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Ba/Ca ratios in the non-spinose planktic foraminifer *Neogloboquadrina dutertrei*: Evidence for an organic aggregate microhabitat

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Abstract

Ba/Ca ratios in many non-spinose planktic foraminifera are markedly higher than those observed in spinose planktic species, but the cause for these high Ba/Ca ratios is not understood. A better understanding of this geochemical anomaly could provide insights into the habitat and/or controls over Ba incorporation in these species and expand their utility in paleoclimate research. In spinose species, shell Ba/Ca depends only on the Ba/Ca ratio of seawater. Proposed explanations for high non-spinose Ba/Ca include (1) the empirical partition coefficient, D_{Ba}, differs from the spinose species, (2) shell Ba varies with seawater temperature and pH, or (3) non-spinose foraminifers have a preference for prey that has elevated Ba. We performed laboratory culture experiments to determine D_{Ba} for the thermocline-dwelling non-spinose planktic foraminifer *Neogloboquadrina dutertrei*. We find that the Ba/Ca ratio of foraminiferal calcite secreted in the laboratory varies linearly with the Ba/Ca ratio of the seawater. The D_{Ba} for this species, 0.11 ± 0.008 (2SE; 95% CL), is similar to the D_{Ba} for spinose species (0.13 ± 0.004, 2SE; 95% CL). As in spinose species, the Ba/Ca ratio of cultured specimens of *N. dutertrei* is not influenced by culture temperature (12–22 °C) or seawater pH_{NBS} (range 7.8–8.3). However, the Ba/Ca ratio of individual plankton-tow *N. dutertrei* specimens that completed their lifecycle in the ocean exceeds the Ba/Ca ratio of cultured specimens by up to three orders of magnitude. It is unlikely this difference between cultured specimens and ocean-grown specimens is due to seawater [Ba] variability, since seawater Ba/Ca ratios calculated using our D_{Ba} are much higher than exist in the ocean. Rather, we suggest that elevated shell Ba/Ca in plankton tow and fossil *N. dutertrei* is due to calcification in the microenvironment of marine organic aggregates such as marine snow, where [Ba] is elevated as a result of Ba release from biogenic particulates.
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Keywords: Non-spinose foraminifera; Barium; Ba/Ca; Marine snow; Habitat

1. INTRODUCTION

Barium (Ba^{2+}) is a divalent cation that substitutes into the calcite lattice of benthic and spinose planktic foraminifera shells in proportion to the [Ba^{2+}] in seawater (Lea and Boyle, 1989; Lea and Spero, 1992; Hönisch et al., 2011). Ba/Ca ratios in thermocline and deeper-dwelling, non-spinose

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planktic foraminifera are often higher than in spinose species (Lea and Boyle, 1991; Hall and Chan, 2004; Bahr et al., 2013) and are also more variable within the shell wall (Kunioka et al., 2006; Hathorne et al., 2009). In the spinose foraminifera *Orbulina universa*, *Globigerinoides sacculifer*, and *Globigerina bulloides*, Ba/Ca is governed solely by seawater Ba/Ca ratios, and is not influenced by secondary controls (Lea and Spero, 1994; Hönisch et al., 2011; Allen et al., 2016). The lack of secondary controls over Ba/Ca in the spinose mixed-layer planktic foraminifera allows for a straightforward interpretation of down-core Ba/Ca records. Thus, Ba/Ca ratios within the shells of spinose planktic foraminifera, which have a wide range in salinity tolerance (S = 27–44), record changes in salinity gradients/freshwater flux in near-shore environments (Weldeab et al., 2007; Schmidt and Lynch-Stieglitz, 2011; Bahr et al., 2013; Weldeab et al., 2014; Evans et al., 2015; Vetter et al., 2017).

The paleoceanographic utility of Ba/Ca ratios in the non-spinose species is less straightforward. In a study that included both spinose and non-spinose planktic foraminifera from core tops, plankton tows, and sediment traps in the Atlantic and Pacific Oceans, Ba/Ca in the non-spinose species was 3–20 times higher than expected, despite rigorous chemical cleaning to remove potential contaminant phases (Lea and Boyle, 1991). The Ba/Ca ratios in sediment-trap *Globorotalia truncatulinoides* and *Neogloboquadrina dutertrei* and in plankton-tow *Globorotalia menardii* were nearly as high as those in core top sediments, suggesting that the enrichment relative to spinose species was not due to sediment contamination. In contrast, shell Ba/Ca of the surface-dwelling spinose species (*G. sacculifer*, *Globigerinoides ruber, Globorotalia conglobatus,* and *O. universa*) from the same study were consistently < 1 μmol/mol, suggesting that Ba/Ca in deeper-dwelling non-spinose foraminifera species is subject to additional environmental controls compared to spinose surface dwellers (Lea and Boyle, 1991). The authors speculated that high Ba/Ca ratios in *G. truncatulinoides* could be due to a depth effect on the partition coefficient for Ba, since this species calcifies at depths of up to 1000 m, and/or an influence of crust addition.

Ba/Ca ratios in *N. dutertrei* and *G. menardii* collected from core-top sediments near the coast of the Amazon and Orinoco Rivers were up to 25 times higher than the spinose species obtained from the same setting (Bahr et al., 2013). While it's tempting to suggest that the high Ba/Ca ratios are due to input of riverine water with elevated Ba, the surface dwellers collected from the same samples had Ba/Ca ratios that rarely exceeded 1 μmol/mol. High Ba/Ca ratios in the non-spinose species may be due to a larger empirical partition coefficient for Ba (D_{Ba}) or greater sensitivity to secondary controls (e.g. temperature, pH) compared to the spinose species (Lea and Boyle, 1991; Hall and Chan, 2004), or to a preference for prey that has elevated Ba (Bahr et al., 2013).

The Ba/Ca ratios in non-spinose foraminifera could, in principle, be related to their subsurface habitat, since seawater Ba concentrations are higher at depth than in surface waters. Barium in the ocean ranges in concentration from ~35–50 nmol/L at the surface to ~150 nmol/L in the habitat depth of non-spinose species (Dehairs et al., 1980; Horner et al., 2015; Hsieh and Henderson, 2017). However, using the $D_{Ba} = 0.13$ for spinose foraminifera (Hönisch et al., 2011) and assuming that seawater [Ca] = 10.3 mmol/L, the maximum Ba/Ca in non-spinose foraminifera should be <2 μmol/mol. Even if we consider the D_{Ba} of 0.22 computed for the non-spinose species by Lea and Boyle (1991), the maximum Ba/Ca ratios in non-spinose species should be <3 μmol/mol, which is still much lower than has been measured in many non-spinose species (Lea and Boyle, 1991; Hathorne et al., 2009; Bahr et al., 2013).

