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Element/Calcium ratios in middle Eocene samples of *Oridorsalis umbonatus* from Ocean Drilling Program Site 1209

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Abstract

Culturing studies and empirical-based calibrations suggest that elemental ratios in benthic foraminifera can be used as proxies to reconstruct past variations in bottom water temperature and saturation state ($\Delta[\text{CO}_3^{2-}]$). However the mechanism(s) linking elemental ratios to $\Delta[\text{CO}_3^{2-}]$ are poorly constrained. We present middle Eocene records of *Oridorsalis umbonatus* Li/Ca, B/Ca, Mg/Ca and Sr/Ca from Ocean Drilling Program Site 1209. We apply calibrations developed from core top samples to estimate middle Eocene variations in intermediate water $\Delta[\text{CO}_3^{2-}]$. The fidelity of bottom water $\Delta[\text{CO}_3^{2-}]$ reconstructions based on single element ratios are assessed by comparing the X/Ca-based reconstructions to each other and to carbon cycle proxy records (benthic foraminifera $\delta^{13}\text{C}$, organic carbon content, foraminifera dissolution indices), and a seawater $\delta^{18}\text{O}$ reconstruction for Site 1209. Discrepancies in the reconstructed $\Delta[\text{CO}_3^{2-}]$ values for the middle Eocene based on these different metal ratios suggests that there are still gaps in our understanding of the parameters influencing X/Ca. The downcore record of *O. umbonatus* Mg/Ca does not exhibit any similarities with the Li/Ca, B/Ca and Sr/Ca records, suggesting that bottom water $\Delta[\text{CO}_3^{2-}]$ is not the dominant influence on Mg/Ca ratios for this species. This hypothesis is supported by the coefficients of multiple linear regression models on new and published Mg/Ca data.

1 Introduction

Model simulations and proxy-based reconstructions hypothesise that early Cenozoic glaciation was closely linked to variations in the global carbon cycle (DeConto and Pollard, 2003; Coxall et al., 2005; Tripathi et al., 2005, 2008; Riesselman et al., 2007; DeConto et al., 2008; Merico et al., 2008; Pearson et al., 2009; Spofforth et al., 2010; Coxall and Wilson, 2011). Large (>1‰) shifts in planktonic, benthic and seawater oxygen isotope ratios and in the accumulation of ice-rafted debris during the middle Eocene to earliest Oligocene (Oi-1) are synchronous with substantial (>500 m) variations in the

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a seawater oxygen isotope reconstruction and (4) by calculating down core estimates of bottom water $\Delta[\text{CO}_3^{2-}]$ and temperature evolution at Site 1209 using multi-element ratios and global minimization solutions.

2 Materials and methods

5 Element/calcium ratios were measured on specimens of *Oridorsalis umbonatus* picked from the $>150\ \mu\text{m}$ size fraction. Samples were processed and cleaned for contaminating phases using the standard Cambridge oxidative procedure that is based on Barker et al. (2003). All down-core B/Ca and Li/Ca ratios and some Mg/Ca and Sr/Ca ratios were determined from matrix-matched intensity ratios on the Q-ICP-MS at the University of Cambridge following the procedure of Yu et al. (2005). Additional down-core Mg/Ca and Sr/Ca measurements were made using the Varin Vista ICP-AES following the method of de Villiers et al. (2002). These two methods yield consistent Sr/Ca and Mg/Ca results based on long-term dual measurements (M. Greaves, personal communication, 2011) All data were screened for contaminating phases using ancillary element ratios (i.e. Al/Ca, Fe/Ca, Si/Ca, Mn/Ca). Any samples that fell outside the range reported by Barker et al. (2003) were excluded. We routinely achieved the analytical accuracy and precision on the X/Ca ratios reported by Yu et al. (2005). The relative standard deviation (% rsd) on replicate benthic foraminifera samples (core top specimens, $n = 3$) is better than 1.2 % for Li/Ca, 1 % for B/Ca, 0.2 % for Mg/Ca and 0.07 % for Sr/Ca.

20 Ocean Drilling Site 1209 ($32^\circ 39.108' \text{ N}$, $158^\circ 30.3564' \text{ E}$) was located in the northern subtropical Pacific Ocean throughout the middle Eocene, with an estimated paleodepth of $\sim 1.9\text{--}2.5\ \text{km}$ (Dutton et al., 2005; Bohaty et al., 2009). The intermediate water depth of Site 1209 was above the Eocene CCD (Tripathi et al., 2005), although carbonate preservation may have been influenced by the relatively shallow Pacific lysocline at this time (Hancock and Dickens, 2005).

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Chronostratigraphic datums for Site 1209 are based on biostratigraphic markers and indicate that the studied interval (140–164 revised meters composite depth, rmcd) is middle Eocene in age (Bralower, 2005; Petrizzo et al., 2005). We use the “best-guess” age model for Site 1209 reported in Dawber and Tripati (2011) but note that due to high planktonic fragmentation in parts of the studied interval and the regional diachrony of middle Eocene calcareous nannofossil datums (Petrizzo et al., 2005; Bohaty et al., 2009), there may be some uncertainty associated with the age model. The age model may be subject to reinterpretation if biostratigraphical datums are later revised.

Specimens of *O. umbonatus* become increasingly fragmented in the upper part of the studied interval. Care was taken to select the best-preserved specimens for analysis (i.e. intact and non-chalky). Foraminiferal dissolution indices are from Dawber and Tripati (2011). The weight percentage of organic carbon was calculated using the “loss on ignition” principal (e.g. Heiri et al., 2001). *O. umbonatus* $\delta^{13}\text{C}$ measurements were made on a homogenized sub-sample of the specimens used to determine Mg/Ca and Sr/Ca via ICP-AES (but separate to X/Ca analyses via Q-ICP-MS). Carbon isotope ratios were determined on two gas source mass spectrometers in the Department of Earth Sciences, University of Cambridge. Long term analytical precision based on replicate analyses of an in-house standard is 0.06‰.

