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

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1483

Abstract

Elemental ratios in benthic foraminifera have been used to reconstruct bottom water temperature and carbonate saturation ($\Delta[\text{CO}_3^{2-}]$). 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 $\Delta[\text{CO}_3^{2-}]$ 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 $\Delta[\text{CO}_3^{2-}]$ are 0.433 ± 0.053 and $0.0561 \pm 0.0084 \mu\text{mol mol}^{-1}$ per $\mu\text{mol kg}^{-1}$ and 0.0164 ± 0.0015 and $0.00241 \pm 0.0004 \mu\text{mol mol}^{-1}$ per $\mu\text{mol kg}^{-1}$, 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 $\Delta[\text{CO}_3^{2-}]$, 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.

1484

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; Tripathi et al., 2005; Tripathi and Elderfield, 2005; Elderfield et al., 2006; Yu and Elderfield, 2007, 2008; Bryan and Marchitto, 2008; Dawber and Tripathi, 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,

1485

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

1486

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).

1493

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 $\Delta[\text{CO}_3^{2-}]$ (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 $\Delta[\text{CO}_3^{2-}]$ in *O. umbonatus* is the through the influence of seawater $\Delta[\text{CO}_3^{2-}]$ on calcification rate, i.e. high seawater $\Delta[\text{CO}_3^{2-}]$ 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 $\Delta[\text{CO}_3^{2-}]$ 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 thought to be a widespread strategy for increasing $[\text{CO}_3^{2-}]$ to promote calcification (Erez, 2003; de Nooijer et al., 2009). Although the energy consumption associated with raising vesicle pH (and $[\text{CO}_3^{2-}]$) 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) $\Delta[\text{CO}_3^{2-}]$. If Rayleigh fractionation occurs in tandem with increased vesicle pH, it follows that foraminifera that vacuolise low $\Delta[\text{CO}_3^{2-}]$ 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 $\Delta[\text{CO}_3^{2-}]$,

1494

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 $\Delta[\text{CO}_3^{2-}]$, 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 $\Delta[\text{CO}_3^{2-}]$ 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- $\Delta[\text{CO}_3^{2-}]$ 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 $\Delta[\text{CO}_3^{2-}]$, rather than reflecting the covariation of $\Delta[\text{CO}_3^{2-}]$ 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 $\Delta[\text{CO}_3^{2-}]$ could be applied to earlier periods of Earth history.

1497

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References

- Anand, P. and H. Elderfield: Variability of Mg/Ca and Sr/Ca between and within the planktonic foraminifers *Globigerina bulloides* and *Globorotalia truncatulinoides*, *Geochem. Geophys. Geosyst.*, 6, Q11D15, doi:10.1029/2004GC000811, 2005.
- Barker, S., Greaves, M., and Elderfield, H.: A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry, *Geochem. Geophys. Geosyst.*, 4, 8407, doi:10.1029/2003GC000559, 2003.
- Bentov, S. and Erez, J.: Novel observations on biomineralization processes in foraminifera and implications for Mg/Ca ratio in the shells, *Geology*, 33, 841–844, doi:10.1130/G21800.1, 2005.
- Bryan, S. P. and Marchitto, T. M.: Mg/Ca–temperature proxy in benthic foraminifera: New calibrations from the Florida Straits and a hypothesis regarding Mg/Li, *Paleoceanography*, 23, PA2220, doi:10.1029/2007PA001553, 2008.
- Corliss, B. H.: Microhabitats of benthic foraminifera within deep-sea sediments, *Nature*, 314, 435–438, doi:10.1038/314435a0, 1985.
- De Nooijer, L. J., Toyofuku, T., and Kitazato, H.: Foraminifera promote calcification by elevating their intracellular pH, *Proc. Nat. Ac. Sci.*, 106, 15374, doi:10.1073/pnas.0904306106, 2009.
- Dickson, A. G.: Thermodynamics of the dissociation of boric-acid in synthetic seawater from 273.15-k to 318.15-k, *Deep-Sea Res. Part A, Oceanogr. Res. Pap.* 37, 755–766, 1990.
- Dickson, A. G. and Millero, F. J.: A comparison of the equilibrium constants for the dissociation of carbonic acid in seawater media, *Deep-Sea Res.*, 34, 1733–1743, 1987.
- Dickson, A. G., Sabine, C. L., and Christian, J. R.: Guide to best practices for ocean CO₂ measurements, *PICES Special Publication*, 3, 191 pp., 2007.
- Dissard, D., Nehrke, G., Reichart, G. J., and Bijma, J.: Impact of seawater pCO₂ on calcification

