**Biogeosciences
Discussions**

Relationships between bottom water carbonate saturation and element/Ca ratios in coretop samples of the benthic foraminifera *Oridorsalis umbonatus*

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Benthic foraminiferal element ratios and carbonate chemistry

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Abstract

Elemental ratios in benthic foraminifera have been used to reconstruct bottom water temperature and carbonate saturation ($\Delta[CO_3^{2-}]$). We present elemental data for the long-ranging benthic foraminifera *Oridorsalis umbonatus* from sediment core tops that span a narrow range of temperatures and a wide range of saturation states. B/Ca, Li/Ca, Sr/Ca and Mg/Ca ratios exhibit positive correlations with bottom water carbonate saturation. The sensitivity of individual element/calcium ratios to bottom water $\Delta[CO_3^{2-}]$ varies considerably, with B/Ca being most sensitive and Sr/Ca the least sensitive. The empirically derived sensitivity of B/Ca, Li/Ca, Mg/Ca and Sr/Ca to bottom water $\Delta[CO_3^{2-}]$ are 0.433 ± 0.053 and $0.0561 \pm 0.0084 \, \mu mol \, mol^{-1}$ per $\mu mol \, kg^{-1}$ and 0.0164 ± 0.0015 and $0.00241 \pm 0.0004 \, \mu mol \, mol^{-1}$ per $\mu mol \, kg^{-1}$, respectively. To assess the fidelity of these relationships and the possibility of applying these relationships to earlier periods of Earth history, we examine the mechanisms governing elemental incorporation into foraminiferal calcite. Empirical partition coefficients for Li and Sr are consistent with Rayleigh fractionation from an internal pool used for calcification. For *O. umbonatus* and other benthic species, we show that the fraction of Ca remaining in the pool is a function of bottom water $\Delta[CO_3^{2-}]$, and can be explained by either a growth rate effect and/or the energetic cost of raising vesicle pH at the site of calcification. Empirical partition coefficients for Mg and B may also be controlled by Rayleigh fractionation, but require that either the fractionation factor from the internal pool is smaller than the inorganic partition coefficient and/or additional fractionation mechanisms. *O. umbonatus* element ratio data may also be consistent with fractionation according to the surface entrapment model and/or the presence of discrete high- and low-Mg calcite phases. However at present we are limited in our ability to assess these mechanisms. The new X/Ca data for *O. umbonatus* provide constraints to test the role of these mechanisms in the future.

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1 Introduction

Elemental ratios in benthic foraminifera can be routinely measured with excellent precision (Yu et al., 2005), and have been used for several decades to investigate past variations in seawater composition and hydrographic parameters (e.g. Lear et al., 2000, 2003, 2010; Rosenthal et al., 1997, 2006; Marchitto et al., 2002, 2007; Tripati et al., 2005; Tripati and Elderfield, 2005; Elderfield et al., 2006; Yu and Elderfield, 2007, 2008; Bryan and Marchitto, 2008; Dawber and Tripati, 2011). However, the mechanism(s) of cation incorporation into foraminiferal calcite and the nature of relationship with hydrographic parameters and seawater chemistry are not well understood and are an area of active research. A number of empirical-based studies have demonstrated that elemental ratios (X/Ca) in benthic foraminifera (e.g. Sr/Ca, Li/Ca and B/Ca) correlate with bottom water carbonate saturation ($\Delta[CO_3^{2-}]$, where $\Delta[CO_3^{2-}]$ is the difference between saturation and in situ $[CO_3^{2-}]$; Lear and Rosenthal, 2006; Yu and Elderfield, 2007, 2008; Dissard et al., 2010), but the basis for the relationship is unknown. Culture studies on two species of planktonic foraminifera report similar relationships between Sr/Ca and U/Ca and ambient pH and/or $[CO_3^{2-}]$, and hypothesize that the relationship reflects a kinetic influence of carbonate chemistry on calcification rate (Lea et al., 1999; Russell et al., 2004). Inorganic calcite precipitation and foraminifera culturing experiments provide clues to the nature of the relationship between foraminifera X/Ca and $\Delta[CO_3^{2-}]$, but at present it is not known which mechanism(s) exerts the dominant influence.

Precipitation experiments report multiple influences on cation (Sr^{2+}, Mn^{2+}, Cd^{2+}, Mg^{2+}, Co^2) incorporation in inorganic calcite, including precipitation rate, temperature and solution and solid composition (e.g. Holland et al., 1964; Lorens 1981; Mucci and Morse 1983; Morse and Bender, 1990, Rimstidt et al., 1998; Nehrke et al., 2007; Tang et al., 2008). The "surface entrapment model" for inorganic calcite precipitation (Watson and Liang, 1995; Watson, 2004; Gabitov and Watson, 2006) has been shown to be consistent with experimental data and provides a viable mechanism for the apparent dependency of Sr partition coefficients on precipitation rate, solution chemistry,

temperature and pH (Lorens, 1981; Gabitov and Watson, 2006; Tang et al., 2008). This model proposes that during inorganic calcite precipitation a transitional surface layer is formed, which may be enriched in Sr (or other ions) due to disequilibrium partitioning. Two kinetic effects are thought to cause this disequilibrium partitioning (Tang et al., 2008): (1) crystal growth behavior, i.e. at faster precipitation rates, more Sr is trapped in the surface layer and (2) ion diffusion behavior, i.e. Sr diffuses back into the surface layer prior to being incorporated into the crystal lattice. The Sr enrichment in the surface layer relative to the crystal interior constitutes an effective partition coefficient, which has been suggested to be a function of temperature (through the dependency on diffusivity), growth rate and/or surface composition (Watson, 2004), and solution chemistry (e.g. pH and ionic strength, though the dependency of surface cation adsorption, Tang et al., 2008). The Surface Entrapment model may also be relevant to other cations, although the magnitude of effective partition coefficient will likely vary between cations to reflect differences in diffusivity and surface adsorption properties.