Here we report results of laboratory culture experiments to determine the D_{Ba} for the non-spinose planktic foraminifer *N. dutertrei* and evaluate the impacts of temperature (12–22 °C) and pH_{NBS} (7.8–8.3) on Ba incorporation in this species. We also collected post-gametogenic (devoid of cytoplasm) shells from plankton tows at the collection site to establish the Ba/Ca variability of *N. dutertrei* specimens that completed their lifecycle in their natural environment. For comparison, we also collected and analyzed post-gametogenic shells of the spinose species *O. universa* and *G. ruber* from the same plankton tows.

2. METHODS

2.1. Sample collection and culture protocols

Juvenile specimens of *N. dutertrei* were collected during July–August 2014 and August 2015, and cultured at the Wrigley Marine Science Center Santa Catalina Island, California. Specimens were collected from a depth of 30–50 m in the San Pedro Basin, Southern California Bight (33°23′N, 118°26′W) using an open-close Puget Sound plankton net (Aquatic Research, 150 μm mesh). The temperature at the collection depth, measured with a Sea-bird Electronics SBE 19plus profiler, ranged from 12 to 16 °C. Seawater used in the experiments was obtained at the collection site after each plankton tow and filtered in the laboratory using 0.22 μm nitrate cellulose filters. In culture experiments with spinose foraminifera, seawater is normally filtered using a 0.8 μm filter, however, we found the 0.22 μm filter reduced bacteria and diatom growth in the culture jars and decreased mortality rates.

Immediately after arrival in the laboratory, live *N. dutertrei* were pipetted from the plankton tow samples, rinsed in filtered seawater, and measured on the longest dimension under an inverted light microscope. Specimens were then transferred into 70 ml polystyrene Falcon® culture flasks containing either ambient or chemically modified filtered seawater. For all experiments, a spike of ^{86}Sr (97.26%) or ^{87}Sr (91.26%) was added to the seawater to identify calcite grown in the laboratory (Table S1). Addition of the spike increased the $^{86}Sr/^{88}Sr$ or the $^{87}Sr/^{88}Sr$ ratio of the seawater by 2x or 4x relative to the natural ratios, respectively. In addition to the isotopic spike, seawater for the D_{Ba} experiment was modified by adding a concentrated $BaCl_2$ solution to ambient seawater to increase the Ba concentration to ~2.5x or ~5x the natural Ba concentration. The maximum concentration of Ba in our experiments (~240 nmol/L) was chosen to prevent barite from precipitating in our culture seawater (Monnin et al., 1999). During the experiments, we did not observe precipitate in the culture flasks. For the pH experiments, we added 0.1 N HCl or 0.1 N NaOH to change the pH of the seawater to 7.8 and 8.3 (NBS scale) for the low and high pH experiments, respectively. Culture baths were illuminated at 55 ± 15 μmol photons m^{-2} s^{-1} using LED XP-E 72 Watt CREE lights (full spectrum) on a 12 h light: 12 h dark cycle. Light levels were monitored daily using a Biospherical Instruments light meter (model QSL-100). Every other day, each foraminifer was fed a 1-day-old previously frozen *Artemia* nauplius by pipetting the thawed *Artemia* onto the specimen's rhizopodial network (Fig. 1A). Specimens were not fed if the rhizopodial network was retracted. All specimens, except those in the high (22 ± 0.1 °C) and low (12 ± 0.1 °C) temperature experiments, were in water baths at a temperature of 16 ± 0.1 °C. The salinity of the seawater used in all experimental was held constant (33.3–33.4). Specimens were maintained in culture until they released gametes or died (Fig. 1B and C). Dead specimens were identified by lack of rhizopodial activity, retraction of cytoplasm into the shell, and failure to release gametes. Post-experiment shells and the post-gametogenic/empty shells of *N. dutertrei*, *O. universa*, and *G. ruber* obtained from the plankton tows were rinsed in DI water, dried, and archived in micropaleontology slides.

2.2. Ambient and experimental seawater sampling and analysis

Seawater samples were collected at 7 depths between 2 and 150 m using a Niskin water sampling rosette at the San Pedro Ocean Time Series (SPOT) station (33°44′N, 118°17 W) on May 21, 2014, to establish the range of Ba concentrations and Ba/Ca ratios in ambient seawater within the presumed habitat depth range of *N. dutertrei* (Table 1, Fig. S1). Water samples were also collected at 10 and 60 m depth at the collection site (33°23′N, 118° 26′W) using a single Niskin bottle on August 27, 2015 (Table 1, Fig. S1). Experimental seawater samples were also collected for analysis of trace element concentrations (Table 2). All seawater samples for trace element analyses were passed through acid-cleaned Millex® polyvinylidene membrane filters (22 μm mesh) into acid-leached 15 mL Nalgene™ bottles and subsequently acidified with 1 μl Optima™ grade concentrated HCl.

Seawater samples were analyzed at the Interdisciplinary Center for Plasma Mass Spectrometry at the University of California, Davis, using an Agilent 7500CE ICP-MS (Agilent Technologies, Palo Alto, CA) equipped with a He collision cell to reduce interferences. Prior to analysis, samples were diluted by a factor of 25 into a solution of 3% HNO_3 acid (Fisher Scientific Trace Element grade) in ultra-pure (18.2 MOhm/cm) water. Counts were collected on ^{42}Ca, ^{85}Rb, ^{86}Sr, ^{87}Sr, ^{88}Sr, ^{137}Ba and ^{138}Ba, and other isotopes not discussed here. Instrument standards for quantification of Ca were diluted from Certiprep ME ICS3 Standard to 1 ppm, 2 ppm, 5 ppm, 10 ppm, and 20 ppm into a 3% HNO_3 solution as above. Single element standards (Inorganic Ventures) for Rb, Sr, and Ba were diluted to 1 ppb, 10 ppb, 50 ppb, 100 ppb, 200 ppb, 500 ppb, and 1000 ppb. The instrument performance and accuracy was evaluated by analyzing the Standard Reference Material 1640A (natural water, National Institute of Standards and Technology) at the beginning of each run. Measured values of Ca (using ^{42}Ca), Sr (using ^{88}Sr) and Ba (using ^{138}Ba) in SRM 1640A were 101.6%, 100.0%, and 98.7% respectively, of the certified values. Quality control standards made from CertiPrep ME ICS3 (5ppm) and single element standards (100 ppb) were analyzed at the beginning and end of the run, as well as every 10th sample, to monitor drift and changes in instrument performance. Recovery of the Ca, Sr, and Ba in the QC standards was 102.6%, 100.1%, and 97.6%, respectively. Internal standards (^{45}Sc for Ca, ^{89}Y for Sr, and ^{115}In for Ba) at a final concentration of 1 ppm were used to correct for within-run variability. These internal standards were prepared using a CertiPrep Sc standard and Inorganic Ventures Ge, Y, In, and Bi standards, diluted to 30 ppm in 3% HNO_3 and introduced to the sample via a tee fitting using a peristaltic pump at a 1:30 IS/sample ratio. The concentration of Ca was calculated using ^{42}Ca, normalized by its natural abundance, because there are no interferences from Sr on this isotope. Total concentrations of Sr and Ba were calculated by constructing calibration curves for each isotope/IS ratio and summing the

Fig. 1. Micrographic observations of the life cycle of *N. dutertrei* in culture. (A) Healthy specimens extend their rhizopodia on the bottom of the culture flasks. (B) Just prior to gametogenesis, the rhizopodia are retracted and the foraminifer turns pale white. Specimens have been observed expelling symbionts during this stage. (C) *N. dutertrei* releasing gametes. See also: https://www.youtube.com/watch?v=iCqcKjeqR4g for a video of gamete release (Fehrenbacher, 2013).

