}O_{seawater} = (\delta^{18}O_{calcite} + 0.27) - 0.25(16.9 - ((Mg/Ca - 1)/0.1))$‰ (Fig. 6B; Table S3).

The estimates of temperature are not greatly sensitive to the value of S_{Mg}. A change in S_{Mg} from 0.1 to 0.078 changes temperature by up to about 0.8 °C. Of course, a change in C_{Mg} will offset temperature by a constant amount and ΔT will be unchanged.

3.2. Evaluation of post-depositional effects

The *Uvigerina* spp. record is characterised by a narrow range in Mg/Ca (Fig. 6). There are two post-depositional issues that first

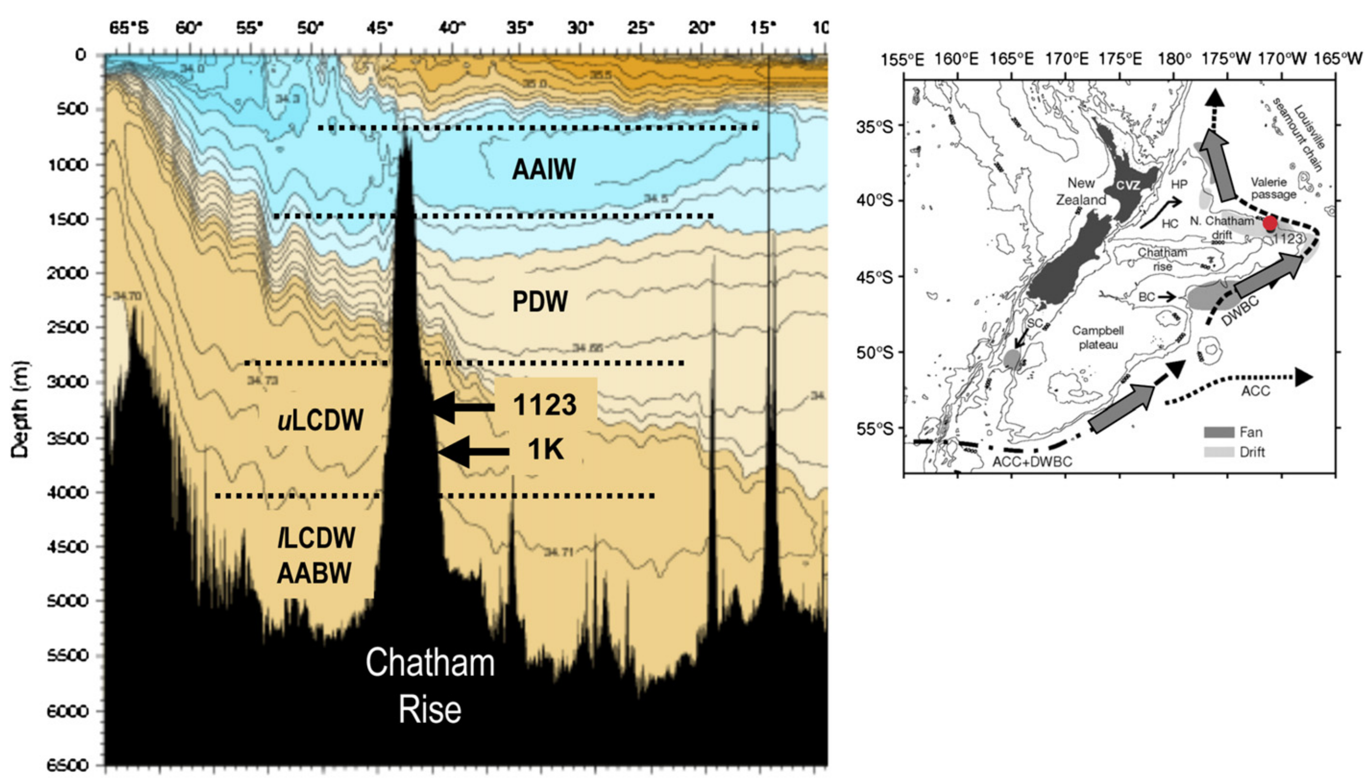


Fig. 5. Study area, showing location of Chatham Rise, and cores ODP 1123 and CHAT 1K. Left: WOCE hydrographic section of salinity from Schlitzer (2000) and major water masses from McCave et al. (2008): AAIW = Antarctic Intermediate Water; PDW = Pacific Deep Water; uLCDP = upper Lower Circumpolar Deep Water; lLCDP = lower Lower Circumpolar Deep Water, including AABW = Antarctic Bottom Water. Arrows show sites of ODP 1123 (3290 m) and CHAT 1K (3556 m) Right: map, from Hall et al. (2001), showing path of DWBC = deep western boundary current and location of ODP 1123.