Empirical partition coefficients for benthic foraminifera (D_X) are notably different to experimentally derived partition coefficients for inorganic calcite (α; e.g. Elderfield et al., 1996). Inorganic partition coefficients are a function of precipitation rate, tending away from α, towards 1, at faster rates (Lorens, 1981; Pingitore and Eastman, 1986; Rimstidt et al., 1998). Sr partition coefficients in cultured planktonic foraminifera ($D_{Sr} < 1$) increase with increased calcification rate (Kisakürek et al., 2008). In contrast, the opposite relationship is observed between D_{Sr} and calcification rate in cultured benthic foraminifera (Erez, 2003). These observations imply that inorganic calcite precipitation is probably an overly simplistic model of foraminifera calcification, which is likely mediated by additional kinetic and/or physiological processes.

Perforate foraminifera are thought to biomineralize through the vacuolization of seawater, which is modified through physiological reactions to increase the pH (and hence $[CO_3^{2-}]$), and perhaps reduce Mg poisoning (Erez et al., 1994; Erez, 2003; de Nooijer et al., 2009). The $[Ca^{2+}]/[CO_3^{2-}]$ of the seawater vacuole may directly influence D_X in a similar manner to inorganic calcite (Nehrke et al., 2007). If so, the physiological

reactions that increase the vacuole pH (and $[CO_3^{2-}]$) may account for the species-specific sensitivities of X/Ca to bottom water $\Delta[CO_3^{2-}]$ (Hall and Chan, 2004; Lear and Rosenthal, 2006; Yu and Elderfield, 2007).

An alternative empirical model that is supported by experimental observations proposes that the D_X in foraminifera and other biogenic carbonates are a function of the amount of Ca remaining in the "internal biomineralization pool" after the precipitation of $CaCO_3$ (Rayleigh fractionation; Elderfield et al., 1996, Erez, 2003; Gagnon et al., 2007). If the fraction of calcium remaining in this internal pool is influenced by $[CO_3^{2-}]$ and/or $\Delta[CO_3^{2-}]$, then the Rayleigh fractionation model may be a valid mechanism to relate foraminifera X/Ca to bottom water $\Delta[CO_3^{2-}]$. Variations in the fraction of calcium utilized may arise from changes in either the calcification rate, the size of the biomineralization reservoir, or the flushing/replenishing time of the pool. Flushing rate may be directly linked to the calcification rate, as the faster the rate of $CaCO_3$ precipitation, the quicker the reservoir may need to be replenished (Elderfield et al., 1996; Erez, 2003).

Recent in vivo experiments of foraminiferal calcification (Bentov and Erez, 2005) observed the precipitation of two types of calcite in perforate foraminifera, a "high-Mg" primary layer sandwiched between thick (90 % of test) "low-Mg" secondary layers (not to be confused with diagenetic inorganic calcite). The concentration of Mg, S and possibly other trace metals differs between high- and low-Mg calcite (Erez, 2003), and the observed inter-test heterogeneity of some trace metals (Szafranek and Erez, 1993; Eggins et al., 2004; Anand and Elderfield, 2005; Sadekov et al., 2005; Kunioka et al., 2006), is consistent with the presence of distinct types of calcite in foraminiferal tests. High Mg calcite is more soluble than low-Mg calcite (Morse and Mackenzie, 1990), and therefore the proportion of primary ("high-Mg") to secondary ("low-Mg") calcite in foraminiferal tests may be controlled by ambient $\Delta[CO_3^{2-}]$. If trace metal concentrations in high- and low-Mg calcite are shown to be different, variations in the proportions of primary and secondary calcite may provide another viable mechanism for relating foraminiferal X/Ca to bottom water $\Delta[CO_3^{2-}]$.

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Here we employ an empirical approach to investigate the sensitivity of elemental ratios (B/Ca, Li/Ca, Sr/Ca and Mg/Ca) in core top specimens of the benthic foraminifera *O. umbonatus* to bottom water $\Delta[CO_3^{2-}]$. We assess the fidelity of these relationships by examining the consistency of the X/Ca data and partition coefficients with the hypoth-
5 esized biomineralziation models discussed. *O. umbonatus* was chosen for this study because it is a shallow-dwelling infaunal species that is commonly found in marine sediments dating back to the late Cretaceous (Corliss 1985; Lear et al., 2000). Better understanding of the systematics of the relationship between *O. umbonatus* X/Ca and bottom water $\Delta[CO_3^{2-}]$ will allow for greater confidence in applying these relationships
10 to earlier periods of Earth history.

2 Materials and methods

Coretop samples were chosen from the Atlantic, Pacific and Indian Oceans (Table 1) to span a large range of bottom water carbonate saturation (−23 to 44 μmol kg^{-1}) and a narrow temperature range (1.1–3.6 °C). Hydrographic data was obtained from the CA-
15 RINA and GLODAP datasets using Ocean Data Viewer (ODV). Post-industrial carbonate system parameters were calculated in ODV using constants from the Best Practices Handbook (Dickson et al., 2007). Pre-industrial carbonate system parameters were calculated using anthropogenic corrected estimates of DIC in CO2SYS, using the set of constants from Mehrbach et al. (1973) as refit by Dickson and Millero (1987) and the
20 K_{HSO_4} formulation of Dickson (1990).

Specimens of *O. umbonatus* were picked from the >150 μm size fraction and cleaned using a standard oxidative-cleaning protocol (Barker et al., 2003). X/Ca ratios were determined from matrix-matched intensity ratios on a quadrapole inductively coupled plasma mass spectrometer at the University of Cambridge (Yu et al., 2005). Samples
25 were screened for contaminating phases including clays, ferromanganese oxides and carbonates, organic matter and silicates using ancillary X/Ca 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). Typical reproducibility of our method based on benthic foraminiferal replicate samples is better than 1.6 % for Mg/Ca, B/Ca and Li/Ca, and better than 0.7 % for Sr/Ca (% relative standard deviation)

5 We also compiled published data on X/Ca ratios in *O. umbonatus* from the literature and calculated bottom water saturation at these sites using the same hydrographic datasets and constants mentioned above. We compare measured X/Ca ratios to all published data for *O. umbonatus* available, with a single exception. We exclude comparisons to Rathmann et al. (2004) and Rathmann and Kuhnert (2008) simply because

10 they used laser ablation techniques to determine X/Ca ratios, and it is unclear how representative values that are measured using this method are of whole test composition.