Table 1
Seawater chemistry near the foraminifer collection site and the SPOT station.

Depth (m)	Location	N	Sr (μmol/L)	Ba (nmol/L)	Ca (mmol/L)	Ba/Ca (μmol/mol)	Sr/Ca (mmol/mol)
10.0	Collection site	2	85.9	40.4	10.4	3.9	8.2
60.0	Collection site	2	86.6	53.9	10.4	5.2	8.3
2.2	SPOT	1	90.3	42.7	10.9	3.9	8.3
9.9	SPOT	1	90.4	43.6	10.9	4.0	8.3
19.7	SPOT	1	90.0	46.1	10.8	4.3	8.3
27.3	SPOT	1	90.0	52.5	10.8	4.9	8.3
40.0	SPOT	1	89.9	55.6	10.8	5.1	8.3
50.2	SPOT	1	89.8	55.2	10.8	5.1	8.3
60.2	SPOT	1	90.0	54.8	10.8	5.1	8.3
150.7	SPOT	1	92.4	56.1	11.1	5.0	8.3

Table 2
Seawater trace element data and pre- and post-experiment alkalinity and pH.

Experiment	Isotope label	$Ba/Ca_{SEAWATER}$ (μmol/mol)	$^{87}Sr/^{88}Sr$ or $^{86}Sr/^{88}Sr$	Pre Exp. Alk/pH	Post Exp. Alk/pH
Ambient Ba	4x ^{87}Sr	4.7 ± 0.1 (N = 4)*	0.342 ± 0.005 (4)*	2208, 8.1 (N = 5)^	2214, 8.1 (N = 4)^
~2.5X	2x ^{86}Sr	13.6 ± 1.2 (N = 2)	0.235 ± 0.001 (2)	2218, 8.2 (N = 2)	2218, 8.2 (N = 3)
~5X	4x ^{87}Sr	21.5 ± 0.01 (N = 2)	0.352 ± 0.001 (2)	2218, 8.2 (N = 2)	2244, 8.2 (N = 2)
12 °C	4x ^{87}Sr	*	*	2205, 8.1 (N = 1)	2215, 8.1 (N = 5)
16 °C	4x ^{87}Sr	*	*	^	^
22 °C	4x ^{87}Sr	*	*	2255, 8.1 (N = 4)	2219, 8.1 (N = 6)
pH 7.8	4x ^{87}Sr	*	*	2075, 7.8 (N = 3)	2072, 7.8 (N = 6)
pH 8.1	4x ^{87}Sr	*	*	^	^
pH 8.3	4x ^{87}Sr	*	*	2406, 8.3 (N = 3)	2411, 8.3 (N = 3)

* and ^ denote averages obtained from seawater samples used for these experiments.

calculated concentrations of Sr or Ba isotopes, respectively. ^{87}Sr counts were obtained by removing the contribution of ^{87}Rb to total counts at mass 87, using ^{85}Rb counts and the $^{85}Rb/^{87}Rb$ natural abundance ratio (0.3856). The reproducibility of sample Ca, Sr, and Ba concentrations, based on analyses of three replicate seawater samples, was 1.0% (Ca), 1.1% (Sr) and 1.8% (Ba).

Pre- and post-experimental seawater alkalinity and pH_{NBS} were determined using a Metrohm 785 autotitrator and electrode. The concentration of titrator acid (0.1 N HCl) was validated by titrating aliquots of oven-dried TRIS buffer dissolved in ultrapure (18 MOhm/cm) water. Accuracy was evaluated by titrating at least one aliquot of Dickson certified reference material (CRM Batch 136) with each batch of samples. The average offset between measured and certified total alkalinity (3 μmol/kg) was within one standard deviation (7 μmol/kg) of repeated titrations of a seawater consistency standard (n = 29). Pre- and post-experimental alkalinity and pH_{NBS} values were constant (within error) throughout all experiments (Table 2).

2.3. Sample preparation and analytical methods

We follow previously published sample cleaning protocols and LA-ICP-MS methods for cultured foraminifers (Fehrenbacher et al., 2017). Specimens were oxidatively cleaned to remove remnant organic matter using 100 μl of a 1:1 solution of 30% H_2O_2:0.1 N NaOH followed by 3 rinses in ultrapure (18 MOhm/cm) water (Mashiotta et al., 1999). Cleaned specimens were mounted onto double-sided carbon tape with the aperture side down. Specimens were analyzed by laser ablation-ICP-MS depth profiling (spot analysis) at the UC Davis Stable Isotope Laboratory in the Department of Earth and Planetary Sciences. Acquisitions were performed from the outside surface to the inside to best quantify the geochemistry of cultured calcite in these specimens, which is added primarily to the outside of the shell (Fehrenbacher et al., 2017). Analytical settings are summarized in Table S2. Isotopes were measured using a rapid peak hopping procedure. Repeat analyses were obtained on chambers that were large enough to permit multiple laser spots. Following our laboratory protocols, we analyzed a fossil *O. universa* to assess Ba/Ca reproducibility within and between analytical sessions (Fehrenbacher et al., 2015). A total of 22 replicate analyses were obtained from the same fossil *O. universa* between October 2013 and May 2015. The mean Ba/Ca ratio from these repeat measurements is 5.43 ± 0.38 μmol/mol (±7%) (1 σ). Trace element to calcium ratios are calculated offline in MS Excel, following established data reduction protocols (Longerich et al., 1996) including screening for outliers, drift correction by bracketing samples with NIST SRM 610 analyses, and subtracting average background counts from each data point. The mean element/Ca ratio for each profile is calculated by normalization to the known trace element concentrations in the drift-corrected bracketed analyses of the NIST SRM 610 standard (Jochum et al., 2011). ^{43}Ca was used as an internal standard. The Ba/Ca ratios of the culture-secreted calcite was obtained by integrating the portion of the shell that contained the isotope label (Fig. S2).