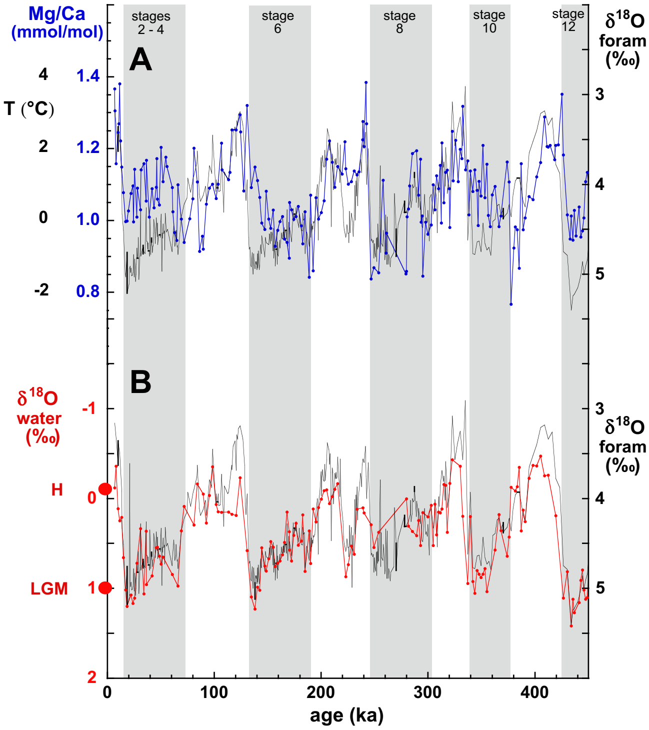


Fig. 6. A. $\delta^{18}O$ (black) and Mg/Ca (blue) for *Uvigerina* spp. from ODP 1123 (Table S3). Also shown is scale for temperature (*T*) estimated using Mg/Ca = 1 + 0.1*T*. B. *Uvigerina* spp. $\delta^{18}O$ (black) and seawater $\delta^{18}O$ (red) from $\delta^{18}O_{seawater} = (\delta^{18}O_{calcite} + 0.27) - 0.25(16.9 - ((Mg/Ca - 1)/0.1))$‰. Circles show modern water temperature and seawater $\delta^{18}O$ (H) and estimated LGM values from pore water modelling.

need to be considered before it can be discussed in terms of bottom water temperature. The first of these is the potential of a dissolution overprint. It is thought that Mg is more homogeneously distributed in the calcite of benthic than planktonic foraminifera and, as such, should be less susceptible to selective loss of Mg-rich portions of the test (e.g., Brown and Elderfield, 1996; Regenberg et al., 2006). For example, Curry and Marchitto (2008) found that distribution within the test walls of *Cibicidoides pachyderma* is Gaussian, suggesting Mg/Ca is present in a single phase. Some evidence from Mg/Ca in planktonic foraminifera from ODP Site 1123 is relevant to this discussion. Mg/Ca in benthic *Uvigerina* spp. shows higher values during interglacial periods and lower values during glacial periods. Were this to reflect dissolution, it would be logical that indicators of dissolution in planktonic foraminifera should exhibit a similar interglacial–glacial pattern. However, measurements of shell weight of *Globigerina bulloides* from the core show lighter values during interglacial periods and heavier values during glacial periods (Greaves, 2008), the opposite to this expectation. In fact, we believe that the shell weight record does not, in the main, reflect dissolution although evidence of dissolution is recognizable in interglacial periods in particular Marine Isotope Stages (MIS) 9 and 11. This observation could still be consistent with a dissolution effect that offset the values to some extent but did not eradicate the glacial/interglacial signal. Nevertheless, this comparison does provide circumstantial evidence that dissolution is not a significant issue for the *Uvigerina* spp. Mg/Ca record. As discussed in the Introduction, use of the shallow infaunal *Uvigerina* spp. for this study should minimize the influence of low $\Delta[CO_3^{2-}]$ bottom waters on Mg/Ca.

The second potential effect is from a diagenetic overprint. We have examined this by comparing the Mg/Ca variability with that of Fe/Ca, Al/Ca and Mn/Ca. We monitored Al with a detection limit of ~5 ppb (0.13 mmol/mol at 60 ppm Ca) and most samples were

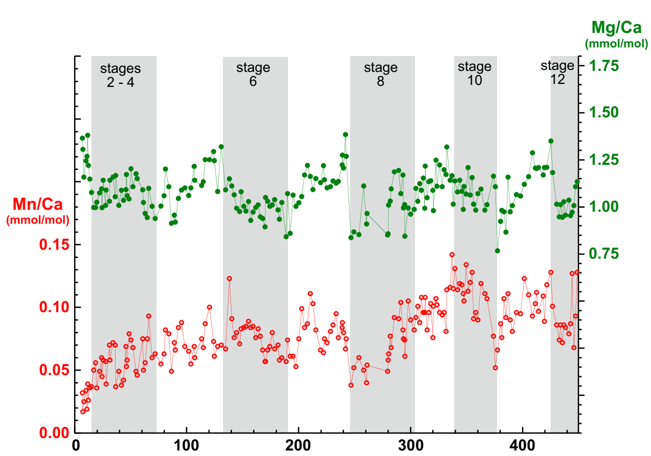


Fig. 7. Comparison of Mg/Ca and Mn/Ca of *Uvigerina* spp. from ODP core 1123.

