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Planktic foraminifers as recorders of seawater Ba/Ca

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ABSTRACT

Recent studies have used the Ba/Ca ratio of planktic foraminifer shells as a proxy for river run-off at oceanic sites near estuaries. Such studies assume that the Ba/Ca ratio in planktic foraminifer shells is primarily controlled by the Ba/Ca concentration of seawater and that other parameters such as salinity, temperature and pH do not compromise the primary Ba concentration relationship. Here we provide new insights from culture experiments and review published studies to confirm that environmental parameters including pH, temperature, salinity, and symbiont photosynthesis do not affect Ba substitution into planktic foraminiferal calcite. The partition coefficient for Ba in spinose planktic foraminifers is estimated as $D_{Ba} = 0.15 \pm 0.05$ (95% confidence limits). The same factor also seems applicable to the non-spinose genus *Neogloboquadrina* but not to specimens of the non-spinose genus *Globorotalia*.

1. Introduction

Environmental information derived from the trace element composition of foraminifer shells is limited by the accuracy with which these calcite shells record ambient seawater chemistry and whether multiple environmental parameters or species-specific differences affect shell chemistry. Continued efforts to improve our understanding of geochemical proxy-relationships in planktic foraminifers have, for instance, revealed a significant pH effect on the Sr/Ca and Mg/Ca ratios (Kisakürek et al., 2008; Lea et al., 1999; Russell et al., 2004), a salinity effect on the Mg/Ca ratio (Kisakürek et al., 2008), and pH and carbonate ion effects on the oxygen and carbon isotopic compositions under conditions of constant $\delta^{13}C_{DIC}$ and $\delta^{18}O$ of seawater (Bijma et al., 1999; Spero et al., 1997). Knowledge of such secondary effects may permit the correction of the primary proxy relationship if the secondary influence can be quantified (e.g. Zeebe, 2001).

Laboratory culture experiments indicate that barium (Ba) is incorporated into the shells of the spinose, symbiont-bearing foraminifers *Orbulina universa* and *Globigerinoides sacculifer* in proportion to seawater concentration and that the incorporation is independent of secondary effects such as temperature, symbiont photosynthesis, and salinity (Lea and Spero, 1992, 1994). Hall and Chan (2004a) and Weldeab et al. (2007a, b) applied this information to planktic foraminifer shells to reconstruct past variations in the Ba/Ca ratio of seawater as a proxy for deglacial meltwater discharge into the Arctic Ocean, and west African river run-off and monsoon intensity, respectively. Similarly, Sprovieri et al. (2008) measured the Ba/Ca ratio in Neogene *O. universa* shells from the Mediterranean and interpreted their record in terms of river discharge and geographical constraints of the Mediterranean Basin. These interpretations of foraminiferal Ba/Ca records are based on the observation that the seawater Ba concentration in estuaries and coastal waters is elevated relative to the open ocean and inversely correlated with salinity, as continental run-off supplies high concentrations of Ba to the ocean.

In the open ocean, dissolved barium ([Ba]) acts as a nutrient-like tracer similar to Cd^{2+} and $\delta^{13}C$ because biological activity extracts these elements from surface waters and transfers them towards the seafloor via sinking particles (e.g. Bernstein et al., 1998). Dissolved Ba thereby covaries with silica and alkalinity (Chan et al., 1977), and although the mechanistic link between alkalinity and [Ba] is not fully understood (Lea, 1993), several studies have used the strong correlation between deep-ocean [Ba] and alkalinity to reconstruct past ocean alkalinity and paleocirculation patterns from Ba/Ca ratios in shells of benthic foraminifers (Hall and Chan, 2004b; Lea, 1993; Lea and Boyle, 1989, 1990a, b).

The underlying assumption for the use of the Ba/Ca ratio as an indicator for alkalinity in the deep ocean or continental run-off in coastal areas and estuaries is that the incorporation into foraminiferal shells depends only on the Ba/Ca ratio in seawater. If Ba partitioning