3. RESULTS

3.1. Seawater Ba, Ca, and Sr

Concentrations of Ba, Ca, and Sr in ambient and experimental seawaters are presented in Table 1. The average Ba, Sr, and Ca concentrations in the upper 10 m in samples taken from the SPOT site (May 2014) and near Santa Catalina Island (August 2015) were [Ba] = 41.8 ± 2.1 nmol/L, [Sr] = 88.1 ± 2.6 μmol/L, and [Ca] = 10.6 ± 0.3 mmol/L (N = 4). This water composition is representative of the ambient seawater used in our experiments. The measured [Ba] is within error of the ambient [Ba] reported by Lea and Spero (1992) ([Ba] = 39.7 ± 0.7 nmol/L), and only slightly higher than the average reported by Hönisch et al., 2011) ([Ba] = 37.8 ± 0.35 nmol/L). The average Ba/Ca ratio for the waters analyzed here was 3.9 ± 0.2 μmol/mol, compared to 4.0 μmol/mol (Lea and Spero, 1992) and 3.7 μmol/mol (Hönisch et al., 2011). The average Sr/Ca ratio for the upper 10 m was 8.3 ± 0.04 μmol/mol. Seawater [Ba] for the SPOT location (May 2014) at 40–150 m were [Ba] = 55.5 ± 0.5 nmol/L (5.1 ± 0.1 μmol/mol) (N = 5). Seawater [Sr] and Sr/Ca at this depth range were 91 ± 1.2 μmol/L and 8.31 ± 0.02 mmol/mol, respectively (Table 1).

3.2. Culture experiment results

Ba/Ca ratios of *N. dutertrei* calcite cultured in the laboratory varies linearly with the Ba/Ca ratios of the experimental seawater ($Ba/Ca_{FORAM} = 0.11 \pm 0.008$ (2 SE) * $Ba/Ca_{SW} + 0.03 \pm 0.1$ (2 SE), Fig. 2A). *N. dutertrei* grown in Ba-free water will have a Ba/Ca ratio = 0 (e.g. the slope is the same, within error, when the equation is forced through the zero-intercept). The average Ba/Ca_{FORAM} ratios of calcite added in culture are 0.57 ± 0.15 (1σ, N = 12), 1.52 ± 0.12 (1 σ, N = 9), and 2.45 ± 0.20 (1 σ, N = 10) μmol/mol for specimens grown in seawater with Ba/Ca_{SW} ratios of 4.7 ± 0.1, 13.6 ± 1.2, and 21.5 ± 0.01 μmol/mol, respectively (Table 2). Data from temperature and pH experiments demonstrate that the Ba/Ca ratio of *N. dutertrei* does not vary with these parameters (Fig. 3, Table 3). The Ba/Ca ratios of specimens grown in seawater with ambient Ba/Ca = 4.7 ± 0.1 μmol/mol, at 12 °C, 16 °C, and 22 °C are not significantly different (Kruskal–Wallis one-way analysis of variance, p = 0.2; Fig. 3A). Similarly, the Ba/Ca ratios of specimens grown in seawater with ambient Ba/Ca (4.7 ± 0.1 μmol/mol (N = 5) at pH_{NBS} 7.8, 8.1, and 8.3 are not different (Kruskal–Wallis one-way analysis of variance, p = 0.5; Fig. 3B).

3.3. Ba/Ca ratios of ocean-grown calcite

Average (whole shell) Ba/Ca ratios of the post-gametogenic *N. dutertrei* shells obtained from the plankton tows range from 4 to 33 μmol/mol (Table S3). Chamber-to-chamber Ba/Ca ratios are not significantly different (Kruskal–Wallis one-way analysis of variance, p = 0.50; Fig. 4). Laser ablation depth profiles from representative specimens demonstrate the highly variable nature of the intrashell Ba/Ca ratios in specimens that completed their lifecycle in the ocean (Fig. 4A) and in the ocean-grown calcite from specimens that completed their lifecycle in culture (Fig. S2). Intrashell Ba/Ca ratios measured in the plankton tow specimens range from ~0.40 to >200 μmol/mol (Figs. 5A and S2).

In cultured specimens, shell Ba/Ca ratios decrease immediately upon transfer into experimental seawater and remain constant within the shell wall (Fig. S2B–D). In the

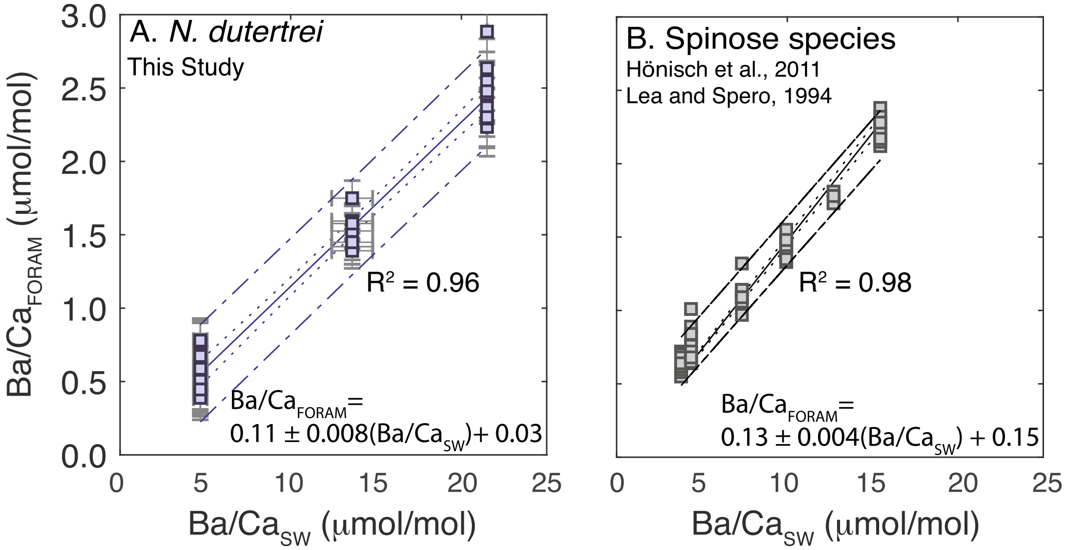

Fig. 2. Average Ba/Ca_{FORAM} ratios vs. seawater Ba/Ca ratios. Average Ba/Ca_{FORAM} ratios (μmol/mol) of the cultured portions of (A) individual *N. dutertrei* (this study) and (B) spinose species (Hönisch et al., 2011; Lea and Spero, 1994) versus Ba/Ca (μmol/mol) of the experimental seawater. Dashed lines on both plots indicate the upper and lower 95% confidence limits; solid lines indicate the upper and lower prediction limits.