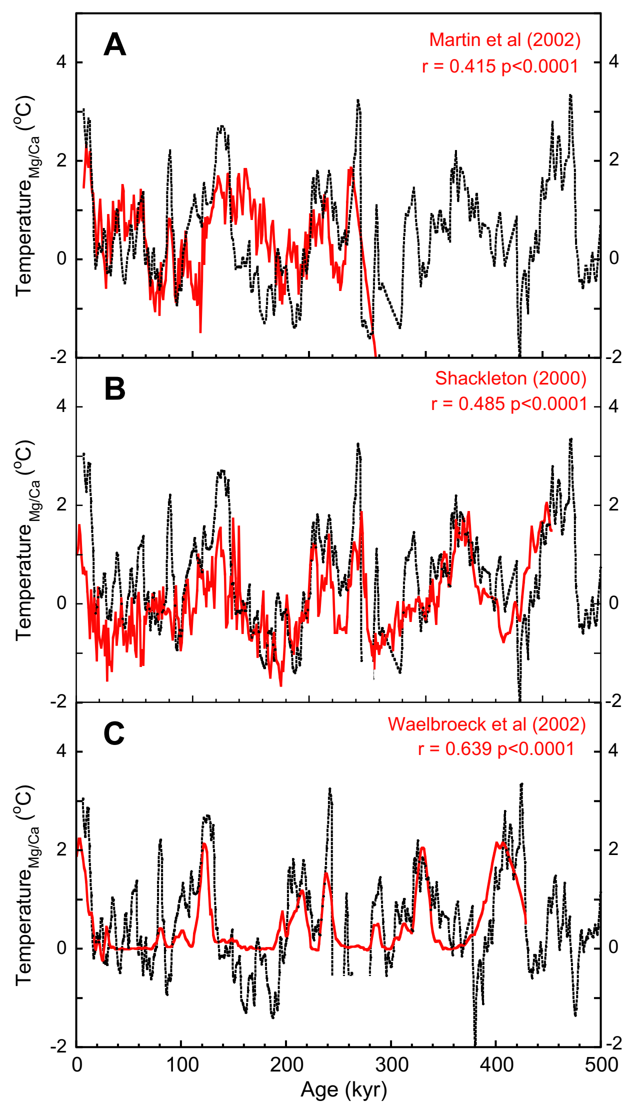
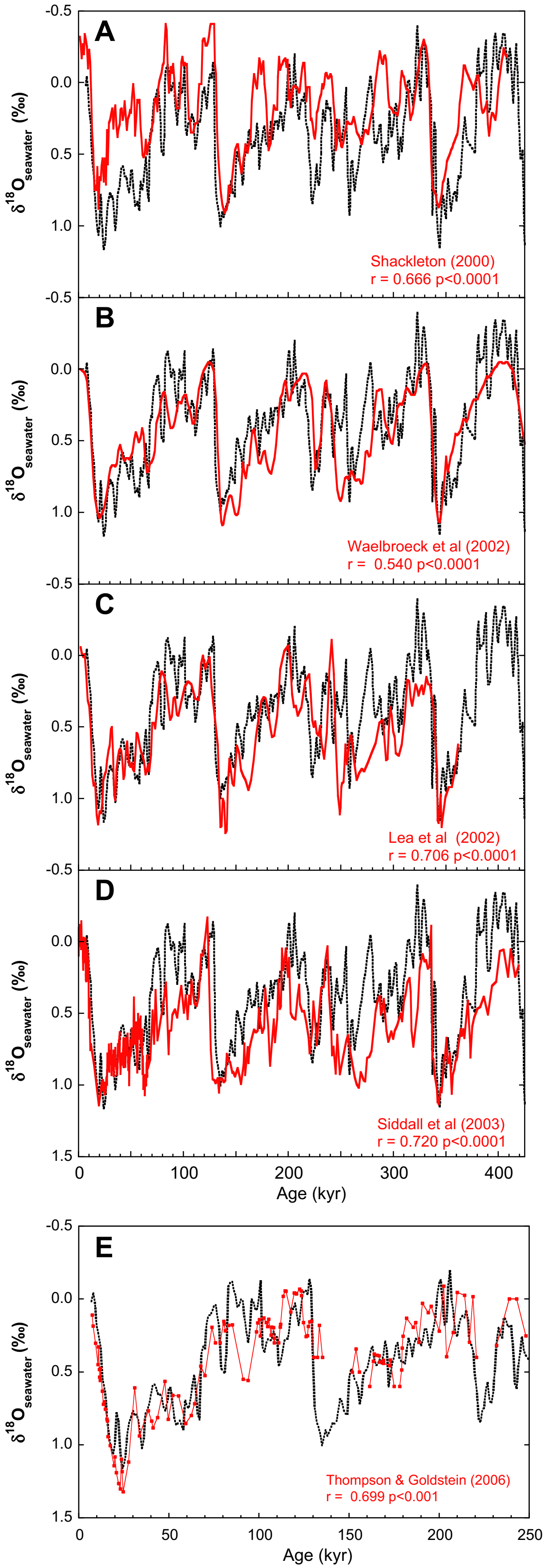


Fig. 8. Comparison of bottom water temperature record from IODP Site 1123 (5 kyr Gaussian interpolation; black) with three other records from the Pacific Ocean (red): A. Martin et al. (2002); B. Shackleton (2000); and C. Waelbroeck et al. (2002).



below detection. We used Al/Ca > 0.4 mmol/mol to identify possible contamination but because Al is more readily contaminated and less precisely determined, it often gives spurious "flyers" so we did not reject Mg/Ca results on the basis of high Al/Ca alone. There was no discernible trend in Al/Ca versus Mg/Ca ($r = 0.015$, $p = 0.59$). Fe/Ca was <0.1 mmol/mol on all except 3 samples and shows no trend versus Mg/Ca ($r = 0.136$, $p = 0.056$) for all samples. The majority of samples have Mn/Ca < 100 μmol/mol (Fig. 7) and the correlation with Mg/Ca is insignificant ($r = 0.134$, $p = 0.059$). Mn/Ca increases down-core from ~20 μmol/mol at core-top to 140 μmol/mol at ~130 ka. Mg/Ca decreases over this range ($r = -0.186$, $p = 0.147$). In samples older than ~130 ka a statistically significant ($r = 0.471$, $p < 0.0001$) pattern is seen where some of the features in the Mg/Ca record are visible in the Mn/Ca record. It is possible that this part of the record indicates some diagenetic imprint affecting Mg although this is known only as a feature of very much higher Mn/Ca ratios up to 400 mmol/mol and Mg/Ca ratios up to 50 mmol/mol (e.g., Pedersen and Price, 1982; Pena et al., 2005). Alternatively, it may be that there has been minor climate-related diagenetic reorganisation of Mn resulting in some superficial similarity in the two records.