3 Results

3.1 Middle Eocene X/Ca ratios

Records of *O. umbonatus* Li/Ca, B/Ca, Mg/Ca and Sr/Ca (Fig. 1) display large amplitude variations on short- and long-time scales during the middle Eocene (up to 25% in $\Delta\text{Sr/Ca}$, 30% in $\Delta\text{Li/Ca}$, 40% in $\Delta\text{Mg/Ca}$ and 56% in $\Delta\text{B/Ca}$). On short time scales (<1 million years), B/Ca ratios do not exhibit any statistically significant correlation with the Li/Ca, Mg/Ca or Sr/Ca records (Fig. 1). Li/Ca and Sr/Ca exhibit the

same increasing trend between ~39 and 37 Ma, but Mg/Ca initially decrease and then increase ca. 37.5 Ma.

3.2 Estimates of middle Eocene $\Delta[\text{CO}_3^{2-}]$

The empirical core top relationships established for *O. umbonatus* Li/Ca, B/Ca, Mg/Ca and Sr/Ca and bottom water $\Delta[\text{CO}_3^{2-}]$ (Table 1, Dawber and Tripathi, 2011) are applied to the middle Eocene X/Ca records from Site 1209. The residence time of Li, B, Mg, Sr and Ca ranges between 10^5 – 10^7 yr (Broecker and Peng, 1982), therefore it is likely that seawater X/Ca were different during the Eocene. Although there are proxy- and model-based constraints for some of the element ratios (e.g. Mg/Ca, Wilkinson and Algeo, 1989; Horita et al., 2002; Coggon et al., 2010), there are notable differences between published estimates. We therefore consider relative changes in middle Eocene intermediate water $\Delta[\text{CO}_3^{2-}]$ implied by each of the X/Ca records (Fig. 1). X/Ca-estimated changes in $\Delta[\text{CO}_3^{2-}]$ are inferred from the smoothed function fitted to the raw data.

Estimates of intermediate water $\Delta[\text{CO}_3^{2-}]$ based on Sr/Ca and Mg/Ca span ~37–45 Ma, with additional estimates from Li/Ca and B/Ca between ~41–37 Ma (measurements of Li/Ca and B/Ca not made on samples prior to 41 Ma). Between ~38.7 and 37 Ma, $\Delta[\text{CO}_3^{2-}]$ estimates based on Sr/Ca and Li/Ca increase ($\sim 60 \mu\text{mol kg}^{-1}$ and $\sim 85 \mu\text{mol kg}^{-1}$ respectively), while estimates based on B/Ca and Mg/Ca show no net change. Although the variability of $\Delta[\text{CO}_3^{2-}]$ based on B/Ca and Mg/Ca is broadly comparable ($\sim 15 \mu\text{mol kg}^{-1}$ and $20 \mu\text{mol kg}^{-1}$ respectively), the structure of the B/Ca and Mg/Ca records is notably different. The discrepancy in the change in $\Delta[\text{CO}_3^{2-}]$ based on the Sr/Ca and Li/Ca records ($\sim 25 \mu\text{mol kg}^{-1}$) may in part reflect the large amount of high frequency variability ($\sim 20\%$) in the Sr/Ca record around 39–38.2 Ma, which is compensated for by the smoothing function. If the change in $\Delta[\text{CO}_3^{2-}]$ between 38.7 and 37 Ma is based on the lower values of the Sr/Ca raw data ($\sim 0.69 \text{ mmol mol}^{-1}$, $n > 15$ samples), rather than the value of the smoothed function, the value ($80 \mu\text{mol kg}^{-1}$) is comparable to the estimate based on the Li/Ca record. On

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long timescales (45–37 Ma) $\Delta[\text{CO}_3^{2-}]$ estimates based on Sr/Ca and Mg/Ca decline by $\sim 70 \mu\text{mol kg}^{-1}$ to $55 \mu\text{mol kg}^{-1}$ respectively. However, during this period there are significant differences in the amplitude and structure of the Sr/Ca and Mg/Ca records on shorter timescales ($< 1 \text{ m yr}^{-1}$).