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also responded to changes in ocean carbonate chemistry or salinity, the ability to estimate past salinity or seawater-Ba/Ca ratio variations would be hampered. One indication that Ba partitioning may be affected by parameters other than dissolved [Ba] comes from a laser ablation study of the symbiont-barren foraminifer *Globorotalia inflata* from sediment traps (Hathorne et al., 2009). Analysis of a single specimen shows a ~6-fold increase in the Ba/Ca ratio from the outer surface towards the inside of the shell wall. Hathorne et al. (2009) observed a strong covariation between Mg/Ca and Ba/Ca ratios in the shell, but the high Ba/Ca ratio of the inner portion of the shell is inconsistent with a supposed shallower growth habitat during early ontogeny of this species, which should reflect the lower Ba/Ca ratio of surface seawater. The cause for the Ba/Ca pattern in this *G. inflata* shell remains unresolved. It may reflect varying environmental parameters during shell secretion but it should be noted that the cleaning methods applied in this laser ablation study do not remove postmortem barite precipitates inside the shells. Lea and Boyle (1991) observed barite contamination in samples from sediments and sediment traps and suggested that barite must partly form in the water column. Lea and Boyle (1991) therefore introduced a cleaning step with alkaline diethylenetriamine-pentaacetic acid (DTPA) for barite removal from sedimentary and trap-collected foraminifer shells, which has since been applied to Ba/Ca ratio measurements by solution chemistry but not for laser ablation studies. In contrast to findings of the laser ablation study, sequential dissolution experiments with DTPA-cleaned shells of *Globigerinoides conglobatus* and *Globorotalia truncatulinoides*, suggested homogeneous Ba/Ca distribution inside the shells (Lea and Boyle, 1991).

Previous studies have examined Ba incorporation into natural samples of *Orbulina* spp., *Globigerinoides ruber*, *G. sacculifer*, *G. conglobatus*, *Neogloboquadrina dutertrei*, and *N. pachyderma* sin. in relation to surface seawater Ba/Ca ratios (Hall and Chan, 2004a; Lea and Boyle, 1991), in cultured *O. universa* as a function of light intensity and seawater Ba concentration at constant temperature (Lea and Spero, 1992), and in cultured *O. universa* and *G. sacculifer* as a function of seawater [Ba], temperature and salinity in two different locations [*O. universa* from Santa Catalina Island in the NE Pacific at 22 °C, S = 33.7, and *O. universa* and *G. sacculifer* from Lee Stocking Island, Bahamas at 29 °C and S = 36.7; Lea and Spero, 1994]. Here we provide new constraints from culture experiments with *O. universa* and the symbiont barren *Globigerina bulloides*, grown under varying seawater pH, temperature, salinity, and two different light levels. Our data confirm and expand the results of previous studies and demonstrate that environmental controls other than the Ba/Ca ratio of seawater have no measurable effect on the Ba/Ca ratio in spinose planktic foraminifers.

2. Foraminifera collection and culturing

Foraminifers for this study were cultured in two field seasons, July–August 2000 and July–August 2008, using previously established methods (e.g. Lea and Spero, 1992; Russell et al., 2004). Juvenile (presphere) *Orbulina universa* and small *G. bulloides* were hand collected by SCUBA divers from surface waters of the San Pedro Basin, approximately 2 km NNE of the Wrigley Institute for Environmental Studies, Santa Catalina Island, California. Surface seawater for culturing was collected at the foraminifer collection site and filtered in the laboratory using acid-cleaned 0.4 μm polycarbonate membrane filters and an acid-leached polysulfone filter holder (2000 field season), and 0.8 μm nitrate cellulose filters on a borosilicate glass filter system (2008 field season).

After collection, each specimen was examined under an inverted light microscope for the purpose of species identification, shell dimension measurement, and inspection of general condition. Individual foraminifers were then transferred to 120 ml glass jars containing the filtered experimental seawater. To avoid contamination of culture water during transfer and feeding of specimens, sample handling was done wearing powder free gloves and using acid-leached glass pipettes for feeding and transferring foraminifers.

Average summer seawater conditions at the collection site are 22 °C, S = 33.5, pH = 8.04 (total scale) and alkalinity = 2250 μmol kg^{-1}. It should be noted that the salinity measurements in 2000 and 2008 used different conductivity meters and yielded slightly different results (S = 33.7 and 33.3, respectively). This difference is likely analytical rather than oceanographic, and it only applies to the pH experiments compared between 2000 and 2008. For comparison, WOCE oceanographic data from the coast of Southern California read S = 33.5.

Foraminifer cultures were maintained in water baths at constant temperature (to ± 0.1 °C) and light levels of 299–406 μmol photons m^{-2} s^{-1} (12-h high light/dark cycle). These light levels exceed the saturation light intensity for the symbiotic dinoflagellates associated with *O. universa* (Rink et al., 1998). Only one parameter was changed per experiment, with all others maintained constant at ambient conditions. Four sets of experiments were performed: *O. universa* was grown under S = 29.9–35.4, T = 18–26 °C, pH = 7.6–8.64 (total scale), and a low light experiment at 23 μmol photons m^{-2} s^{-1} (12-h low light/dark cycle). This light intensity falls below the light compensation point for the dinoflagellates' photosynthetic activity (Rink et al., 1998). *G. bulloides* was grown over a pH range of 7.61–8.52 (total scale). *G. bulloides* and *O. universa* were fed a 1-day old *Artemia* sp. nauplius (brine shrimp) every other or every third day, respectively.