3.3. *Bottom water temperature and* Uvigerina *spp.* $\delta^{18}O$ *records*

Given the narrow range in Mg/Ca ratios, the benthic foraminiferal Mg/Ca record for Southern Ocean ODP Site 1123 shows striking variability that correlates with climate oscillations, with an obvious resemblance to the benthic $\delta^{18}O$ *Uvigerina* spp. record (Fig. 6). Comparison of paired data (Fig. S1A) shows that the estimated bottom water temperature and *Uvigerina* spp. $\delta^{18}O$ are significantly correlated ($r = -0.6336$, $p < 0.0001$). Each glacial interval has similar minimum Mg/Ca ratios, equivalent to a temperature of approx. −1.5 °C (Fig. 6), with values increasing prior to the glacial termination observed in the benthic $\delta^{18}O$ (best seen for MIS 10 and 6). Interglacial MIS 5, 9 and 11 (and perhaps 7) have somewhat higher Mg/Ca compared with Holocene values. The resolution of the record is insufficient to define changes confidently in Mg/Ca at millennial resolution.

Three other records are available of bottom water temperature for the Pacific Ocean (Fig. 8; Fig. S2). In order to apply correlation statistics, data have been converted to 5 kyr Gaussian interpolations. The correlations between bottom water temperatures derived from ODP 1123 and the previous studies all are significant ($p < 0.0001$).

The record of Martin et al. (2002) from the eastern tropical Pacific is also derived from benthic Mg/Ca and may be expected to be most similar to the ODP 1123 record. The two records are significantly correlated ($r = 0.415$; $p < 0.0001$) but do exhibit differences. Notably Stage 4 is colder and Stage 5.1 and 5.4 warmer in the 1123 record. Termination II is weaker in the Martin et al. (2002) record and starts to warm earlier than in the 1123 record. Martin et al. (2002) show that the low values during MIS 5 are associated with evidence from fragmentation of intense dissolution and this may have affected Mg/Ca. The two records track each other for the older part of the record but towards the end of MIS 7 values are higher than in the 1123 record, perhaps suggesting age-model related offsets.

The record of Shackleton (2000) is the residual obtained by correcting $\delta^{18}O_{calcite}$ from Pacific core V19-30 for global $\delta^{18}O_{seawater}$

Fig. 9. Comparison of $\delta^{18}O_{seawater}$ record from IODP Site 1123 (black; 5 kyr Gaussian interpolation) with five other records (red): A. Shackleton (2000); B. Waelbroeck et al. (2002); C. Lea et al. (2002); D. Siddall et al. (2003); and E. Thompson and Goldstein (2006).

(itself derived from $\delta^{18}O_{air}$ and an estimate of the Dole effect). The two records are significantly correlated ($r = 0.485$; $p < 0.0001$). There have been criticisms of this approach (Jouzel et al., 2002; Waelbroeck et al., 2002), mainly because of its assumption of a purely precessionally driven Dole effect with implications for relative sea level (RSL), and these will be discussed below.

The record of Waelbroeck et al. (2002), based on $\delta^{18}O_{calcite}$ and sea level estimates is striking in that it shows near constant glacial temperatures of about 0 °C over the four glacial stages represented. This is in contrast to the records from Martin et al. (2002), Shackleton (2000) and ODP Site 1123. In part this may reflect smoothing. However, interglacial values are strikingly similar to ODP Site 1123 and the two records are significantly correlated ($r = 0.639$; $p < 0.0001$) with the highest correlation of the three comparisons (Fig. S2). To a first approximation the two records in Fig. 8C are similar in that Waelbroeck et al. (2002) show deep water cooling occurring soon after the peak interglacials but slightly later in ODP 1123. The principal difference is that ODP Site 1123 shows variability, especially over glacial periods, not seen in Waelbroeck et al. (2002). The factors determining that curve are discussed in Waelbroeck et al. (2002). In brief, it assumes the Pacific benthic calcite $\delta^{18}O$ represents the global ocean (but this is implicit in our interpretation of the record from ODP Site 1123) and that temperature is simply the difference between benthic calcite $\delta^{18}O$ and ice volume $\delta^{18}O$. Waelbroeck et al. (2002) suggest the correlation between these parameters may be more complex than assumed. Comparison of the two temperature records on a scatter plot (Fig. S2) suggests the temperature construction truncates at a minimum value of about 0 °C. However, glacial bottom water temperatures were cooler than this, including -1.2 ± 0.5 °C at the site of ODP 1123, as have been estimated by Adkins et al. (2002).

In summary, comparison of the ODP Site 1123 record with the three other records of Pacific bottom water temperature (Fig. 8; Fig. S2) reveals strong similarities but also differences. Given that derivation of two of the records did not involve Mg/Ca they provide independent support that the benthic Mg/Ca record presented here represents bottom water temperature; and that secondary factors seem to be minor.

Of relevance to the interpretation of all four records is the broader question as to whether local hydrographic changes affect what may be considered as a global record. In the case of the Atlantic Ocean the answer is well known (e.g., Waelbroeck et al., 2002; Skinner and Shackleton, 2005). It is safer to assume that the Pacific Ocean deep water is a reasonable representation of the global ocean, at least on timescales where changes in global ocean are greater than gradients in hydrography.

3.4. Bottom water temperature and seawater $\delta^{18}O$ records

A test of the fidelity of the temperature record is to combine Mg/Ca-based temperature and *Uvigerina* spp. $\delta^{18}O$ to estimate seawater $\delta^{18}O$ (Fig. 6) and to make comparison with previous records (Fig. 9; Fig. S3). Where necessary published sea level values have been converted to $\delta^{18}O_{seawater}$ using a scaling of 1‰ per 100 m. These estimates are not greatly sensitive to the value of S_{Mg} but are very sensitive to S_O. For example, a change from 0.25‰/°C to 0.27‰/°C changes $\delta^{18}O_{seawater}$ by 0.32 ± 0.02‰, about 30 m sea level equivalent. In order to apply correlation statistics data have been converted to 5 kyr interpolations. The correlations between seawater $\delta^{18}O$ derived from ODP Site 1123 and these previous studies all are significant ($p < 0.0001$).