1498

- and Mg/Ca and Sr/Ca ratios in benthic foraminifera calcite: results from culturing experiments with *Ammonia tepida*, *Biogeosciences*, 7, 81–93, doi:10.5194/bg-7-81-2010, 2010.
- Eggins, S. M., Sadekov, A., and De Deckker, P.: Modulation and daily banding of Mg/Ca in *Orbulina universa* tests by symbiont photosynthesis and respiration: a complication for sea-water thermometry? *Earth Planet. Sci. Lett.*, 225, 411–419, doi:10.1016/j.epsl.2004.06.019, 2004.
- Elderfield, H., Bertram, C. J., and Erez, J.: A biomineralization model for the incorporation of trace elements into foraminiferal calcium carbonate, *Earth Planet. Sci. Lett.*, 142, 409–423, 1996.
- Elderfield, H., Yu, J., Anand, P., Kiefer, T., and Nyland, B.: Calibrations for benthic foraminiferal Mg/Ca paleothermometry and the carbonate ion hypothesis, *Earth Planet. Sci. Lett.*, 250, 633–649, 2006.
- Erez, J.: The Source of Ions for Biomineralization in Foraminifera and Their Implications for Paleoclimatographic Proxies, *Rev. Mineral. Geochem.*, 54, 115–149, doi:10.2113/0540115, 2003.
- Erez, J., Bentov, S., Tishler, C., and Szafrank, D.: Intracellular calcium storage and the calcification mechanism of perforate foraminifera, *Paleobios*, 16, 30, 1994.
- Gabitov, R. I. and Watson, E. B.: Partitioning of strontium between calcite and fluid, *Geochem. Geophys. Geosyst.*, 7, Q11004, doi:10.1029/2005GC001216, 2006.
- Gagnon, A. C., Adkins, J. F., Fernandez, D. P., and Robinson, L. F.: Sr/Ca and Mg/Ca vital effects correlated with skeletal architecture in a scleractinian deep-sea coral and the role of Rayleigh fractionation, *Earth Planet. Sci. Lett.*, 261, 280–295, 2007.
- Hall, J. M. and Chan, L. H.: Li/Ca in multiple species of benthic and planktonic foraminifera: thermocline, latitudinal, and glacial-interglacial variation, *Geochim. Cosmochim. Acta*, 68, 529–545, 2004.
- Healey, S. L., Thunell, R. C., and Corliss, B. H.: The Mg/Ca-temperature relationship of benthic foraminiferal calcite: New core-top calibrations in the < 4 °C temperature range, *Earth Planet. Sci. Lett.*, 272, 523–530, doi:10.1016/j.epsl.2008.05.023, 2008.
- Hemming, N. G., Reeder, R. J., and Hanson, G. N.: Mineral-fluid partitioning and isotopic fractionation of boron in synthetic calcium carbonate, *Geochim. Cosmochim. Acta*, 59, 371–379, 1995.
- Holland, H., Holland, H., and Munoz, J.: The coprecipitation of cations with CaCO₃-II. The coprecipitation of Sr⁺² with calcite between 90° and 100°C, *Geochim. Cosmochim. Acta*,

