Calcification rate and shell chemistry response of the planktic foraminifer *Orbulina universa* to changes in microenvironment seawater carbonate chemistry

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**A B S T R A C T**

We use LA-ICP-MS depth profiling to explore the sensitivity of shell chemistry of the symbiotic planktic foraminifer *Orbulina universa* to diurnal changes in the holobiont physiology, over a wide range of seawater pH and DIC compositions. B/Ca and U/Ca vary in concert with diurnal Mg/Ca banding, forming compositional bands that are qualitatively consistent with physiological modification of seawater carbonate chemistry ([pH, [B(OH)\(_2\)/HCO\(_3^-\)] and [CO\(_2^-\)]) within the foraminiferal microenvironment by the net effects of photosynthesis, respiration and calcification. The amplitude of B/Ca banding broadly conforms to banding predicted using the bulk-shell B/Ca sensitivity to the carbonate chemistry changes in the foraminiferal microenvironment. U/Ca banding tends to be greater than predicted using the published bulk-shell sensitivity of this proxy to carbonate chemistry. This either suggests that carbonate chemistry changes in the foraminiferal microenvironment are greater than predicted by modeling and/or the published bulk shell calibration does not accurately reflect the U/Ca sensitivity at the micro-scale. A fourfold increase in seawater DIC composition (1026 to 4019 μmol kg\(^{-1}\)) is associated with significant increases in Sr/Ca and Mg/Ca partitioning, and a decrease in Mn/Ca partitioning into shell calcite. The accompanying fourfold increase in calcite saturation produces only a twofold increase in calcification rate (0.14 to 0.28 ±0.02 μm hr\(^{-1}\)), suggesting that seawater carbonate chemistry exerts only a small effect on foraminiferal calcification rates, but does have a significant influence on trace element incorporation at both the inter-shell and bulk-shell scale.

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1. Introduction

The trace element and stable isotope compositions of calcium carbonate precipitated by planktic foraminifera differ significantly from inorganic calcite compositions precipitated from seawater. This includes many of the major proxies used for seawater temperature and carbonate system reconstruction (Mg/Ca, B/Ca, δ\(^{11}\)B, δ\(^{18}\)O; see Allen et al., 2011, 2012; Bijma et al., 1999; Lea et al., 1999; McCrea, 1950; Morse and Bender, 1990; Sanjal et al., 1996, 2000; Uchikawa et al., 2015). The reasons for the differences between biologically precipitated and inorganic minerals remain poorly understood and are often simply attributed to unspecified biological "vital effects" (Urey et al., 1951; Weiner and Dove, 2003). The uncertain influence of vital effects on trace element incorporation into foraminifer shells remains a significant impediment to our ability to reconstruct past seawater conditions from geochemical proxies.

In planktic foraminifera, vital effects include physiological processes (e.g., photosynthesis, respiration and calcification) that modify seawater chemistry in the external boundary layer (microenvironment), and internal processes that regulate the precipitation rate, composition, polymorph type, topology and orientation of calcium carbonate (de Nooijer et al., 2014). Several studies have documented large diurnal carbonate chemistry variations within the microenvironment of symbiotic foraminifera (Jorgensen et al., 1985; Köhler-Rink and Kühl, 2005; Rink et al., 1998), which can be explained by changes in the balance between respiration and photosynthesis of the host foraminifer and algal symbionts (Wolf-Gladrow et al., 1999; Zeebe et al., 1999, 2003). Daytime photosynthetic activity of algal symbionts consumes CO\(_2\) and raises pH in the microenvironment, whereas nighttime respiration of the host foraminifer and symbionts releases CO\(_2\) and lowers pH in the microenvironment. This drives a large diurnal change of almost one pH unit adjacent to the shell sur-
face of *Orbulina universa* (Köhler-Rink and Kühl, 2005; Rink et al., 1998). Seawater in the microenvironment provides the source of ions for biomineralization (de Nooijer et al., 2014), although the chemistry of the internal calcification environment is modified by physiochemical processes used to promote or regulate calcification (Bentov et al., 2009; de Nooijer et al., 2009; Glas et al., 2012; Zeebe and Sanyal, 2002). The extent of the connection between the external microenvironment and internal calcification environment is unknown, although they are certainly linked, given the architecture of the calcification site (Fig. 1).