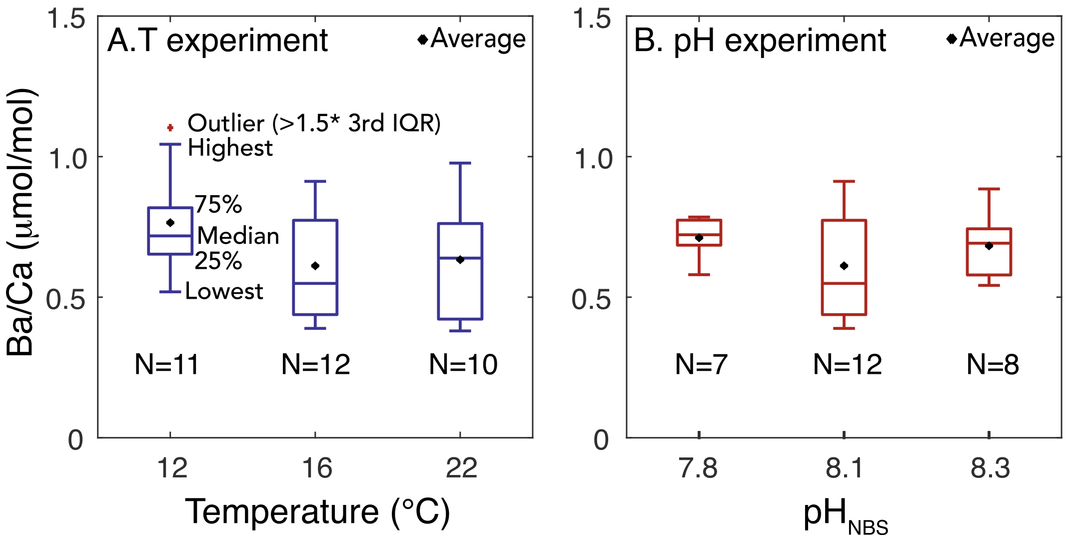

Fig. 3. Average Ba/Ca_{FORAM} ratios vs. culture temperature and pH. Box and whisker plots of the Ba/Ca_{FORAM} ratios in cultured portions of *N. dutertrei* versus (A) calcification temperature and (B) seawater pH. Black dot denotes sample mean. Upper and lower box bounds represent the 75% and 25% quantile, respectively. Middle line within the box marks the median. The upper and lower 'whiskers' denote the maximum and minimum values (excluding outliers), respectively. Red dot denotes an outlier that exceeds 1.5 times the value of the 3rd interquartile range (IQR).

Table 3
Average Ba/Ca_{FORAM} ratios of cultured specimens, listed by experiment.

Ambient Ba/Ca, 16 °C, pH 8.1[a]	D_{Ba} experiment (16 °C, pH 8.1)		Temperature experiment (pH 8.1)		pH experiment (16 °C)	
Ba/Ca_{SW}: 4.7 (μmol/mol)	Ba/Ca_{SW}: 13.6 (μmol/mol)	Ba/Ca_{SW}: 21.5 (μmol/mol)	12 °C	22 °C	7.80	8.30
0.41	1.58	2.88	0.65	0.80	0.79	0.89
0.43	1.75	2.30	1.04	0.56	0.72	0.76
0.39	1.59	2.64	1.10	0.42	0.77	0.69
0.59	1.42	2.46	0.66	0.98	0.58	0.56
0.46	1.53	2.55	0.82	0.73	0.72	0.64
0.75	1.42	2.37	0.52	0.56	0.69	0.54
0.59	1.58	2.24	0.72	0.76		0.71
0.51	1.39	2.29	0.77	0.72		
0.45	1.45	2.30	0.69	0.42		
0.67		2.48	0.64	0.38		
0.77			0.80			
0.78						
Avg. 0.57	1.52	2.45	0.77	0.63	0.71	0.68
St. Dev. 0.15	0.12	0.20	0.17	0.20	0.07	0.12

[a] Note: This data is used as the control group in all three experiments.

ocean-grown specimens, patterns of intrashell Ba/Ca variability differ from specimen-to-specimen (Fig. 5A). In some specimens (ND3, ND4, and ND21), we observe elevated Ba/Ca ratios within the inner chamber wall region (initial chamber calcite) and lower Ba/Ca ratios in the outer region of the chamber wall (Fig. 5A). In contrast, (ND6 and ND9), we find that some specimens display moderately high and variable Ba/Ca throughout the entire chamber wall. Intrashell Ba/Ca variability and high Ba/Ca ratios in field collected *N. dutertrei* contrast with the low and generally constant intrashell Ba/Ca ratios measured in the chamber walls of the plankton tow collected spinose species *O. universa* and *G. ruber* obtained from the same plankton tow samples (Fig. 5B and C, respectively).

4. DISCUSSION

Our experimental data demonstrate that the Ba/Ca ratios of *N. dutertrei* vary linearly with seawater [Ba] and that the D_{Ba} for *N. dutertrei*, 0.11 ± 0.008 (2 SE), is similar to the D_{Ba} reported for spinose species, 0.13 ± 0.004 (2 SE) (Fig. 2B) (Hönisch et al., 2011). Similar to the spinose species, the D_{Ba} for *N. dutertrei* is not affected by variation in calcification temperature or seawater pH. These results

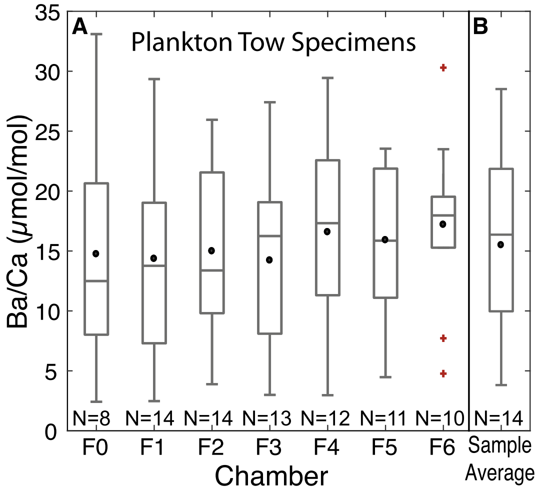

Fig. 4. Chamber-to-chamber and average Ba/Ca ratios of the plankton tow specimens. Box and whisker plots of (A) chamber-to-chamber ratios and (B) whole shell average trace element ratios Ba/Ca ratios. The black dots represent chamber averages. Red+ symbols denote outliers. See Fig. 3 caption for additional details on how to interpret box-and-whisker plots. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

imply that *N. dutertrei* shell Ba/Ca ratios should be similar to the Ba/Ca ratios of spinose foraminifera collected from the same plankton tows (e.g. <1 μmol/mol) if they calcified in the ambient seawater environment. Furthermore, *N. dutertrei* Ba/Ca should vary little within the shell wall. Based on our experimental D_{Ba} for *N. dutertrei* ($D_{Ba} = 0.11 \pm 0.008$ (2 SE) and the measured seawater Ba/Ca at the depth of collection (∼5 μmol/mol), *N. dutertrei* Ba/Ca ratio should be ∼0.5 μmol/mol.