The record of Shackleton (2000), Fig. 9A, shows higher sea level (lower $\delta^{18}O_{seawater}$) than this study and other records. Bard (quoted in Jouzel et al., 2002) has suggested that MIS 6.5 (at 175 kyr) should provide a good test of sea level estimates as the record from Argentarola Cave suggests a sea level of −50 m relative to today (Bard et al., 2002). The Shackleton (2000) record shows a relatively high sea level whereas this study, Waelbroeck et al. (2002) and Siddall et al. (2003) show about −50 to −70 m.

Comparison with the $\delta^{18}O_{seawater}$ reconstructions of Waelbroeck et al. (2002), Fig. 9B, points to age model differences with this study, particularly at MIS 8 and 5–4 and Termination III. Similar issues arise in comparison with Siddall et al. (2003), Fig. 11D, particularly at MIS 5 and Termination II. However, in general, there is good agreement with these two reconstructions, given the different approaches taken. The record of Lea et al. (2002), Fig. 9C, is based on a detrended planktonic Mg/Ca record of temperature and again shows broad similarities with this study.

The records shown in Fig. 9A–D all involve benthic $\delta^{18}O$ data in their derivation. The record of Thompson and Goldstein (2006), Fig. 9E, is a sea level curve from a compilation of coral data and is of interest because it, alone of the records shown for comparison, is derived independently of the benthic $\delta^{18}O$ record. The record from the present study captures most of the features of the coral-based record and the correlation with seawater $\delta^{18}O$ derived from ODP 1123 is significant ($r = 0.72$; $p < 0.0001$; Fig. S4). A notable difference is that this study suggests that sea level at MIS 5.1 and 5.3 is similar to MIS 5.5 whereas the coral compilation (but not all coral-based sea level records; see Thompson and Goldstein, 2005) and the Red Sea record (Siddall et al., 2003) show lower sea level at MIS 5.1 and 5.3.

3.5. Correlation and phasing of Mg/Ca (temperature), benthic $\delta^{18}O$ and seawater $\delta^{18}O$ records

Comparison of paired data (Fig. S1A) shows that the estimated bottom water temperature (Mg/Ca) and *Uvigerina* spp. $\delta^{18}O$ are significantly correlated ($r = -0.634$, $p < 0.0001$). When bottom water temperature (Mg/Ca) and seawater $\delta^{18}O$ are compared (Fig. S1B) the correlation is weak but significant ($r = -0.128$, $p < 0.00907$). These differences occur because the correlation statistics are influenced by different phase offsets at different periodicities between the paired records. To demonstrate this effect, correlation statistics were compiled where leads of Mg/Ca in the range −5 kyr to +28 kyr were imposed on the records (Fig. 10).

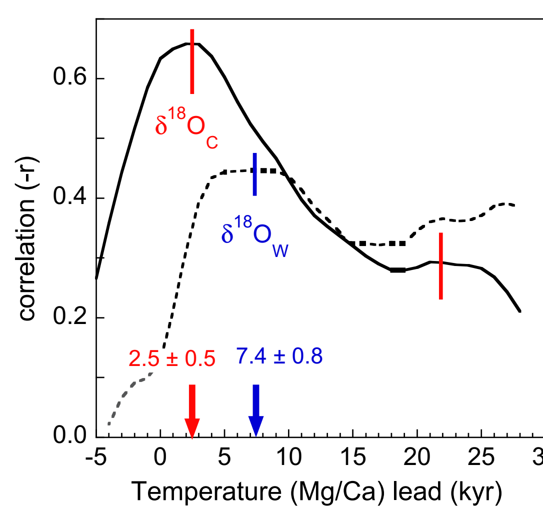


Fig. 10. Coefficients of correlation of temperature (Mg/Ca) with calcite $\delta^{18}O$ ($\delta^{18}O_C$) and seawater $\delta^{18}O$ ($\delta^{18}O_W$) with lead from −5 to +28 kyr. Arrows show temperature lead for maximum correlations also marked with vertical lines together with secondary maximum at ~20 ka discussed in text.