Foraminiferal partition coefficients are calculated using measured foraminifera X/Ca and the X/Ca of seawater (Mg/Ca $\sim 5.3 \, \text{mol} \, \text{mol}^{-1}$; B/Ca $\sim 0.040 \, \text{mol} \, \text{mol}^{-1}$; Li/Ca $\sim 2.52 \, \text{mmol} \, \text{mol}^{-1}$ and Sr/Ca $\sim 8.72 \, \text{mmol} \, \text{mol}^{-1}$). The fraction of Ca remaining

15 after a batch of calcification (F, as shown in Figs. 4 and 5) is calculated according to Elderfield et al. (1996), and using values of 0.044 (Kitano et al., 1971) and 0.004 (Okumura and Kianto, 1986) for the Sr and Li inorganic calcite partition coefficients, respectively.

3 Results

20 B/Ca, Li/Ca, Sr/Ca and Mg/Ca ratios in coretop specimens of *O. umbonatus* are regressed against bottom water $\Delta[\text{CO}_3^{2-}]$ (Fig. 1, Table 2). All X/Ca ratios exhibit a significant correlation with bottom water $\Delta[\text{CO}_3^{2-}]$, although regression parameters differ depending on which hydrographic dataset is used (Table 2). This empirical approach assumes that that it is appropriate to compare core top sediment with modern hy-

25 drographic values. Depending on local sedimentation rates, the upper centimeter of the sediment column could represent several tens to thousands of year's accumulation. Some hydrographic parameters can be assumed to be relatively constant on

these timescales; however over the last century the inventory of dissolved inorganic carbon (DIC) in the ocean has changed as a result of anthropogenic CO_2 emissions. Several attempts have been made to estimate anthropogenic carbon uptake (see review in Sabine and Tanhua, 2010), including a study that utilized the GLODAP data set (Waugh et al., 2006). It is possible therefore to calculate pre-industrial DIC and $\Delta[CO_3^{2-}]$ by correcting measured DIC for anthropogenic uptake, and this approach has been adopted previously (Yu and Elderfield, 2007; Lear et al., 2010). Anthropogenic carbon uptake is spatially heterogeneous (Sabine et al., 2004), and large areas of the oceans are poorly represented in the GLODAP data set. As a result, pre-anthropogenic DIC estimates may contain significant bias if hydrographic data needs to be interpolated over significant distances. The empirical strategy adopted here has been to utilize the data sets with the greatest spatial coverage (i.e. to use both CARINA and GLODAP data sets). We also note that anthropogenic carbon uptake has not yet penetrated many of the bottom water environments examined in this study, and that the majority of core top samples in this study lack unequivocal pre- or post-industrial age constraints (Rose Bengal staining or ^{14}C-AMS dates). We calculate regression statistics for both modern $\Delta[CO_3^{2-}]$ and pre-industrial $\Delta[CO_3^{2-}]$ scenarios, but illustrate only the uncorrected $\Delta[CO_3^{2-}]$ regressions (Fig. 1).

The sensitivity of X/Ca to bottom water $\Delta[CO_3^{2-}]$ varies, with B/Ca ratios being the most sensitive and Mg/Ca the least sensitive. There is some indication that the sensitivity of Sr/Ca ratios may be different in the separate ocean basins (Fig. 1c). *O. umbonatus* Sr/Ca from the Pacific Ocean appear to exhibit a greater sensitivity to bottom water $\Delta[CO_3^{2-}]$. The source of this difference is unclear, but it does not appear to reflect a specific $\Delta[CO_3^{2-}]$-threshold as has been reported for benthic Mg/Ca (Elderfield et al., 2006). The relationship between Li/Ca and bottom water $\Delta[CO_3^{2-}]$ (Fig. 1a) is consistent with that published for *O. umbonatus* from a coretop depth transect in the Norwegian Sea irrespective of whether or not bottom water $\Delta[CO_3^{2-}]$ is corrected for anthropogenic DIC (Lear and Rosenthal, 2006; Lear et al., 2010). The narrow

temperature range of the core top dataset limits our ability to rigorously evaluate the influence of temperature on X/Ca ratios.

Linear regressions of the individual X/Ca ratios (Fig. 2) demonstrate that some component of the observed coretop variability may be explained by a common factor, possibly bottom water $\Delta[CO_3^{2-}]$. However, it is clear that other parameters must also influence some/all of the X/Ca ratios, and that the sensitivity of individual X/Ca ratios to these additional parameters may be different.

4 Discussion

Core top element data suggests that there is a relationship between *O. umbonatus* Li/Ca, B/Ca, Mg and Sr/Ca and bottom water $\Delta[CO_3^{2-}]$. However with an empirical basis, it is not always clear if the correlations between X/Ca and bottom water $\Delta[CO_3^{2-}]$ reflect a genuine causal relationship or reflect the covariation of $\Delta[CO_3^{2-}]$ with other hydrographic parameters that influence X/Ca. One strategy to assess the fidelity of these apparent relationships is to examine the mechanistic cause. A second strategy, presented elsewhere (Dawber and Tripati, in review at Climate of the Past), is to apply these relationships to down core records of *O. umbonatus* X/Ca and assess the consistency of the $\Delta[CO_3^{2-}]$ reconstructions based on multi-element data and comparisons with other proxy data. Here, we examine the compatibility of the *O. umbonatus* X/Ca with hypothesized models of inorganic and foraminiferal mineralization.