4 Discussion

If the sensitivity of X/Ca to $\Delta[\text{CO}_3^{2-}]$ established from modern core top samples is appropriate for the middle Eocene, the X/Ca records for Site 1209 imply significant changes in intermediate water $\Delta[\text{CO}_3^{2-}]$ between 45 and 37 Ma. For example, the increase in Sr/Ca and Li/Ca between ~ 38.7 and 37 Ma may indicate a change in $\Delta[\text{CO}_3^{2-}]$ of up to $60\text{--}85 \mu\text{mol kg}^{-1}$. This estimate is larger than the calculated increase in equatorial Pacific deep water $\Delta[\text{CO}_3^{2-}]$ during the Oi-1 glacial expansion in the earliest Oligocene ($\sim 54 \mu\text{mol kg}^{-1}$ at ODP Site 1218, Lear and Rosenthal, 2006). The estimated change in bottom water $\Delta[\text{CO}_3^{2-}]$ at Site 1218 is based on a Li/Ca record also derived from *O. umbonatus* and a core top calibration from one site in the Norwegian Sea (Lear and Rosenthal, 2006), which gives a similar relationship to the core top calibration used here (Dawber and Tripathi, 2011). Sediment accumulation at Site 1218 provide corroborating evidence for a large increase in $\Delta[\text{CO}_3^{2-}]$ across Oi-1, which resulted in an $\sim 1.2 \text{ km}$ deepening of the calcite saturation horizon (CCD, Tripathi et al., 2005). Independent evidence for a similarly large change in intermediate water $\Delta[\text{CO}_3^{2-}]$ at Site 1209 during the late middle Eocene ($\sim 38.7\text{--}37 \text{ Ma}$) is more equivocal (Fig. 2). Records of weight percent calcium carbonate at Sites 1209 (Hancock and Dickens, 2005), 1218 and 1219 (Tripathi et al., 2005; Lyle et al., 2005) support an increase in Pacific deep and intermediate water $\Delta[\text{CO}_3^{2-}]$ between 40 and 37 Ma and an $\sim 0.5 \text{ km}$ deepening of the CCD (carbon-accumulation event 4 (CAE-4) of Lyle et al., 2005). In contrast, foraminifera dissolution indices at Site 1209 (Hancock and Dickens, 2005; Dawber and Tripathi, 2011) suggest increasingly corrosive pore waters beginning

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at ~40.5 Ma to at least 38 Ma. The *O. umbonatus* $\delta^{13}\text{C}$ record for Site 1209 also shows a small decrease (0.3–0.4‰) during CAE-4, which may reflect a decrease in carbon isotope composition of pore waters as a result of organic carbon remineralization.

The apparent discrepancy between the Site 1209, 1218 and 1219 weight percent CaCO_3 records, the CCD reconstruction, the Site 1209 Sr/Ca and Li/Ca estimates of $\Delta[\text{CO}_3^{2-}]$ and the Site 1209 foraminifera dissolution indices during CAE-4 is somewhat of a paradox. Taken at face value, these trends may indicate a decoupling of the CCD and lysocline and/or bottom water and pore water $\Delta[\text{CO}_3^{2-}]$ at Site 1209. During earlier carbonate accumulation events in the middle Eocene, foraminifera dissolution indices are consistent with the weight percent CaCO_3 records for Site 1209, 1218 and 1219 (Fig. 2). The Site 1209 Sr/Ca record also exhibits small increases, equivalent to $\sim 20 \mu\text{mol kg}^{-1}$, during CAE-3 at ~ 41 Ma, and CAE-2 at ~ 44.5 Ma. The Mg/Ca record shows the opposite response to the Sr/Ca record, the foraminifera dissolution indices and CCD reconstruction during CAE-4, CAE-3 and CAE-2, suggesting that $\Delta[\text{CO}_3^{2-}]$ is not the dominant influence on Mg/Ca. During CAE-3 there is no change in the Site 1209 *O. umbonatus* $\delta^{13}\text{C}$ and weight percent organic carbon records, or in the *O. umbonatus* $\delta^{13}\text{C}$ record across CAE-2. *O. umbonatus* $\delta^{13}\text{C}$ and weight percent organic carbon are influenced by additional processes, e.g. $\text{CaCO}_3\text{:C}_{\text{organic}}$ rain rate, which may be obscuring changes in these proxies due to bottom water and/or pore water $\Delta[\text{CO}_3^{2-}]$.

Qualitatively, the Sr/Ca and Li/Ca based estimates for the change in $\Delta[\text{CO}_3^{2-}]$ at Site 1209 are consistent with the reconstruction of the Pacific CCD on million year timescales. However, quantitatively the Sr/Ca and Li/Ca based estimates of $\Delta[\text{CO}_3^{2-}]$ across CAE-4 are inconsistent both with each other and with the estimated change in the depth of the CCD, assuming a similar scaling to the Oi-1 glaciation (i.e. 1.2 km deepening of the CCD and an estimated change of $54 \mu\text{mol kg}^{-1}$ in Pacific deepwater $\Delta[\text{CO}_3^{2-}]$; Lear and Rosenthal, 2006). The thermal and carbonate saturation profile of the equatorial Pacific during the Eocene are not well constrained, therefore it is unclear whether large changes in deepwater $\Delta[\text{CO}_3^{2-}]$, as implied by the substantial changes in

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the depth of the CCD, would propagate to intermediate water depths. Nonetheless, the discrepancies in the structure and amplitude of the X/Ca records at Site 1209 indicate that either the sensitivity to $\Delta[\text{CO}_3^{2-}]$ established from core tops is not appropriate for the Eocene or that secondary parameters contribute to, or may indeed be the dominant influence on *O. umbonatus* X/Ca .

Yu and Elderfield (2007) report changes in North Atlantic Ocean intermediate water (BOFS 17K) $\Delta[\text{CO}_3^{2-}]$ of 20–30 $\mu\text{mol kg}^{-1}$ between the Last Glacial Maximum (LGM) and the Holocene based on a record of *Cibicidoides mundulus* B/Ca. For comparison, Sr/Ca data for the same core (from *C. wuellerstorfi*, Lear et al., 2003), when normalised to *O. umbonatus* using the species offsets of Lear et al. (2003) and converted into $\Delta[\text{CO}_3^{2-}]$ using the core top calibration from Dawber and Tripathi (2011), yield a LGM-Holocene change of $\sim 70 \mu\text{mol kg}^{-1}$. Although this comparison of LGM-Holocene $\Delta[\text{CO}_3^{2-}]$ estimates may be overly simple and biased by inaccuracies in the species corrections, core top calibrations, and the analytical uncertainty associated with measurements on different instruments, it illustrates that there are also discrepancies between different X/Ca - $\Delta[\text{CO}_3^{2-}]$ reconstructions during the Pleistocene. For Li, B, Mg and Sr, seawater composition across the LGM-Holocene transition should be similar to modern, minimizing any potential influence on the X/Ca sensitivity to $\Delta[\text{CO}_3^{2-}]$. Therefore discrepancies between the different X/Ca - $\Delta[\text{CO}_3^{2-}]$ reconstructions likely indicates the influence of secondary parameters.