1499

- 28, 1287–1301, doi:10.1016/0016-7037(64)90130-9, 1964.
- Katz, A.: The interaction of magnesium with calcite during crystal growth at 25-90 C and one atmosphere, *Geochim. Cosmochim. Acta*, 37, 1563-1578, 1973.
- Kisakürek, B., Eisenhauer, A., Böhm, F., Garbe-Schönberg, D., and Erez, J.: Controls on shell Mg/Ca and Sr/Ca in cultured planktonic foraminifera, *Globigerinoides ruber* (white), *Earth Planet. Sci. Lett.*, 273, 260–269, doi:10.1016/j.epsl.2008.06.026, 2008.
- Kitano, Y., Kanamori, N., and Oomori, T.: Measurements of distribution coefficients of strontium and barium between carbonate precipitate and solution – Abnormally high values of distribution coefficients measured at early stages of carbonate formation, *Geochem. J.*, 4, 183–206, 1971.
- Kunioka, D., Shirai, K., Takahata, N., Sano, Y., Toyofuku, T., and Ujiie, Y.: Microdistribution of Mg/Ca, Sr/Ca, and Ba/Ca ratios in *Pulleniatina obliquiloculata* test by using a NanoSIMS: Implication for the vital effect mechanism, *Geochem. Geophys. Geosyst.*, 7, Q12P20, doi:10.1029/2006GC001280, 2006.
- Lea, D., Mashioita, T., and Spero, H.: Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing, *Geochim. Cosmochim. Acta*, 63, 2369–2379, 1999.
- Lear, C. and Rosenthal, Y.: Benthic foraminiferal Li/Ca: Insights into Cenozoic seawater carbonate saturation state, *Geology*, 34, 985–988, 2006.
- Lear, C., Elderfield, H., and Wilson, P.: Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite, *Science*, 287, 269–272, doi:10.1126/science.287.5451.269, 2000.
- Lear, C., Rosenthal, Y., and Slowey, N.: Benthic foraminiferal Mg/Ca-paleothermometry: A revised core-top calibration, *Geochim. Cosmochim. Acta*, 66, 3375–3387, 2002.
- Lear, C., Elderfield, H., and Wilson, P.: A Cenozoic seawater Sr/Ca record from benthic foraminiferal calcite and its application in determining global weathering fluxes, *Earth Planet. Sci. Lett.*, 208, 69–84, 2003.
- Lear, C. H., Mawbey, E. M., and Rosenthal, Y.: Cenozoic benthic foraminiferal Mg/Ca and Li/Ca records: Toward unlocking temperatures and saturation states, *Paleoceanography*, 25, PA4215, doi:10.1029/2009PA001880, 2010.
- Lorens, R. B.: A study of biological and physical controls on the trace metal content of calcite and aragonite, Ph.D. dissertation. Univ. of Rhode Island, 1978.
- Lorens, R. B.: Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite

1500

- precipitation rate, *Geochim. Cosmochim. Acta*, 45, 553–561, 1981.
- Marchitto, T. M., Oppo, D. W., and Curry, W. B.: Paired benthic foraminiferal Cd/Ca and Zn/Ca evidence for a greatly increased presence of Southern Ocean Water in the glacial North Atlantic, *Paleoceanography*, 17, 1038, doi:10.1029/2000PA000598, 2002.
- 5 Marchitto, T. M., Bryan, S. P., Curry, W. B., and McCorkle, D. C.: Mg/Ca temperature calibration for the benthic foraminifer *Cibicides pachyderma*, *Paleoceanography*, 22, PA1203, doi:10.1029/2006PA001287, 2007.
- Mehrbach, C., Culberso, C. H., Hawley, J. E., and Pytkowic, R. M.: Measurement of apparent dissociation-constants of carbonic-acid in seawater at atmospheric-pressure, *Limnol. Oceanogr.*, 18, 897–907, 1973.
- 10 Morse, J. and Bender, M.: Partition coefficients in calcite: Examination of factors influencing the validity of experimental results and their application to natural systems, *Chem. Geol.*, 82, 265–277, 1990.
- Morse, J. W. and Mackenzie, F. T.: *Geochemistry of Sedimentary Carbonates*, *Develop. Sediment.*, 48, 1990.
- 15 Mucci, A. and Morse, J. W.: The incorporation of Mg²⁺ and Sr²⁺ into calcite overgrowths: Influences of growth rate and solution composition, *Geochim. Cosmochim. Acta*, 47, 217–233, 1983.
- Nehrke, G., Reichart, G. J., Van Cappellen, P., Meile, C., and Bijma, J.: Dependence of calcite growth rate and Sr partitioning on solution stoichiometry: Non-Kossel crystal growth, *Geochim. Cosmochim. Acta*, 71, 2240–2249, 2007.
- 20 Okumura, M. and Kitano, Y.: Coprecipitation of alkali metal ions with calcium carbonate, *Geochim. Cosmochim. Acta*, 50, 49–58, 1986.
- Pingitore Jr., N. E. and Eastman, M. P.: The coprecipitation of Sr²⁺ with calcite at 25°C and 1 atm, *Geochimica et Cosmochimica Acta*, 50, 2195–2203, doi:10.1016/0016-7037(86)90074-8, 1986.
- 25 Rathmann, S. and Kuhnert, H.: Carbonate ion effect on Mg/Ca, Sr/Ca and stable isotopes on the benthic foraminifera *Oridorsalis umbonatus* off Namibia, *Mar. Micropaleo.*, 66, 120–133, 2008.
- 30 Rathmann, S., Hess, S., Kuhnert, H., and Mulitza, S.: Mg/Ca ratios of the benthic foraminifera *Oridorsalis umbonatus* obtained by laser ablation from core top sediments: Relationship to bottom water temperature, *Geochem. Geophys. Geosyst.*, 5, Q12013, doi:10.1029/2004GC000808, 2004.