4.1 Surface Entrapment Model

Experimentally determined Sr inorganic calcite partition coefficients are controlled by precipitation rate and are temperature sensitive (Tang et al., 2008). Sr incorporation in inorganic calcite is consistent with the Surface Entrapment Model (SEMO, Watson and Liang, 1995, Watson, 2004; Tang et al., 2008) and to a first approximation Sr inorganic partition coefficients can be used as an indicator of precipitation rate if changes in pH

and temperature are not significant (Tang et al., 2008). Empirical partition coefficients (D_X) for *O. umbonatus* and other species of benthic foraminifera as a function of bottom water $\Delta[CO_3^{2-}]$ are shown in Fig. 3. Li, B, Mg and Sr empirical partition coefficients increase with increasing bottom water $\Delta[CO_3^{2-}]$. Assuming that the positive relationship

5 between seawater $[CO_3^{2-}]$ and calcification rate established for planktonic foraminifera (Russell et al., 2004) is also applicable to benthic foraminifera, *O. umbonatus* Li, B, Mg and Sr partition coefficients positively correlate with calcification rate, suggesting that Li, B, Mg and Sr incorporation could be consistent with the SEMO. In the SEMO, the increase in Sr inorganic partition coefficients with increasing precipitation rate reflects the

10 progressive retainment of Sr from the enriched surface layer as the precipitation rate exceeds Sr lattice diffusion rates. It is interesting that Li, B, Mg and Sr exhibit similar relationships with $\Delta[CO_3^{2-}]$ (and calcification rate) given their differences in ionic radius, charge and potential site location in the calcite lattice (i.e. interstitial or Ca site) and presumably, their diffusion coefficients. It should be possible to further check whether

15 *O. umbonatus* empirical partition coefficients are consistent with the SEMO by checking the relative sensitivity of D_X with the relative diffusion coefficients in calcite. Unfortunately, to our knowledge, there are no estimates of low temperature cation diffusion coefficients in calcite. From high temperature experiments, it is clear that diffusion coefficients in calcite cannot simply be estimated from size and charge considerations, and

20 knowledge of the diffusion pathway (i.e. interstitial or vacancies) is important (Cherniak, 2010). Inorganic calcite precipitation experiments over the temperature and pressure range of *O. umbonatus* habitats are needed to constrain cation diffusion coefficients in order to better define any similarities between *O. umbonatus* biomineralization and the SEMO. Interestingly, other species of benthic foraminifera exhibit a negative correlation

25 between Li empirical partition coefficients and bottom water $\Delta[CO_3^{2-}]$ (and presumably calcification rate, Fig. 3), which suggests that Li incorporation and perhaps other ions in foraminiferal calcite does not follow the SEMO.

4.2 Rayleigh fractionation

Seawater vacuoles are thought to be the main source of ions in foraminiferal calcite (Erez, 2003). In a conceptual model, Elderfield et al. (1996) described the evolution of empirical partition coefficients as a function of the amount of Ca remaining in an internal pool serving calcification. In the semi-enclosed pool, cations are incorporated into foraminiferal calcite with a constant fractionation factor, assumed to be the inorganic partition coefficient. Empirical Sr and Li partition coefficients for *O. umbonatus* (0.09–0.11 and 0.005–0.0075, respectively) are larger than the inorganic calcite partition coefficients (0.04 and 0.004, Lorens, 1978, 1981; Elderfield et al., 1996; Okumura and Kitano, 1986), but less than one, consistent with calcification from a semi-enclosed pool that is modified via Rayleigh fractionation. In contrast, Mg and B empirical partition coefficients for *O. umbonatus* (0.00017–0.00068 and 0.0005–0.0014, respectively) are significantly lower than the inorganic partition coefficients (0.0573 and 0.38–4.0, respectively, Katz, 1973; Gabitov et al., 2011; Hemming et al., 1995). This observation does not preclude a Rayleigh fractionation mechanism in *O. umbonatus*, but indicates that for Mg and B, either the fractionation factor from the internal pool is significantly smaller than the inorganic partition coefficient, or there are additional mechanisms contributing to the partition coefficients.

If Rayleigh fractionation is controlling partition coefficients in *O. umbonatus,* Sr partition coefficients imply that ∼84–92 % of the Ca in the internal pool is consumed in a single batch of calcification (Fig. 4). Similar calculations for three other benthic species (Elderfield et al., 1996) indicate that they use a slightly larger proportion of the internal pool (94–99 %) compared to *O. umbonatus. O. umbonatus* Li partition coefficients have a much wider range, indicating that ∼37–77 % of the Ca is used during each batch of calcification (Fig. 5). This range in the proportion of Ca used from the internal pool overlaps the range observed in other benthic species (Fig. 5). But interestingly, the infaunal species (*O. umbonatus* and *U. peregrina*) appear to use a greater proportion of the Ca in the internal pool than the epifaunal species (Fig. 5).

For Sr and Li partition coefficients in *O. umbonatus* there is a well defined, positive correlation between the fraction of the internal Ca pool is used for calcification and ambient seawater $\Delta[CO_3^{2-}]$ (refer to colour versions of Figs. 4 and 5). In contrast, the opposite relationship is observed for the four other benthic species for which Li/Ca data is available (Fig. 5). One way to account for the positive correlation between the apparent fraction of the Ca pool consumed during calcification and ambient seawater $\Delta[CO_3^{2-}]$ in *O. umbonatus* is the through the influence of seawater $\Delta[CO_3^{2-}]$ on calcification rate, i.e. high seawater $\Delta[CO_3^{2-}]$ results in high calcification rates that consume a greater proportion of Ca in the internal pool before replenishing/flushing. This scenario assumes a somewhat constant replenishing/flushing rate of the internal Ca pool. It is not known whether the replenishing/flushing rate would also be dependent on calcification rate, for example, if flushing rate positively correlates with calcification rate, the higher frequency of flushing expected at higher seawater $\Delta[CO_3^{2-}]$ would correlate with proportionally lesser amounts of Ca consumption per batch. This prediction is opposite to that observed in *O. umbonatus*, but is consistent with the Li partition coefficients for the four other benthic species.

Recently, it has been observed that benthic foraminifera raise the pH of vesicles at the site of calcification, which is though to be a widespread strategy for increasing $[CO_3^{2-}]$ to promote calcification (Erez, 2003; de Nooijer et al., 2009). Although the energy consumption associated with raising vesicle pH (and $[CO_3^{2-}]$) is unconstrained, and is likely a complex process that will depend on the presence of other ions (e.g. Mg, Zeebe and Sanyal, 2002), it is a reasonable first order assumption that it will be inversely related to initial vacuole (and therefore seawater) $\Delta[CO_3^{2-}]$. If Rayleigh fractionation occurs in tandem with increased vesicle pH, it follows that foraminifera that vacuolise low $\Delta[CO_3^{2-}]$ seawater require more energy to raise vesicle pH. Hence it would be energetically more efficient to replenish/flush the internal pool less frequently; therefore presumably a greater proportion of the pool would be consumed during each batch of calcification. This hypothesis predicts a negative correlation between the fraction of Ca consumed from the internal pool and bottom water $\Delta[CO_3^{2-}]$,

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which is observed in *U. peregrina, C. pachyderma, P. foveolata* and *P. ariminensis* but is opposite to the trend observed in *O. umbonatus* (Fig. 5).