The large diurnal changes in pH, DIC and other carbonate system parameters in the foraminiferal microenvironment (Köhler-Rink and Kühl, 2005; Rink et al., 1998; Wolf-Gladrow et al., 1999) have the potential to influence and modify the incorporation of pH- and carbonate-system sensitive trace elements such as B/Ca and U/Ca. The proportions of dissolved boron species, boric acid (B(OH)3) and borate (B(OH)4−), in seawater are governed by acid-base equilibria, whereby most boron exists in the form of B(OH)3 at low pH, and B(OH)4− at high pH (Hershey et al., 1986). If only the charged B(OH)4− ion is thought to be included into foraminiferal calcite, as proposed by Hemming and Hanson (1992), the B/Ca of foraminifer shells can be used to infer information about past ocean carbonate system chemistry. However, recent calcite precipitation experimental studies have shown the exclusive incorporation of B(OH)4− might not be the case (e.g., Uchikawa et al., 2015). Despite this, the B/Ca ratio in foraminifer shells can be empirically related to the product of seawater and B(OH)4−/[HCO3−] ratio and the effective exchange coefficient (Yu et al., 2007):

\[
B/\text{Ca} = K_{D,\text{B/Ca}} \cdot \left( [\text{B(OH)}_4^-]/[\text{HCO}_3^-] \right)
\]

(1)

where the square brackets indicate seawater concentrations, and *K_{D,\text{B/Ca}}* is the apparent (stoichiometric) exchange coefficient. Experimental culture studies confirm that the B/Ca ratio in planktic foraminifer shells increases with seawater pH (Allen et al., 2011, 2012; Henehan et al., 2013), as high pH drives higher [B(OH)4−] and lower [HCO3−] in solution, increasing the [B(OH)4−]/[HCO3−] ratio. Thus, while the precise mechanisms behind B uptake into foraminifera are uncertain, we may relate B/Ca in our cultured specimens to changes in microenvironment [B(OH)4−]/[HCO3−] and pH.

The U/Ca composition of foraminiferal calcite is also sensitive to seawater carbonate chemistry, and shows a non-linear decrease with increasing [CO3^2−] in pH experiments (Russell et al., 2004). The incorporation of uranium into coral aragonite is suggested to occur as a uranyl carbonate complex, most likely the triscarbonato ion, (UO2(CO3)3−), which is the dominant uranyl species over the range of modern seawater pH (see Djögic et al., 1986). The [UO2(CO3)3−] ion likely requires a coordination change to fit into the calcite lattice (Reeder et al., 2000):

\[
\text{CaCO}_3(s) + \text{UO}_2\text{(CO}_3^3^-)(\text{aq}) \leftrightarrow \text{UO}_2\text{(CO}_3^3^-)(\text{aq}) + \text{Ca}^{2+}(\text{aq}) + 3\text{CO}_3^{2-}(\text{aq})
\]

(2)

This reaction has been used to describe the U/Ca composition of calcite as a function of the triscarbonato species and effective exchange coefficient (Russell et al., 2004):

\[
\text{U/Ca} = K_{D,\text{U/Ca}} \cdot \left[ \text{UO}_2\text{(CO}_3^3^-)/[\text{Ca}^{2+}] \cdot [\text{CO}_3^{2-}]^3 \right]
\]

(3)

As the carbonate ion concentration and seawater pH increase, the cubic nature of the carbonate ion term in the partition coefficient denominator drives an exponential decrease in the sensitivity of U/Ca with carbonate ion activity in seawater.

To explore the response of shell trace element chemistry to seawater DIC and pH, and the importance of physiologically controlled microenvironment effects, we conducted a small number of culture experiments on the symbiotic planktonic foraminifer *Orbulina universa*. *Orbulina universa* is an ideal species for this purpose, as it calcifies continuously to produce a simple spherical shell comprising sequential diurnal growth bands (Eiggins et al., 2004; Spero et al., 2015). Here, we use a laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) depth profiling technique (Eiggins et al., 2004) to measure banded variations in Mg/Ca, B/Ca and U/Ca through the shell. We interpret changes in the magnitude and phase of banding in these elements in context of a physiological diusis–reaction model of the foraminifer-symbiont system, and estimate growth rates from the well-established regular pacing of Mg/Ca banding. The magnitude of B/Ca and U/Ca banding is compared with the modeled diurnal variations in pH, [B(OH)4−]/[HCO3−] and [CO3^2−] at the shell surface, combined with published sensitivities of the B/Ca and U/Ca proxies (Allen et al., 2011; Russell et al., 2004) to determine whether microenvironment changes are sufficient to drive B/C and U/Ca banding in *O. universa* (Fig. 2).

2. Methods

2.1. Foraminifer collection and culturing

*Orbulina universa* were cultured using established methods (e.g., Russell et al., 2004) during August 2013 at the Wrigley Institute for Environmental Studies (WIES), on Santa Catalina Island, California. Small juvenile foraminifers were either hand collected by SCUBA divers, or by plankton tow in the San Pedro Basin surface waters approximately 2 km NNE of WIES. Individual foraminifers were identified to species level and their largest diameter was measured under an inverted microscope before being transferred into 120 mL soda-lime glass jars (Wheaton®). The jars were filled with experimental seawater and sealed with a snap cap lid lined with Parafilm™ M laboratory film to limit gas exchange with the laboratory atmosphere. Foraminifers collected by plankton tow were transferred into experimental seawater only after they had regrown their spines, and in two cases, this transfer followed initial formation of their final spherical chamber.