During the 7- to 10-day culture period *O. universa* secretes and calcifies a spherical chamber, whereas *G. bulloides* forms between two and four new chambers. After the foraminifers underwent gametogenesis, empty shells were rinsed in ultrapure or deionized water and archived for later analysis. In addition, samples of the culture solutions were acidified, and analyzed to verify that seawater Ba and Ca concentrations remained constant over the course of the experiments.

Experimental pH, [CO_3^{2-}] and total alkalinity (AT) were simultaneously modified by the addition of ultrapure HCl to lower these quantities or the addition of ultrapure NaOH to increase them. Initial and final seawater pH were measured and alkalinity was determined by Gran-titration with a Metrohm 785 Titrino auto-titrator. In the year 2000 samples were also taken for dissolved inorganic carbon (DIC), collected at the beginning and end of each experiment, poisoned with a few drops of a saturated $HgCl_2$ solution and measured coulometrically at the Alfred Wegener Institute. pH, AT and DIC were all normalized to Dickson certified reference material, which was measured in parallel to the experimental seawaters.

Experimental seawater salinity was modified by either addition of deionized water or evaporation of filtered seawater under a heat lamp. All salinity experiments were conducted in 2008 and initial and final salinity were measured with a handheld Fisher Scientific 3-Star conductivity meter.

3. Sample preparation for analysis

Only gametogenic shells were used for analysis. All specimens were rinsed in distilled water to remove sea salts, dried and weighed. Chambers secreted under controlled conditions in the laboratory were separated from the juvenile portion of the shell grown in the ocean before collection. Shells grown in 2000 were prepared and analyzed at the University of California in Santa Barbara following the methods of Lea and Martin (1996), whereas shells grown in 2008 were prepared and analyzed in the Godwin Laboratory at Cambridge University following the methods of Yu et al. (2005).

O. universa shells grown in 2000 were cracked open with a disposable scalpel and the juvenile test (if present) was removed with a small brush. The fragments were then transferred to 0.5 ml polypropylene centrifuge vials. Individual shells of *O. universa* were analyzed where possible, but for the smallest individuals, two or three shells were pooled to obtain at least 40 μg of uncleaned calcite. For *G. bulloides*, chambers grown in the laboratory were identified by

comparing the size of the specimen at collection with the size of the postgametogenic shell. The laboratory-grown chambers were amputated with a scalpel, pooled (25–35 chambers per sample) and loaded into 0.5-ml polypropylene centrifuge vials. Samples were then subjected to a series of physical and chemical treatments including: oxidation in hot (70 °C) buffered H_2O_2–NaOH (0.1 N NaOH, 15% v/v H_2O_2 Seastar) solution to remove organic matter, 2–3 weak acid leaches (0.001 N HNO_3) and repeated rinses in ultrapure water. The amputation and cleaning procedures followed methods established by Mashiotta et al. (1997). DTPA cleaning is not necessary for cultured foraminifer shells, as they were dried and archived immediately upon gametogenesis. Sample analysis followed the multi-element inductively coupled plasma mass spectrometry (ICP-MS) method described by Lea and Martin (1996). After cleaning, 20–30 μg size samples of purified foraminifer shells were dissolved in 0.5 ml of a 0.1 N HNO_3 solution containing calibrated concentrations of ^{135}Ba and ^{45}Sc. The solutions were aspirated into a Finnigan Element2 high-resolution magnetic sector ICP-MS. The ^{135}Ba/^{138}Ba and ^{45}Sc/^{48}Ca ratios were determined by pulse counting and analog acquisition modes, respectively. The concentrations of Ba and Ca were then determined by isotope dilution and internal standard calculation, respectively. Na/Ca was determined to be certain that the hydrogen peroxide–sodium hydroxide solution used in the sample preparation was completely rinsed out. Several analyses of a consistency standard with Ba and Ca concentrations similar to the foraminiferal samples had a standard deviation of 0.4% for Ba, 1% for Ca, and 1.25% for the Ba/Ca ratio. An average of 2–4 replicates was determined on *O. universa*. Due to the small sample yield in *G. bulloides* only one Ba/Ca analysis per experiment could be collected for this species.

