



PII S0016-7037(00)00563-9

Experimental determination of trace element partition coefficients in cultured benthic foraminifera

SUZANNE M. HAVACH,¹ G. THOMAS CHANDLER,^{1,3} AMY WILSON-FINELLI,² and TIMOTHY J. SHAW^{1,2,*}¹Marine Science Program, University of South Carolina, Columbia, South Carolina 29208, USA²Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, USA³Department of Environmental Health Sciences, University of South Carolina, Columbia, South Carolina 29208, USA

(Received January 3, 2000; accepted in revised form August 23, 2000)

Abstract—We present the first trace metal partition coefficients obtained from reproducing cultures of deep-sea benthic foraminifera. Paleoceanographically important species, including juvenile *Bulimina marginata*, *Cibicidoides pachyderma*, and *Uvigerina peregrina*, were maintained in sediment microcosms at 10°C, 35 psu, and pH 8 for 1–3 years. Juvenile foraminifera were separated, cleaned, and dissolved under clean conditions for determination of trace metal partition coefficients on recently deposited (1–3 months) foraminiferal calcite. In addition to the deep-sea species, we analyzed a shallow water benthic foraminifer, *Ammonia beccarii*. Overlying water samples were collected from the microcosms concurrent to the period of calcification (3 months prior to separation). Ba/Ca partition coefficients (D_{Ba}) were measured in replicate for benthic foraminifera species *Bulimina marginata* (0.24 ± 0.07), *Uvigerina peregrina* (0.24 ± 0.06), *Ammonia beccarii* (0.20 ± 0.04). The D_{Ba} for *Bulimina marginata* and *Uvigerina peregrina* were found to closely match the range from the Ontong Java Plateau. Sample size limitations allowed for only one analysis of D_{Ba} for *Cibicidoides pachyderma*. However, our nonreplicated D_{Ba} of 0.5 ± 0.1 falls within the accepted range of core top samples (0.37 ± 0.06). We report a D_{Cd} for *Ammonia* of 1.0 ± 0.5 , for *Cibicidoides* of 4 ± 2 , for *Bulimina* of 3 ± 1 , and for *Uvigerina* 2 ± 1 which all fall within the ranges reported for core top calibrations. The large uncertainties in D_{Cd} reflect variation in dissolved Cd concentration in the artificial seawater reservoir due to loss and replacement of Cd during the course of the experiment. The variability between species is probably the result of variability in pore water Cd in the sediment culture system and may reflect habitat effects. Copyright © 2001 Elsevier Science Ltd

1. INTRODUCTION

Investigations of ocean circulation, climate change, and ocean chemistry have utilized planktonic and benthic foraminifera for nearly half a century (Emiliani, 1955; Boyle and Keigwin, 1982; Broecker, 1982; Boyle, 1986; Boyle and Keigwin, 1985/86; Delaney and Boyle, 1987; Boyle, 1988; Lea and Boyle, 1990a,b; Dymond et al., 1992; Lynch-Stieglitz and Fairbanks, 1994; Lea, 1995; Ohkouchi et al., 1995; McIntyre et al., 1997; Rosenthal et al., 1997). The calcareous tests of the foraminifera serve as isotopic and trace element tracers of ocean water chemistry at the time of shell formation. Boyle (1981) recognized that if a simple partition coefficient behavior could be demonstrated to control the trace element chemistry of foraminiferal tests, then trace elements like barium and cadmium could be used as proxies for past ocean chemistry. Trace elements with distributions similar to those of nutrients have found specific utility as nutrient proxies. Barium is used as a tracer for silica (refractory nutrients) and alkalinity, while cadmium is useful to describe the distribution of phosphorus (labile nutrients) (Boyle et al., 1976; Chan et al., 1977). The utility of these proxies is dependent on the incorporation of trace elements into foraminiferal calcite at a concentration proportional to their concentration in surrounding waters.