1501

- Rimstidt, J. D., Balog, A., and Webb, J.: Distribution of trace elements between carbonate minerals and aqueous solutions, *Geochim. Cosmochim. Acta*, 62, 1851–1863, 1998.
- Rosenthal, Y., Boyle, E. A., and Slowey, N.: Temperature control on the incorporation of magnesium, strontium, fluorine, and cadmium into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline paleoceanography, *Geochim. Cosmochim. Acta*, 61, 3633–3643, 1997.
- 5 Rosenthal, Y., Lear, C. H., Oppo, D. W., and Linsley, B. K.: Temperature and carbonate ion effects on Mg/Ca and Sr/Ca ratios in benthic foraminifera: Aragonitic species *Hoeglundina elegans*, *Paleoceanography*, 21, PA1007, doi:10.1029/2005PA001158, 2006.
- 10 Russell, A. D., Hönisch, B., Spero, H. J., and Lea, D. W.: Effects of seawater carbonate ion concentration and temperature on shell U, Mg, and Sr in cultured planktonic foraminifera, *Geochim. Cosmochim. Acta*, 68, 4347–4361, 2004.
- Sabine, C. L. and Tanhua, T.: Estimation of Anthropogenic CO₂ Inventories in the Ocean, *Annu. Rev. Marine. Sci.*, 2, 175–198, doi:10.1146/annurev-marine-120308-080947, 2010.
- 15 Sabine, C. L., Feely, R. A., Gruber, N., Key, R. M., Lee, K., Bullister, J. L., Wanninkhof, R., Wong, C. S., Wallace, D. W. R., Tilbrook, B., Millero, F. J., Peng, T. H., Kozyr, A., Ono, T., and Rios, A. F.: The Oceanic Sink for Anthropogenic CO₂, *Science*, 305, 367–371, doi:10.1126/science.1097403, 2004.
- Sadekov, A. Y., Eggins, S. M., and De Deckker, P.: Characterization of Mg/Ca distributions in planktonic foraminifera species by electron microprobe mapping, *Geochem. Geophys. Geosyst.*, 6, Q12P06, doi:10.1029/2005GC000973, 2005.
- 20 Szafranek, D. and Erez, J.: Chemistry of Mg, SO₄²⁻, Sr, Na and Cl in live foraminifera shells, *Abstract. Int. Symp. On Biomineralization*, Monaco, Biomineralization, 93, 1993.
- Tang, J., Köhler, S. J., and Dietzel, M.: Sr²⁺/Ca²⁺ and 44Ca/40Ca fractionation during inorganic calcite formation: I. Sr incorporation, *Geochim. Cosmochim. Acta*, 72, 3718–3732, 2008.
- 25 Watson, E. B.: A conceptual model for near-surface kinetic controls on the trace-element and stable isotope composition of abiogenic calcite crystals, *Geochim. Cosmochim. Acta*, 68, 1473–1488, 2004.
- 30 Watson, E. B. and Liang, Y.: A simple model for sector zoning in slowly grown crystals: Implications for growth rate and lattice diffusion, with emphasis on accessory minerals in crustal rocks, *American Mineralogist*, 80, 1179–1187, 1995.
- Wauth, D. W., Hall, T. M., McNeil, B. I., Key, R. M., and Matear, R.: Anthropogenic CO₂ in the