Culture jars containing foraminifers were placed in circulating water baths held at constant temperature, 21.92 ± 0.13°C, monitored with HOBO Tidbit® loggers. A 12–12 h light-dark cycle was imposed for the duration of the culture experiments using Osram Lumilux T5 skywhite high output bulbs to deliver a PAR irradiance...
level greater than or equal to 285 ± 23 μmol photons m⁻² s⁻¹), to ensure light saturation of symbiotic photosynthesis (Rink et al., 1998). Light intensity was monitored every 7–10 days with a Biospherical Instruments QSP-2000 light meter. Foraminifers were fed a 1-day old brine shrimp (Artemia sp. nauplius, San Francisco Bay strain) every second day. Foraminifers typically underwent gametogenesis several days after forming their adult-stage spherical shell. Following gametogenesis, empty shells were rinsed in deionized water, air-dried and archived before being cleaned and analyzed at the ANU.

Seawater obtained from the foraminifer collection site was filtered (0.8 μm) prior to use in experiments, and its pH and DIC adjusted to produce high and low DIC and high and low pH compositions (Table 1). Artificial seawater with the observed salt composition of seawater from Millero (1974) was made containing no DIC, and mixed with ambient seawater to produce experimental seawater with low DIC concentration (1026 μmol kg⁻¹). Sodium bicarbonate was added to ambient seawater to produce experimental seawater with double the ambient DIC concentration (4019 μmol kg⁻¹). Seawater pH was titrated with 0.1 M NaOH or 0.1 M HCl to produce target pH values of 7.53, 7.96/7.97 and 8.44 (total scale). Uranium and boron were enriched in experimental seawaters to facilitate subsequent microanalysis of B/Ca in foraminifer shells. Enrichment was achieved by addition of a uranium chloride and boric acid stock solutions, to levels of 50× ambient seawater U and 5× ambient seawater B concentration, except for the low DIC seawater which was enriched to just below half this level.

The total alkalinity of experimental seawater was measured by Gran-titration using a Metrohm 809 open cell autotitrator that was standardized using Dickson certified reference seawater. Sea-
water pH was measured with a Metrohm pH electrode that had been calibrated to the NBS scale using low ionic strength pH buffers (pH 4.00, 7.00 and 10.00; Fisherbrand). The pH and alkalinity of experimental seawaters were measured at the beginning and end of all experiments to monitor the consistency of carbonate system chemistry during experiments. Calculation of the carbonate system equilibrium, and conversion from pH(NBS) to the pH\textsubscript{TOTAL} scale, were performed using a modified version of the Van Heuven et al. (2011) Matlab script (CO2SYS.m) that accommodates changes to seawater [Br\textsuperscript{−}] independent of salinity. Uranium speciation was calculated from \([\text{U}]\) using aqueous thermodynamic data from Djogic et al. (1986). Small samples of experimental seawater were filtered using 0.22 μm Millipore syringe filters, transferred to acid cleaned 15 ml plastic vials and acidified to pH ~4 with optima grade HNO\textsubscript{3} for later trace element analysis at the ANU.

2.2. Sample preparation and analysis

Seawater trace metal concentrations were measured using a Varian Vista Pro Axial ICP-AES and a Varian 820 Quadrupole ICP-MS at the Research School of Earth Sciences, the Australian National University (RSES, ANU; Supplementary material, Table S1). Seawater samples were diluted 10× with 2% HNO\textsubscript{3} for analysis by ICP-AES using a three-point external calibration curve, run at the beginning and end of each analytical session, and a standard-sample-standard bracketing protocol to correct for instrument drift. Seawater B/Ca, Mg/Ca, and Sr/Ca molar ratios were measured with a reproducibility of ±1.25%, ±0.13%, and ±0.16% (1σ) based on repeated analysis of the CASS-4 seawater reference material (NRC, Canada). We also measured seawater by ICP-MS to measure Mn/Ca and U/Ca, which were below or near the detection limits of ICP-AES, and to validate B/Ca, Mg/Ca and Sr/Ca measurements. For ICP-MS analysis seawater samples were diluted 100× with 2% HNO\textsubscript{3}. Instrument drift was monitored and corrected using a combination of internal standards (\(^{136}\)Ba, \(^{45}\)Sc, \(^{88}\)Y, \(^{115}\)In, and \(^{235}\)U) and measurement of a synthetic seawater standard every five samples. Seawater B/Ca, Mg/Ca, Mn/Ca, Sr/Ca, and U/Ca molar ratios were measured with a precision of ±0.9%, ±1.3%, ±1.5%, ±1.0%, and ±2.1% (1σ) respectively, based on repeat analyses of CASS-4 seawater. Accuracy relative to average seawater ratios for B/Ca, Mg/Ca, Sr/Ca and U/Ca is 1.0%, 1.5%, 3.7% and 14% and Mn/Ca relative to CASS-4 is 1.9%.