4.1 Influence of secondary parameters on middle Eocene X/Ca records

4.1.1 Temperature

Mg/Ca ratios in core top specimens of *O. umbonatus* exhibit a strong correlation with bottom water temperature (Lear et al., 2002, 2004; Rathmann et al., 2004; Healey et al., 2008; Dawber and Tripathi, 2011), although the systematics of this relationship are poorly understood. A number of studies have used the Mg/Ca ratio of *O. umbonatus* to

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reconstruct past temperature variations on the assumption that the sensitivity of Mg/Ca to bottom water $\Delta[\text{CO}_3^{2-}]$ and other parameters is minor/negligible (e.g. Lear et al., 2000, 2004; Billups and Schrag, 2003; Dutton et al., 2005; Triпати and Elderfield, 2005; Triпати et al., 2005; Sosdian and Rosenthal, 2009; Dawber and Triпати, 2011). Multiple linear regression of new and published core top *O. umbonatus* Mg/Ca against bottom water temperature and $\Delta[\text{CO}_3^{2-}]$ yields a more significant relationship than simple linear regression on either parameter (Table 2, significance assessed by regression r^2 value, p-values of parameter coefficients and the Akaike information criterion). We consider several subsets of the combined Mg/Ca data as uncorrected anthropogenic DIC data is not available for all localities, and some studies have questioned the reliability of some of the published Mg/Ca data due to potential issues arising from contamination or diagenetic alteration (i.e. Marchitto et al., 2007). Regardless of the data subset used in the multiple linear regression, the Mg/Ca sensitivity to temperature is an order of magnitude greater than the sensitivity to $\Delta[\text{CO}_3^{2-}]$ ($\sim 0.0103 \text{ mmol mol}^{-1} \text{ C}^{-1}$ and $\sim 0.013 \text{ mmol mol}^{-1} \mu\text{mol}^{-1} \text{ kg}^{-1}$; Table 2). Multiple linear regression is not however, an infallible test of the relative influence of temperature and $\Delta[\text{CO}_3^{2-}]$ on *O. umbonatus* Mg/Ca as these two parameters exhibit a high degree of covariation in the oceans leading to issues of spatial autocorrelation in the regression. As similar approach to that adopted by Yu and Elderfield (2008), which examines depth dependent variations in benthic Mg/Ca across the last Glacial Maximum-Holocene transition at a site with well constrained bottom water temperature and $\Delta[\text{CO}_3^{2-}]$ histories, would provide a secondary assessment of the relative influence of these parameters. Nonetheless, the structure of the Mg/Ca record for Site 1209 is consistently different to the Li/Ca, B/Ca and Sr/Ca records during the middle Eocene, further suggesting that it is temperature, rather than $\Delta[\text{CO}_3^{2-}]$, that is the dominant influence on *O. umbonatus* Mg/Ca.

Unfortunately, measurements of core top *O. umbonatus* Li/Ca, B/Ca and Sr/Ca that span a significant temperature range are not available, so it is not possible to rigorously assess the temperature influence on these element ratios. However, we note that a weak, negative relationship between Li/Ca and temperature has been reported for

several species of benthic and planktonic foraminifera (Hall and Chan, 2004; Marriott et al., 2004; Bryan and Marchitto, 2008; Lear et al., 2010).

4.1.2 Seawater composition

Foraminifera are thought to calcify through the vacuolization of seawater (Erez et al., 1994; Erez, 2003), so foraminifera X/Ca may reflect changes in the magnitude and/or X/Ca of cation fluxes into and out of the ocean. Sequence stratigraphic and geochemical proxy reconstructions support highly variable sea level during the middle Eocene (Browning et al., 1996; Miller et al., 2005; Tripathi et al., 2005; Dawber and Tripathi, 2011; Dawber et al., 2011). Increases in the Ca flux from continental weathering when unaccompanied by carbonate compensation is a mechanism of lowering seawater X/Ca , and has been proposed as one way to account for the apparent increase in seawater [Ca] during the middle Miocene glacial expansion (Griffith et al., 2008). During the Neogene the magnitude of seawater [Ca] variations on time scales of 2–4 Myr is ~20% (Fantle and DePaolo, 2005), which is similar to the long-term variability in the middle Eocene Sr/Ca and Mg/Ca records at Site 1209. However, it is difficult to conceive that seawater [Ca] could be decoupled over million year periods from calcite compensation. Griffith et al. (2008) suggest that changes in the rate of dolomitization and or the Ca: HCO_3^- of riverine inputs are possible processes to decouple the Ca and C cycle, but additional work is required to evaluate these hypotheses. Short-term (<1 Myr) variations in the X/Ca at Site 1209, if solely due to changes in seawater [Ca], would require extremely large and unrealistic changes over a geologically rapid time (~15% in [Ca] in <400 kyr).

The release of Sr into the ocean via the erosion and/or recrystallisation of continental shelf aragonite may be an important control on seawater Sr/Ca over a range of time scales, and is hypothesized to drive Pleistocene glacial-interglacial variations of up to ~12% (Stoll and Schrag, 1998, Stoll et al., 1999). Switching the locus of carbonate deposition between the shelf and deep sea may amplify changes in seawater Sr/Ca since most aragonite calcifying species live on the continental shelf (Martin et al., 1999). The

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effect of aragonite weathering fluxes on seawater Li- and B concentrations is not well constrained because partition coefficients for biogenic aragonite species are largely undetermined.