If Sr and Li discrimination in benthic foraminifera is controlled by Rayleigh fractionation from an internal pool, our observations suggest that there may be significant differences in the replenishing/flushing dynamics between species. To reconcile the positive correlation between the fraction of the internal pool consumed per batch of calcification and bottom water $\Delta[CO_3^{2-}]$ in *O. umbonatus,* the replenishing/flushing frequency of the internal pool must be relatively invariant to $\Delta[CO_3^{2-}]$. With an approximately constant replenishing/flushing rate, *O. umbonatus* specimens that vacuolise low $\Delta[CO_3^{2-}]$ seawater and require greater energy to raise vesicle pH to overcome calcification barriers, calcify more slowly and therefore use less of the internal pool.

4.3 Multiple calcite phases in foraminifera test

The inter-test heterogeneity of some elements in foraminiferal tests (Szafranek and Erez, 1993; Eggins et al., 2004; Anand and Elderfield, 2005; Sadekov et al., 2005; Kunioka et al., 2006) may reflect the presence of distinct types of calcite. Alternating bands of "high-Mg" (7.0–10.0 mmol mol^{-1}) and "low-Mg" (~3.0–5.5 mmol mol^{-1}) calcite are observed in *O. universa* and *Globigerinoides* sp. High Mg calcite is more soluble than low-Mg calcite (Morse and Mackenzie, 1990) therefore the alternating bands of high- and low-Mg may reflect diurnal variations in the pH (up to 0.9 pH units, Eggins et al., 2004), and $\Delta[CO_3^{2-}]$ of the foraminiferal microenvironment as a result of the day-night, photosynthesis-respiration cycle of the algal symbionts (Eggins et al., 2004; Sadekov et al., 2005). This mechanism cannot account for the Mg/Ca variability reported in some non-symbiotic species and benthic species (Erez, 2003; Bentov and Erez, 2005), however a similar control on the micro-environment pH by the foraminifera is feasible, possibly through changes in respiration or metabolism (Eggins et al., 2004; Sadekov et al., 2005). If empirical partition coefficients in *O. umbonatus* primarily reflect changes in the proportion of high- and low-Mg calcite phases, the trend of increasing

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D_X with bottom water $\Delta[CO_3^{2-}]$ would predict that the Li, B and Sr concentrations would be higher in the high-Mg calcite phase. This hypothesis is testable and future micro-analysis studies should aim to characterize the minor and trace element composition of the alternating bands in foraminiferal tests. We note that our inferences about the Li and Sr composition of the high-Mg calcite phase are consistent with inorganic calcite precipitation experiments, in which Li and Sr inorganic calcite partition coefficients increase with increasing Mg concentration in the parent solution and solid (Mucci and Morse, 1983; Okumura and Kitano, 1986).

5 Summary

The B/Ca, Li/Ca, Sr/Ca and Mg/Ca ratios and empirical partition coefficients for core-top specimens of the benthic foraminifera *O. umbonatus* exhibit significant, positive correlations with bottom water $\Delta[CO_3^{2-}]$. Mg and B empirical partition coefficients are significantly smaller than inorganic partition coefficients suggesting that their incorporation into foraminiferal calcite is not primarily controlled by the Surface Entrapment Model (Watson and Liang, 1995; Watson, 2004; Tang et al., 2008). Furthermore, the observation that Li, B, Mg and Sr empirical partition coefficients all exhibit a similar relationship with bottom water $\Delta[CO_3^{2-}]$, despite their presumed differences in lattice diffusivity, may also argue against these elements being incorporated according to the SEMO. However, calcite lattice diffusion coefficients are not well constrained. Inorganic precipitation experiments at low temperatures are needed to better define relative cation diffusivities, which should help elucidate any similarities between Li, B, Mg and Sr incorporation in *O. umbonatus* and the SEMO.

The Sr and Li data for *O. umbonatus* is consistent with the Rayleigh fractionation mechanism of Elderfield et al. (1996). We demonstrate that the proportion of the internal Ca pool used for calcification is a function of seawater $\Delta[CO_3^{2-}]$, possibly through a direct influence on growth rate and/or the energetic cost of raising the internal vesicle pH. Our observations for Li partition coefficients for several species suggest that

if Rayleigh fractionation is the correct model of ion discrimination, there may be significant differences in the replenishing/flushing dynamics of the internal pool between species. Rayleigh fractionation may also control Mg and B incorporation, but to account for the small empirical partition coefficients either the fractionation factor from the internal pool must be much smaller than the inorganic partition coefficient and/or additional fractionation mechanisms operate. In situ sampling of the minor and trace element composition of foraminiferal vesicles will provide constraints on the Mg and B fractionation factor (α) and insights into the possible role of ion transport fractionation. The presence of two phases of Mg-calcite, whose proportions reflect changes in $\Delta[CO_3^{2-}]$, cannot be vigorously assessed because the Li, B and Sr composition of these phases is unknown at present. However, if this mechanism is the dominant influence on empirical partition coefficients, the similarity of the relationships between Li, B, Mg and Sr and $\Delta[CO_3^{2-}]$ would predict that the high-Mg calcite phase would have higher concentrations of Li, B and Sr than the low-Mg calcite phase. The relevance of this biomineralization mechanism for *O. umbonatus* can be tested by characterizing the minor and trace element composition of the two Mg-calcite phases and comparing it to the predicted composition based on the X/Ca-$\Delta[CO_3^{2-}]$ relationships presented here.