Whereas the Ba/Ca ratios of *G. ruber* and *O. universa* shells collected in plankton tows simultaneously with specimens used in our culture experiments are within the ratios expected based upon seawater [Ba], the Ba/Ca ratios of post-gametogenic plankton tow collected *N. dutertrei* (∼4–33 μmol/mol) are 8-65x higher than expected. In addition, these specimens display variable Ba/Ca in their shell walls (intrashell variability ranges from 0.5 to 200 μmol/mol) that far exceed the constant Ba/Ca observed in specimens grown in culture (Fig. S2). If we assume that shell Ba varies only as a function of seawater [Ba], then *N. dutertrei* would have to calcify in water with a Ba/Ca ratio that ranges between 3 and 1800 μmol/mol ($[Ba]_{sw} =$ ∼40–18,000 nmol/L) to explain the average and intrashell Ba/Ca ratios observed in the plankton tow specimens (∼ < 1–200 μmol/mol). Such dissolved seawater barium concentrations are not observed in open seawater environment. Additionally, it is difficult to reconcile intrashell Ba/Ca

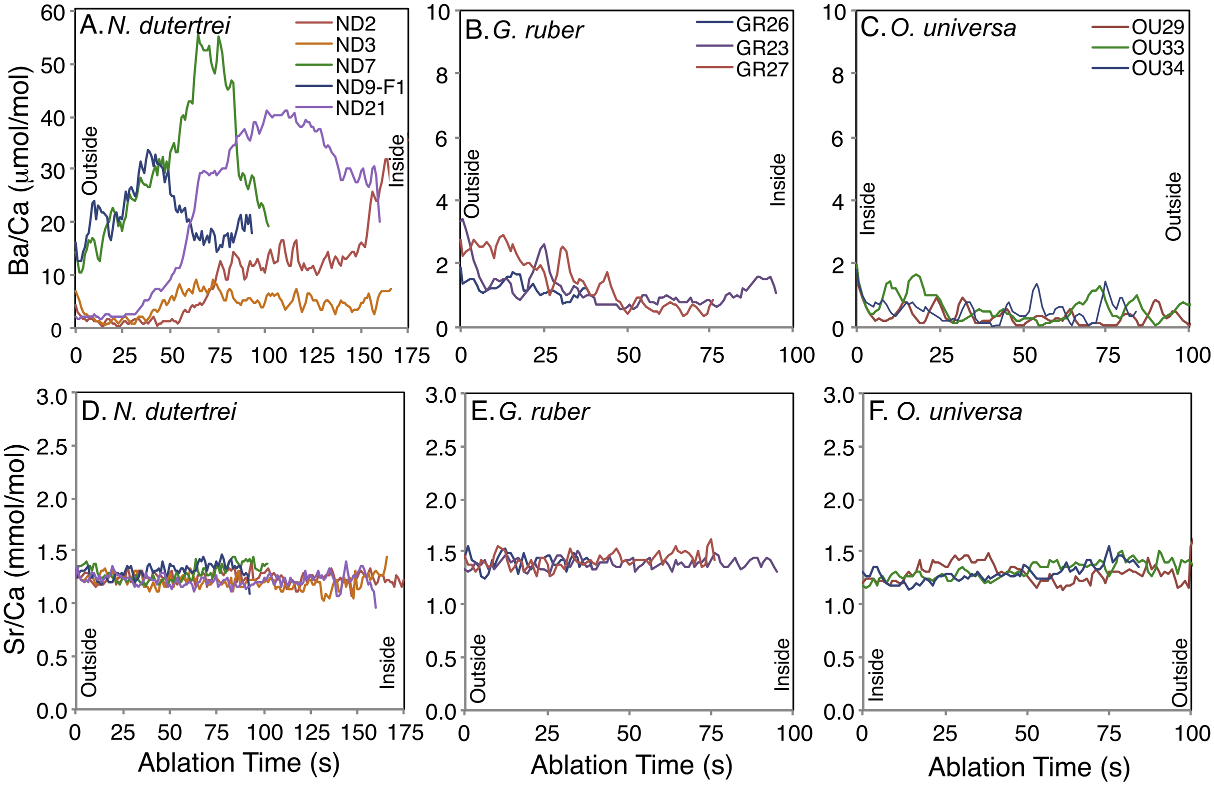

Fig. 5. Representative laser ablation depth profiles of the Ba/Ca and Sr/Ca ratios in the plankton tow specimens. Intrashell Ba/Ca (A-C) and Sr/Ca (D-F) ratios measured in (A, D) plankton tow specimens of *N. dutertrei*; (B, E) *G. ruber*; and (C, F) *O. universa*. The Ba/Ca ratio is highly variable and elevated in *N. dutertrei* (A) compared to the low and generally constant Ba/Ca ratios measured in *G. ruber* (B) and *O. universa* (C). The Sr/Ca ratios are similar among all three species and do not display intrashell variability (D-F).

variability with the relatively constant $[Ba]_{SW}$, even accounting for a slight increase in $[Ba]_{SW}$ from the surface to 150 m (Table 1, Fig. S1).

4.1. Possible mechanisms for elevated Ba/Ca ratios in *N. dutertrei*

4.1.1. Preference for prey with elevated Ba

One potential explanation for elevated shell Ba/Ca ratios could be a preference for prey that has elevated Ba compared to seawater. Of the potential prey that might be consumed by *N. dutertrei* (e.g. copepods, diatoms, Acantharia), only Acantharia and diatoms are known to concentrate Ba. Acantharia have skeletons composed of the mineral celestite ($SrSO_4$), and the Ba/Sr ratio in Acantharia skeletal material is higher than the surrounding seawater due to their higher partition coefficient ($D_{Ba/Sr}$) for Ba (where $D_{Ba/Sr} = (Ba/Sr)_{Acantharia}/(Ba/Sr)_{SW} = 3.4$ (Bernstein et al., 1998)). Feeding studies with spinose foraminifer species suggested they either do not eat Acantharia or they ingest the cytoplasm only and discard the skeletal material (Spindler et al., 1984). If *N. dutertrei* were to ingest Acantharia and their skeletal structure, we would also expect to see elevated Sr in *N. dutertrei* because Acantharia skeletons are composed of ~48% Sr. However, Sr/Ca and Ba/Ca ratios do not covary in *N. dutertrei* ($R^2 = 0.0$, $p = 0.20$). Furthermore, in contrast to the highly variable intratest Ba/Ca we observe within single chambers of the plankton tow *N. dutertrei* specimens, intrashell Sr/Ca ratios are not variable (Fig. 5D–F). Nevertheless, we can estimate the Sr/Ca ratio one would expect to see if the excess Ba in *N. dutertrei* is due to the ingestion of Acantharia. Using a *N. dutertrei* specimen with a Ba/Ca ratio of 10 μmol/mol in the ocean-grown portion of the chamber, and assuming an Acantharia Ba/Ca ratio of 4×10^{-3} μmol/mol (Arrhenius, 1963; Rieder et al., 1982), the incorporation of Sr from ingested Acantharian skeletons would yield a Sr/Ca ratio of >3.4 mmol/mol (Supplementary Materials). This is far higher than the Sr/Ca ratio measured in the plankton-tow specimens (average $Sr/Ca = 1.40 \pm 0.09$). We infer from these calculations that Acantharia are not directly responsible for the elevated and variable Ba/Ca ratios in *N. dutertrei*.