Orbulina universa shells were oxidatively cleaned to remove organic material prior to LA-ICP-MS analysis by cracking shells open with a scalpel blade, followed by immersion in a 50:50 solution of 30% hydrogen peroxide and 0.1 M NaOH in a water bath at 55 ± 5°C for ~10 min (Pak et al., 2004). The buffered solution was then removed and the shell repeatedly rinsed with ultra-pure milli-Q water before being mounted on carbon tape for analysis (Eiggins et al., 2003, 2004). Trace element/Ca (TE/Ca) ratios were measured using a Varian 820 Quadrupole ICP-MS coupled to an ArF excimer laser (λ = 193 nm, pulse width = 25 ns FWHM) via an ANU Helex laser ablation system at the RSES, ANU following Eiggins et al. (2003, 2004; Supplementary material, Table S2). Laser ablation sampling was conducted using 70 μm diameter circular spots at a laser pulse rate of 3 Hz at an fluence of ~2 J/cm\textsuperscript{2}. A mixed He–Ar gas stream was used to transfer ablation products to the ICP-MS. A rapid peak hopping protocol, employing 10 to 30 ms dwell times per isotope depending on abundance, was applied to measure selected analyte isotopes (\(^{18}\)O, \(^{118}\)B, \(^{24}\)Mg, \(^{25}\)Mg, \(^{28}\)Al, \(^{43}\)Ca, \(^{44}\)Ca, \(^{55}\)Mn, \(^{87}\)Sr, \(^{88}\)Sr, and \(^{238}\)U) repeatedly every ~0.35 s for a duration of 30–90 s, depending on shell thickness. Three profiles were measured from inside to outside through each foraminifer shell.

The ICP-MS instrument response was calibrated using SRM NIST610 glass and corrected for variation in ablation yield and instrument drift by normalizing to the measured internal standard isotope (\(^{43}\)Ca and \(^{44}\)Ca) intensities during each mass spectrometer cycle. An in-house carbonate standard was measured periodically to monitor the consistency of carbonate ablation relative to the SRM NIST 610. LA-ICP-MS data reduction followed well-established procedures for time-resolved analysis (Longerich, 1996), including the initial screening of mass-time spectra for outliers and subtracting mean background intensities (measured with laser off). The mean TE/Ca ratio obtained from each compositional profile was averaged to produce a bulk shell composition for each specimen. Multiple profiles obtained from each foraminifer shell were combined to produce an average profile by identifying and aligning common peaks using the Linage function in AnalySeries v1.2, following Allen et al. (2011). To isolate only the banding patterns in our data, a Butterworth bandpass Fourier filter (Butterworth, 1930) was applied to the LA-ICP-MS profiles to remove low frequency (period > 5 μm) trends and high frequency (period < 0.5 μm) noise using the scipy.signal python package (Jones et al., 2001). The long period patterns are the gradually increasing trends of Mg/Ca, B/Ca and U/Ca that occur through the test from the inside of the POS to the outside of the shell, and short period patterns are instrumental noise.

The time taken to measure each shell compositional profile was converted to shell wall thickness and depth relative to the internal shell surface, assuming each laser pulse removed a 0.1 μm thick layer of calcite (Eiggins et al., 2003). Linear calcification rate can then be converted to rate with units of mass per unit surface area per unit time using the density of calcite.

3. Results

3.1. Intra-shell trace element compositional variation

The diurnal phasing of the variation shown by different trace elements is determined by comparison to the diurnal pattern of Mg/Ca banding (Fig. 3), which is characterized by high Mg bands formed at night and low Mg bands during the day (Spero et al., 2015). Measured trace element/Ca ratio profiles through the final spherical chamber wall of O. universa shells all show significant compositional growth banding (Figs. 3–5). In most cases, the diurnal Mg/Ca banding is accompanied by a trend of increasing Mg/Ca away from the primary organic sheet (POS) towards the outside of the shell (see Fig. 3).

The POS is located in a band of relatively low Mg/Ca near the inner shell surface and in some cases associated with an anomalous high U/Ca band (Eiggins et al., 2004; Sadekov et al., 2005). The number of low and high Mg/Ca band pairs developed between the POS and external surface is consistent with the number of days each foraminifer lived in experimental culture after formation of its final spherical chamber, as recorded in daily culture logs.

