

RESEARCH ARTICLE

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Incorporation of Mg, Sr, Ba, U, and B in High-Mg Calcite Benthic Foraminifers Cultured Under Controlled $p\text{CO}_2$ C. Not^{1,2} , B. Thibodeau^{1,2} , and Y. Yokoyama³ 

Key Points:

- High-Mg calcite foraminifers have higher E/Ca ratio than low-Mg calcite
- The incorporation of Mg, Sr, Ba, U, and B does not vary linearly with $p\text{CO}_2$ in *Baculogypsina sphaerulata* and *Amphisorus hemprichii*
- Both modes of calcification (porcelaneous and hyaline) incorporate similar Mg/Ca, Sr/Ca, Ba/Ca, and B/Ca

Supporting Information:

- Supporting Information S1
- Data Set S1

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Abstract Measurement of elemental ratios (E/Ca) has been performed in two symbiont-bearing species of high-Mg calcite benthic foraminifers (hyaline, *Baculogypsina sphaerulata* and porcelaneous, *Amphisorus hemprichii*), cultured under five $p\text{CO}_2$ levels, representing preindustrial, modern, and three predicted future values. E/Ca ratios were analyzed by Laser Ablation coupled with Inductively Coupled Plasma Mass Spectrometer (LA-ICP-MS). We measured several E/Ca, such as Mg/Ca, Sr/Ca, Ba/Ca, U/Ca, and B/Ca simultaneously. We observed that high-Mg calcite benthic foraminifers possess higher E/Ca than low-Mg calcite foraminifers, irrespective of their calcification mode (hyaline or porcelaneous). In both modes of calcification, Mg, Sr, Ba, U, and B incorporation could be controlled by Rayleigh fractionation. However, more data are needed to validate and quantify the relative importance of this process and closely investigate the presence/absence of other mechanism. Therefore, it highlights the need for a multielemental approach when looking at trace element incorporation. Finally, no significant relationship was observed between the different ratios and the $p\text{CO}_2$ of the water, suggesting that none of the Mg/Ca, Sr/Ca, Ba/Ca, U/Ca, and B/Ca is sensitive to bottom water $p\text{CO}_2$ or pH for these species.

1. Introduction

The geochemistry of foraminifer tests (shells) often reflects the environmental conditions in which foraminifers calcified and offers an opportunity to reconstruct past environmental changes (e.g., Lea & Boyle, 1989; Nürnberg et al., 1996). Multiple elements incorporated into the shells have been used to reconstruct hydrographic parameters (e.g., Mg for temperature, Na for salinity), seawater chemistry (e.g., B for carbonate chemistry), biogeochemical cycling and ocean circulation (Lear et al., 2002, 2003; Wit et al., 2013; Yu & Elderfield, 2007, 2008). However, the mechanisms by which trace elements are incorporated into the shell and associated with carbonate are still controversial as contradictory behaviors have been observed (de Nooijer et al., 2009; Elderfield et al., 1996; Nehrke et al., 2013). While it has been widely accepted that the endocytosis of seawater is required for the calcification process to happen (Bentov & Erez, 2006; Erez, 2003), the ensuing evolution of the encapsulated seawater is different according to the foraminifer test structure. In foraminifers from porcelaneous/miliolid species, which form imperforate shells, the encapsulated seawater is modified and subsequently transported in the cell to create a unique internal pool (containing dissolved inorganic carbon [DIC], calcium and trace element [E]) for calcification (Bentov & Erez, 2006; de Nooijer et al., 2009, 2014). The high-Mg calcite needles produced during calcification are transported and released out of the test to form the new chamber wall (de Nooijer et al., 2009). In hyaline species, which form perforate shells, the encapsulated seawater is modified and transported in the cell to create distinct internal pools for DIC and cations such as Ca^{2+} or Mg^{2+} (Erez, 2003). Thus, in both type of calcification, the encapsulated seawater is chemically modified. Elderfield et al. (1996) suggested that this modification is a response to Rayleigh distillation and the E/Ca of the shell is a function of the calcium remaining in the internal pool. However, a recent study advocated for the existence of an alternative process (Nehrke et al., 2013). The authors proposed that the transmembrane transport via Ca-channel is responsible for the incorporation of Ca, Mg, and Sr (and probably other elements) and therefore for the discrimination between Mg or Sr and Ca. The combination of the transmembrane transport and the passive transport of seawater by diffusion of cations through gaps in the pseudopodial network and vacuolization of seawater allow Mg/Ca to reach values observed in low-Mg and high-Mg calcite (Nehrke et al., 2013). Furthermore, the existence of a

metastable carbonate phase from which planktonic foraminifers form their shell was recently demonstrated (Jacob et al., 2017). Thus, the processes by which trace elements are incorporated to foraminifer shell and the rationale for the species-specific aspect of E/Ca is still equivocal. In addition, experimental data set on the incorporation processes of trace elements in foraminifers focus mainly on the incorporation of Mg and Sr (e.g., Erez, 2003; Nehrke et al., 2013) although other trace element ratios (Ba/Ca, U/Ca, B/Ca, etc.) are described in foraminifer shells. Unfortunately, most of the studies focus on one or two ratios separately and only a limited number of studies (Gussone et al., 2016; Nehrke et al., 2013; van Dijk et al., 2017) have tried to find incorporation processes that would explain the ratio of several trace elements in foraminifer shells.

However, strong relationships between empirical data and trace element ratios in benthic foraminifer shells have been widely observed and used to reconstruct environmental conditions. While Mg/Ca is widely used as a temperature proxy (Rathmann et al., 2004; Rosenthal et al., 1997), and carbonate geochemistry (Dissard et al., 2010), Sr/Ca has been linked to different parameters such as DIC (Keul et al., 2016), temperature and/or CO_3^{2-} concentration (Reichert et al., 2003; Rosenthal et al., 2006), hydrostatic pressure (Elderfield et al., 1996), and Sr/Ca of seawater (Lear et al., 2003; Yu et al., 2014). The strong correlation between Ba concentration in deep water and alkalinity allowed the estimation of past ocean alkalinity using Ba/Ca in benthic foraminifers (Hall & Chan, 2004). More recently, a relationship between Ba/Ca in calcite and seawater Ba/Ca have been observed (de Nooijer et al., 2017). U/Ca in foraminifers is thought to be negatively correlated to carbonate ion concentrations (Keul et al., 2013) and carbonate ion saturation state (Raitzsch et al., 2011b). Finally, B/Ca has been used to reconstruct the carbonate ion concentration and pH of water masses (Raitzsch et al., 2011a; Yu & Elderfield, 2007). In this study, we measured Mg/Ca, Sr/Ca, Ba/Ca, U/Ca, and B/Ca in two benthic foraminifer species *Baculogypsina sphaerulata* and *Amphisorus hemprichii* cultured at five $p\text{CO}_2$ levels (260, 360, 580, 770, and 970 μatm), in order to document trace element incorporation (Mg, Sr, Ba, U, and B) in two symbiont-bearing, high-Mg calcite, benthic foraminifers. The two species are commonly found in coral-reef environment in the northwest Pacific (Hohenegger, 1994) and play a key role on the carbonate production of the reef. In addition, at similar $p\text{CO}_2$ high-Mg calcite has been found to exceed the solubility of aragonite, and therefore of calcite, which means that high-Mg calcite foraminifers could be highly sensitive to change of $p\text{CO}_2$. Thus, we investigated the influence of carbonate chemistry ($p\text{CO}_2$) to the incorporation of trace elements. Moreover, we compared our findings with trace element ratios from other benthic foraminifers to decipher systematic pattern for the incorporation of trace elements in benthic foraminifer shells.

2. Materials and Methods

Two species of algal symbiont-bearing benthic foraminifers were used in this study. *B. sphaerulata* and *A. hemprichii* are important primary and carbonate producers in coral-reef ecosystem of the north-west Pacific (Fujita & Fujimura, 2008; Hohenegger, 2006). Both species produce high-Mg calcite shells (at approximately 11 mol % MgCO_3 , Saraswati et al., 2004), but possess different shell structures. *B. sphaerulata* has a perforated hyaline shell, whereas *A. hemprichii* has an imperforated porcelaneous shell. Also, the symbiont of *B. sphaerulata* is a diatom, whereas the symbiont of *A. hemprichii* is a dinoflagellate.