Barium contained in or on diatoms could be responsible for the elevated Ba/Ca ratios in shell calcite if diatoms are a dominant food source for *N. dutertrei*. Barium within marine diatoms can be elevated above ambient seawater [Ba] by a factor of two or more via passive leakage through ion channels, driven by the negative potential of cell cytoplasm relative to the external medium (Sternberg et al., 2005). Studies have shown that the Ba concentration of cultured diatoms is primarily associated with extracellular Fe oxides (FeO_x) adsorbed to the cell surface, and that cellular Ba increases with seawater iron concentration (Ganeshram et al., 2003; Sternberg et al., 2005; Tang and Morel, 2006).

Foraminifera feeding experiments and transmission electron microscopy (TEM) imaging of the cytoplasm (detailing diatom-like structures) suggest that *N. dutertrei* and other non-spinose foraminifer species ingest both diatoms and zooplankton (Anderson et al., 1979; Spindler et al., 1984; Hemleben et al., 1989). However, these studies do not quantify the relative proportion of phytoplankton:zooplankton prey that is naturally consumed. Recent advances in biomarker geochemistry show that fatty acid biomarker analysis (e.g. Suhr et al., 2003; LeKieffre et al., 2017) and 16S RNA gene metabarcoding combined with TEM imagery (Bird et al., 2017, 2018) are superior methods for quantifying feeding behavior and trophic interactions in foraminifera. For example, fatty acid analyses revealed that some benthic foraminifer species have a preference for specific phytodetritus, even when they have access to other potential food items (Suhr et al., 2003). 16S RNA gene metabarcoding of two specimens of *N. dutertrei* from our plankton tows did not contain sufficient diatom RNA to suggest that this species regularly consumes diatoms (Bird et al., 2018). Because of the limited sample size, however, we cannot eliminate diatoms as a potential source for some of the excess Ba recorded in field collected *N. dutertrei* shells.

4.1.2. Calcification in microhabitat enriched in Ba relative to seawater

A calcifying environment that is rich in Ba is needed to explain the unusually high and variable Ba/Ca ratios we observe in field-collected *N. dutertrei*. We propose a novel hypothesis for the ecological microhabitat of *N. dutertrei*. We hypothesize that *N. dutertrei*, and perhaps other non-spinose species, calcify within microenvironments containing Ba-rich fluids associated with organic particulates such as marine snow. These microenvironments often contain elevated trace element concentrations relative to bulk seawater (Hebel et al., 1986). The chemistry (O_2, pH, silicic acid, dissolved organic carbon, and amino acids) of these fluids is distinctly different from that of bulk and varies as a function of particle size seawater (Alldredge and Cohen, 1987; Brzezinski et al., 1997; Alldredge, 2000). The strong chemical gradients between bulk seawater and the interstitial fluids can be maintained by slow diffusion rates due to the complex geometry of marine snow particles (Alldredge, 2000). Although seawater is undersaturated with respect to barite (Monnin et al., 1999; Rushdi et al., 2000; Monnin et al., 2006), marine snow can contain barite crystals, potentially aided by microbial activity (Chow and Goldberg, 1960; Alldredge and Cohen, 1987; Gonzalez-Munoz et al., 2012), an indication that the Ba concentration within the marine snow can reach and exceed saturation with respect to barite (Dehairs et al., 1980; Stroobants et al., 1991).

We can calculate the dissolved Ba concentration and Ba/Ca_{SW} of a model microenvironment, if we assume that a *N. dutertrei* individual with a shell Ba/Ca = 15 μmol/mol calcified at 50 m depth, with seawater [Ca] = 10.2 mmol/L. Under these conditions, the [Ba] in the microenvironment would be ~1500 nmol/L (Ba/Ca_{SW} ~150 μmol/mol), suggesting supersaturation with respect to barite (Ω~9, using K_{sp} from Rushdi et al., 2000). This calculated Ba concentration is a factor of 10 higher than that observed in the deep Pacific Ocean. Such a high saturation state suggests that barite precipitation may be inhibited by kinetic factors or by other chemical conditions within the microenvironment, analogous to the crystal poisons in seawater that prevent spontaneous $CaCO_3$ precipitation in the surface ocean, despite supersaturated conditions.

Dissolved Acantharia tests and diatoms would contribute indirectly to the geochemistry of *N. dutertrei* by increasing the [Ba] of the interstitial fluids contained in marine snow. Researchers have previously proposed that diatom degradation and release of adsorbed Ba is a source of Ba for barite precipitation within marine snow particles (Dehairs et al., 1980; Fisher et al., 1991; Ganeshram et al., 2003). Barium adsorption to FeO_x decreases with increasing pH (Sternberg et al., 2005); hence Ba released from diatom FeO_x within the marine snow could drive far greater shell Ba/Ca enrichments. Microelectrode measurements of pH and O_2 within marine snow showed pH depletion of 0.22 units and O_2 depletion by as much as 45% in the largest particles (under dark conditions) (Alldredge and Cohen, 1987; Ploug et al., 1999; Ploug, 2001). A pH depletion of 0.22 units could decrease the Ba/Fe ratio of adsorbed FeO_x on the cell surface by ~50% (see Fig. 4, Sternberg et al., 2005), releasing Ba into the marine snow fluids. In large particles, there is also the potential to release adsorbed Ba by reducing particulate Fe (III) to the soluble form Fe(II). Dissolved Acantharia tests could further increase not only the [Ba] of the interstitial fluids within marine snow relative to seawater, but also the [Sr] concentration (de Villiers, 1999). Interestingly, the Sr/Ca ratio of the cultured calcite (average $Sr/Ca = 1.15 \pm 0.05$) is ~17% lower (p-value $\ll 0.001$) than the ocean-grown calcite (average $Sr/Ca = 1.4 \pm 0.09$), in spite of the 10% (^{86}Sr) or 20% (^{87}Sr) increase in the Sr/Ca ratio of culture seawater due to the addition of the Sr-isotope labels (Fig. 6). We therefore suggest that the elevated Sr/Ca_{FORAM} ratios of the ocean-grown calcite compared to cultured calcite could arise from elevated Sr concentration in marine snow particles due to remineralization of Acantharia in the water column (de Villiers, 1999).

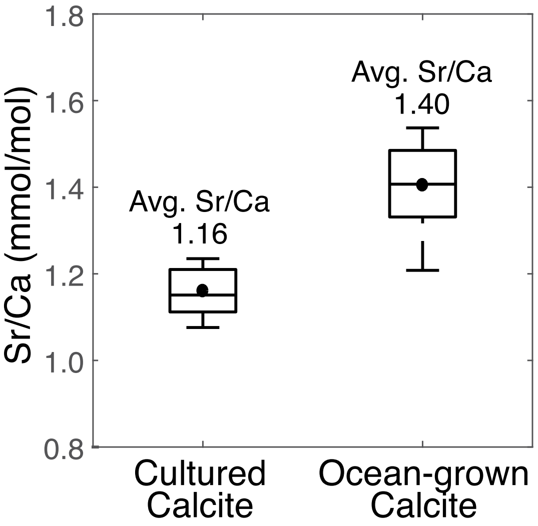

Fig. 6. Sr/Ca ratios measured in the cultured vs. ocean-grown portions of the same specimens. Sr/Ca ratios of the cultured portions of *N. dutertrei* shells were determined by averaging the Sr/Ca ratio of calcite that grew in culture (identified using the Sr-isotope labels). The ocean-grown portions of the shell were determined by averaging the Sr/Ca ratios of the portions of the shell that did not contain the Sr-isotope label. Ocean-grown calcite has significantly higher Sr/Ca ratios (p-value $\ll 0.001$).