During parts of the middle Eocene, the Site 1209 B/Ca record is positively correlated with the seawater $\delta^{18}\text{O}$ reconstruction for this site (Fig. 3, Dawber and Tripathi, 2011). A notable exception is between ~ 38.7 and 38 Ma when seawater $\delta^{18}\text{O}$ decreases, but B/Ca increases (Fig. 3). In contrast, the *O. umbonatus* Sr/Ca and Li/Ca records are negatively correlated with seawater $\delta^{18}\text{O}$ throughout the middle Eocene (Fig. 3). Between 41 and 40.5 Ma, Li/Ca appear to be decoupled from Sr/Ca and seawater $\delta^{18}\text{O}$, although the significance of this trend is unclear as it is supported by only a few data points. Sr/Ca values of *O. umbonatus* decrease by $\sim 21\%$ across the $\sim 1.1\text{‰}$ positive shift in seawater $\delta^{18}\text{O}$ commencing at ~ 41 Ma, which is interpreted as a major episode of glacial expansion associated with a glacioeustatic lowering (Dawber and Tripathi, 2011). If aragonite weathering was primarily responsible for seawater Sr/Ca variations, the *O. umbonatus* Sr/Ca record should be positively correlated with the seawater $\delta^{18}\text{O}$ reconstruction. Our observations suggest that glacially mediated variations in the continental and shelf flux of Sr to the ocean are not the primary influence on *O. umbonatus* Sr/Ca. Li and B partition coefficients for biogenic shelf aragonite are needed to evaluate this effect on Li/Ca and B/Ca ratios in *O. umbonatus*.

4.2 Estimates of $\Delta[\text{CO}_3^{2-}]$ and temperature based on multi-element ratios

The comparisons of the Site 1209 middle Eocene *X*/Ca records with each other, independent carbon cycle proxies and a seawater $\delta^{18}\text{O}$ reconstruction indicate that element ratios in *O. umbonatus* are not controlled solely by bottom water $\Delta[\text{CO}_3^{2-}]$. Recently, Gaetani and Cohen (2006) and Gaetani et al. (2011) introduced an application of the global minimization technique to solve variations in multiple parameters based on multi-element ratios in corals. Global minimization of multi-element ratio data in foraminifera is potentially a powerful paleoproxy tool for investigating the relative sensitivity of *X*/Ca to several environmental parameters and a means of estimating down

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4.3 Influence of pore water chemistry?

A potential uncertainty of investigating *O. umbonatus* X/Ca ratios as proxies for bottom water $\Delta[\text{CO}_3^{2-}]$ is its reported infaunal habitat, in the upper 0–4 cm in the sediment (Corliss, 1985; Rathburn and Corliss, 1994). Models predict that pore water $\Delta[\text{CO}_3^{2-}]$ may be substantially different (up to 25 %) from bottom waters and vary considerably within the upper few centimeters of the sediment (Martin and Sayles, 1996) as a result of pore water processes (e.g. respiratory oxidation of organic matter in sediments) and acid neutralization reactions (Emerson and Bender, 1981; Archer 1991). In saturated bottom waters where pore water $\Delta[\text{CO}_3^{2-}]$ is predicted to decrease rapidly relative to bottom waters (Martin and Sayles, 1996), or in environments with high rates of respiratory driven dissolution, the reported sensitivity of benthic foraminiferal X/Ca ratios to bottom water $\Delta[\text{CO}_3^{2-}]$ may be underestimated for infaunal taxa. However, it would be difficult to quantifying this uncertainty. In addition, infaunal foraminifera may migrate within the sediment in response to food availability, temperature, and carbonate saturation (Gross, 2000), which may introduce additional inaccuracies into the core-top calibration.

Pore water borate concentrations may also become decoupled from bottom water levels, as the speciation of dissolved boron is pH-dependent (e.g. Hemming and Hanson, 1992). Borate is the species thought to be incorporated into calcium carbonate (Hemming and Hanson, 1992), therefore a shift in the speciation of the pore water boron reservoir as a result of respiratory driven dissolution and acid neutralization reactions may introduce some bias into B/Ca-based reconstructions of $\Delta[\text{CO}_3^{2-}]$ from infaunal taxa. The lower B/Ca sensitivity to bottom water $\Delta[\text{CO}_3^{2-}]$ reported for coretop specimens of the infaunal genus *Uvigerina* compared to the epifaunal genus *Cibicides* (Yu and Elderfield, 2007) is consistent with this hypothesis.

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4.4 Possible implications for middle Eocene climate

If the seawater $\delta^{18}\text{O}$ reconstruction for Site 1209 accurately reflects changes in continental ice storage (Dawber and Tripathi, 2011), the observed variations in *O. umbonatus* $\delta^{13}\text{C}$, Li/Ca, B/Ca and Sr/Ca records support the hypothesis that middle Eocene glaciation was closely coupled to the carbon cycle. Although, the lack of a consistent correlation between all four records throughout the middle Eocene likely indicates that additional parameters are influencing the Li/Ca, B/Ca and Sr/Ca records and that the processes linking the records are complex.