1502

- oceans estimated using transit-time distributions, *Tellus B*, 58, 376–389, 2006.
- Yu, J. and Elderfield, H.: Benthic foraminiferal B/Ca ratios reflect deep water carbonate saturation state, *Earth Planet. Sci. Lett.*, 258, 73–86, 2007.
- Yu, J. and Elderfield, H.: Mg/Ca in the benthic foraminifera *Cibicides wuellerstorfi* and *Cibicides mundulus*: Temperature versus carbonate ion saturation, *Earth Planet. Sci. Lett.*, 276, 129–139, 2008.
- Yu, J., Day, J., Greaves, M., and Elderfield, H.: Determination of multiple element/calcium ratios in foraminiferal calcite by quadrupole ICP-MS, *Geochem. Geophys. Geosyst.*, 6, Q08P01, doi:10.1029/2005GC000964, 2005.
- 10 Zeebe, R. E. and Sanyal, A.: Comparison of two potential strategies of planktonic foraminifera for house building: Mg²⁺ or H⁺ removal?, *Geochim. Cosmochim. Acta*, 66, 1159–1169, doi:10.1016/S00167037(01)00852-3, 2002.

1503

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

1504

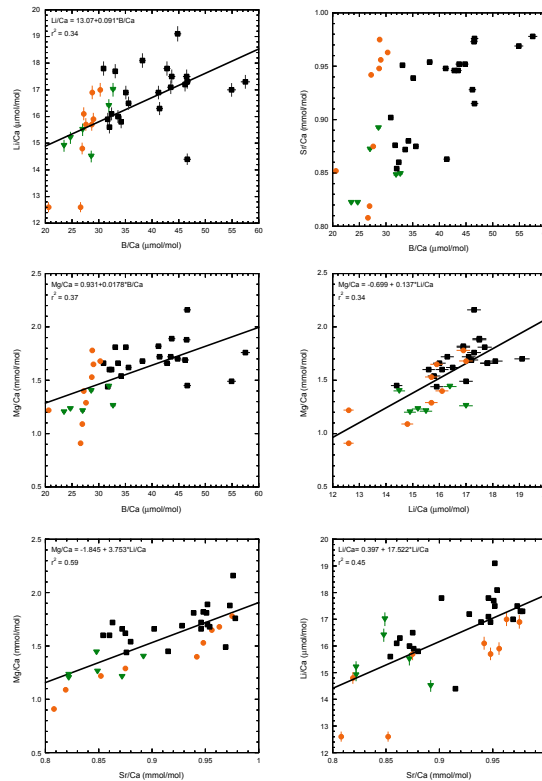


Fig. 2. Cross-plots of *O. umbonatus* coretop X/calcium ratios. Error bars denote analytical precision (as in Fig. 1) and dashed lines are linear least square regressions. Symbols denote ocean basin, as in Fig. 1.