Verification of foraminiferal metal proxies, for benthic species, have relied on trace metal distributions measured on

foraminifera collected from core tops and the overlying seawaters. Lea and Boyle (1989) found that recent core-top foraminifera had Ba/Ca ratios that increased linearly with increasing Ba concentration in the bottom water, resulting in the currently accepted D_{Ba} of 0.37 ± 0.06 . More recently, McCorkle et al. (1995) analyzed core-top *Cibicidoides wuellerstorfi* from the Ontong Java Plateau and found that D_{Ba} , D_{Cd} , and D_{Sr} decreased with water depth. McCorkle et al. (1995) attributed this decrease to a possible preferential loss of the trace elements through dissolution. Hester and Boyle (1982) showed cadmium incorporation into foraminiferal shells, in proportion to overlying bottom water, for core-top species. Boyle (1988) enlarged upon the 1982 study and concluded D_{Cd} was 2.9 ± 0.6 , the currently used value for deep-sea cores. Other cadmium studies have shown that Cd/Ca ratios in benthic foraminifera are proportional to the seawater Cd concentration, but that they depend on the depth of calcification (Boyle, 1992; Ohkouchi et al., 1995). Boyle (1992) derived an empirical water depth vs. D_{Cd} relationship from his global core-top data. Ohkouchi et al. (1995) provided a similar equation for a depth-dependent partition coefficient using their core-top data from the Pacific Ocean. However, scatter was greater than the standard deviation of laboratory standards for Boyle (1988). It was suggested that scatter may result from biological effects, mixing of recent and fossil foraminifera, differences in depth habitat (i.e., pore water vs. bottom water environment), or imperfections in the cleaning procedure prior to analysis.

Culturing experiments with living planktonic foraminifera have also been used to investigate the reliability of foraminifera

* Author to whom correspondence should be addressed (shaw@mail.chem.sc.edu).

as paleotracers and to help resolve scatter observed in foraminifera collected from core tops. Lea and Spero (1992; 1994) concluded that the incorporation of Ba in *Globigerinoides sacculifer* and *Orbulina universa* covaried with seawater concentration, and that Ba uptake does not appear to vary significantly with temperature, salinity, or by individual shells. Delaney (1989) investigated the uptake of radioactive cadmium in solution by planktonic foraminifera and found that Cd/Ca ratios were comparable to D_{Cd} from fossil core-top versus water estimates. Recently published work by Mashiotta et al. (1997) gives contrasting D_{Cd} values for two different planktonic species and found that the species that lacked symbionts was the more faithful recorder of Cd content in the seawater.

Benthic foraminifera may be susceptible to a greater number of potential sources of variability than are planktonic foraminifera due to their environment of calcification. Isotope studies have demonstrated that infaunal species have lower ^{13}C values than epifaunal species, reflecting the difference between pore water composition and bottom water (Grossman, 1984; Corliss, 1985; McCorkle et al., 1990; Wilson-Finelli et al., 1988). The sediment-water interface is strongly influenced by microbial activity, organic matter diagenesis, and calcium carbonate dissolution; in fact, diagenesis of sediments can produce trace element maxima and sharp gradients at and across the interface (Shaw et al., 1990; McCorkle and Klinkhammer, 1991; Paytan and Kastner, 1996).

To begin to assess the impact environment of deposition on trace element uptake, we have utilized our successful microcosm culture facility to measure uptake of Ba and Cd in recently deposited foraminiferal calcite. In this study we present the first partition coefficients obtained from benthic foraminifera in a culture environment. While *Cibicides pachyderma* and *Uvigerina peregrina* are extensively used in core-top studies, other valuable species such as *Melonis barleeanum* (used for Cd data in Rosenthal et al., 1997) and *Bulimina marginata* are abundant in our cultures. *Bulimina marginata* is most often used as a diagnostic species to characterize the marine environment. For example, Sejrup and Knudsen (1993) associated the distribution of *Bulimina marginata* with interglacial periods and differences in ocean circulation patterns. The ability to use this species as a proxy for metal concentrations will provide further information about past ocean conditions. To assess the reliability of foraminifera as tracers, it is essential to identify factors that control benthic foraminiferal partition coefficients through controlled experiments with living cultures.