Both species were cultured in seawater tanks and were exposed to five different $p\text{CO}_2$ levels 260, 360, 580, 770, and 970 μatm (Table 1). The $p\text{CO}_2$ level was maintained using a high precision $p\text{CO}_2$ control system

Table 1
Experimental Conditions of Foraminifer Culturing Experiments

Treatment	T (°C)	pH at 25°C	$p\text{CO}_2$ (μatm)	$[\text{CO}_3^{2-}]$ ($\mu\text{mol kg}^{-1}$)	$[\text{HCO}_3^-]$ ($\mu\text{mol kg}^{-1}$)	DIC ($\mu\text{mol kg}^{-1}$)	Ω cal	Ω arg
T1 (Preindustrial)	27.5	8.17 ± 0.03	261 ± 29	263	1,526	1,796	6.39	4.24
T2 (Present)	27.4	8.07 ± 0.03	360 ± 19	219	1,637	1,865	5.32	3.53
T3	27.5	7.93 ± 0.04	580 ± 30	161	1,781	1,958	3.91	2.6
T4	27.5	7.83 ± 0.04	774 ± 56	131	1,855	2,007	3.18	2.11
T5	27.6	7.76 ± 0.04	972 ± 43	111	1,906	2,043	2.69	1.78

Note. Values of dissolved inorganic carbon (DIC), saturation state of seawater with respect to calcite (Ω cal) and to aragonite (Ω arg) were calculated from the total alkalinity (constant at 2,188 $\mu\text{mol kg}^{-1}$) and $p\text{CO}_2$.

(see details in Fujita et al., 2011). During the whole experiment (12 weeks), seawater within the tank was maintained at a constant temperature of $28.5 \pm 0.7^\circ\text{C}$ and a light intensity of $60 \mu\text{mol m}^{-2} \text{s}^{-1}$, with an exposure period of 12 h. Twice a week, salinity, alkalinity, and pH were measured during the 12 weeks period of the experiment. Salinity was constant at 34.4, alkalinity averaged around $2,188 \mu\text{mol kg}^{-1}$ and pH varies between the different $p\text{CO}_2$ as detailed in Table 1.

Three foraminifers of each species were selected from each $p\text{CO}_2$ treatment for laser ablation analyses. In order to limit the size dependency of the shell chemistry (Elderfield et al., 2002; Friedrich et al., 2012), we selected foraminifer specimens of approximately equal shell size and close to the mean size of each treatment (supporting information Table S1). Prior to analysis, foraminifers were cleaned with hydrogen peroxide, in order to eliminate organic matter residue, rinsed with ultraclean water ($>18 \text{ M}\Omega$), and dried in an oven at 40°C for approximately 30 min. Foraminifers were fixed with double-sided adhesive tape and mounted onto a glass slide. Five spots were ablated for each *A. hemprichii* shell and four spots for each *B. sphaerulata* shell due to the smaller shell size. Ablation spots were spread evenly over the shell and tended to be in the same location for each foraminifer shell ablated. For each group of three foraminifers, which correspond to 12 and 15 spots for *B. sphaerulata* and *A. hemprichii*, respectively, three pairs of standard (NIST614 and JCp-1) were analyzed.

Elements were measured with a Resonetics M50 laser ablation system ($\lambda = 193 \text{ nm}$) connected to a Thermo-Finnigan ElementXR sector field inductively coupled plasma mass spectrometer at the Atmosphere and Ocean Research Institute of the University of Tokyo (Kawakubo et al., 2014). Stability and reproducibility were monitored using NIST614 glass reference material and a pressed pellet of carbonate standard JCp-1 (Inoue et al., 2004; Okai et al., 2002). Foraminifers were ablated using a laser beam spot with a pulse rate of 2 Hz, a spot size of $60 \mu\text{m}$, and an energy of 100 mJ with 85% attenuation, giving a fluency of $\sim 2 \text{ J cm}^{-2}$. Standards (NIST and JCp-1) were ablated using a laser beam spot with a pulse rate of 5 Hz, a spot size of $60 \mu\text{m}$, and energy of 100 mJ with 50% attenuation, giving a fluency of $\sim 6 \text{ J cm}^{-2}$. The ablation was done with a helium flux of 650 mL min^{-1} and high purity nitrogen flux of 4 mL min^{-1} . The ablated material carried by the helium was mixed with argon before entering the plasma. Data acquisition time was 60 s in total, with approximately the first 20 s for blank signal acquisition (no ablation), 25 s for the shell ablation, and 15 s to ensure the return to blank condition. The average signal of the first 20 s acquired was used to correct for the blank. Higher signal, if present at the beginning of the ablation, was not considered for the estimation E/Ca, since it is considered as surficial contamination (Rathmann et al., 2004). E/Ca was calculated from the visually estimated stable part of the ablation signal which consist of 18–23 analyses depending of the sample out of the 25 measurements done during the 25 s period of ablation.

Nine elements (^{11}B , ^{25}Mg , ^{27}Al , ^{43}Ca , ^{55}Mn , ^{66}Zn , ^{86}Sr , ^{137}Ba , ^{238}U) were measured and corrected for the background signal. Elements were normalized to ^{43}Ca and the machine drift was corrected using the average of the JCp-1 standard sensitivity which enclosed samples in the sequence. Measured intensity ratios were normalized to reference values by comparison with the intensity ratio of the coral standard JCp-1 (Inoue et al., 2004; Okai et al., 2004). The normalization was done according to the equation:

$$E/\text{Ca}_F \text{ mol mol}^{-1} = E/\text{Ca}_F \text{ cps} / E/\text{Ca}_S \text{ cps} \times E/\text{Ca}_S \text{ mol mol}^{-1} \quad (1)$$

where F subscript indicates, the ratio obtained on foraminifer shells, whereas S indicates the ratio obtained on a standard. Ratios labeled with cps subscript correspond to intensity ratio in counts per second (after blank correction) and ratios labeled with mol mol^{-1} corresponds to the concentration ratio.

The reproducibility of the JCp-1 measurement (2σ Standard Error (SE), $n = 42$) was estimated at 1.4% for Mg/Ca, 2.6% for Sr/Ca, 14% for Ba/Ca, 0.9% for U/Ca, and 4.8% for B/Ca. Accuracy of the measurements was monitored for each of the three foraminifers during the sequence using the difference between the JCp-1 E/Ca measured and the certified value after normalization to NIST614, following equation (1). Foraminifers were cultured in filtered seawater (water passed through a $10 \mu\text{m}$ and a $1 \mu\text{m}$ filter) in which the colloidal fraction could cause detrital contamination. Since no special cleaning was applied to eliminate detrital material, Al/Ca and Mn/Ca were monitored to identify possible contamination (mainly from clay and surface coating) and the degree of covariance between these ratios and Mg/Ca, Sr/Ca, Ba/Ca, U/Ca, and B/Ca were analyzed. No statistically significant correlations were observed ($R^2 < 0.5$ and $p < 0.05$); thus, all measurements were considered for further interpretations (Bolton et al., 2011). Average E/Ca ratio for each

foraminifer test and each treatment have been calculated with their two-sigma standard deviation (SD) to represent the intratest and intertest variability, respectively. The E/Ca ratio of each measurement for each $p\text{CO}_2$ was analyzed by one-way analysis of variance (ANOVA) to establish if the difference between each mean value is statistically significant. Finally, a Tukey posthoc test was performed. These statistical analyses were performed with R Studio (R Team, 2017).

3. Results

3.1. Element to Calcium Ratio and Partition Coefficient

Average Mg/Ca values ranged from 158 to 177 mmol mol^{-1} for *B. sphaerulata* and 162 to 168 mmol mol^{-1} for *A. hemprichii* (Figure 1 and Table 2) without significant differences between the two species. The intratest variability (SD) ranged from 1% to 7% in *A. hemprichii* and from 2% to 10% in *B. sphaerulata*. The intertest variability (SD) was estimated at 1–4% for *A. hemprichii* and 1–7% in *B. sphaerulata*.