Profiles of Mg/Ca, B/Ca and U/Ca with the associated noise and background trends removed with a Butterworth bandpass filter are plotted in Fig. 4. B/Ca banding is generally out of phase with Mg/Ca, and where present U/Ca banding is broadly in phase with Mg/Ca in most shells (Fig. 4). Given the diurnal nature of Mg/Ca (Spero et al., 2015), this suggests that high B/Ca bands precipitate during the day and low B/Ca bands precipitate during the night, and the converse applies to U/Ca. While the number of specimens considered here is small, we observe that B/Ca and U/Ca banding are most clearly developed in the low pH and low DIC experiments (Fig. 4a–d). U/Ca banding in the high DIC experiments is less well developed and possibly absent (Fig. 4e–f).
Mn/Ca banding is notable for occurring in shells grown in low DIC seawater, but is not obvious in other experiments (Fig. 5). Sr/Ca shows no evidence of diurnal banding, although significant variations do occur in many shells. In particular, Sr/Ca ratios tend to be lower between the POS and inner shell surface (Fig. 5). Other notable features are the presence of relatively high Mn/Ca and Mg/Ca ratios at the inner shell surface (Fig. 5).

3.2. TE/Ca variations with carbonate system variables

The mean bulk shell compositions of each experimental group (Fig. 6) are calculated using the average profile compositions of each shell, excluding the contribution of calcite precipitated prior to the experiment. Our bulk shell composition estimates have significant uncertainties, due to the small number of shells analyzed.
in each experiment and the variable compositions between individual shells. Accordingly, we caution against using the results reported here for the purpose of proxy calibration and reconstruction of seawater carbonate system parameters.

Bulk shell Mg/Ca and Sr/Ca compositions correlate with DIC, with the increase in Sr/Ca from 1.19 ± 0.07 to 1.71 ± 0.02 mmol/mol being highly significant (Pearson R correlations: Sr/Ca–DIC, R = 0.98, p = 0.02, n = 4; Mg/Ca–DIC, R = 0.99, p < 0.01, n = 4).

The B/Ca of shells measured in this study is high compared to natural specimens because of the elevated [B] in our experimental seawaters. To compare data between our experiments, the B/Ca of the low DIC specimens must be corrected for the two-fold lower [B] than other treatments. This correction is made using the B/Ca−[B(OH)₂] relation of Allen et al. (2011) for O. universa (B/Ca = 1.4 + [B(OH)₂] − 39.5). After correction, bulk B/Ca has a positive trend with seawater [CO₂⁻] (R = 0.74) and a positive trend with seawater pH (R = 0.90), although the correlations are not significant at the 95% confidence level (p = 0.26 and 0.09, respectively).

Measured shell U/Ca values in the low DIC experiment are corrected for the 3.1 × lower seawater [U] in this experiment, assuming a linear relationship between shell U/Ca and seawater [U] (Russell et al., 2004). The resulting set of corrected shell U/Ca compositions form a negative non-linear trend with [CO₂⁻] (R = 0.86, p = 0.14, n = 4), although the correlation is not significant.

Shell Mn/Ca values are low (<1 μmol/mol), except in the low DIC experiment, which had 4.7 × higher [Mn] than other experiments (Fig. 5a–b). The measured shell Mn/Ca in this experiment was linearly corrected to a 4.7 × lower Mn/Ca value assuming partitioning scales with [Mn] concentration (Eggins, unpublished results). Strong negative relationships are observed between Mn/Ca and both DIC (Mn/Ca–DIC, R = −0.96, p = 0.04, n = 4).

3.3. Partition coefficient changes with calcification rate

Mean linear growth rates are determined by dividing the shell wall thickness (profile length) by the observed number of diurnal growth band pairs (each of which reflects 24 hrs of growth). These rate estimates increase in experimental order from low DIC < low pH < high pH < high DIC (Supplementary material, Table S2), but are notable for falling in a narrow range between 0.14 ± 0.02 and 0.28 ± 0.02 μm hr⁻¹ despite the large range of saturation state (Ω) across these experiments. Our linear calcification rates measured for O. universa correspond to values of R (log₁₀ Rate mol m⁻² s⁻¹) = −6.5 and −6.1. Although the calcification rate uncertainties are large due to the small number of individuals grown in each experiment, a general increase in calcification rate with increasing calcite saturation state is apparent.