Although it is not possible to unequivocally distinguish the source of element fractionation in *O. umbonatus*, the new X/Ca data provide testable constraints for biomineralization models. The consistency of the *O. umbonatus* minor and trace element partition coefficients with several of the hypothesized models of biomineralization in foraminifera illustrates that there is likely a mechanistic cause for the empirical correlation observed between X/Ca and bottom water $\Delta[CO_3^{2-}]$, rather than reflecting the covariation of $\Delta[CO_3^{2-}]$ with other hydrographic parameters that influence X/Ca. This assessment provides some confidence that the core top relationships between *O. umbonatus* X/Ca and bottom water $\Delta[CO_3^{2-}]$ could be applied to earlier periods of Earth history.

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Table 1. Location details of core top samples used in this study.

Core	Depth	Basin	Latitude °N	Longitude °W	Water depth m
BOFS 5K	core top	Atlantic Ocean	50.70	21.90	3547
BOFS 8K	core top	Atlantic Ocean	52.50	22.10	4045
CD 113A SITE A	core top	Atlantic Ocean	52.92	16.92	3600
NEAP 17B	core top	Atlantic Ocean	56.10	27.20	2734
NEAP 19B	core top	Atlantic Ocean	52.45	30.20	3283
NEAP 20B	core top	Atlantic Ocean	42.29	28.24	2878
T86 15B	core top	Atlantic Ocean	30.48	36.95	3271
T86 5B	core top	Atlantic Ocean	46.90	25.40	3121
T88 11B	core top	Atlantic Ocean	45.40	25.40	2741
T88 12B	core top	Atlantic Ocean	44.10	24.90	3052
T88 15AB	core top	Atlantic Ocean	38.90	25.00	2738
T88 17B	core top	Atlantic Ocean	35.40	29.40	2934
T88 19B	core top	Atlantic Ocean	31.31	30.48	3726
T90 10B	core top	Atlantic Ocean	45.36	27.15	2162
T90 13B	core top	Atlantic Ocean	44.00	20.02	4016
T90 15B	core top	Atlantic Ocean	47.60	20.92	4177
T90 2B	core top	Atlantic Ocean	53.10	20.80	2731
T90 4B	core top	Atlantic Ocean	47.20	21.39	3945
T90 7B	core top	Atlantic Ocean	46.30	23.61	3752
T90 8B	core top	Atlantic Ocean	46.20	23.72	3393
T90 11B	core top	Atlantic Ocean	45.00	24.66	3208
WIND 10B	core top	Indian Ocean	−29.12	−47.55	2871
WIND 1B	core top	Indian Ocean	−35.12	−35.54	4156
WIND 3B	core top	Indian Ocean	−32.64	−48.49	3731
WIND 5B	core top	Indian Ocean	−31.57	−47.57	3684
1123C 1−1	3−5 cm	Pacific Ocean	−0.02	−161.02	3411
2.5BC37	core top	Pacific Ocean	0.00	−159.48	2445
1.5BC33	core top	Pacific Ocean	−1.00	−157.85	2015
2BC13	core top	Pacific Ocean	0.01	−158.91	2301
4BC51	core top	Pacific Ocean	−0.02	−161.02	3411
5.5BC58	core top	Pacific Ocean	−0.01	−162.22	4341
1BC3	core top	Pacific Ocean	−2.24	−157.00	1616

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Table 2. Linear least square regression models fitted through X/Ca and $\Delta[CO_3^{2-}]$ data.