The *O. umbonatus* Sr/Ca record exhibits the most striking correlation with the seawater $\delta^{18}\text{O}$ reconstruction, but as discussed, the relationship is opposite to what might be expected if *O. umbonatus* Sr/Ca was controlled by seawater composition related to shelf aragonite recrystallisation. If *O. umbonatus* Sr/Ca ratios are primarily governed by bottom water $\Delta[\text{CO}_3^{2-}]$, the reconstructions imply that during middle Eocene glacial intervals, carbonate saturation was reduced at Site 1209. Detailed records of CaCO_3 MARs for Sites 1218 and 1219 (Lyle et al., 2005; Tripathi et al., 2005), and a compilation of carbonate content for other tropical Pacific sites have been interpreted to record increased deep water carbonate preservation associated with glacial expansion (ca. 41.5 Ma), as a result of a deepening of the saturation horizon (ca. 41.5 Ma; Lyle et al., 2005; Tripathi et al., 2005). The apparent discrepancy between records from Site 1209 and other Pacific sites may reflect local differences in carbonate saturation. It is also possible that the lysocline and CCD were decoupled during the middle Eocene (Site 1209 would have been closest to the paleo-lysocline). Alternately *O. umbonatus* Sr/Ca ratios may not primarily reflect changes in bottom water $\Delta[\text{CO}_3^{2-}]$.

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5 Summary

Detailed records of *O. umbonatus* Li/Ca, B/Ca, Mg/Ca and Sr/Ca from ODP Site 1209 exhibit well-defined and large amplitude shifts on a number of time-scales during the middle Eocene. Bottom water $\Delta[\text{CO}_3^{2-}]$ may be an important influence on X/Ca, however discrepancies in the nature and magnitude of downcore X/Ca records at Site 1209 suggest that either empirically derived coretop regression models are not appropriate for the early Cenozoic and/or X/Ca are influenced by secondary parameters. The *O. umbonatus* Mg/Ca record for Site 1209 is consistently different to the Li/Ca, B/Ca and Sr/Ca records suggesting that bottom water $\Delta[\text{CO}_3^{2-}]$ is not the dominant control on Mg/Ca ratios for this species. This hypothesis is supported by the order of magnitude difference in the relative sensitivity of *O. umbonatus* Mg/Ca to temperature and $\Delta[\text{CO}_3^{2-}]$, as determined from multiple linear regression. Additional culturing work and down core multi-element studies records are required to further assess the potential of *O. umbonatus* X/Ca ratios as proxy archives for bottom water $\Delta[\text{CO}_3^{2-}]$.

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Table 1. Linear least square regression models fitted through X/Ca and $\Delta[\text{CO}_3^{2-}]$ data.

X/Ca	Dataset used	T range (°C)	$\Delta[\text{CO}_3^{2-}]$ range ($\mu\text{mol kg}^{-1}$)	n	$\Delta[\text{CO}_3^{2-}]$ not corrected for Anthropogenic DIC				$\Delta[\text{CO}_3^{2-}]$ corrected for Anthropogenic DIC			
					Slope ($\text{mmol mol}^{-1} \mu\text{mol}^{-1} \text{kg}^{-1}$ except for B/Ca and Li/Ca – $\mu\text{mol mol}^{-1} \mu\text{mol}^{-1} \text{kg}^{-1}$)	Intercept	R^2	p-value	Slope ($\text{mmol mol}^{-1} \mu\text{mol}^{-1} \text{kg}^{-1}$ except for B/Ca and Li/Ca – $\mu\text{mol mol}^{-1} \mu\text{mol}^{-1} \text{kg}^{-1}$)	Intercept	R^2	p-value
B/Ca	This study	1.1 to 3.6	–23 to 44	37	0.433 ± 0.053	29.7 ± 1.1	0.65	1.5e–9	0.369 ± 0.045	29.9 ± 1.1	0.66	1.3e–9
Li/Ca	All datasets	–0.8 to 3.6	–23 to 45	44	0.0526 ± 0.0084	15.53 ± 0.19	0.46	1.1e–7	0.0466 ± 0.0091	15.60 ± 0.22	0.43	1.2e–5
	This study	1.1 to 3.6	–23 to 44	37	0.0561 ± 0.0105	15.56 ± 0.22	0.45	6.2e–6				
	Lear et al. (2006)	–0.8 to 0.6	6 to 45	9	0.0515	15.3	0.69	0.00149				
Sr/Ca	This study	1.1 to 3.6	–23 to 44	37	0.00241 ± 0.0004	0.8756 ± 0.0074	0.57	7.4e–8	0.00207 ± 0.0003	0.8764 ± 0.0072	0.58	5.2e–8
Mg/Ca	All datasets (except Rathmann and Kuhnert (2007))	–0.9 to 10.5	25 to 70	83	0.0164 ± 0.0016	1.381 ± 0.0366	0.59	1.7e–9	0.0102 ± 0.0014	1.413 ± 0.05	0.41	9.6e–11
	Same but multiple linear regression (Table 3)	–0.9 to 10.5	25 to 70	83	0.017 ± 0.002	1.199 ± 0.055	1.472 ± 0.043	1.5e–14	0.0083 ± 0.001	1.215 ± 0.054	0.56	3.2e–9
	This study	1.1 to 3.6	–23 to 44	37	0.0122 ± 0.0016	1.400 ± 0.034	0.61	1.8e–8	0.00992 ± 0.0015	1.412 ± 0.036	0.56	1.6e–7
	Healey et al. (2006)	1.2 to 4	–3 to 39	24	0.0227 ± 0.0049	1.355 ± 0.105	0.49	1.3e–4				
	Elderfield et al. (2006)	–0.9 to –0.8	6 to 36	6					0.0024 ± 0.0019	1.422 ± 0.048	0.27	0.298
	Lear et al. (2002)	0.8 to 10.5	–22 to 0	16	0.0190 ± 0.0032	1.382 ± 0.087	0.76	1.3e–5				
Rathmann and Kuhnert (2008)	1.6 to 10.4	–25 to 21	6	–0.0092 ± 0.0119	2.137 ± 0.217	0.13						

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Table 2. Linear least square regression models fitted through Mg/Ca, Temperature and $\Delta[\text{CO}_3^{2-}]$ data.