The partition coefficient of element was calculated as follows:

$$D_E = E/\text{Ca}_F / E/\text{Ca}_{SW} \quad (2)$$

where E/Ca_F and E/Ca_{SW} correspond to the trace element Ca ratio in the foraminifer calcite and in seawater, respectively. Trace elements in seawater were not measured during the culture experiment, and average value from the literature were used for partition coefficient estimation. Therefore, no potential changes in the seawater trace element concentration can be observed between the different treatments and the coefficient partition calculated are thus only representing the species variability. Value of coastal Okinawa seawater (Armid et al., 2011) was used to estimate the magnesium partition coefficient. Considering a Mg/Ca_{SW} of $4.77 \pm 0.10 \text{ mmol mol}^{-1}$ (Armid et al., 2011), D_{Mg} ranged from 0.033 to 0.038 for both *B. sphaerulata* and *A. hemprichii* (Table 3).

Sr/Ca values were different between the two species; they ranged from 2.4 to 2.7 mmol mol^{-1} and from 1.8 to 2.1 mmol mol^{-1} for *B. sphaerulata* and *A. hemprichii*, respectively (Figure 1 and Table 2). The intratest variability was 4–14% and 2–18% for *B. sphaerulata* and *A. hemprichii* and the intertest variability was estimated at 2–8% and between 2% and 9% for *B. sphaerulata* and *A. hemprichii*, respectively. D_{Sr} was estimated using equation (2) and an average Sr/Ca_{SW} value of $8.36 \pm 0.25 \text{ mmol mol}^{-1}$ (Armid et al., 2011). In *B. sphaerulata*, D_{Sr} ranged from 0.28 to 0.31, whereas in *A. hemprichii*, it ranged from 0.22 to 0.25 (Table 3).

The mean Ba/Ca varied from 3 to 33 $\mu\text{mol mol}^{-1}$ in *B. sphaerulata* and from 10 to 24 $\mu\text{mol mol}^{-1}$ in *A. hemprichii* (Figure 1 and Table 2). The intratest variability was estimated at 7–54% and 3–32% for *B. sphaerulata* and *A. hemprichii*, respectively, and the intertest variability was estimated at 14–77% and between 17% and 59% for *B. sphaerulata* and *A. hemprichii*, respectively. No Ba/Ca or Ba concentrations were available for Okinawa seawater; thus, we used a Ba/Ca average from world surface seawater to estimate D_{Ba} , however we would like to point out that such estimation can lead to large variability linked to possible spatial variation of the Ba concentration. Using equation (2) and Ba/Ca_{SW} of $3.50 \pm 0.08 \mu\text{mol mol}^{-1}$ (de Villiers, 1998; Kunioka et al., 2006), D_{Ba} ranged from 9.5 to 0.7 in *B. sphaerulata* and *A. hemprichii* (Table 3).

The U/Ca in *B. sphaerulata* specimens varied from 45 to 65 nmol mol^{-1} , whereas the U/Ca in *A. hemprichii* was almost one order of magnitude higher and varied from 223 to 284 nmol mol^{-1} (Figure 1 and Table 2). The intratest variability was estimated between 3–35% and 3–21% for *B. sphaerulata* and *A. hemprichii*, respectively and the intertest variability was estimated between 17–24% and 5–19% for *B. sphaerulata* and *A. hemprichii*, respectively. Estimation of D_U , based on equation (2) and U/Ca_{SW} of $1.07 \pm 0.08 \mu\text{mol mol}^{-1}$ (Armid et al., 2011), ranged from 0.04 to 0.06 in *B. sphaerulata* and from 0.21 to 0.26 in *A. hemprichii* (Table 3).

B/Ca in *B. sphaerulata* varied from 415 to 1,399 $\mu\text{mol mol}^{-1}$ and from 342 to 1,093 $\mu\text{mol mol}^{-1}$ in *A. hemprichii* (Figure 1 and Table 2). The intratest variability was estimated between 4–44% and 5–32% for *B. sphaerulata* and *A. hemprichii*, respectively and the intertest variability was estimated between 7–11% and 8–19% for *B. sphaerulata* and *A. hemprichii*, respectively. D_B was estimated using the world ocean value for seawater B/Ca of 40 mmol mol^{-1} as used in Allen et al. (2011) and Dawber and Tripathi (2012), resulting in D_B ranging from 0.015 to 0.027, with no differences between the two species studied (Table 3).

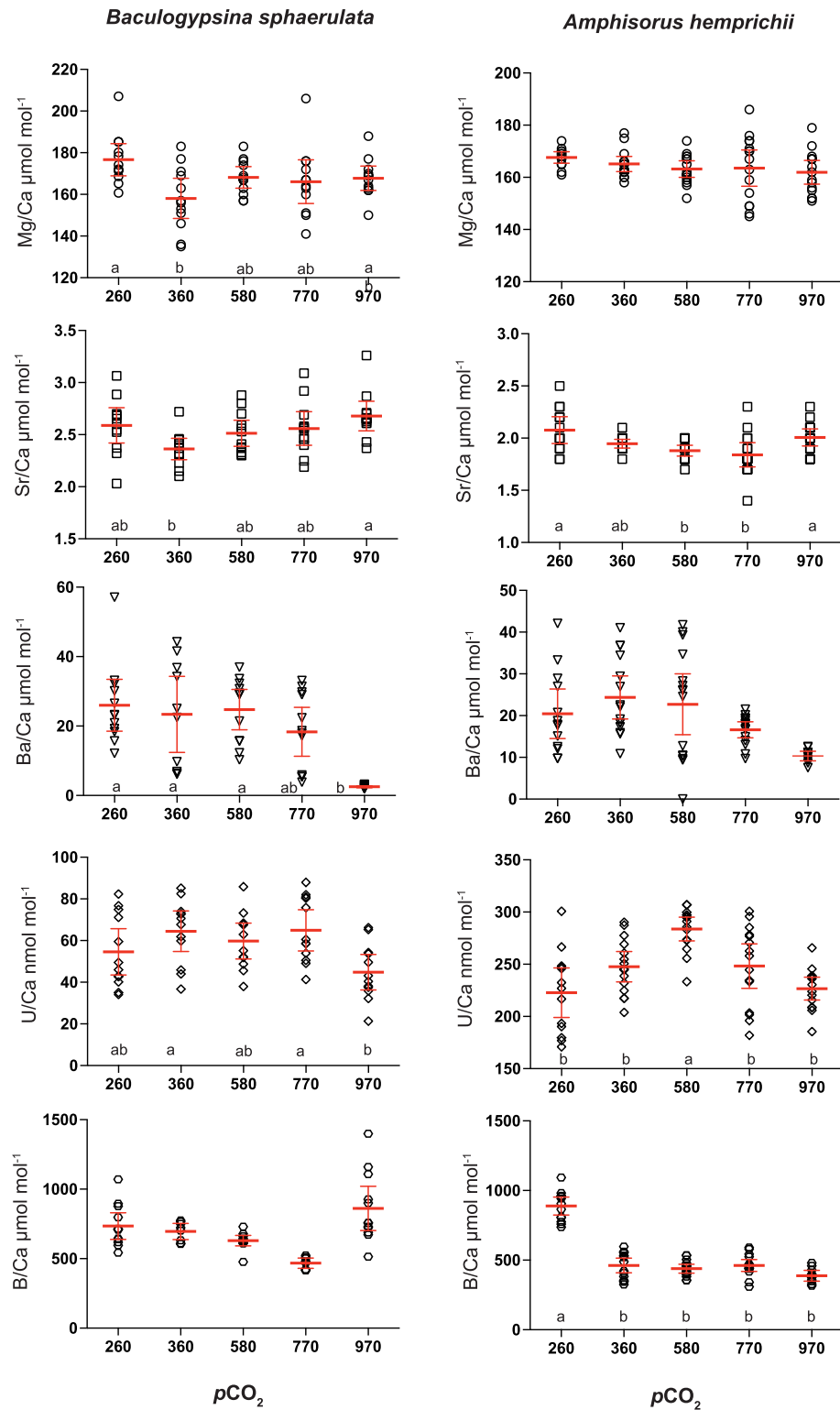


Figure 1. Single analyses (open symbol), mean value with 95% confidence interval (in red) for Mg/Ca (circle), Sr/Ca (square), Ba/Ca (triangle), U/Ca (diamond), and B/Ca (hexagon) at the five different pCO₂ used for cultured *Baculogypsina sphaerulata* (high-Mg calcite, benthic, diatom symbiont-bearing) and *Amphisorus hemprichii* (high-Mg calcite, benthic, dinoflagellate symbiont-bearing).