2. METHODS

2.1. Collection of Tests and Seawater Samples

Deep-sea benthic foraminiferal species were maintained in continuous high-density cultures in a circulating, filtered, artificial (Instant Ocean) seawater system. The foraminifera and sediments for the deep-sea cultures were collected from a depth of 200–250 m and approximately 70 miles off Charleston, SC, at the Charleston Bump Site (31°55'N, 79°11'W). The cultures were kept in sediments in a 10°C environmental chamber and in darkness at a salinity of 35 psu (as chlorinity) and pH 8. The calcite saturation index for the Instant Ocean at 35 psu, 10°C and atmospheric pressure was calculated to be ~3 based on pH and alkalinity measurements using solubility and acid dissociation constants from Stumm and Morgan (1995). The foraminifera, *Ammonia beccarii* and sediments for shallow water cultures

were collected from pristine North Inlet, South Carolina. The shallow water cultures were kept at a salinity of 30 psu and maintained at room temperature with 12 hour light/dark intervals to simulate natural conditions. Sediment was sieved, washed, and autoclaved (after Chandler, 1986). Cultures were fed twice weekly on a diet of centrifuged phytoplankton including *Dunaliella tertiolecta* and *Isochrysis galbana* for the deep-sea cultures and heat-shocked centrifuged algae including the diatom *Phaeodactylum tricorutum* for the shallow water cultures.

To obtain D_{TE} for the stock cultures, juvenile *Bulimina marginata*, *Cibicides pachyderma*, and *Uvigerina peregrina* were collected between 90 and 150 μ m stainless steel sieves. The size fraction used in this study (<150 μ m) was smaller than used in published studies, but was necessary to insure that only juvenile foraminifera containing recently precipitated calcite were analyzed. The collected sediment fraction was stained with Rose Bengal to distinguish live from empty individuals and to facilitate sorting of juveniles with a small paint brush. Juveniles were collected because their calcification period could be constrained to within a few months. Water samples were collected concurrently with the calcification period, beginning at least 3 months prior to separation of the juvenile foraminifera. Water samples were extracted from the culture chambers with an acid cleaned syringe and expressed through an acid cleaned 0.2 μ m Gelman Supor® filter in an acid cleaned 4 ml polystyrene sample vial. Samples were later acidified with double-distilled HNO_3 to a pH < 2.

2.2. Cleaning of Tests

The collected foraminiferal tests were subjected to a cleaning procedure to ensure that only the barium and cadmium incorporated into the calcite shell was measured. The original protocol from Boyle (1981) and Boyle and Keigwin (1985/86) has been slightly modified for our samples. The initial cleaning step was designed to remove all traces of protoplasm from the tests. This was the essential step since our cultured foraminifera were full of algal-rich material. The tests were placed in 35 × 10 mm petri dishes and soaked for three consecutive 24 hour periods in bleach (sodium hypochlorite 5.25% by weight) with five deionized water rinses between each bleaching period. After the final water rinse the dishes were placed in a 100°C oven for at least 12 hours to completely dry the tests. Replicates of each species were then weighed on a Sartorius S4 microbalance and the tests were transferred intact to acid-cleaned Teflon 0.5 ml centrifuge vials. Approximately 150–250 individual foraminifera yielded samples of 165–261 μ g, substantially less than those samples routinely extracted from the field (e.g., Lea and Boyle, 1990b). Therefore, we had to allow adjustments in sample handling to accommodate our smaller sample size. Normally the tests are crushed between glass plates before they are brushed into vials. However, preliminary trials indicated substantial material was lost when the extremely fine fragments resulting from the crushed juveniles were transferred, and this step was omitted.