X/Ca	Dataset used	T range (°C)	$\Delta[CO_3^{2-}]$ range (μmol kg^{-1})	n	$\Delta[CO_3^{2-}]$ not corrected for Anthropogenic DIC				$\Delta[CO_3^{2-}]$ corrected for Anthropogenic DIC			
					Slope (μmol mol^{-1} per μmol kg^{-1}) except for B/Ca and Li/Ca − (μmol mol^{-1} per μmol kg^{-1})	Intercept	R^2	p-value	Slope (μmol mol^{-1} per μmol kg^{-1}) except for B/Ca and Li/Ca − (μmol mol^{-1} per μmol 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	1.5×10^{-9}	0.369 ± 0.045	29.9 ± 1.1	0.66	1.3×10^{-9}
Li/Ca	All datasets	−0.8 to 3.6	−23 to 45	44	0.0526 ± 0.0084	15.53 ± 0.19	0.46	1.1×10^{-7}				
	This study	1.1 to 3.6	−23 to 44	37	0.0561 ± 0.0105	15.56 ± 0.22	0.45	6.2×10^{-6}	0.0466 ± 0.0091	15.60 ± 0.22	0.43	1.2×10^{-5}
	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	7.4×10^{-8}	0.00207 ± 0.0003	0.8764 ± 0.0072	0.58	5.2×10^{-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	1.7×10^{-9}	0.0102 ± 0.0014	1.413 ± 0.05	0.41	9.6×10^{-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	1.5×10^{-14}	0.0083 ± 0.001	1.215 ± 0.054	0.56	3.2×10^{-9}
	This study	1.1 to 3.6	−23 to 44	37	0.0122 ± 0.0016	1.400 ± 0.034	0.61	1.8×10^{-8}	0.00992 ± 0.0015	1.412 ± 0.036	0.56	1.6×10^{-7}
	Healey et al. (2008)	1.2 to 4	−3 to 39	24	0.0227 ± 0.0049	1.355 ± 0.105	0.49	1.3×10^{-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	1.3×10^{-5}				
	Rathmann and Kuhnert (2008)	1.6 to 10.4	−25 to 21	6	−0.0092 ± 0.0119	2.137 ± 0.217	0.13					
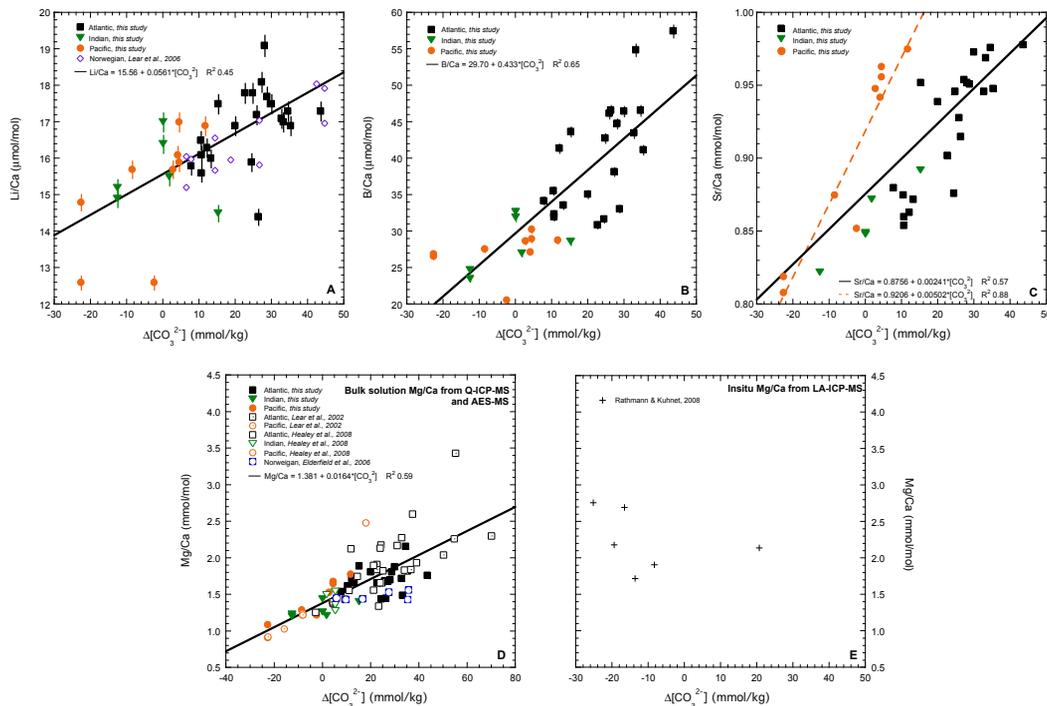
Fig. 1. Correlation of coretop *O. umbonatus* X/Ca with bottom water $\Delta[CO_3^{2-}]$. **(A–E)** show data for different X/Ca ratios: **(A)** Li/Ca, **(B)** B/Ca, **(C)** Sr/Ca, and **(D)** and **(E)** Mg/Ca ratios. Data are displayed by basin (squares denote Atlantic Ocean samples, inverted triangles denote Indian Ocean, circles denote Pacific Ocean, locations detailed in Table 1). Refer to individual panel key for sources of published data. All data, with the exception of Rathmann and Kuhnert, was attained by bulk solution ICP-MS and Mg/Ca has been corrected for differences in the cleaning protocol (i.e. oxidative vs reductive cleaning). The data from Rathmann and Kuhnert (2008) was attained from laser-ablation ICP-MS **(E)**. Error bars denote the analytical precision of Li/Ca and B/Ca ratios measured in this study is ~2 % (relative standard deviation, rsd). The error on Sr/Ca and Mg/Ca values is smaller the values represented by the size of the data symbols. Lines denote linear least square regressions. Regression equations, uncertainties and statistics are shown in Table 2.
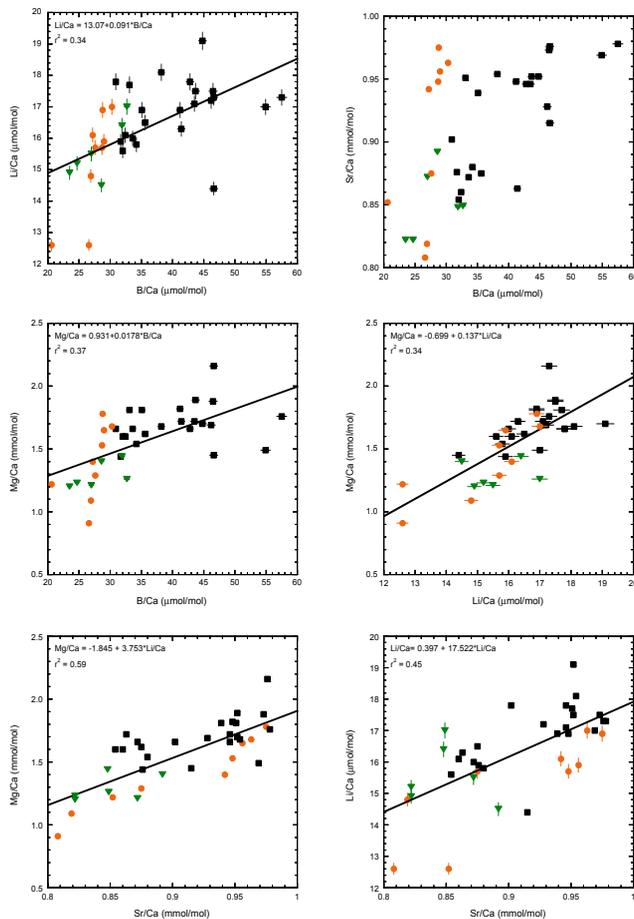
Fig. 2. Cross-plots of *O. umbonatus* coretop X/calcium ratios. Error bars denote analytical precision (as in Fig. 1) and dashed lines are linear least square regressions. Symbols denote ocean basin, as in Fig. 1.