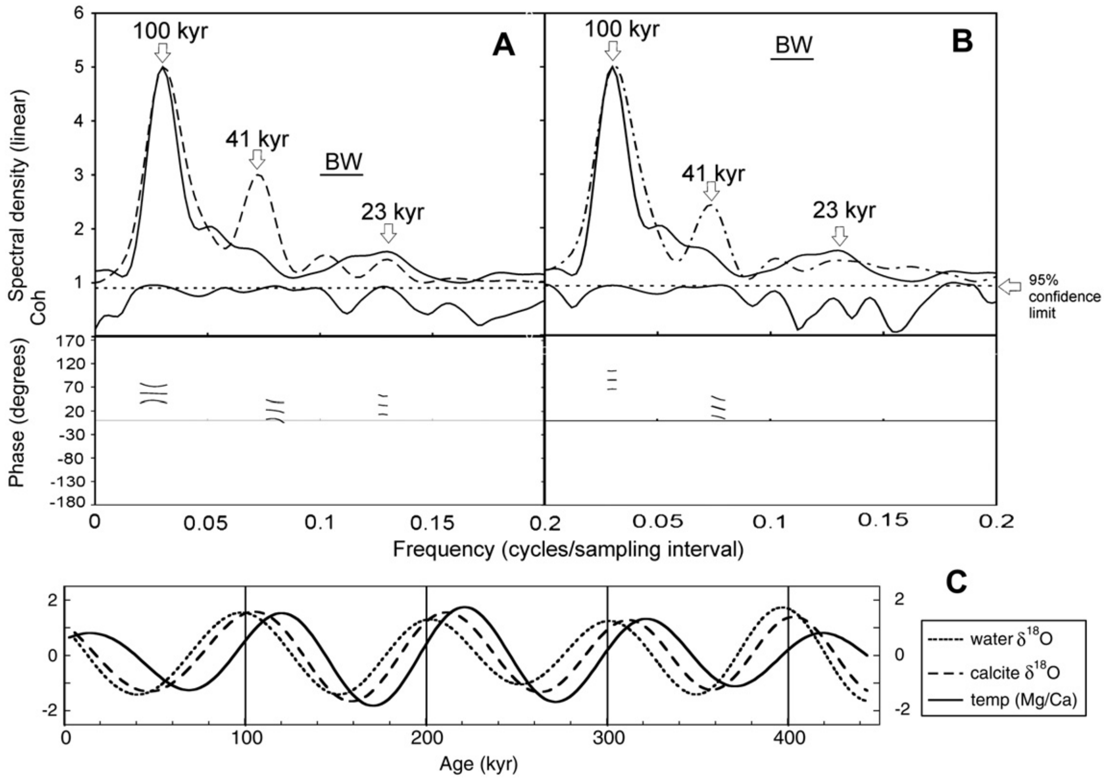


Fig. 11. Spectral analyses of ODP 1123 Mg/Ca based temperature (solid line) versus (A) ODP 1123 calcite $\delta^{18}O$ (dashed) and (B) 1123 seawater $\delta^{18}O$ (dashed–dotted). Bar labelled "BW" indicates bandwidth. "Coh" indicates coherency plot with 95% confidence limit (dotted). Phase panel beneath each cross-spectrum indicates phase relationships, with 95% confidence limits, for orbital bands above coherency significance criterion. C. Phase relationships between 100-kyr bandpass-filtered parameters versus time.

Temperature and benthic $\delta^{18}O$ records are significantly correlated ($p < 0.0001$) over the whole of this range but the correlation is at a maximum for a temperature (Mg/Ca) lead over benthic $\delta^{18}O$ of 2.5 ± 0.5 kyr. This improves the correlation slightly ($r = -0.681$; Fig S1C). The temperature and seawater $\delta^{18}O$ records are more poorly correlated but reach a maximum at a temperature lead of 7.4 ± 0.8 kyr. This improves the correlation significantly ($r = -0.428$; Fig. S1D).

Linear correlation does not, of course, identify phasing at particular periodicities and defines a lag/lead that is some function of the relative influences of the main component periodicities and their respective leads and lags.

In spite of the short data range, the power at tilt and to a limited extent at precession shared between $\delta^{18}O_{calcite}$ and $\delta^{18}O_{water}$ permits a phase estimate to be made at these periodicities (Fig. 11). In both cases the phase offsets are within error zero: $\delta^{18}O_{calcite}$ lags $\delta^{18}O_{water}$ by 2 ± 3 kyr for tilt and 5 ± 8 kyr for precession. In contrast, cross-spectral analysis indicates that at eccentricity periods there is a ca 16 ± 5.5 kyr lead of temperature over calcite $\delta^{18}O$ and a ca 24 ± 5.6 kyr lead over water $\delta^{18}O$ (using ARAND software, Howell, 2001); similar values were obtained using Analyseries software (Paillard et al., 1996). This is apparent in the smoothed data sets using a 100 kyr filter (Fig. 11). The phase offset at eccentricity is also present as a minor peak in Fig. 10. Seawater $\delta^{18}O$ lags calcite $\delta^{18}O$ by 6 ± 3 kyr; clearly the inclusion of temperature in the calcite $\delta^{18}O$ signal produces this offset, which represents the difference between oceanic temperature change and ice volume changes. Shackleton (2000) identified a 14 ± 5 kyr phase lag of global ice volume to changes in eccentricity. In this data set temperature leads eccentricity by ~ 7 kyr, a phenomenon that will be investigated in future work.

4. Conclusion

A methodological study has been made to assess the use of benthic foraminiferal Mg/Ca in the infaunal *Uvigerina* spp. for estimation of bottom water temperature. Use of a Holocene–LGM comparison of Mg/Ca and $\delta^{18}O_{calcite}$ data allowed definition of the temperature sensitivity of Mg/Ca and supports data at the higher sensitivity core-top calibration values. $\Delta[CO_3^{2-}]$ seems not to be an important influence on Mg/Ca for this species. A test of this approach has been made by generation of a *Uvigerina* spp. record for the Southern Ocean over the past 440,000 years from ODP Site 1123 (Chatham Rise). The record shows variability that correlates with climate oscillations. Transformation to temperature allows estimates to be made of changes in seawater temperature and $\delta^{18}O$ for this period. These are very sensitive to choice of the slope of the paleotemperature equation but the values estimated for *Uvigerina* spp. appear reliable. Comparisons with published records provide independent circumstantial support for the estimates of bottom water temperature and seawater $\delta^{18}O$. Given the estimation of temperature sensitivity obtained from this study, the possibility exists for future work applying this approach at higher resolution.

Acknowledgments

We thank Jimin Yu and Nick McCave for discussions and Claire Waelbroeck and Eelco Rohling for providing data. The reviews by David Lea and a second reviewer were very helpful. Mike Hall and James Rolfe are thanked for laboratory support and Nick McCave for samples from CHAT 1K. We thank IODP for provision of samples from Site 1123 and John Firth and colleagues at the College Station repository for their assistance during sampling. This work was supported in part by funding from the NERC QUEST DESIRE programme (NE/E007597).

H.E. thanks members of the EPICA team for the opportunity to contribute to their annual meetings, and discussions, and to this Special Issue.

Appendix. Supplementary material

Supplementary material can be found, in the online version, at doi:10.1016/j.quascirev.2009.07.013

References

Adkins, J.F., McIntyre, K., Schrag, D.P., 2002. The salinity, temperature, and $\delta^{18}O$ of the glacial deep ocean. Science 298, 1769–1773.