The remaining cleaning procedures were conducted in a class 10,000 clean room under a class 100 laminar flow hood. The protocol continued with a series of E-pure™ (18 M Ω cm water) and clean methanol rinses in between ultrasonic agitation to remove fine clays. The reducing reagent reaction time was adjusted downward for our small sample size. We did not employ the DTPA treatment designed to remove sedimentary barite (after Lea and Boyle, 1993) because DTPA dissolves both barite and calcite, making it a concern for small sample sizes. After the samples were transferred to new, clean, Teflon 0.5 ml centrifuge vials, a single weak acid (0.001 N HNO_3) leach was performed but removed as soon as the tests had resettled in the tube. Once the cleaning was complete the tests were dissolved in double-distilled 0.075 N HNO_3 . To determine if dissolution was complete and Ca concentrations were uniform, a few μ l of each sample was placed on pH paper (after Lea and Boyle, 1993). All pH values were 1.0–1.5.

2.3. Analysis by Isotope Dilution ICP-MS

Foraminiferal and seawater samples were analyzed on our Finnigan Element ICP-MS. Sample metal concentrations were quantified by isotope dilution to compensate for changes in instrumental sensitivity/matrix effects during any particular run. Samples were spiked with isotope-enriched solutions, analyzed for isotope ratios, and quantified

using the appropriate isotope dilution equation (after Klinkhammer and Chan, 1990).

Two independent standards were measured during each run to assess mass fractionation and error involved with isotope dilution on our ICP-MS. First, the natural ratio of an isotope pair was monitored with nonspiked consistency standards. These included an artificial seawater standard and a coral standard (provided by Glen Shen). The machine-measured ratio was substituted into the isotope dilution equation for the ideal ratio to correct for mass fractionation and resulted in a correction of less than 1% in concentration calculations. A second standard, made from spiked Ultragrade Ba and Ca standards, was used to monitor the accuracy of the method. For the seawater runs, these standards had an error of 2–3% and a precision (or RSD) of 3%. The precision of the coral standard during Ba/Cd and Ca foraminiferal runs was 2% or less, while the RSD for duplicate analysis of calcium in a foraminifera sample was 2%.

2.3.1. Barium and cadmium in seawater

A ^{135}Ba and ^{111}Cd enriched spike with known ^{138}Ba and ^{114}Cd was used to analyze barium and cadmium in both the seawater samples and foraminiferal calcite. Seawater samples were diluted by a factor of 10 with 5% HNO_3 to minimize matrix effects. Samples were then spiked with an aliquot of the $^{135}\text{Ba}/^{111}\text{Cd}$ spike to obtain a ratio of $^{135}/^{138}\text{Ba}$ near 1.55 and a $^{111}/^{114}\text{Cd}$ ratio near 8.4. These target ratios are the geometric mean of the ratio of spike isotope: quantified isotope occurring naturally and in the spike and give the minimum amount of random error (Webster, 1960). Our ratios ranged from 5.06 to 21.71 for cadmium and 0.89 to 1.56 for barium, an acceptable range for accurate ICP-MS results (Klinkhammer and Chan, 1990). During all cadmium runs, ^{120}Sn was monitored so that a correction could be made for the ^{114}Sn isobar interfering on ^{114}Cd . Seawater and foram samples were run using the CETAC MCN 6000 to minimize oxide interferences from Mo species. Natural ratios were monitored to detect possible interfering oxide species. We observed a variation in the Cd concentration in the artificial seawater reservoirs over time associated with loss of Cd to the sediments, loss to the carbon filter system and regular addition of a new Instant Ocean. Thus the range in Cd concentration reported represents a concentration range, not analytical error (discussed below).