Seventeen water samples were randomly selected for analysis of trace and minor element concentrations over the course of the experiment. These samples yield ambient seawater concentrations of 37.8 ± 0.35 nmol kg^{-1} for [Ba] and 10.24 ± 0.09 mmol kg^{-1} for [Ca]. The amount of Ba incorporated into the foraminiferal shell is negligible compared to the total [Ba] present in the experimental seawater (Lea and Spero, 1992). However, it is conceivable that problems could arise from barium contamination (e.g. during feeding) or adsorption onto the culture jar walls. Although one of the water samples showed [Ba] elevated by 11%, the average change in seawater [Ba] was only 0.9%, indicating that barium adsorption was negligible and contamination unlikely. Nevertheless, we cannot rule out the possibility that some foraminifers experienced Ba concentrations that may have differed from the average of 37.8 nmol kg^{-1}.

Only *O. universa* were grown in 2008. Samples consisting of ~15 shells were cracked and then cleaned in the same way as described above. Elemental analysis of this sample set was carried out in the Godwin Laboratory at Cambridge University following the methods of Yu et al. (2005). Calcium concentrations were first measured by ICP-AES. Aliquots of the same solution were diluted to 100 ppm [Ca] to minimize matrix effects during subsequent analysis by ICP-MS (PerkinElmer SCIEX Elan DRC II). Standards prepared with Milli-Q$^+$ allowed a Ba/Ca detection range of 0.09–4.84 μmol/mol. Standard solutions were measured every 3–5 samples, giving a ~1.7% relative standard deviation (RSD). Only a few samples could be measured in duplicate with this method.

4. Results

4.1. Carbonate chemistry, light level, and foraminifer species

The experimental matrix and Ba/Ca results are summarized in Table 1 and shown in Fig. 1a–d. Figs. 1a, b and 2 show Ba/Ca ratios of the same experiments relative to pH, [CO_3^{2-}] and total alkalinity, respectively. *O. universa* shells grown in 2000 and 2008 and measured in different labs give the same Ba/Ca ratio within error: 0.67 ± 0.04 (Santa Barbara) and 0.69 ± 0.03 (Cambridge). Two *O. universa* analyses from this data set deviate by more than 2σ from the experimental mean (Table 1). Both analyses were done on single large shells and although their interpretation would not change the conclusions from this study, we suspect these specimens may have suffered from elevated [Ba] in their respective culture jars, and have therefore excluded them from the figures and further evaluation.

G. bulloides has not been calibrated for Ba/Ca before. The primary observation from our experiments is that Ba/Ca ratios of the two

Table 1
Experimental seawater conditions and Ba/Ca data for new culture experiments performed in 2000 and 2008.

Experiment	Light	Salinity	Temperature (°C)	Alkalinity (μmol kg^{-1})	pH (total scale)	Calc. DIC (μmol kg^{-1})	Calc. [CO_3^{2-}] (μmol kg^{-1})	Ba/Ca – 1 (μmol/mol)	N	Ba/Ca – 2 (μmol/mol)	N	Ba/Ca – 3 (μmol/mol)	N	Ba/Ca – 4 (μmol/mol)	N
O. universa															
BH1	LL	33.6	22	**2253 ± 10**	**8.03 ± 0.02**	2000*	**182**	0.61	1	0.70	3	0.57	2	0.59	2.0
BH2	HL	33.8	22	2268 ± 5	8.07 ± 0.02	1993*	196	0.63	1	0.71	2	0.67	2	(1.06)	1.0
BH3	HL	33.7	22	**2047 ± 15**	**7.61 ± 0.03**	1965*	**76**	0.76	3	0.67	2				
BH4	HL	33.7	22	**2632 ± 12**	**8.52 ± 0.02**	1979*	**468**	0.56	1	0.58	2	0.60	3	0.57	1.0
BH5	HL	33.7	22	**2436 ± 21**	**8.30 ± 0.01**	1997*	**311**	0.65	1	0.64	1	0.56	1	(1.01)	1.0
BH6	HL	33.7	22	**2122 ± 6**	**7.81 ± 0.01**	1979*	**111**	0.60	1	0.60	2	0.57	2	0.70	
KA1	HL	33.2	**18**	2233 ± 21	8.08 ± 0.03	1990	175	0.69	15						
KA2	HL	33.0	**20**	2229 ± 5	8.03 ± 0.01	2000	166	0.62	15						
KA3	HL	33.3	22	2239 ± 5	8.01 ± 0.02	2001	173	0.71	15	0.67	15				
KA4	HL	33.0	**26**	2237 ± 10	7.95 ± 0.01	2001	173	0.63	15						
KA5	HL	33.3	22	**2058 ± 2**	**7.60 ± 0.02**	1991	**70**	0.67	15						
KA6	HL	33.3	22	**2425 ± 4**	**8.27 ± 0.02**	2009	**297**	0.66	15						
KA7	HL	33.3	22	**2803 ± 7**	**8.64 ± 0.03**	2013	**577**	0.62	15						
KA8	HL	**29.9**	22	2040 ± 9	8.03 ± 0.03	1828	153	0.70	15	0.68	15				
KA9	HL	**31.5**	22	2163 ± 13	7.99 ± 0.05	1949	157	0.68	15	0.71	15				
KA10	HL	**35.4**	22	2385 ± 0	7.98 ± 0.03	2137	182	0.64	15						
G. bulloides															
BH1	LL	33.6	22	2253 ± 10	8.03 ± 0.02	2000*	182	0.65	35						
BH2	HL	33.8	22	2268 ± 5	8.07 ± 0.02	1993*	196	0.55	25						
BH3	HL	33.7	22	**2047 ± 15**	**7.61 ± 0.03**	1965*	**76**	0.69	25						
BH4	HL	33.7	22	**2632 ± 12**	**8.52 ± 0.02**	1979*	**468**	0.70	25						