1507

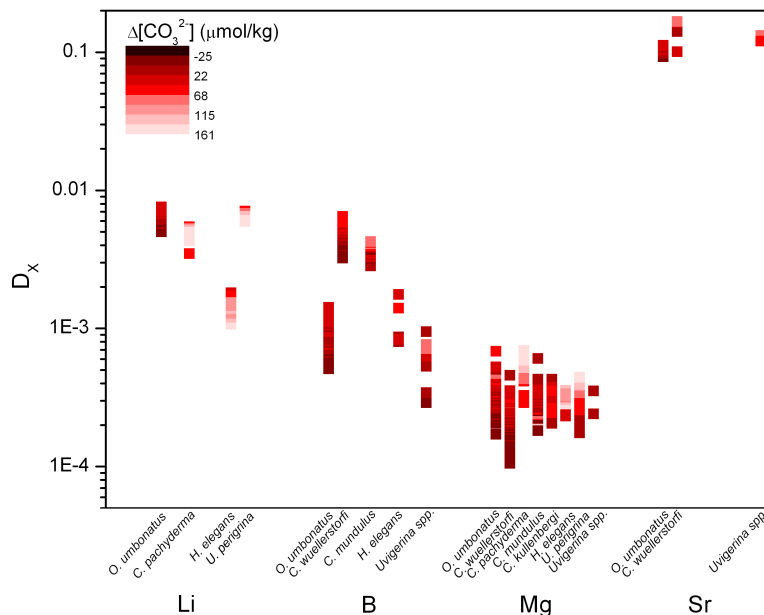


Fig. 3. Benthic foraminifera empirical partition coefficients as a function of bottom water $\Delta[CO_3^{2-}]$. Partition coefficients calculated from new and published benthic foraminifera element ratios (Lear et al., 2002, 2003; Lear and Rosenthal, 2006; Elderfield et al., 2006; Yu and Elderfield,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

1508

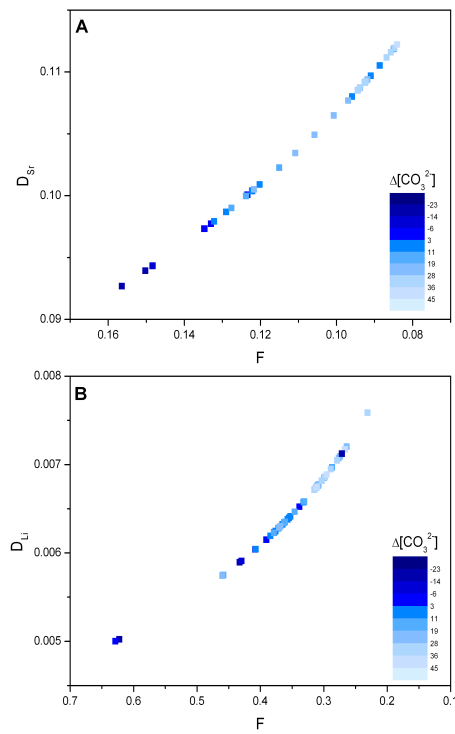


Fig. 4. Relationships between *O. umbonatus* empirical partition coefficients (**A**, D_{Sr} ; **B**, D_{Li}), the fraction of Ca remaining in the internal pool after one batch of calcification (F) and bottom water $\Delta[CO_3^{2-}]$.

1509

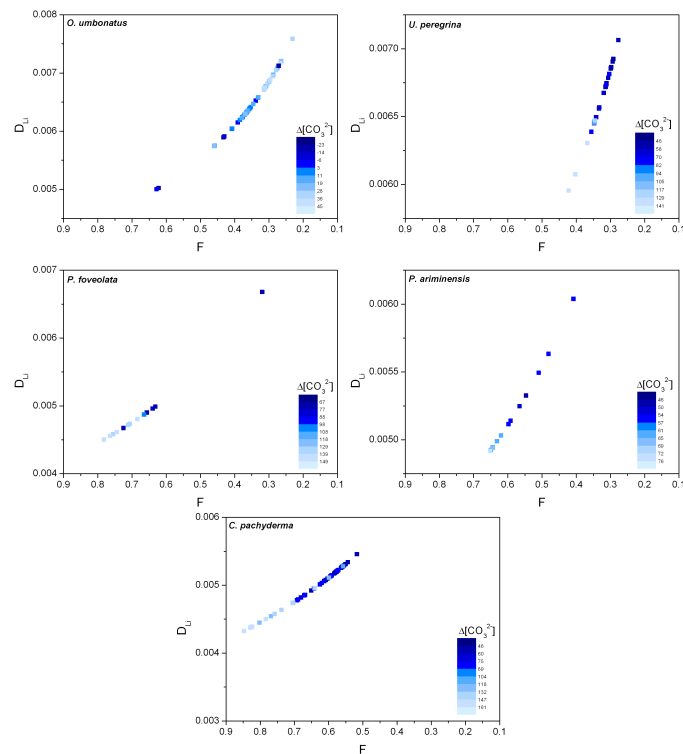


Fig. 5. The relationship between Li empirical partition coefficients, the fraction of Ca remaining in the internal pool after calcification and bottom water $\Delta[CO_3^{2-}]$ for *O. umbonatus* and other benthic species. Empirical partition coefficients and data sources as in Fig. 3.

1510