2.3.2. Barium and cadmium in foraminiferal calcite

The barium and cadmium concentrations in the foraminiferal calcite were measured similarly to the seawater samples. The 40 μl of dissolved foraminiferal solution was spiked with 40 μl of ^{135}Ba and ^{111}Cd enriched spike and diluted to 120 μl with 0.075 N HNO_3 . Barium target ratios for values included in computed averages ranged from 0.94 to 3.02, while the cadmium ratios for averaged values ranged from 3.74 to 18.38. All raw data was checked for unusual variation (signal spikes) and signal suppression. We observed evidence of signal suppression in the raw data at count rates greater than 5×10^6 counts per second (cps) for the Ba analysis. These high count rates were only observed at the peak center (when the center of the ion beam was focussed on the detector). Therefore, we calculated ratios based on a narrow mass window by integrating the counts from the leading edge of the ion beam (the leading peak shoulder rather than the peak center). All ratios for Ba were calculated for the same narrow mass window. Replicate ratios for the coral standard measured on the peak shoulder had a precision of better than 1%. The peak shoulder integrations were below detector saturation for all samples and precision standards. However, the accuracy standard for the foraminiferal calcite analyses showed excessive counts even on the shoulder of the ^{138}Ba peak (right at 6×10^6 cps). This resulted in obvious signal suppression through the run (even affecting the Cd counts). Thus we used the more conservative accuracy results from subsequent artificial seawater analyses for our error calculations (better than 5%).

2.3.3. Calcium in the seawater and foraminiferal calcite

Ca was also measured by isotope dilution using a ^{43}Ca enriched spike with known ^{44}Ca . Ca has previously been measured in seawater and foraminiferal calcite by flame atomic absorption (e.g., Lea and Spero, 1992; Lea and Boyle, 1993; Lea and Spero, 1994). Lea and

Martin (1996) used internal calibration with scandium to measure calcium on a VG Elemental PlasmaQuad 2+ Turbo ICP-MS. The VG PlasmaQuad used in Lea and Martin's study was a quadrupole-based instrument as opposed to our ICP mass spectrometer which is a double focusing sector field instrument. An advantage of a sector field instrument such as the Finnigan MAT Element is the ability to work at higher resolution settings to determine accurate ratios of elements that have interferences (Vanhaecke et al., 1997). Thus, we used a medium resolution setting ($R = 3,000$) to resolve the calcium analyte signal from several interferences (such as ^{40}Ar). Seawater samples were diluted 1 to 50 with 5% HNO_3 and spiked to achieve the target ratio for $^{43}\text{Ca}/^{44}\text{Ca}$ of 1.08. Actual target values during the seawater runs were 1.07–1.54. Dissolved foraminifera aliquots of 20 μl were spiked with 10 μl of ^{43}Ca -enriched spike and brought to a final volume of 500 μl with 0.075 N HNO_3 . Foraminiferal target ratios were 0.68–1.36.

The resulting Ba and Ca concentrations were used to construct a partition coefficient for each foraminiferal replicate according to the following expression:

$$D_{\text{Ba}} = (\text{Ba}/\text{Ca})_{\text{calcite}}/(\text{Ba}/\text{Ca})_{\text{seawater}}$$

Similarly, Cd/Ca ratios in the foraminiferal calcite were calculated or matched with the Cd/Ca ratio in the culture seawater for D_{Cd} .

3. RESULTS AND DISCUSSION

3.1. Calculated Partition Coefficients

3.1.1. Barium in foraminiferal calcite and partition coefficients

Table 1 illustrates the concentrations of Ba/Ca ratios in the artificial seawater and element ratios in the foraminiferal calcite. Artificial seawater had a Ba concentration higher than the range of typical deep ocean waters. The seawater barium concentrations in the deep-sea cultures were $0.50 \pm 0.03 \mu\text{mol}/\text{kg}$. In the *Ammonia* cultures, seawater concentrations were $0.46 \pm 0.01 \mu\text{mol}/\text{kg}$ barium. Artificial seawater had a Ca concentration slightly lower than the range of typical deep ocean waters. Calcium concentrations were $8.6 \pm 0.9 \text{ mmol}/\text{kg}$ and $7.5 \pm 0.1 \text{ mmol}/\text{kg}$ in the deep-sea and *Ammonia* culture seawater, respectively. The range in concentrations for Ca and Ba reflect actual variations over the course of the experiment rather than analytical uncertainty. Much of the variation in Ca and Ba was due to evaporation and periodic dilution, thus the absolute concentrations tended to co-vary with time, resulting in a lower range in the ratio.