Apparent partition coefficients (K₀’s) are calculated for Mg/Ca, Sr/Ca and Mn/Ca by dividing the respective shell TE/Ca by seawater TE/Ca ratios. Because B and U do not substitute for Ca²⁺, shell B/Ca and U/Ca are divided by ([B(OH)₂]·[HCO₃⁻]) and ([UO₂²⁺·CO₂⁻·HCO₃⁻]/[Ca²⁺·CO₂⁻]) (Equations (1) and (3)), from carbon and boron species concentrations calculated in CO2SYS, and for uranium species concentrations calculated from Djogić et al. (1986) for each experimental condition. There are significant increases in K₀,Mg/Ca and K₀,Sr/Ca with calcification rate (Fig. 7; R = 0.95, 0.95, and p = 0.05, 0.05, respectively, n = 4), and a significant decrease in K₀,Mn/Ca with calcification rate (Fig. 7; R = −0.99, and p < 0.01, n = 4). No consistent relationship is observed for either K₀,B/Ca or K₀,U/Ca with growth rate.

4. Discussion

4.1. Intrashell composition response to microenvironmental carbonate system variations

The B/Ca and U/Ca compositional banding we document in O. universa shells is qualitatively consistent with the expected variation of these geochemical proxies due to diurnal changes in the effects of net photosynthesis–respiration on pH, [B(OH)₂/HCO₃⁻] and [CO₂⁻] within the microenvironment of O. universa (Fig. 2). The spatial coherence of high B/Ca bands with low Mg/Ca bands that are formed during the day (Spero et al., 2015) (Fig. 4), is consistent with the daytime photosynthetic drawdown of CO₂ and resulting elevation of pH and [B(OH)₂/HCO₃⁻] in the microenvironment of O. universa. Similarly, the synchronicity of high U/Ca bands with high Mg/Ca bands that are formed during the night, is
consistent with an increase in net respired CO₂ at night and resulting decrease in microenvironmental pH and [CO₃²⁻]. The phasing of high U/Ca bands with high Mg/Ca bands are clearest in the low DIC and low pH experiments (Fig. 4a–d). This is consistent with the enhanced sensitivity of U/Ca at the lower concentrations of [CO₃²⁻] of these experiments, described by both theory (Equation (3)) and the empirical bulk shell calibration of Russell et al. (2004). Conversely, the absence of strong U/Ca banding in specimens grown in high DIC and high pH experiments is likely the result of the lower sensitivity of U/Ca to [CO₃²⁻] at high concentrations of [CO₃²⁻] (Russell et al., 2004) driving any U/Ca variations below our analytical precision.

In an effort to quantify the extent of the microenvironmental influence on shell chemistry, we combine the proxy calibrations of Allen et al. (2011) and Russell et al. (2004) with the diffusion–reaction model developed by Zeebe et al. (2003) to predict compositional changes in shell B/Ca and U/Ca arising from the carbonate chemistry variation over diurnal cycles. The diffusion–reaction model was run for both light and dark conditions, using the results for the different seawater chemistries of each experiment as a basis for comparing observed and predicted shell compositions and diurnal variation. The model calculates concentration profiles of the carbonate system parameters in the chemical microenvironment of the foraminifer using fixed rates of photosynthesis, respiration and calcification of respectively 10, 2 and 3 nmol Chr⁻¹ in the light, and 0, 2 and 1 nmol Chr⁻¹ in the dark (Lea et al., 1995; Rink et al., 1998; Zeebe et al., 2003). The carbonate chemistry calculated at the shell surface in the dark (night) and the light (day) is then used to estimate the diurnal changes in B/Ca and U/Ca compositions based on published sensitivities to seawater carbonate
The amplitude of observed B/Ca banding between the POS and outer surfaces of shells generally matches the predicted compositional variation. However, the measured U/Ca variation is generally much greater than the predicted amplitude of U/Ca banding (Fig. 8b, d, f, h). Possible explanations for this could be a greater U/Ca−[CO$_3^{2−}$] sensitivity than previously reported by bulk calibrations (equal to or greater than 3 times) or differences in the relative carbon fluxes used in the model of Zeebe et al. (2003) to describe foraminiferal physiology. Differences in the strength of photosynthesis and calcification might explain some of the differences in banding within and between individuals (e.g., Fig. 8i–j). However, varying calcification, photosynthesis and respiration carbon fluxes in the model over a range that exceeds the observed carbon flux values cannot explain the variation measured in both B/Ca and U/Ca bands (Fig. 8i–j). This suggests that disparities from modeled bands could be the result of limitations associated with bulk calibrations. This may be explained by the fact that, bulk shell calibrations integrate day and night calcite, thereby varying the individual contributions of light-dependent physiological processes on the internal carbonate system of the foraminifer. Disparities from predictions could also arise from internal biomineralization processes that influence U/Ca and B/Ca differently. For example, if foraminifers employ either carbon concentrating or proton pumping mechanisms, the associated changes to either DIC and/or pH will affect U and B incorporation differently, through their individual sensitivities to DIC and pH.