BH experiments were performed in 2000, KA experiments in 2008. Experiments BH2 and KA3 were performed at average ambient conditions of the collection site, data in bold mark experimental modifications from ambient conditions. pH values measured at 25 °C on the NBS scale were converted to the total scale and corrected for the respective experimental water temperature. Asterisks in the DIC column indicate measured data, others were calculated from measured alkalinity and pH. N indicates the number of chambers analyzed for each sample. Two Ba/Ca data in brackets deviate by more than 2σ from the experimental mean and were not interpreted further.

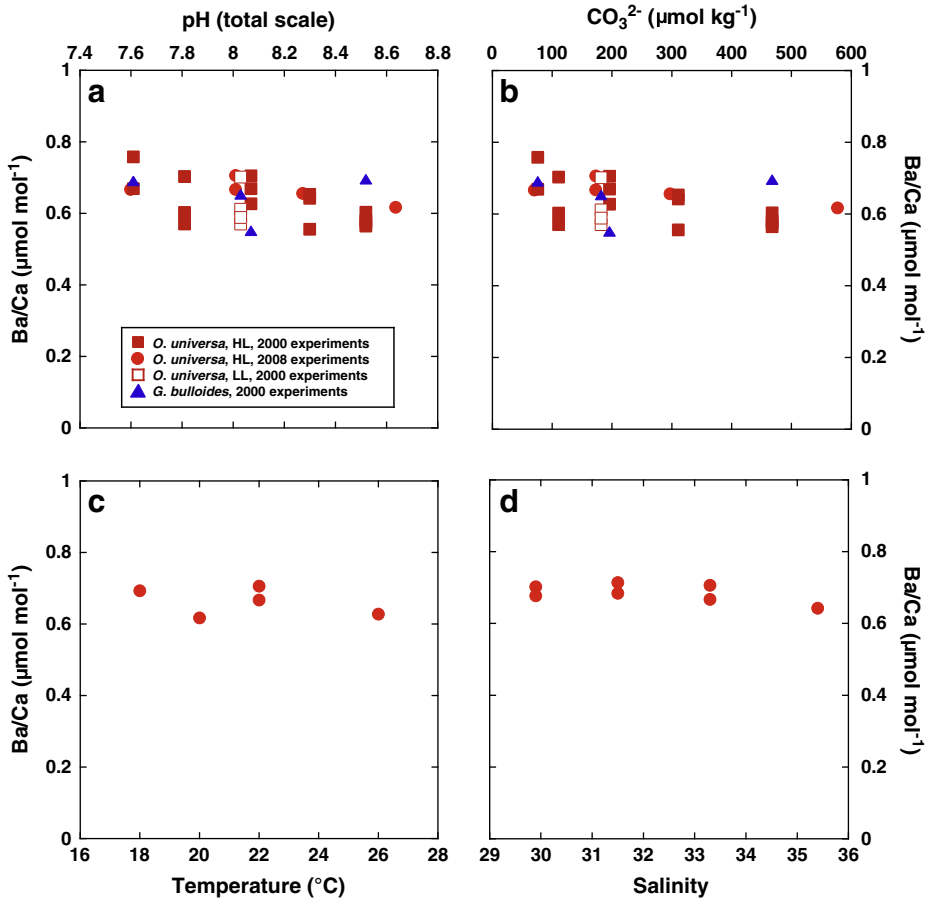

Fig. 1. Ba/Ca data from culture experiments: a and b show HL and LL experiments with *O. universa* and *G. bulloides* relative to seawater pH and [CO_3^{2-}], c and d show *O. universa* relative to temperature and salinity. The Ba/Ca ratio is independent of pH, light level, temperature, salinity or foraminifer species.