Bard, E., Antonioli, F., Silenzi, S., 2002. Sea-level during the penultimate interglacial period based on a submerged stalagmite from Argentarola Cave (Italy). Earth Planet Sci Lett 196, 135–146.

Barker, S., Greaves, M., Elderfield, H., 2003. A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry. Geochem Geophys Geosyst 4 (9). doi:10.1029/2003GC000559.

Barker, S., Cacho, I., Benway, H., Tachikawa, K., 2005. Planktonic foraminiferal Mg/Ca as a proxy for past oceanic temperatures: a methodological overview and data compilation for the Last Glacial Maximum. Quaternary Sci Rev 24, 821–834.

Brown, S., Elderfield, H., 1996. Variations in Mg/Ca and Sr/Ca ratios of planktonic foraminifera caused by postdepositional dissolution: evidence of shallow Mg-dependent dissolution. Paleoceanography 11, 543–551.

Bryan, S.P., Marchitto, T.M., 2008. Mg/Ca-temperature proxy in benthic foraminifera: new calibrations from the Florida Straits and a hypothesis regarding Mg/Li. Paleoceanography 23. doi:10.1029/2007PA001553 PA2220.

Carter, R.M., McCave, I.N., Richter, C., Carter, L., et al., 1999. Proc ODP, Init Repts, 181 [Online]. Available from: <http://www-odp.tamu.edu/publications/181_IR/181ir.htm>.

Curry, W.B., Marchitto, T.M., 2008. A secondary ionization mass spectrometry calibration of *Cibicidoides pachyderma* Mg/Ca with temperature. Geochem Geophys Geosyst 9 (4). doi:10.1029/2007GC001620 Q04009.

de Villiers, S., Greaves, M., Elderfield, H., 2002. An intensity ratio method for the accurate determination of Mg/Ca and Sr/Ca of marine carbonates by ICP-AES. Geochem Geophys Geosyst 3. doi:10.1029/2001GC000169.

Elderfield, H., Ganssen, G., 2000. Past temperature and $\delta^{18}O$ of surface ocean waters inferred from foraminiferal Mg/Ca ratios. Nature 405, 442–445.

Elderfield, H., Bertram, C.J., Erez, J., 1996. A biomineralization model for the incorporation of trace elements in foraminiferal calcium carbonate. Earth Planet Sci Lett 142, 409–423.

Elderfield, H., Yu, J., Anand, P., Kiefer, T., Nyland, B., 2006. Calibrations for benthic foraminiferal Mg/Ca paleothermometry and the carbonate ion hypothesis. Earth Planet Sci Lett 250, 633–649.

Erez, J., 2003. The source of ions for biomineralization in foraminifera and their implications for paleoceanographic proxies. Rev Mineral Geochem 54, 115–149. doi:10.2113/0540115.

Greaves, M.J., 2008. Trace Elements in Marine Biogenic Carbonates: Analysis and Application to Past Ocean Chemistry. PhD thesis. University of Southampton, 194 pp.

Greaves, M., Caillon, N., Rebaubier, H., Bartoli, G., Bohaty, S., Cacho, I., et al., 2008. Interlaboratory comparison study of calibration standards for foraminiferal Mg/Ca thermometry. Geochem Geophys Geosyst 9. doi:10.1029/2008GC001974 Q08010.

Hall, I.R., McCave, I.N., Shackleton, N.J., Weedon, G.P., Harris, S.E., 2001. Intensified deep Pacific inflow and ventilation in Pleistocene glacial times. Nature 412, 809–812.

Howell, P., 2001. ARAND Time Series and Spectral Analysis Package for the Macintosh, Brown University: IGBP PAGES/World Data Center for Paleoclimatology Data Contribution Series 2001–044. NOAA/NGDC Paleoclimatology Program, Boulder, Colorado.

Jouzel, J., Hoffman, G., Arrenin, F., Waelbroeck, C., 2002. Atmospheric oxygen 18 and sea-level changes. Quaternary Sci Rev 21, 307–314.

Kim, S.-T., O'Neill, J.R., 1997. Equilibrium and nonequilibrium oxygen isotope effects in synthetic calcites. Geochim Cosmochim Acta 61, 3461–3475.

Lea, D.W., Martin, P.A., Pak, D.A., Spero, H.J., 2002. Reconstructing a 350 kyr history of sea level using planktonic Mg/Ca and oxygen isotope records from a Cocos Ridge core. Quaternary Sci Rev 21, 283–293.

Lean, C.M.B., McCave, I.N., 1998. Glacial to interglacial mineral magnetic and palaeoceanographic changes at Chatham Rise, SW Pacific Ocean. Earth Planet Sci Lett 163, 247–260.

Lear, C.H., 2007. Mg/Ca palaeothermometry: a new window into Cenozoic climate change. In: Haywood, W.M. (Ed.), Deep-Time Perspectives on Climate Change: Marrying the Signal from Computer Models and Biological Proxies. The Micropalaeontological Society, Special Publications. The Geological Society, London, pp. 313–322.

Lear, C.H., Rosenthal, Y., 2006. Benthic foraminiferal Li/Ca: insights into Cenozoic seawater carbonate saturation state. Geology 34, 985–988. doi:10.1130/G22792A.1.

Lear, C.H., Rosenthal, Y., Slowey, N., 2002. Benthic foraminiferal Mg/Ca-paleothermometry: a revised core-top calibration. Geochim Cosmochim Acta 66, 3375–3387.

Lisiecki, L.E., Raymo, M.E., 2005. A Pliocene–Pleistocene stack of 57 globally distributed benthic $\delta^{18}O$ records. Paleoceanography 20. doi:10.1029/2004PA001071 PA1003.