Data set	N	Model	A	B	C	R^2	AIC	p-value	Residual standard error	Ratio B/C*
1	83	Mg/Ca = 1 (null)					99.7			
		Mg/Ca = A + B · BWT	1.360 ± 0.071	0.161 ± 0.026		0.32	69.1	A: 2.0e-16 B: 1.9e-8	0.36	
		Mg/Ca = A + C · $\Delta[\text{CO}_3^{2-}]$	1.472 ± 0.043		0.017 ± 0.002	0.51	40.7	A: 2.0e-16 C: 1.5e-14	0.30	
		Mg/Ca = A + B · BWT + C · $\Delta[\text{CO}_3^{2-}]$	1.355 ± 0.057	0.073 ± 0.025	0.014 ± 0.002	0.56	34.1	A: 2.0e-16 B: 0.00402 C: 2.6e-09	0.29	5.2
2	79	Mg/Ca = 1 (null)					66.2			
		Mg/Ca = A + B · BWT	1.329 ± 0.077	0.169 ± 0.033		0.24	45.3	A: <2e-16 B: 2.5e-06	0.31	
		Mg/Ca = A + C · $\Delta[\text{CO}_3^{2-}]$	1.486 ± 0.039		0.015 ± 0.002	0.43	22.8	A: <2e-16 C: 3.2e-11	0.27	
		Mg/Ca = A + B · BWT + C · $\Delta[\text{CO}_3^{2-}]$	1.289 ± 0.061	0.110 ± 0.028	0.012 ± 0.002	0.52	9.9	A: <2e-16 B: 0.000160 C: 2.2e-09	0.25	9.2
3	77	Mg/Ca = 1 (null)					104.9			
		Mg/Ca = A + B · BWT	1.247 ± 0.090	0.200 ± 0.032		0.34	65.9	A: <2e-16 B: 2.0e-08	0.36	
		Mg/Ca = A + C · $\Delta[\text{CO}_3^{2-}]$	1.486 ± 0.042		0.018 ± 0.002	0.57	32.0	A: <2e-16 C: 1.1e-15	0.29	
		Mg/Ca = A + B · BWT + C · $\Delta[\text{CO}_3^{2-}]$	1.446 ± 0.078	0.023 ± 0.037	0.017 ± 0.003	0.57	33.6	A: <2e-16 B: 0.547 C: 1.1e-08	0.29	1.4
4	73	Mg/Ca = 1 (null)					65.2			
		Mg/Ca = A + B · BWT	0.967 ± 0.119	0.317 ± 0.050		0.35	34.2	A: 1.1e-11 B: 1.7e-08	0.30	
		Mg/Ca = A + C · $\Delta[\text{CO}_3^{2-}]$	1.495 ± 0.038		0.016 ± 0.002	0.50	14.9	A: <2e-16 C: 1.18e-12	0.2608	
		Mg/Ca = A + B · BWT + C · $\Delta[\text{CO}_3^{2-}]$	1.296 ± 0.122	0.103 ± 0.061	0.013 ± 0.003	0.52	13.9	A: 3.5e-16 B: 0.0924 C: 4.1e-06	0.26	7.9

Data sets 1 All data except Rathmann and Kuhnert (2007). 2 All data except Rathmann and Kuhnert (2007) and Little Bahama Bank data from Lear et al. (2002). 3 All data except Rathmann and Kuhnert (2007) and Norwegian Sea data from Elderfield et al. (2006). 4 All data except Rathmann and Kuhnert (2007), Little Bahama Bank data from Lear et al. (2002) and Norwegian Sea data from Elderfield et al. (2006).

* Ratio BWT: $\Delta[\text{CO}_3^{2-}]$ coefficients (per unit Mg/Ca change)

Element/Calcium ratios in middle Eocene samples

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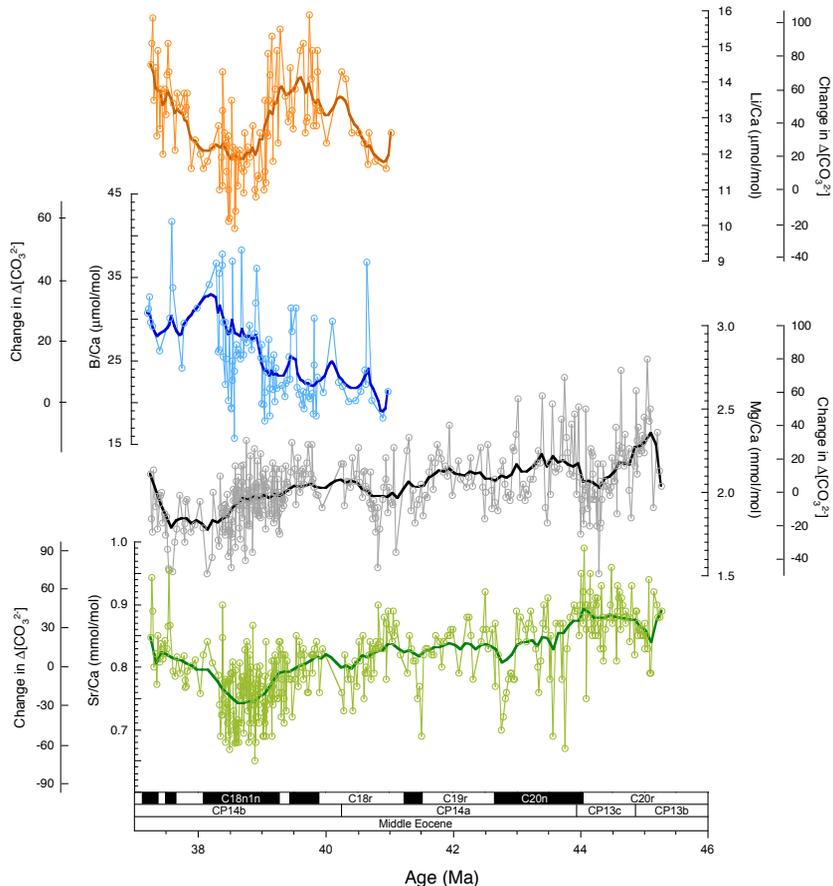