foraminifer species and the high light (HL) and low light (LL) experiments are indistinguishable within the individual data variability. Statistical evaluation (student *t*-test, using Matlab) of the pH relationship measured in *O. universa* shells yields a negative relationship with a slope (m) of −0.09 µmol/mol per 1 pH unit. Although the relationship is significant (i.e. $m \neq 0$) at a 95% confidence level, the regression only explains 28% of the Ba/Ca variance ($R^2 = 0.28$). For comparison, the average 2σ standard deviation of replicates within each experimental group is ±0.08 µmol/mol. With a glacial/interglacial pH-difference of ~0.15 pH units (Foster, 2008; Hönisch and Hemming, 2005; Sanyal et al., 1995) the glacial/interglacial Ba/Ca change predicted by this observed relationship would not be detectable.

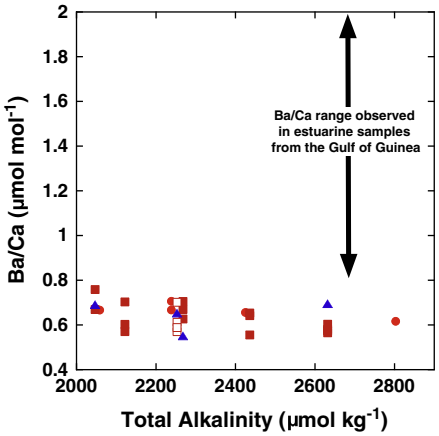

Fig. 2. Same data as in Fig. 1a and b relative to total alkalinity of experimental seawater. Although the individual data variability may be large relative to repeat analysis of consistency standards, the Ba/Ca range is small compared to the large variation observed in natural samples such as estuarine foraminiferal Ba/Ca ratios from the Gulf of Guinea (Weldeab et al., 2007a).

4.2. Temperature and salinity

Fig. 1c and d show Ba/Ca ratios in shells of *O. universa* as a function of culture water temperature and salinity, respectively. No change in the Ba/Ca ratio is observed in response to either parameter.

5. Discussion

The comparison between symbiont-bearing and symbiont-barren foraminifers, as well as the differing light level experiments with *O. universa* may be seen as an extension of pH experiments. This is because symbiont photosynthetic activity and the associated CO_2 sequestration in planktic foraminifers are known to increase pH at the site of calcification, and this effect is larger at higher light intensities (Hönisch et al., 2003; Jørgensen et al., 1985; Rink et al., 1998). In contrast, pH in the microenvironment of symbiont-barren foraminifers such as *G. bulloides* is dominated by the CO_2-producing processes of respiration and calcification, which lower pH at the site of calcification (Hönisch et al., 2003). Ba/Ca ratios of *O. universa* grown under high-light and low-light conditions agree at a 95% confidence level (0.67 ± 0.04 and 0.62 ± 0.05 µmol/mol, respectively), suggesting that variable light intensities and corresponding pH changes at the site of calcification do not significantly affect Ba incorporation. In general, the data variability (±0.08 µmol/mol, 2σ) is large compared to the analytical uncertainty of ~0.009 µmol/mol, but small compared to the Ba/Ca range observed over

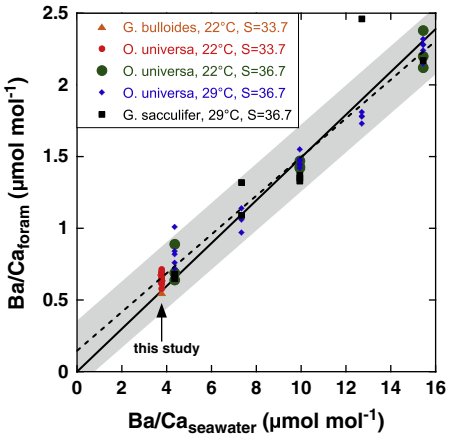

Fig. 3. Ba/Ca ratios in shells of cultured *O. universa* (Lea and Spero, 1994; this study), *G. sacculifer* (Lea and Spero, 1994) and *G. bulloides* (this study) relative to the Ba/Ca ratio of experimental seawater. Data by Lea and Spero (1992) are not included in this figure, as their analytical procedure was subsequently improved and earlier data were suspected elevated (Lea and Spero, 1994). Three different foraminifer species were grown at various salinities and temperatures and yet all species (symbiont-bearing and symbiont-barren) and experiments fall on the same partitioning line. The linear regression through this data set is $Ba/Ca_{shell} = 0.13 + 0.14 * Ba/Ca_{seawater}$ (dashed line). When forced through the origin, the Ba/Ca partitioning for this data set can be described as $Ba/Ca_{shell} = 0.15 (\pm 0.05) * Ba/Ca_{seawater}$ (solid line) and the linear and forced regression agree on a 95% confidence level (grey bar).

the past 20 ky in the Arctic Ocean (~1.3–2.3 µmol/mol, Hall and Chan, 2004a), over the past 155 ky in the Gulf of Guinea (~0.8–2.1 µmol/mol, Fig. 2, Weldeab et al., 2007a), and over the past 8 My in the Mediterranean (~0.5–9.5 µmol/mol, Sprovieri et al., 2008). The sum of our new data and the light experiments performed by Lea and Spero (1992, 1994), suggests that seawater carbonate chemistry does not affect Ba partitioning in spinose planktic foraminifer shells.