Calcite results for *Bulimina marginata*, *Cibicidoides pachyderma*, *Uvigerina peregrina*, and *Ammonia beccarii*, when matched with appropriate seawater concentrations, give values for D_{Ba} . Our *Cibicidoides* D_{Ba} value of 0.5 ± 0.1 falls in the range of the accepted mean value of 0.37 ± 0.06 , while the D_{Ba} s for other species (*Bulimina marginata* 0.24 ± 0.07 , *Uvigerina peregrina* 0.24 ± 0.06 , *Ammonia beccarii* 0.20 ± 0.04) are similar to the range of values (0.313–0.221) obtained by McCorkle et al. (1995).

3.1.2. Cadmium in foraminiferal calcite and partition coefficients

Table 2 summarizes the Cd/Ca ratios in the foraminiferal calcite, cadmium concentrations in the *Ammonia* culture seawater, and the resulting D_{Cd} for *Ammonia beccarii*. While barium values in Instant Ocean were considerably higher than those found in the modern ocean (Chan et al., 1977), average cadmium concentrations were slightly above the high end of

Table 1. Barium partition coefficients, D_{Ba} , from barium and calcium analyses in foraminiferal calcite and culture seawater. Results from previous field studies are included for comparison. Sample size is the weight of foraminiferal calcite per sample before the cleaning procedure was performed.

	D_{Ba}	Ba/Ca calcite $\mu\text{mol/mol}$	Ba/Ca seawater $\mu\text{mol/mole}$	Sample size $\mu\text{g calcite}$
<i>Cibicides pachyderma</i>	0.5 ± 0.1	29 ± 2	55 ± 2	44
<i>Uvigerina peregrina</i>	0.19	10.79		181
<i>Uvigerina peregrina</i>	0.28	16.02		221
<i>Uvigerina peregrina</i>	0.23	13.11		232
Mean ± 1σ	0.24 ± 0.06	13 ± 3		
<i>Bulimina marginata</i>	0.27	15.84		217
<i>Bulimina marginata</i>	0.17	10.00		206
Mean ± 1σ	0.24 ± 0.07	13 ± 2		
<i>Ammonia beccarii</i>	0.20	12.4	62 ± 2	207
<i>Ammonia beccarii</i>	0.20	12.6		165
Mean ± 1σ	0.20 ± 0.04	12.5 ± 0.6		
Lea and Boyle (1989)	0.37 ± 0.06	1.8–5.0	5–13	600
<i>Uvigerina</i> spp., <i>C. wuellerstorfi</i> , <i>C. kullenbergi</i>	water depth generally ≥2.5 km			
McCorkle et al. (1995)	0.313–0.221	2.8–3.9	11–13	300–700
<i>C. wuellerstorfi</i>	decreasing with depth 1–4 km			

bottom water values (Boyle et al., 1976) at 1.1 ± 0.5 nm/kg. We observed that the Cd concentration in our culture systems was not conservative over time, varying as a function of loss of Cd to the sediments/carbon filter system and regular addition of Cd with the new Instant Ocean. The frequency of the variation was relatively short (less than 1 month) compared to the period

of calcification for the juvenile foraminifera (1–3 months). Thus the range in Cd concentration reported represents an average concentration range during calcification, not analytical error. We were able to maintain the Cd concentration in a relatively narrow concentration range over the course of the experiments (9 months). However, we report the short-term

Table 2. Cadmium partition coefficients, D_{Cd} , from cadmium and calcium analyses in foraminiferal calcite and culture seawater. Results from previous field studies are included for comparison.