The diffusion–reaction model results are influenced by how far the symbiont swarm extends from the surface of the shell. As noted in our culture logs, in culture experiments, the density and position of the symbiont swarm can vary greatly between individual foraminifers and throughout their ontogeny. This could also vary systematically with different experimental conditions as the symbionts might adjust their position subject to both light and carbon availability. Despite these caveats, the model demonstrates that the geochemical banding observed within O. universa shells is broadly consistent with diurnal changes in microenvironment carbonate chemistry produced by photosynthesis, respiration and calcification.

This is the first study to evaluate B/Ca and U/Ca banding in symbiotic planktic foraminifers, and extends the observations on O. universa reported by Allen et al. (2011). Comparable B data have been reported by Branson et al. (2015) who, using a high-resolution scanning transmission X-ray microscope, observe B bands that peak just after Mg bands in the benthic foraminifer Amphistegina lessonii. Although this appears to conflict with our result, it is important to note that this species belongs to a different suborder than O. universa, and that Mg/Ca banding in A. lessonii has been linked to chamber addition rather than having a diurnal origin (Bentov and Erez, 2005; Erez, 2003). The phasing of B/Ca and Mg/Ca banding in this species is therefore likely to be driven by a distinct mechanism rather than the diurnal processes active in O. universa.

In contrast to good agreement between modeled and observed B/Ca in foraminifer shells outside the POS, predicted B/Ca does not match what was observed between the POS and the inner shell surfaces (see Fig. 8a, c, e, g). Anomalous high U/Ca values at the position of the POS are a prominent feature in many shells, particularly in the low pH and high DIC experiments (Fig. 3c–d, e–f). The origin of these elevated U/Ca bands is unclear, and might reflect initial calcification of the spherical adult chamber of O. universa at significantly lower [CO$_3^{2−}$] than during subsequent shell calcification. Alternatively, high uranium contents associated with the POS might be a product of uranium adsorption or accumulation at this organic layer, in a similar manner to the sequestration of uranium carbonate complexes onto cell surfaces and associated components in marine cyanobacteria (Acharya et al., 2009). This feature might also be at the limit of LA-ICP-MS depth resolution, and therefore is not fully resolved in all shells.

Several assumptions underpin our ability to predict diurnal changes in shell compositions using the diffusion–reaction model. Firstly, the empirical proxy relationships we apply to our data have been calibrated using bulk shell compositions and over a range of seawater compositions that are much narrower than our DIC experiments. Secondly, the rates of photosynthesis and respiration are constant in the model, although they have been observed to change daily with changes in symbiont productivity (Spero and Parker, 1985) and throughout the foraminifer’s ontogeny as it grows and symbiont numbers increase (Fujiki et al., 2014; Spero and Parker, 1983; Takagi et al., 2016). This might explain why B/Ca and U/Ca banding overlie broader compositional trends that occur with shell thickening over multiple days of growth (Fig. 3).

4.2. Bulk-shell TE/Ca composition response to carbonate system variations

The bulk B/Ca and U/Ca systematics observed here are qualitatively consistent with those documented for O. universa cultures.
by Allen et al. (2011) and Russell et al. (2004) (Fig. 6). Shell B/Ca compositions show a positive correlation with \([\text{B(OH)}_2^-]/\text{HCO}_3^-]\) as expected based on equation (1), albeit with a significant positive intercept (Fig. 9). The trend and intercept are broadly consistent with results from previous studies, after taking into account the [B\(_2\)] difference between studies.

The lack of Mg/Ca-pH relationship is notable, given previously reported 7 ± 5% Mg/Ca sensitivity to pH (Russell et al., 2004). The absence of this relationship may be attributable to the high variability of Mg/Ca between individual foraminifers (Sadek et al., 2005; Spero et al., 2015), combined with the limited specimen numbers in our study. The variability of TE/Ca ratios between individuals could be due to a range of factors, for example, organism size, growth rate and genetic factors (Boyle, 1995), as well as the size, growth rate and location of the symbiont population.

4.3. Calcification rate effects on trace element incorporation

The twofold increase of foraminifer calcification rate over the large experimental range of DIC and \(\Omega\) is significantly lower than the precipitation rate increase predicted for inorganic calcite. Using calcite precipitation rate calculations of Burton and Walter (1987), increasing solution saturation state from 2 to 8 results in an increase of inorganic precipitation rate by 20 times, this is an order of magnitude larger than for \(O.\ universa\). The twofold increase in calcification rate from the low DIC to high DIC experiments (low to high \([\text{CO}_3^{2-}]\)) is broadly consistent with a twofold increase in shell thickness over a ten-fold increase of \([\text{CO}_3^{2-}]\) observed by Bijma et al. (1999) and Russell et al. (2004), who attributed this observation to increased shell calcification rates. Our log\(_{10}\) Rate values are consistent with previous rate estimates for other planktonic foraminifers (i.e. \(R = -6.6 \) to \(-6.0\)) grown over a similar range of seawater \(\Omega\) (see Fante and Tipper, 2014, and calculated using calcium isotope data from Gusson et al., 2003 and Ksakurek et al., 2011).