The lack of a temperature or salinity effect is consistent with the earlier work of Lea and Spero (1994), who compared Ba/Ca ratios in *O. universa* grown at 22 and 29 °C and S = 36.7 on Lee Stocking Island, Bahamas, and at 22 °C and S = 33.7 on Santa Catalina Island (Lea and Spero, 1992), and found no significant difference between 33.7 and 36.7 salinity or their temperature experiments. It is remarkable how similar the foraminiferal Ba/Ca ratio is from these different studies and at different salinities and temperatures (see also Fig. 3). Our new data thus expand the temperature and salinity range over which no change in Ba/Ca ratio can be observed to 18–29 °C and S = 29.9–36.7.

In contrast, precipitation experiments have shown that Ba/Ca ratios are strongly anti-correlated with temperature in synthetic and scleractinian coral aragonite (Gaetani and Cohen, 2006). Gaetani and Cohen (2006) noted that the temperature correlation is not an equilibrium process and attributed their observation to surface entrapment of Ba during aragonite growth and coralline vital effects (active Ba discrimination into the calcifying fluid and temperature and/or light dependent enzymatic ion pumping). Ba^{2+} has an ion radius much larger than Ca^{2+} and does not substitute as easily into calcite as into aragonite. Ba/Ca ratios in calcitic foraminifer shells are therefore much lower than in aragonitic coral skeletons (<1 µmol/mol vs. >4 µmol/mol) and the lack of a temperature or pH effect is consistent with expectations based on the aqueous chemistry of dissolved Ba. Approximately 96% of dissolved Ba in seawater exists as a free hydrated metal ion, and only 4% of Ba may be complexed by sulfate (Byrne et al., 1988). Temperature and pH exert only a very small influence on such weakly complexed metal ions (Byrne et al., 1988) and thus do not give rise to significant variations in availability for incorporation into marine carbonates. In addition, our empirical calibrations demonstrate that if there were any change of calcification rate in response to higher pH and temperature, it did not result in measurable discrimination against Ba incorporation. Vital effects within and between species do not seem to exist for Ba uptake into spinose planktic foraminifer shells. Barium has no reported biochemical function, and because symbiont-bearing *O. universa* grown at high and low light levels record the same Ba/Ca ratio as the symbiont-barren *G. bulloides*, Ba partitioning between seawater and foraminiferal calcite does not appear to be influenced by symbiont photosynthetic activity.

Ba partitioning into the shells can be described by a simple partition coefficient $D_{Ba} = Ba/Ca_{foram} / Ba/Ca_{seawater}$. The partition coefficients estimated from our new culture data are $D_{Ba} = 0.17 \pm 0.04$ (2σ) for *G. bulloides* and 0.17 ± 0.02 (2σ) for *O. universa*. *Globigerinoides sacculifer* and *O. universa* grown by Lea and Spero (1994) yield a D_{Ba} of 0.15 ± 0.02. The combined partition coefficients of core-top fossil spinose planktic foraminifers yield $D_{Ba} = 0.19 \pm 0.05$ (Lea and Boyle, 1991), and Hall and Chan (2004a) observed $D_{Ba} = 0.22 \pm 0.02$ for coretop *N. pachyderma* sin. Statistical evaluation (student *t*-test) of these data reveals that the D_{Ba} values derived from laboratory culture (this study, Lea and Spero, 1994), where the Ba/Ca ratio of the culture medium was measured, agree at a 95% confidence level. The combined laboratory culture D_{Ba} value also agrees with the coretop D_{Ba} from Lea and Boyle (1991) at a 96% confidence level. However, the D_{Ba} from Hall and Chan (2004a) does not agree with the laboratory cultures. It should be noted that we have excluded culture data by Lea and Spero (1992) from this evaluation. That study estimated a D_{Ba} of 0.16 ± 0.01 for cultured *O. universa* (regression forced through zero) but Lea and Spero (1994) later improved their analytical technique and suspected their earlier analyses of foraminiferal Ba/Ca ratios may be too high. Following that line of argument, the coretop study by Lea and Boyle (1991) may also be less reliable than samples measured in/after 1994. Moreover, the coretop studies used average surface ocean $Ba/Ca_{seawater}$ values for the respective ocean basins rather than $Ba/Ca_{seawater}$ which was not measured at each core site. In particular for the Arctic Ocean, where the Lena and Mackenzie Rivers discharge high Ba concentrations of 130 and 520 nmol/l, respectively, the average surface value of 65 nmol/l used by Hall and Chan (2004a) to estimate D_{Ba} for *N. pachyderma* may not be accurate for the core site. For future studies estimating $Ba/Ca_{seawater}$ from foraminiferal Ba/Ca, we therefore recommend to use D_{Ba} established from culture studies as the most accurate coefficient. We determine this D value via a regression through our new culture data combined with previously published *O. universa* and *G. sacculifer* data (Lea and Spero, 1994). We assume that a foraminifer grown in Ba-free water will not incorporate any Ba into its shell, and accordingly have forced the linear regression shown in Fig. 3 through the origin. Seawater Ba/Ca ratios can thus be estimated from foraminiferal Ba/Ca ratios as