Table 2

Average E/Ca in *Baculogypsina sphaerulata* (High-Mg Calcite, Benthic, Diatom Symbiont-Bearing) and *Amphisorus hemprichii* (High-Mg Calcite, Benthic, Dinoflagellate Symbiont-Bearing) for Each pCO₂, With Two-Sigma Standard Deviation From the Individual Measurement

pCO ₂ (μatm)	<i>Baculogypsina sphaerulata</i>					<i>Amphisorus hemprichii</i>				
	Mg/Ca (mmol mol ⁻¹)	Sr/Ca (mmol mol ⁻¹)	Ba/Ca (μmol mol ⁻¹)	U/Ca (nmol mol ⁻¹)	B/Ca (μmol mol ⁻¹)	Mg/Ca (mmol mol ⁻¹)	Sr/Ca (mmol mol ⁻¹)	Ba/Ca (μmol mol ⁻¹)	U/Ca (nmol mol ⁻¹)	B/Ca (μmol mol ⁻¹)
260	177 ± 7	2.59 ± 0.15	26 ± 7	55 ± 10	735 ± 87	168 ± 2	2.09 ± 0.10	20 ± 5	223 ± 20	888 ± 55
360	158 ± 9	2.36 ± 0.10	23 ± 8	64 ± 9	696 ± 40	165 ± 3	1.95 ± 0.04	24 ± 5	248 ± 14	462 ± 49
580	168 ± 5	2.51 ± 0.11	25 ± 5	60 ± 8	630 ± 34	163 ± 3	1.88 ± 0.05	24 ± 6	284 ± 11	439 ± 30
770	166 ± 9	2.56 ± 0.15	18 ± 6	65 ± 9	468 ± 25	163 ± 6	1.84 ± 0.11	16 ± 2	248 ± 20	462 ± 40
970	168 ± 5	2.68 ± 0.13	2.5 ± 0.2	45 ± 8	861 ± 14	162 ± 4	2.02 ± 0.07	10 ± 1	227 ± 10	388 ± 35

3.2. Elemental Ratio Under Different pCO₂ Exposure

Mg/Ca, Sr/Ca, Ba/Ca, U/Ca, and B/Ca and their relative partition coefficients responded differently to pCO₂ variations in cultured experiments. However, in absence of direct measurements of trace element concentrations in the culture water, we used regional (for Mg, Sr, and U) and global (for Ba and B) data; therefore, the same E/Ca in seawater was used for all pCO₂, which means that the variation trend of D_E was controlled by the E/Ca variation in the foraminifer. This is coherent with the fact that measured seawater salinity suggesting that trace element concentrations within the culture water did not vary significantly.

No significant relationships between Mg/Ca, Sr/Ca, Ba/Ca, U/Ca, or B/Ca and pCO₂ were observed for any of the two species studied. However, some average E/Ca were significantly different between pCO₂ levels even with the absence of a general trend for the total range of pCO₂ studied. In *B. sphaerulata*, Mg/Ca was significantly lower at the pCO₂ value of 360 μatm and higher at the pCO₂ value of 260 μatm but showed relatively similar values for the other treatments (p = 0.017; Figure 1 and supporting information Table S2). No significant variation in Mg/Ca was observed in *A. hemprichii* specimens from 260 to 970 μatm (Figure 1). For Sr/Ca in *B. sphaerulata*, lower values were at pCO₂ of 360 μatm and higher values were at pCO₂ of 970 μatm (p = 0.017; supporting information Table S2), whereas in *A. hemprichii*, values were lower at pCO₂ of 770 μatm and values were higher at pCO₂ of 260 μatm (p < 0.001; supporting information Table S2). As for Mg/Ca, no significant difference was observed for Ba/Ca in *A. hemprichii*, whereas in *B. sphaerulata*, lower values were observed in higher pCO₂ (970 μatm) and the highest values were observed in the other pCO₂ levels with no significant difference between them (p < 0.001; supporting information Table S2). For U/Ca in *B. sphaerulata*, lower values were at pCO₂ of 970 μatm and higher values were at pCO₂ of 360 and 770 μatm (p = 0.11; supporting information Table S2), whereas in *A. hemprichii*, lower values were at pCO₂ of 260 μatm and higher values were at pCO₂ of 580 μatm (p < 0.001; supporting information Table S2). Finally, B/Ca in *B. sphaerulata* showed no significant variation, whereas in *A. hemprichii*, higher values were at pCO₂ of

Table 3

Partition Coefficient in Inorganic Calcite and High-Mg Calcite Benthic Foraminifera (*Baculogypsina sphaerulata* and *Amphisorus hemprichii*)

	Inorganic	<i>Baculogypsina sphaerulata</i>	<i>Amphisorus hemprichii</i>
Mg	0.057	0.035 ± 0.003	0.034 ± 0.001
Sr	0.04	0.31 ± 0.03	0.23 ± 0.02
Ba	0.08	5.99 ± 6.61	5.49 ± 3.38
U	0.05–0.2	0.05 ± 0.02	0.23 ± 0.05
B	0.38–4.0	0.02 ± 0.01	0.01 ± 0.01

Note. Inorganic partition coefficients are from Elderfield et al. (1996) and Dawber and Tripathi (2012). D_{Mg}, D_{Sr}, and D_U were calculated using seawater E/Ca at 26°C from Armid et al. (2011), i.e., Mg/Ca_{SW} = 4.77 ± 0.1 mmol mol⁻¹, Sr/Ca_{SW} = 8.36 ± 0.25 mmol mol⁻¹, and U/Ca_{SW} = 1.07 ± 0.08 μmol mol⁻¹. D_{Ba} was calculated using the average surface Ba/Ca of seawater, i.e., Ba/Ca_{SW} = 3.5 ± 0.08 μmol mol⁻¹ (Chan et al., 1976; de Villiers, 1998; Kunioka et al., 2006) and D_B was calculated using the average surface B/Ca of seawater, i.e., B/Ca_{SW} = 40 mmol mol⁻¹ (Allen et al., 2011; Dawber & Tripathi, 2012).

260 μatm and all the other treatments showed significantly lower B/Ca with no difference between these lower values ($p < 0.001$; supporting information Table S2).