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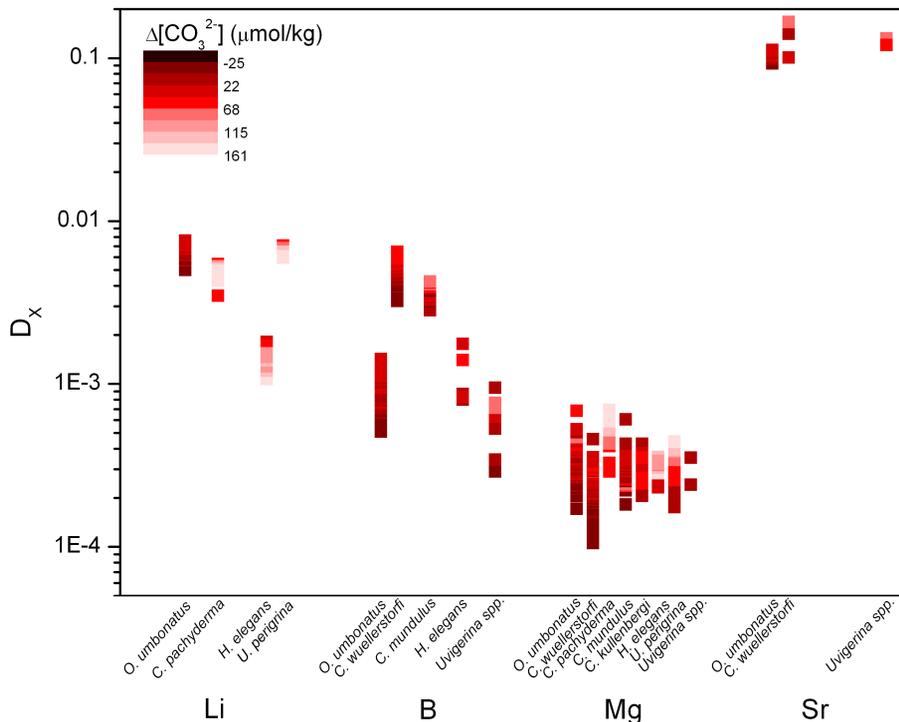
Fig. 3. Benthic foraminifera empirical partition coefficients as a function of bottom water $\Delta[CO_3^{2-}]$. Partition coefficients calculated from new and published benthic foraminifera element ratios (Lear et al., 2002, 2003; Lear and Rosenthal, 2006; Elderfield et al., 2006; Yu and Elderfield, 2007, 2008; Bryan and Marchitto, 2008; Healey et al., 2008) and modern seawater composition (Li/Ca $\sim$ 0.00252 mol mol^{-1}, B/Ca $\sim$ 0.0404 mol mol^{-1}, Mg/Ca $\sim$ 5.31 mol mol^{-1} and Sr/Ca $\sim$ 0.00872 mol mol^{-1}).

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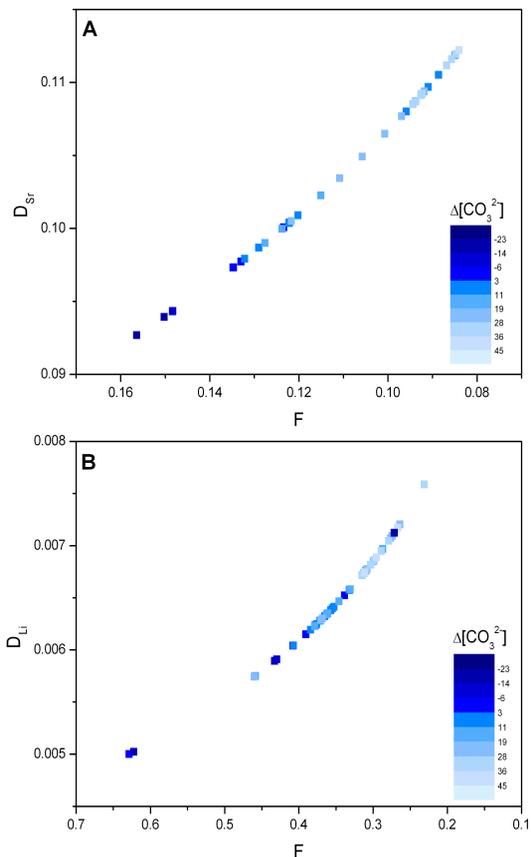
Fig. 4. Relationships between *O. umbonatus* empirical partition coefficients (**A**, D_{Sr}; **B**, D_{Li}), the fraction of Ca remaining in the internal pool after one batch of calcification (F) and bottom water $\Delta[CO_3^{2-}]$.
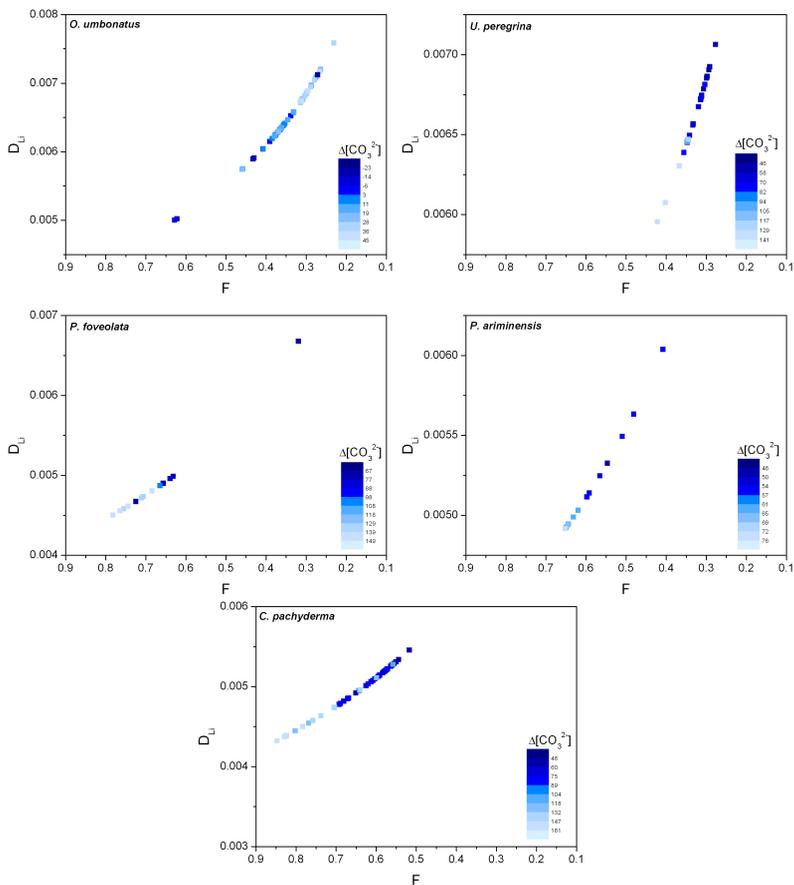
Fig. 5. The relationship between Li empirical partition coefficients, the fraction of Ca remaining in the internal pool after calcification and bottom water $\Delta[CO_3^{2-}]$ for *O. umbonatus* and other benthic species. Empirical partition coefficients and data sources as in Fig. 3.

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