Marchitto, T.M., Curry, W.B., Oppo, D.W., 2000. Zinc concentrations in benthic foraminifera reflect seawater chemistry. Paleoceanography 15, 299–306.

Marchitto, T.M., Lynch-Stieglitz, J., Hemming, S.R., 2005. Deep Pacific $CaCO_3$ compensation and glacial–interglacial atmospheric CO_2. Earth Planet Sci Lett 231, 317–336. doi:10.1016/j.epsl.2004.12.024.

Martin, W.R., Sayles, F.L., 1996. $CaCO_3$ dissolution in sediments of the Ceara Rise, western equatorial Atlantic. Geochim Cosmochim Acta 60, 243–263.

Martin, P.A., Lea, D.W., Rosenthal, Y., Shackleton, N.J., Sarnthein, M., Papenfuss, T., 2002. Quaternary deep sea temperature histories derived from benthic foraminiferal Mg/Ca. Earth Planet Sci Lett 198, 193–209.

Mashiotta, T.A., Lea, D.W., Spero, H.J., 1999. Glacial–interglacial changes in Subantarctic sea surface temperature and $\delta^{18}O$–water using foraminiferal Mg. Earth Planet Sci Lett 170, 417–432.

McCave, I.N., Carter, L., Hall, I.R., 2008. Glacial–interglacial changes in water mass structure and flow in the SW Pacific Ocean. Quaternary Sci Rev 27, 1886–1908.

McCorkle, D.C., Martin, P.A., Lea, D.W., Klinkhammer, G.P., 1995. Evidence of a dissolution effect on benthic foraminiferal shell chemistry: $\delta^{13}C$, Cd/Ca, Ba/Ca, and Sr/Ca results from the Ontong Java Plateau. Paleoceanography 10, 699–714.

O'Neil, J.R., Clayton, R.N., Mayeda, T.K., 1969. Oxygen isotope fractionation in divalent metal carbonates. J Chem Phys 51, 5547–5558.

Paillard, D., Labeyrie, L., Yiou, P., 1996. Macintosh program performs time-series analysis. EOS Transactions AGU 77, 379.

Pedersen, T.F., Price, N.B., 1982. The geochemistry of manganese carbonate in Panama Basin sediments. Geochim Cosmochim Acta 46, 69–74.

Pena, L.D., Calvo, E., Cacho, I., Eggins, S., Pelejero, C., 2005. Identification and removal of Mn–Mg-rich contaminant phases on foraminiferal tests: implications for Mg/Ca past temperature reconstructions. Geochem Geophys Geosyst 6. doi:10.1029/2005GC000930.

Regenberg, M., Nürnberg, D., Steph, S., Groeneveld, J., Garbe-Schönberg, D., Tiedemann, R., Dullo, W.C., 2006. Assessing the effect of dissolution on planktonic foraminiferal Mg/Ca ratios: evidence from Caribbean core tops. Geochem Geophys Geosyst 7. doi:10.1029/2005GC001019 Q07P15.

Rosenthal, Y., Lear, C.H., Oppo, D.W., Linsley, B.K., 2006. Temperature and carbonate ion effects on Mg/Ca and Sr/Ca ratios in benthic foraminifera: aragonitic species *Hoeglundina elegans*. Paleoceanography 21. doi:10.1029/2005PA001158.

Schlitzer, R., 2000. Electronic atlas of WOCE hydrographic and tracer data now available. EOS Transactions AGU 81 (5), 45. <http://www.wewoce.org/>.

Shackleton, N.J., 1974. Attainment of isotopic equilibrium between ocean water and the benthonic foraminifera genus *Uvigerina*: isotopic changes in the ocean during the last glacial. Cent Nat Rech Sci Colloq Int 219, 203–209.

Shackleton, N.J., 2000. The 100,000 year ice-age cycle identified and found to lag temperature, carbon dioxide, and orbital eccentricity. Science 289, 1897–1902.

Siddall, M., Rohling, E.J., Almogi-Labin, A., Hemleben, C., Meischner, D., Schmelzer, I., et al., 2003. Sea-level fluctuations during the last glacial cycle. Nature 423, 853–858.

Skinner, L.C., Shackleton, N.J., 2005. An Atlantic lead over Pacific deep-water change across Termination I: implications for the application of the marine isotope stage stratigraphy. Quaternary Sci Rev 24, 571–580.

Tachikawa, K., Elderfield, H., 2002. Microhabitat effects on Cd/Ca and $\delta^{13}C$ of benthic foraminifera. Earth Planet Sci Lett 202, 607–624.

Thompson, W.G., Goldstein, S.L., 2005. Open-system coral ages reveal persistent suborbital sea-level cycles. Science 308, 401–404.

Thompson, W.G., Goldstein, S.L., 2006. A radiometric calibration of the SPECMAP timescale. Application of the marine isotope stage stratigraphy. Quaternary Sci Rev 25, 3207–3215.

Waelbroeck, C., Labeyrie, L., Michel, E., Duplessy, J.C., McManus, J.F., Lambeck, K., et al., 2002. Sea-level and deep water temperature changes derived from benthic foraminifera isotopic records. Quaternary Sci Rev 21, 295–305.

Weaver, P.P.E., Carter, L., Neil, H.L., 1998. Response of surface water masses and circulation to late Quaternary climate change east of New Zealand. Paleoceanography 13, 70–83.

Yu, J., Elderfield, H., 2007. Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state. Earth Planet Sci Lett 258, 73–86.

Yu, J., Elderfield, H., 2008. Mg/Ca in the benthic foraminifera *Cibicidoides wuellerstorfi* and *Cibicidoides mundulus*: temperature versus carbonate ion saturation. Earth Planet Sci Lett 276, 129–139.