4. Discussion

4.1. Variation of E/Ca in Benthic Foraminifers

Table 4 summarizes the data from this study and the data available in the literature for Mg/Ca, Sr/Ca, Ba/Ca, U/Ca, and B/Ca in benthic foraminifers. Mg/Ca ranged from ~ 160 to $180 \text{ mmol mol}^{-1}$ in both species (Table 2 and Figure 1), which is in accordance with Mg/Ca from other high-Mg calcite species (Dueñas-Bohórquez et al., 2011; Gacutan et al., 2017; Raitzsch et al., 2010; Raja et al., 2005; Toyofuku et al., 2000; van Dijk et al., 2017). Whereas *B. sphaerulata* and *A. hemprichii* have different calcification process; no significant difference in Mg/Ca is observed between the two species. This absence of impact of the mode of calcification on Mg/Ca is also observed by the data assembled in Table 4. However, the Mg/Ca from hyaline foraminifer, which produces both low-Mg and high-Mg calcite depending on the species, appears to be at least genus specific for high-Mg calcite (Table 4) since, for example, Mg/Ca from *Heterostegina depressa* varies from around $150 \pm 10 \text{ mmol mol}^{-1}$ (Dueñas-Bohórquez et al., 2011; Raitzsch et al., 2010), while it ranges around $128 \pm 11 \text{ mmol mol}^{-1}$ for *Planoglabratella opercularis* (Toyofuku et al., 2000) or $60 \pm 20 \text{ mmol mol}^{-1}$ for *Amphistegina lessonii* (Mewes et al., 2015; Raja et al., 2005; Segev & Erez, 2006). Yet, a recent study on two foraminifer species from the Calcarinidae family suggest that Mg/Ca is similar within this family, as Mg/Ca varies from ~ 146 to ~ 163 in *Calcarina Capricornia* and between ~ 134 and ~ 160 in *B. sphaerulata* (Gacutan et al., 2017). On the other hand, porcelaneous foraminifers always produce high-Mg calcite shells, and species variability is also observed (Table 4) as *Quinqueloculina yabei* Mg/Ca ranges $112 \pm 11 \text{ mmol mol}^{-1}$ (Toyofuku et al., 2000), *Marginopora kudakajimaensis* Mg/Ca ranges from $316 \pm 37 \text{ mmol mol}^{-1}$ (Raja et al., 2005) or *Sorites marginalis* Mg/Ca ranges $144 \pm 1 \text{ mmol mol}^{-1}$ (van Dijk et al., 2017). In this study, *A. hemprichii* Mg/Ca ranged from 145 to $186 \text{ mmol mol}^{-1}$ which is slightly lower than the Mg/Ca range of 224 to $256 \text{ mmol mol}^{-1}$ observed from the same species by Raja et al. (2005). The difference observed between Mg/Ca from *A. hemprichii* in the present study and the one from Raja et al. (2005) could be linked to the combination of (1) the temperature difference between the two studies (27.5°C in the present study versus $28\text{--}30^\circ\text{C}$, which would affect the Mg/Ca by about 28 mmol mol^{-1} based on the Mg/Ca-T correlation (Raja et al., 2005) and (2) the intraspecies variability, since Mg/Ca ranges between 294 and $360 \text{ mmol mol}^{-1}$ for a set temperature of 25.2°C (Raja et al., 2005).

The Sr/Ca of *B. sphaerulata* and *A. hemprichii* ranged, respectively, from 2.4 to $2.7 \text{ mmol mol}^{-1}$ and from 1.8 to $2.1 \text{ mmol mol}^{-1}$. This is coherent with previous data collected on high-Mg calcite foraminifers (Allison et al., 2011; Dueñas-Bohórquez et al., 2011; Elderfield et al., 2002; Gacutan et al., 2017; Raitzsch et al., 2010; Raja et al., 2005; van Dijk et al., 2017). Sr/Ca from *A. hemprichii* (porcelaneous) is on average $\sim 2 \text{ mmol mol}^{-1}$ (Elderfield et al., 2002; Raja et al., 2005, and this study) whereas Sr/Ca from *H. depressa* and *Baculogypsina sphaerulata* (hyaline) are higher $\sim 2.5 \text{ mmol mol}^{-1}$ (Dueñas-Bohórquez et al., 2011; Gacutan et al., 2017; Raitzsch et al., 2010, and this study) suggesting that the mode of calcification could influence the Sr/Ca in these species. However, this is not consistent with other high-Mg benthic foraminifer species where hyaline species do not systematically have higher Sr/Ca than porcelaneous species (see Table 4).

Ba/Ca ratios in low-Mg calcite planktonic and benthic foraminifers vary from ~ 0.4 to $\sim 20 \mu\text{mol mol}^{-1}$, with higher ratios in benthic foraminifers (Hall & Chan, 2004; Havach et al., 2001; Hintz et al., 2006; Hönisch et al., 2011; Lea & Boyle, 1991, 1989; Lea & Martin, 1996; Lea & Spero, 1994; van Dijk et al., 2017). Here, in high-Mg calcite benthic foraminifers, we observed Ba/Ca values slightly higher (ranging from 2 to $\sim 30 \mu\text{mol mol}^{-1}$) than in low-Mg calcite benthic foraminifers. Only two other studies reported Ba/Ca in high-Mg calcite with an average ratio of $\sim 90 \mu\text{mol mol}^{-1}$ in *Rosalina vilardeboana* (Hintz et al., 2006) and Ba/Ca ranging 14–23 $\mu\text{mol mol}^{-1}$ in four porcelaneous species and ranging 3–11 $\mu\text{mol mol}^{-1}$ in four hyaline species (van Dijk et al., 2017). Taken together, this suggests that high-Mg foraminifers tend to incorporate higher quantities of Ba. No systematic variation in Ba/Ca of high-Mg calcite benthic foraminifers was observed, suggesting that Ba/Ca in high-Mg calcite foraminifers do not depend on the mode of calcification (hyaline versus porcelaneous) or on the nature of the symbiont.

We reported here, to the best of our knowledge, the first measurement of U/Ca in high-Mg benthic foraminifers. U/Ca average was around 60 nmol mol^{-1} for *B. sphaerulata* and $\sim 250 \text{ nmol mol}^{-1}$ for *A. hemprichii*

Table 4
Compilation of Mg/Ca, Sr/Ca, Ba/Ca, U/Ca, and B/Ca in Benthic Foraminifera Published in the Literature

Species	Symbiont		Specie	Epifaunal/ Infaunal	Cultured/ Natural Env.	Dead/ Living	Cleaning methods	Mg/Ca mmol/ mol	Sr/Ca ±	Ba/Ca ummol/ mol	U/Ca nmol/ mol	B/Ca ummol/ mol	References	
	LMC- HMC	Hyaline/ Porcelaneous												
<i>Cibicides wuellerstorfi</i>	L	H	N	E	NE	Mix	Reductive + Oxidative	2.7	0.8				Lea and Boyle (1989)	
					NE	D	Reductive + Oxidative						McCorkle et al. (1995)	
					Mix	Mix	Reductive + Oxidative	1.7	0.3	1.3	0.2	0.4		Russell et al. (1994)
					NE	D	Reductive + Oxidative				9.2	1.0		Lea and Martin (1996)
					NE	Mix	Reductive + Oxidative			1.2	0.0	0.4		Elderfield et al. (1996)
					NE	D	Mix Leach and Reduc- tive and Oxidative	1.1	0.2	1.3	0.1			Martin and Lee (2002)
					NE	L	Reductive + Oxidative	1.4	0.4					Lear et al. (2002)
					NE	Mix	Reductive + Oxidative	1.1	0.3				200	Elderfield et al. (2006)
					NE	D	Mix Reductive and Oxidative						21	Yu and Elderfield (2007)
					NE	L	No	1.4	0.3					Raitzsch et al. (2008)
					NE	D	Reductive + Oxidative + Citrate	1.2	0.3					Yu and Elderfield (2008)
					NE	D	Mix Reductive and Oxidative	1.2	0.2			216	21	Yu et al. (2010)
					NE	D	Oxidative					193	21	Rae et al. (2011)
	<i>Cibicides kullenbergi</i>	L	H	N	E	NE	Mix	Reductive + Oxidative	2.8	0.8				Lea and Boyle (1989)
					NE	L	Reductive + Oxidative	5.4	0.4					Lear et al. (2002)
					NE	D	Mix Reductive and Oxidative					131	8	Yu and Elderfield (2007)
					NE	L	No	1.6	0.9					Raitzsch et al. (2008)
					NE	D	Mix Reductive and Oxidative	1.6	0.3					Yu and Elderfield (2008)
					NE	D	Mix Reductive and Oxidative	1.2	0.1			174	7	Yu et al. (2010)
					NE	D	Oxidative					164	17	Rae et al. (2011)
					NE	D	No				10.3	5.6		Raitzsch et al. (2011a, 2011b)
					NE	D	Oxidative	4.3	0.5					Tisserand et al. (2013)
					NE	D	Reductive + Oxidative			1.2	0.1			Yu et al. (2014)
					NE	D	Mix Reductive and Oxidative				5.9	1.4		Chen et al. (2017)
					NE	D	Oxidative					166		Rae et al. (2011)
					NE	D	Oxidative					107		Rae et al. (2011)
<i>Cibicides lobatus Cibicides robertsonianus</i>		L	H	Y	I	NE	Mix	Reductive + Oxidative						Lea and Boyle (1989)
					NE	Mix	Reductive + Oxidative						Elderfield et al. (1996)	
					NE	L	Reductive + Oxidative	1.6	1.6					Lear et al. (2002)
					NE	D	Mix Reductive and Oxidative					45	3	Yu and Elderfield (2007)
					NE	D	Reductive + Oxidative	1.6	0.3					Brian and Marchitto (2008)
					NE	D	Reductive + Oxidative			3.1	1.0			Yu et al. (2014)
					NE	D	Oxidative	1.4	0.4					Gussone et al. (2016)
					C	L	Reductive + Oxidative			13.0	3.0			Havach et al. (2001)
					NE	Mix	Reductive + Oxidative	1.2	0.3					Elderfield et al. (2006)
					NE	D	Oxidative	1.4	0.4					Rae et al. (2011)
					NE	D	Oxidative	1.3	0.3					Tisserand et al. (2013)
					NE	D	Oxidative			1.0	0.1			Gussone et al. (2016)
	<i>Uvigerina sp.</i>	L	H	Y	I	NE	D	Reductive + Oxidative	1.3	0.3				Lea and Boyle (1989)
						NE	D	Oxidative						