Although the higher Sr/Ca_{FORAM} ratios in the ocean-grown calcite may point to Acantharia as a food source, our measurements show that Ba/Ca_{FORAM} and Sr/Ca_{FORAM} variability is not coupled. For example, in the ocean-grown specimens with the highest and most variable Ba/Ca_{FORAM} ratios, the Sr/Ca_{FORAM} ratios remain constant (e.g. Fig. 5, specimens ND6 and ND9). Thus, the incorporation mechanism need not be linked to food, but instead could be linked to the chemistry of the interstitial seawater within the marine snow particles and biomineralization mechanisms.

Evidence from our observations and the behavior of *N. dutertrei* in culture lends support to the marine snow/organic aggregate microhabitat hypothesis. Non-spinose planktic foraminifers captured in our plankton nets are often attached to or associated with macroscopic organic aggregates (marine snow or other debris, Fig. 7). Although spinose species are far more abundant, we rarely observed them embedded within organic particulates. In addition, when in culture, *N. dutertrei* show a clear preference for attachment to a surface during growth stages. Healthy, thinly calcified *N. dutertrei* specimens attach to the bottom of the culture flasks by extending a rhizopodial network (Fig. 1A). They retract their rhizopodia and detach from the bottom of the flask when they are preparing to undergo gametogenesis (Fig. 1B). Gametogenesis commences within a few days and gametes are released into the jar (Fig. 1C).

If *N. dutertrei* behavior is similar in the ocean, individuals may attach to marine snow and/or other organic aggregates in the water column (when such material is abundant) during early growth stages (e.g. during chamber formation processes). When the rhizopodia retract and the specimens prepare for gametogenesis perhaps they dislodge from particles and then float briefly in the open ocean before gamete release. An organic aggregate habitat could also explain the highly variable specimen-to-specimen Ba/Ca ratios which would vary depending on the unique chemistry of each organic particle in the water column (e.g. Figs. 5 and S2).

Our hypothesis may explain observations of inter-species differences in the nitrogen isotopic composition of organics bound within the shells of foraminifera (termed foraminiferal bound (FB-) $\delta^{15}N$). Non-spinose species have higher FB-$\delta^{15}N$ compared to shallow-dwelling spinose species. An herbivorous (diatom-rich) diet would decrease the FB-$\delta^{15}N$, opposite of what is found in these species. Thus, the authors attributed the elevated FB-$\delta^{15}N$ to the consumption of suspended particulate organic matter, which has elevated $\delta^{15}N$ (Altabet et al., 1999), by the non-spinose species (Ren et al., 2012).

Our laboratory observations of *N. dutertrei* and other non-spinose species such as *G. menardii* (Mielke, 2001) show that in culture these species exhibit behavior that is similar to benthic foraminifera. Perhaps a microhabitat on marine snow or other organic particulates allows these species to live a quasi-benthic existence within the water column. Although Lea and Boyle (1991) suggested enriched

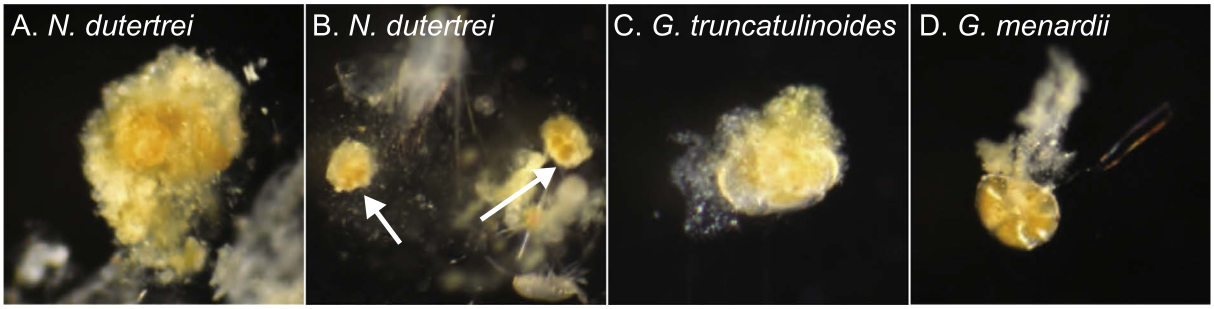

Fig. 7. Micrographic observations of specimens in organic particulates. (A-D): Micrographs of non-spinose planktic foraminifer specimens attached to marine snow/organic particulates. (A-B) *N. dutertrei*, (C) *G. truncatulinoides*, and (D) *G. menardii*. δ.

Ba in fossil specimens of non-spinose species such as *G. truncatulinoides*, *G. menardii*, and *N. dutertrei* were due to diagenetic overprinting, we speculate that these and other non-spinose planktic species display elevated shell Ba/Ca because they have similar habitat strategies. If our hypothesis is correct, Ba/Ca and Sr/Ca ratios in non-spinose foraminifera might yield information on past aggregate microenvironment chemistry, but cannot be used as a pure water column elemental proxy. A microhabitat calcification environment may also complicate the utility of boron isotopes in aggregate-dwelling species as a proxy for pH since the pH of POM may be lower than ambient seawater (Alldredge and Cohen, 1987). For example, the δ^{11}B composition *of N. dutertrei* is the lowest of all deep-dwelling species calibrated to date (Foster, 2008; Anagnostou et al., 2016).

5. CONCLUSION

Culture experiments demonstrate that the Ba/Ca ratios of *N. dutertrei* vary linearly as a function of seawater Ba/Ca ratios, with a $D_{Ba} = 0.11 \pm 0.008$, similar to the D_{Ba} of spinose species ($D_{Ba} = 0.13 \pm 0.004$), and are not influenced by temperature or pH. Nevertheless, intrashell and average Ba/Ca ratios of ocean-grown *N. dutertrei* collected at the same time as cultured specimens are significantly higher and more variable than predicted from Ba/Ca$_{SW}$ and laboratory calibrations in filtered seawater. We suggest that the Ba/Ca geochemistry of *N. dutertrei* is elevated and variable due to calcification in a microenvironment enriched in Ba such as marine snow or other organic particulates. If other deeper dwelling non-spinose species behave similarly in the ocean, this may explain the higher than expected Ba/Ca ratios in *G. truncatulinoides* (Lea and Boyle, 1991), *G. menardii* (Lea and Boyle 1991; Bahr et al., 2013), and *G. scitula* (Hathorne et al., 2009).

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APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.gca.2018.03.008.

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