Fig. 1. High-resolution middle Eocene records of *O. umbonatus* Li/Ca, B/Ca, Mg/Ca and Sr/Ca from ODP Site 1209, equatorial Pacific Ocean. Heavier lines denote a weighted smoothing function. Bottom water $\Delta[\text{CO}_3^{2-}]$ ($\mu\text{mol kg}^{-1}$) scale bar is based on the core top calibrations of Dawber and Triпати (2011) shown in Table 1.

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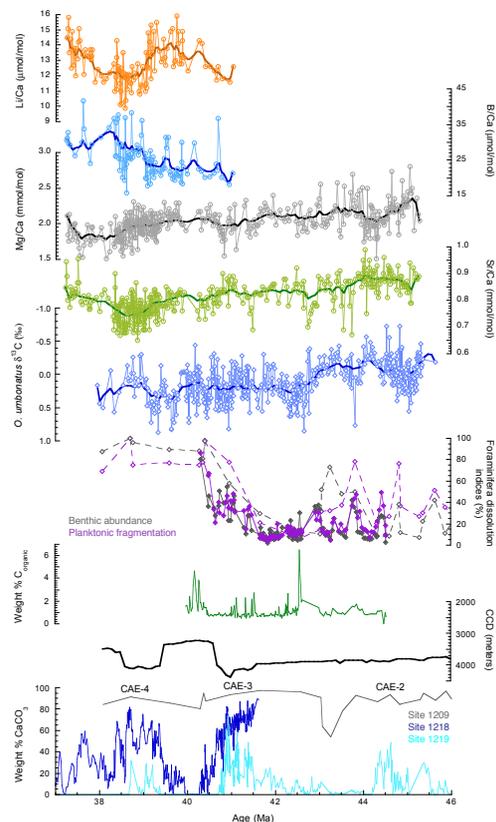


Fig. 2. Comparison of Site 1209 *O. umbonatus* X/Ca records with independent carbon cycle proxies. Benthic abundance (%) and planktonic fragmentation, proxies for carbonate dissolution, are shown in grey and pink respectively, solid lines denote data from this study and dashed lines are data from Hancock and Dickens (2005). Differences in absolute values reflect the different size fractions used to define the “coarse” fraction. The records of weight percentage of CaCO_3 are from Hancock and Dickens (2005), Tripati et al. (2005) and Lyle et al. (2006). CAE is an abbreviation for the carbonate-accumulation events documented by Lyle et al. (2006). The calcite compensation depth (CCD) reconstruction is from Tripati et al. (2005).

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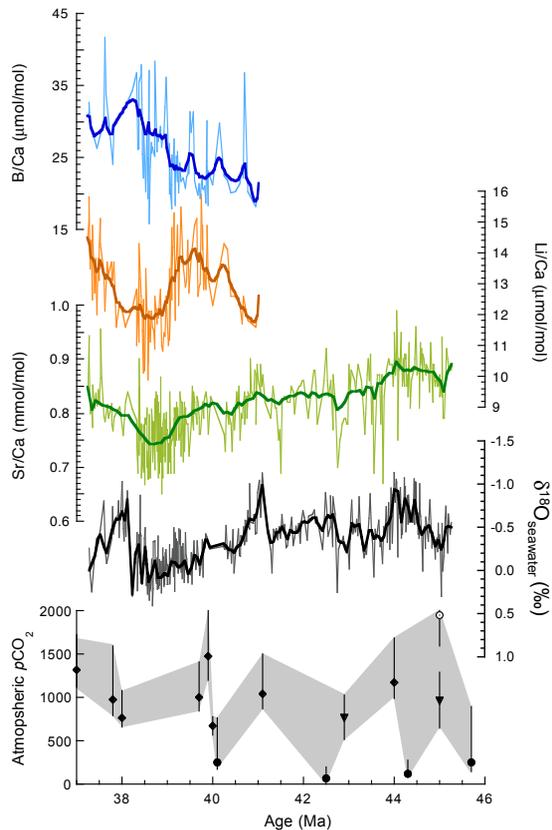


Fig. 3. Comparison of the down core *O. umbonatus* X/Ca records with the seawater $\delta^{18}\text{O}$ reconstruction from ODP Site 1209 (Dawber and Tripathi, 2011). Shown for reference are estimates of atmospheric $p\text{CO}_2$ based on alkenones (diamonds, Pagani et al., 2005; Freeman and Hayes, 1992); boron isotopes in carbonates (circles, Demicco et al., 2003); stomatal indices (inverted triangle, McElwain, 1998; Kurschner et al., 2001); and paleosol carbon isotopes (open circle with dot, Ekart et al., 1999).

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