Table 4. (continued)

Species	LMC-HMC		Hyaline/ Porcellaneous	y/h	Symbiont		Epifaunal/ Infaunal	Cultured/ Natural Env.	Dead/ Living	Cleaning methods	Mg/Ca mmol/ mmol	Sr/Ca ±	Ba/Ca ummol/ mmol	U/Ca nmol/ mmol	B/Ca ummol/ mmol	References
	L	H			Specie	Env.										
<i>Cibicides pachyderma</i>	L	H			E	NE	NE	D	Leach	5.7	2.3					Rosenthal et al. (1997)
<i>Oridorsalis umbonatus</i>	L	H			I	NE	NE	L	Reductive + Oxidative	1.7	0.6					Lear et al. (2002)
<i>Planulina sp.</i>	L	H				NE	NE	L	No	2.8	0.8					Rathman et al. (2004)
<i>Planulina ariminensis</i>	L	H			E	NE	NE	D	Oxidative	2.6	0.7	1.0	0.1		44	Rathmann and Kuhnert (2008)
	L	H			E	NE	NE	D	Reductive + Oxidative	1.7	0.5	0.9	0.1		60	Rae et al. (2011)
	L	H			E	NE	NE	D	Oxidative	2.6	0.3				35	Brown et al. (2010)
	L	H			E	NE	NE	D	Reductive + Oxidative	2.4	0.5				20	Dawber and Tripathi (2012)
	L	H			E	NE	NE	D	Oxidative	2.0	0.7	0.9	0.1			Tisserand et al. (2013)
	L	H			E	NE	NE	D	Oxidative	3.3	2.3	1.2	0.3			Gussone et al. (2016)
<i>Elphidium sp.</i>	L	H		N	E	NE	NE	D	Oxidative	3.0	1.0	1.4	0.2			Allison et al. (2011)
<i>Elphidium williamsoni</i>	L	H		N	E	NE	NE	D	Oxidative	1.5	0.7	1.0	0.1			Gussone et al. (2016)
<i>Ammonia spp.</i>	L	H		N	E	NE	NE	D	Oxidative	2.4	0.9	1.4	0.8			Keul et al. (2017)
<i>Ammonia tepida</i>	L	H		N	E	NE	NE	D	Bleach (NaClO)	1.1	0.3	1.4	0.2			Raitzsch et al. (2010)
	L	H		N	E	NE	NE	D	No	1.8	0.2	1.4	0.1			Dissard et al. (2010)
	L	H		N	E	NE	NE	D	NaOCl	5.0						Duenas-Bohorquez et al. (2011)
	L	H		N	E	NE	NE	D	Bleach (NaClO)	3.2			166.8	261.0		Keul et al. (2013)
<i>Ammonia aamoriensis</i>	L	H		N	E	NE	NE	D	Yes	3.8	1.9					de Nooijer et al. (2014)
<i>Ammonia beccarii</i>	L	H		N	E	NE	NE	D	No	1.7	0.4					Mewes et al. (2015)
	L	H		N	E	NE	NE	D	Reductive + Oxidative	2.1	0.3	12.5	0.6		64	Havach et al. (2001)
	L	H		N	E	NE	NE	D	Oxidative	2.5	0.4	1.2	0.0		58	Rae et al. (2011)
<i>Melonis zaandamae</i>	L	H		N	E	NE	NE	D	Oxidative	1.4	0.5	1.0	0.1		130	Brown et al. (2010)
<i>Nuttallides umbonifera</i>	L	H		N	E	NE	NE	D	Reductive + Oxidative	128.2	11.3					Toyofuku et al. (2000)
<i>Bulimina aculeata</i>	L	H		N	E	NE	NE	D	Oxidative	3.8	2.1	22.8				Hintz et al. (2006)
<i>Bulimina marginata</i>	L	H		N	E	NE	NE	D	Reductive + Oxidative	1.7	0.4	13.0	2.0			Havach et al. (2001)
<i>Bulimina inflata</i>	L	H		N	E	NE	NE	D	Bleach (NaClO)	2.1	0.3					Wit et al. (2012)
<i>Gyroidinoides sp.</i>	L	H		N	E	NE	NE	D	Oxidative	2.5	0.4	1.2	0.0			Tisserand et al. (2013)
<i>Cassidulina laevigata</i>	L	H		N	E	NE	NE	D	Oxidative	1.4	0.5	1.0	0.1			Gussone et al. (2016)
<i>Planoglobatella operculis</i>	L	H		N	E	NE	NE	D	Oxidative	235.6	17.8	2.0	0.1			Gussone et al. (2016)
<i>Neorotalia calcar</i>	L	H		N	E	NE	NE	D	Oxidative	136.0	5.3	2.5	0.1			Toyofuku et al. (2000)
<i>Rosalina viardeboana</i>	L	H		N	E	NE	NE	D	Oxidative	128.2	11.3					Toyofuku et al. (2000)
<i>Heterostegina depressa</i>	L	H		N	E	NE	NE	D	Oxidative	235.6	17.8	2.0	0.1			Raja et al. (2005)
	L	H		N	E	NE	NE	D	Methanol + Oxidative	53.0	3.4	91.4				Hintz et al. (2006)
	L	H		N	E	NE	NE	D	Oxidative	148.9	5.4	2.8	1.4			Raitzsch et al. (2010)
	L	H		N	E	NE	NE	D	No	136.0	5.3	2.5	0.1			Duenas-Bohorquez et al. (2011)
	L	H		N	E	NE	NE	D	Bleach (NaClO)	136.0	5.3	2.5	0.1			Duenas-Bohorquez et al. (2011)

Table 4. (continued)