$$Ba/Ca_{shell} = 0.149(\pm 0.05) * Ba/Ca_{seawater}$$

Forcing the regression through the origin has little overall effect, as the linear and forced regression agree on a 95% confidence level.

Importantly, we remind the reader that Lea and Boyle (1991) found much higher $D_{Ba} \approx 1$ for specimens of the non-spinose Globorotaliid family, i.e. *Globorotalia truncatulinoides*, *G. hirsuta* and *G. menardii*. Lea and Boyle (1991) argued that this may be attributed to a different calcification mechanism but their data are too variable to permit estimation of a coherent D_{Ba} for the Globorotaliids. One parameter that the Globorotaliids have in common is that they all live in the subsurface, at water depths >70–300 m (Farmer et al., 2007), except for *G. truncatulinoides* which has been reported to live as deep as 700 m (Mulitza et al., 1999; Steph et al., 2009). Although the seawater Ba concentration increases with depth and may explain higher Ba/Ca ratios in deep living *G. truncatulinoides*, the seawater Ba concentration in the upper 300 m of the water column is similar to the surface layer, and accordingly we need to consider how [Ba] could be increased in the microenvironment of this particular group of foraminifer species. With no biological function reported, it seems unlikely that foraminifers would actively increase [Ba] in their microenvironment, so the only conceivable ways to increase Ba incorporation include reduced

discrimination against Ba during calcification or preying on organisms that concentrate Ba. The Ba/Sr partition coefficient in the skeletal material of Acantharia, i.e. celestite ($SrSO_4$), is very large with an average value of 3.4, and celestite remineralization takes place largely in the subsurface (Bernstein et al., 1998). Given the Globorotaliids' habitat depth in the subsurface, and the concurrence with the zone of celestite remineralization, we suggest that acantharian celestite could be the source of excess Ba if Globorotaliids feed on this abundant group of zooplankton at depth. This hypothesis could be tested in laboratory feeding experiments with *G. menardii*, which is frequently collected in plankton nets off Santa Catalina Island. If correct, the analysis of Ba/Ca ratios in fossil specimens of deep-dwelling planktic foraminifers could even be useful to constrain the evolutionary history of Acantharia, which do not preserve in seafloor sediments.

The D_{Ba} established here is strictly only applicable to species of the spinose Globigerinidae, including *O. universa*, *G. sacculifer*, *G. ruber*, *G. bulloides* and *G. conglobatus*. *Neogloboquadrina pachyderma* and *N. dutertrei* are phylogenetically more closely related to the *Globorotalia* species but the D_{Ba} is similar to that of the spinose Globigerinidae.

6. Conclusions

Our new culture experiments confirm that pH, temperature, salinity and light level do not significantly affect the Ba incorporation into shells of the planktic foraminifers *O. universa* and *G. bulloides*. There is no discernable difference in Ba/Ca shell compositions of these two foraminifer species when grown in the same water. These observations, in addition to earlier experiments on the Ba incorporation as a function of the seawater Ba/Ca ratio, reinforce the notion that paleo-Ba concentrations of seawater can be estimated from spinose planktic foraminifer shells, and the D_{Ba} is 0.15 ± 0.05. However, our measurements show that the variability of Ba/Ca ratios recorded by individual shells is large compared to the analytical reproducibility of consistency standards. Since bioturbation and potential barite contamination of sedimented shells pose additional complications for paleoreconstructions, we emphasize the need to analyze and replicate samples of multiple foraminifer shells.

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