A wealth of experimental data and an extensive theoretical basis underpin evidence for the effect of calcification rate on trace element incorporation into calcite (see DePaolo, 2011; Gabitov and Watson, 2006; Lorens, 1981; Nielsen et al., 2012; Tesoriero and Pankow, 1996). In general, in inorganic calcite, Sr and other incompatible trace elements (\(K_0 < 1\)) exhibit larger partition coefficients with increasing calcite precipitation rate, whereas Mn and other compatible trace elements (\(K_0 > 1\)) experience smaller partition coefficients with increased precipitation rate (Dromgoole and Walter, 1990; Lorens, 1981; Tang et al., 2008; Tesoriero and Pankow, 1996). At faster precipitation rates trace element behavior tends toward kinetic fractionation, whereas at slower precipitation rates equilibrium partitioning dominates (DePaolo, 2011). The apparent sensitivity of bulk shell Mg/Ca, Sr/Ca and Mn/Ca compositions to seawater carbonate system parameters could reflect the effect of these parameters on calcification rate, with Sr/Ca and Mg/Ca in-
creasing and Mn/Ca decreasing with increasing calcification rate (and Ω). These results lend support to the previous suggestion of increasing Sr/Ca ratios in planktic foraminifers with increasing calcification rate (Dueñas-Bohórquez et al., 2009; Ksakurek et al., 2008; Lea et al., 1999). Variation in calcification rates might also contribute to observed compositional differences between calcite precipitated on either side of the POS in individual shells. Very thin diurnal Mg/Ca bands on the inside of the POS indicate calcification proceeds about 5 times slower at the inner shell surface than the outer surface in O. universa (Spero et al., 2015). These slower calcite-DIC rates might explain the higher Mn/Ca compositions and tendency toward lower Sr/Ca compositions between the inner surface and the primary organic sheet (see Figs. 5 and 7). Whether differences in day and night calcification rates might also be sufficient to modulate the amplitude of diurnal banding remains to be established. This will require further use of higher resolution analysis methods to constrain day and night calcification rates.

Calcification rates slower than R = −6.0 are within the range where kinetic effects influence Sr and Mn partitioning into calcite (DePaolo, 2011; Lorenz, 1981; Tang et al., 2008; Tesoriero and Pankow, 1996). However, they fall below the rates where kinetic effects have been shown to strongly influence inorganic B partitioning into calcite (i.e. R > −6, Uchikawa et al., 2015). The narrow range of shell calcification rates exhibited by O. universa further suggests that calcification rate is unlikely to exert a large influence on bulk shell B/Ca compositions. We suggest that both B/Ca and U/Ca are much more sensitive to ambient seawater carbonate chemistry at the intra-shell scale than rate, given that O. universa and other planktic foraminifers appear to regulate their shell calcification rates within narrow limits.

5. Conclusions

It is important to understand how and why trace elements vary within foraminiferal shells, in order to constrain “vital effects” on trace element to calcium ratio proxies recorded in foraminiferal calcite. In O. universa the B/Ca compositional banding is out-of-phase with diurnal Mg/Ca banding, and U/Ca banding, where present, is in-phase with Mg/Ca banding. B/Ca banding and in many cases U/Ca banding are qualitatively consistent with the respective proxy responses to diurnal changes in the carbonate system chemistry within the chemical microenvironment of the foraminifer, based on B/Ca and U/Ca relationships established using bulk analytical methods. These carbonate system changes result from the net effects of respiration, calcification, and the photosynthetic activity of symbionts. However, there is a greater variation of U/Ca, and of B/Ca (in the high and low DIC experiments), within individual shells than predicted by microenvironment modeling. It is not clear whether this is due to limitations with the sensitivities of the bulk shell proxy calibrations used, to the sizes of the net carbon fluxes attributed to photosynthesis and respiration in the modeled microenvironment, or additional factors that are specific to the biomineralization process. Thus, our current understanding of diurnal microenvironmental variability is sufficient to explain the relative phasing, but not amplitude of Mg/Ca, B/Ca and U/Ca banding.

A quadrupling of DIC and calcite saturation state of seawater only results in a doubling of shell calcification rates. The small number of foraminifers cultured and analyzed in this study reveal that DIC concentration and calcification rate have positive correlations with bulk shell Sr and Mg partitioning, and a negative correlation with bulk Mn partitioning. No significant calcification rate effect is observed for bulk shell B and U partitioning. This may be a consequence of the small (factor of two) range in calcification rate, and greater sensitivity of these elements to seawater pH and DIC.

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Appendix A. Supplementary material

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References