Species	LMC-HMC		Hyaline/ Porcelaneous		Symbiont		Cleaning methods	Mg/Ca mmol/mol	Sr/Ca ±	Ba/Ca ummol/mol ±	U/Ca nmol/mol ±	B/Ca ummol/mol ±	References						
					Epifaunal/ Infaunal	Cultured/ Natural Env.								Dead/ Living	Specie	y/n			
<i>Gyroidina soldanii</i>			H		I	NE	D	Oxidative				41	11	Rae et al. (2011)					
<i>Lenticulina vortex</i>			H		I	NE	D	Oxidative				74	11	Rae et al. (2011)					
<i>Amphistegina lessonii</i>	H		H	Y	E	NE	L	Methanol + Oxidative Bleach (NaClO)	77.0	6.1	1.7	0.1		Raja et al. (2005) Segev and Erez (2006) Mewes et al. (2015) Segev and Erez (2006) van Dijk et al. (2017)					
<i>Amphistegina lobifera</i>	H		H	Y	E	C	L	No	49.3										
<i>Amphistegina gibbosa</i>	H		H	Y	E	C	L	Bleach (NaClO)	47.8	4.5									
<i>Baculogypsina sphaerulata</i>	H		H	Y	E	C	L	Oxidative	58.6	0.6	1.7	0.02	3.4	0.5	van Dijk et al. (2017)				
			H	Y	E	C	L	No	167.3	6.6	2.5	0.1	19.0	9.7	57.7	8.4	678	144	This study
						NE	L	Oxidative	147.00	29.30	2.70	0.30							Gacutan et al. (2017)
<i>Calcarina capricornia</i>	H		H	Y	E	NE	L	Oxidative	154.60	13.80	2.80	0.60							Gacutan et al. (2017)
<i>Asterigerina carinata</i>	H		H		E	C	L	Oxidative	28.5	2.4	1.9	0.01	6	0.5					van Dijk et al. (2017)
<i>Heterostegina antillarum</i>	H		H		E	C	L	Oxidative	141.3	0.3	2.7	0.02	10.7	0.5					van Dijk et al. (2017)
<i>Planorbulina acervalis</i>	H		H		E	C	L	Oxidative	139.1	1.2	3.1	0.02	11.3	0.5					van Dijk et al. (2017)
<i>Hoeglundina elegans</i>	Aragonite		H		E	NE	Mix	Oxidative	1.1	0.4	1.9	0.6							Rosenthal et al. (2006)
						NE	D	Mix Reductive and Oxidative					39	10	Yu and Elderfield (2007)				
<i>Marginopora vertabralis</i>	H		P	Y	E	NE	D	Reductive + Oxidative	1.7	0.9					Bryan and Marchitto (2008)				
<i>Marginopora kudakajimaensis</i>	H		P	Y	E	NE	L	Methanol+Oxidative	315.9	37.3	3.2	0.4			Raja et al. (2005)				
<i>Quinqueloculina sp.</i>	H		P	N	E	NE	D	Oxidative	71.2	16.6	1.8	0.1			Gussone et al. (2016)				
<i>Quinqueloculina yabei</i>	H		P		E	C	L	Oxidative	112.3	10.5					Toyofuku (2000)				
<i>Amphisorus hemprichii</i>	H		P	Y	E	NE	L	Methanol+Oxidative	238.0	16.3	1.8	0.1			Raja et al. (2005)				
						C	L	No	164.3	2.2	2.0	0.1	19.2	5.9	245.8	24.2	528	204	This study
<i>Pyrgo sp.</i>	H		P		I	NE	D	Oxidative	40.9	39.7	2.0	0.1			Gussone et al. (2016)				
<i>Sorites marginalis</i>	H		P		E	C	L	Oxidative	144.2	0.8	2	0.1	23.1	0.5					van Dijk et al. (2017)
<i>Laevipeneroplis bradyi</i>	H		P		E	C	L	Oxidative	136.2	0.7	2.2	0.1	14.2	0.5					van Dijk et al. (2017)
<i>Archaias angulatus</i>	H		P		E	C	L	Oxidative	137.7	0.5	2.2	0.01	14.6	0.5					van Dijk et al. (2017)
<i>Peneroplis pertusus</i>	H		P		E	C	L	Oxidative	126.1	1.8	2.1	0	18	0.5					van Dijk et al. (2017)

Note. Foraminifera are classified by their content of magnesium between Low-Mg calcite (LMC), aragonite and High-Mg calcite (HMC).

(Figure 1), which falls in the range of U/Ca measured in calcite foraminifers (Keul et al., 2013; Raitzsch et al., 2011b; Russell et al., 2004). However, U/Ca in low-Mg calcite benthic foraminifer seems to be lower than from high-Mg calcite foraminifer, where U/Ca from low-Mg calcite species such as *Cibicidoides wuellerstorfi* range from 4.6 to 23.0 nmol mol⁻¹ or *Cibicidoides kullenbergi* range from 4.5 to 20.9 nmol mol⁻¹. An exception to the lower U/Ca in low-Mg calcite shells was observed during culture experiments of *Ammonia* sp. under large ranges of pCO₂, where U/Ca ranges from 25 to 797 nmol mol⁻¹ (Keul et al., 2013). Looking at the present-day condition, *Ammonia* sp. U/Ca is around 40 nmol mol⁻¹, supporting the idea of higher U/Ca ratios in foraminifer that produce high-Mg calcite.

In the literature, B/Ca have been measured in both planktonic and benthic low-Mg calcite. In benthic foraminifers, it ranges from 20 to 240 μmol mol⁻¹ with species-specific variability, where B/Ca in *C. wuellerstorfi* ranges from 140 to 240 μmol mol⁻¹ (Brown et al., 2010; Rae et al., 2011; Yu & Elderfield, 2007) and in *Oridorsalis umbonatus* it ranges from 20 to 80 μmol mol⁻¹ (Brown et al., 2010; Dawber & Tripathi, 2012; Rae et al., 2011). B/Ca in high-Mg calcite is higher than B/Ca reported for low-Mg calcite, and we observed species specificity, where B/Ca was close to 500 μmol mol⁻¹ for *A. hemprichii* and around 830 μmol mol⁻¹ for *B. sphaerulata*. However, to our knowledge, no other B/Ca have been reported for high-Mg calcite foraminifers.

Based on these data, we observed that all E/Ca measured in this study (Mg/Ca, Sr/Ca, Ba/Ca, U/Ca, and B/Ca) were higher in high-Mg benthic foraminifers than in low-Mg benthic foraminifers. No systematic difference was observed based on the mode of calcification or the presence/absence of the symbiont and its nature, its habitat (epi/infaunal) or the cleaning method used (Table 4). This suggests that the incorporation of a specific element is probably linked to several processes that can be species specific; as a change in the relative contribution of transmembrane transport and passive transport (van Dijk et al., 2017). However, it is difficult to assess the robustness of this observation since almost only Mg/Ca and Sr/Ca are reported in the literature for high-Mg calcite foraminifers.

4.2. Incorporation Process of E/Ca

4.2.1. Imperforate Versus Perforate Shells

Different calcification processes characterize the two-studied species. *B. sphaerulata*, a hyaline foraminifer precipitates perforate shell of high-Mg calcite, whereas *A. hemprichii*, a porcelaneous foraminifer produces imperforate shell of high-Mg calcite. As described in the section 1, imperforate shells are produced via the formation of small calcite crystals within the intracellular vesicle that are transported later on to the chamber site formation. The incorporation of trace elements is believed to go through the intracellular vesicle where the calcite crystals are formed (Bentov & Erez, 2006). Perforate shells seem to have a more complex or at least less understood calcification process, since it is still unknown if the calcification site is open or closed and if there is a presence or absence of intracellular ion reservoirs (de Nooijer et al., 2014). While it is clear that the seawater E/Ca is modified, the modification processes involved; Rayleigh distillation, passive transport, ion pump, transmembrane transporter or double fractionation mechanism, are still controversial (de Nooijer et al., 2014; Jacob et al., 2017; Nehrke et al., 2013).

Even if the two species have different calcification processes, they both produce high-Mg calcite, with similar Mg/Ca values, indicating that the different processes involved in the incorporation of Mg in both calcification modes can incorporate the same level of Mg/Ca. By looking at the other elements, no general difference appears between the elements based on the calcification mode, Sr/Ca and B/Ca are higher in *B. sphaerulata* (hyaline shell), and U/Ca are higher in *A. hemprichii* (porcelaneous shell). This trend is also observed when considering other published value for high-Mg calcite foraminifers, where Sr/Ca is higher on average for hyaline than porcelaneous (Table 4). Interestingly our data show similar Ba/Ca for both species whereas average published values are higher for porcelaneous foraminifers.

4.2.2. Partition Coefficient

Partition coefficients (D_x) of the different elements measured in this study are presented in Table 3 and compared with the inorganic partition coefficient. Except for D_U , all partition coefficients are similar for both species studied here. The partition coefficient for Mg and B is smaller compared to the inorganic partition coefficient while Sr and Ba are higher than the inorganic value and U is similar. This suggests that the calcification process segregates Mg and B while concentrating Sr and Ba for both species.

D_{Mg} obtained for *B. sphaerulata* and *A. hemprichii*, were similar to D_{Mg} published for high-Mg calcite (Dueñas-Bohórquez et al., 2011; Raitzsch et al., 2010; Toyofuku et al., 2000) and close to the D_{Mg} of *A. hemprichii* (Raja et al., 2005). In all cases, the D_{Mg} was lower than the inorganic partition coefficient but higher than the low-Mg calcite benthic foraminifer partition. Comparable results were observed in D_B values, which were always found below the inorganic partition coefficient (e.g., Dawber & Tripathi, 2012). D_{Sr} was higher in high-Mg calcite foraminifer than in low-Mg calcite shells, where D_{Sr} is estimated between 0.15 and 0.18 (Dissard et al., 2010; Elderfield et al., 2000). In high-Mg calcite foraminifers D_{Sr} is estimated at between 0.2 and 0.3 (Dueñas-Bohórquez et al., 2011; Raitzsch et al., 2010; Raja et al., 2005, and this study), which is higher than the inorganic partition coefficient but lower than one. D_U was within the range of D_U observed in *Ammonia* sp. (Keul et al., 2013) and was similar to inorganic calcite that varies from 0.046 to 0.2 (Table 3, Elderfield et al., 1996). Average D_{Ba} in *B. sphaerulata* and *A. hemprichii* were higher than the D_{Ba} observed in planktonic foraminifers, where D_{Ba} ranges between ~ 0.17 and ~ 1 (Hönisch et al., 2011; Lea & Boyle, 1991; Lea & Spero, 1992) and benthic foraminifers, where D_{Ba} ranges between ~ 0.4 and ~ 2.6 (van Dijk et al., 2017).

Partition coefficient higher than the inorganic partition coefficient but lower than one, suggests a calcification from a semi-enclosed pool where the element is modified via Rayleigh fractionation (Dawber & Tripathi, 2012). Here this is the case for Sr and Ba. However, lower partition coefficients, as observed for Mg and B, can also be explained by Rayleigh fractionation if the fractionation factor from the internal pool is smaller than the inorganic one (Dawber & Tripathi, 2012). While we are aware that other mechanisms could be involved (e.g., surface entrapment model) our dataset do not allow to make such distinction.

Our high D_{Ba} needs to be considered carefully because no Ba/Ca or barium concentration was available for the culture ambient water and thus we had to use the global ocean average Ba/Ca. However, in coastal environments, influence of freshwater rich in barium (like river or even more importantly groundwater) can affect the Ba/Ca. In order to investigate the importance of such a variability of Ba/Ca, we calculated the concentration required to reach the D_{Ba} observed in previous studies. Barium concentration of $\sim 1,500$ nmol kg^{-1} and ~ 250 nmol kg^{-1} would be needed obtain a D_{Ba} of 0.17 and 1, respectively. Such concentrations are reported in different groundwater systems (Santos et al., 2011), highlighting the possibility that we underestimated the concentration of Ba/Ca when using global ocean data and thus overestimated our D_{Ba} . Therefore, it appears difficult to discuss the incorporation pathway of Ba in foraminifer with this data set.

The range of D_U observed in our data is similar to inorganic calcite, which can indicate that incorporation of uranium in these two species is driven by inorganic processes such as Rayleigh fractionation and/or surface entrapment model. In addition, U/Ca was the only ratio that was correlated to the weight of the foraminifer shell (indicator of precipitated mass; supporting information Table S2), highlighting the predominance of inorganic processes of U incorporation.

4.3. Effect of $p\text{CO}_2$ on Mg/Ca, Sr/Ca, Ba/Ca, U/Ca, and B/Ca

Several empirical studies have shown a correlation between carbonate system parameters such as CO_2 , HCO_3^- , CO_3^{2-} concentrations, pH or DIC and E/Ca in benthic foraminifers (Dissard et al., 2010; Yu & Elderfield, 2007, 2008). However, it is difficult to single out their respective importance in the incorporation of trace elements because the basis of these relationships is unknown. Based on our experimental setting, only $p\text{CO}_2$ changes can be discussed below and no discrimination with covarying carbonate chemistry parameters as pH can be examined. While it has been suggested that the calcite saturation state and pH could influence the Mg/Ca in benthic foraminifers (Elderfield et al., 2006), no evidence of the influence of neither $[\text{CO}_3^{2-}]$ nor pH in the incorporation of Mg in foraminifer species *Ammonia tepida*, *Heterostegina depressa*, and *Elphidium williamsoni* was observed before (Allison et al., 2011; Dissard et al., 2010; Dueñas-Bohórquez et al., 2011). The same equivocal evidence can be found in regards to the incorporation of Sr/Ca in benthic foraminifers (Dueñas-Bohórquez et al., 2011). Until recently no evidence has been found that carbonate system parameters could affect the incorporation of Ba/Ca since only the Ba concentration in seawater has been found to affect Ba/Ca in foraminifer (Hintz et al., 2006; Lea & Boyle, 1989). However van Dijk et al. (2017) suggested a positive linear correlation between Ba/Ca and $p\text{CO}_2$ for several benthic species, both hyaline and porcelaneous species. It has been observed that carbonate system parameters, particularly CO_3^{2-} , can control the U/Ca incorporated in different species because pH affects the proportion of the different forms of U in seawater (Keul et al., 2013; Raitzsch et al., 2011b). Finally, B/Ca have been identified to

correlate with CO_3^{2-} in several studies (Yu & Elderfield, 2007; Yu et al., 2010) but also with pH (Howes et al., 2017; Kaczmarek et al., 2015).

In *B. sphaerulata* and *A. hemprichii*, there was no significant relationship between the carbonate system parameters and any E/Ca measured. Ba/Ca in both foraminifer was significantly lower at higher $p\text{CO}_2$ (970 μatm) but the large interspecimen variability within the other $p\text{CO}_2$ treatments limits further conclusion. In *A. hemprichii*, B/Ca was also significantly lower when $p\text{CO}_2$ was 260 μatm . There is no available data in the incorporation of trace elements under variable $p\text{CO}_2$ in high-Mg calcite, except for *H. depressa* where the influence of carbonate system parameters on Mg/Ca and Sr/Ca was estimated (Dueñas-Bohórquez et al., 2011; Raitzsch et al., 2010). Based on this data set, we observed limited influence of the $p\text{CO}_2$ on the ratio of Mg, Sr, Ba, U, and B in high-Mg calcite shells, even though it has been demonstrated that the calcification rate of the two species decreases at higher $p\text{CO}_2$ (Fujita et al., 2011). Finally, as of now, Mg/Ca, Sr/Ca, Ba/Ca, U/Ca, and B/Ca in *A. hemprichii* and *B. sphaerulata* do not appear to be sensitive to changes in carbonate chemistry. However, since Mg/Ca was not influenced by any changes in $p\text{CO}_2$ or other carbonate system parameters, it suggests that both species can be good candidates to reconstruct the paleotemperature of the coastal environment.

5. Summary and Concluding Remarks

In summary, Mg/Ca, Sr/Ca, Ba/Ca, U/Ca, and B/Ca ratios in benthic high-Mg calcite shells were higher compared to low-Mg calcite benthic foraminifers. Despite a different mode of calcification between the two species studied here (hyaline versus porcelaneous), most of the ratios were in the same order of magnitude. U/Ca was the only ratio that shows a distinct difference between the two species, where U/Ca was significantly higher in *A. hemprichii*. In addition, we did not observe any link between the incorporation of the different elements and the mode of calcification, suggesting that the processes, probably Rayleigh fractionation, involved in the calcification of hyaline and porcelaneous shells can produce the same magnitude of E/Ca ratios. No relationship with carbonate chemistry of the surrounding water was observed within the data set. Some significant differences were present, especially for Ba/Ca and B/Ca, but no clear trend can be distinguished; therefore, it seems that these two species are not sensitive to change in the carbonate chemistry of the water. However, it is worthwhile to note that Ba/Ca, U/Ca, and B/Ca data are very limited for benthic foraminifers, even more so for high-Mg calcite benthic foraminifers, and therefore the conclusions here would benefit from additional data. From a general point of view, the multi-element approach of shell chemistry is needed to develop an integrative understanding of the incorporation processes and the mechanisms involved in the incorporation of each element. Future research using cultured samples focusing on the relationships between environmental factors and biological signatures may be a key to unveiling the mechanisms of E/Ca in foraminifer tests.

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