	D_{Cd}	Cd/Ca calcite $\mu\text{mol/mol}$	Cd/Ca seawater $\mu\text{mol/mole}$	Sample size $\mu\text{g calcite}$
<i>Cibicides pachyderma</i>	4 ± 2	0.49 ± 0.07	0.12 ± 0.05	44
<i>Uvigerina peregrina</i>		0.15		181
<i>Uvigerina peregrina</i>		0.12		221
<i>Uvigerina peregrina</i>		0.28		232
Mean ± 1σ	2 ± 1	0.18 ± 0.09		
<i>Bulimina marginata</i>		0.38		217
<i>Bulimina marginata</i>		0.37		209
Mean ± 1σ	3 ± 1	0.38 ± 0.06[#]		
<i>Ammonia beccarii</i>	0.8	0.14	0.17 ± 0.08	207
<i>Ammonia beccarii</i>	1.1	0.19		165
Mean ± 1σ	1.0 ± 0.5	0.17 ± 0.04		
Boyle (1988)		0.050–0.25	0.01–0.08	
<i>Uvigerina</i> spp., <i>C. wuellerstorfi</i> , <i>C. kullenbergi</i> , <i>N. umbonifera</i>	2.9 ± 0.6 water depth generally ≥3 km			
Boyle (1992)	1.3 for depth <1,150 m Empirically defined for 1–3 km	0.050–0.25	0.02–0.09	
<i>Uvigerina</i> spp., <i>C. wuellerstorfi</i> , <i>C. kullenbergi</i> , <i>N. umbonifera</i>	2.9 for depth > 3,000 m			
McCorkle et al. (1995)	2.54–1.30	0.09–0.20	0.07–0.09	
<i>C. wuellerstorfi</i>	decreasing with depth 1–4 km			
Ohkouchi et al. (1995)	1.3 for depth < 1,150 m Empirically defined for 1–4 km	0.08–0.30	0.05–0.2	
<i>C. wuellerstorfi</i>	2.3 for depth > 4,000 m			

[#] *Bulimina* mean Cd/Ca is significantly different ($P < 0.10$) from the mean Cd/Ca for *Uvigerina* or *Ammonia*.

variability as uncertainty to reflect the limitations on our reported partition coefficients produced by the nonconservative behavior of Cd in our culture system. The calculated D_{Cd} for *Ammonia* of 1.0 ± 0.5 , for *Cibicidoides* of 4 ± 2 , for *Bulimina* of 3 ± 1 , and for *Uvigerina* 2 ± 1 all fall within the ranges reported for core top calibrations. Even with the variability associated with the cadmium concentrations in the seawater, the precision of ratios in foraminiferal calcite replicates allows us to make comparisons among the four species.

3.2. Variation in Calculated Partition Coefficients

3.2.1. Interspecies differences

The *Cibicidoides* value appears to be higher relative to the other species for both Ba/Ca and Cd/Ca and is most similar to the available field data for samples collected from greater than 3 km depth. There is no published data to indicate that significant interspecies differences in metal uptake exists, although Lea and Boyle (1989) speculated that *Cibicidoides* was a more reliable indicator because the relationship between barium in its calcite and barium in the seawater showed the least scatter. In addition to the observed difference between *Cibicidoides* and other species, our data show that there is a statistically significant difference ($P < 0.10$) between the Cd/Ca in the tests of *Bulimina* when compared to Cd/Ca in *Uvigerina* or *Ammonia* tests. This interspecific variability may be the result of a habitat effect. Habitat or depth preference effects have been demonstrated in our cultures (Chandler et al., 1996; Wilson-Finelli et al., 1998). For example, Wilson-Finelli et al. (1998) found that, in culture, *Uvigerina* juveniles were more often found at greater depths than were *Bulimina* juveniles. While field studies do not allow an absolute depth assignment for each species in this study, we include field observations for comparison. Field data indicate that *Cibicidoides pachyderma* lives epifaunally, while *Uvigerina peregrina* is described as shallow infaunal or simply infaunal (e.g., Corliss, 1991; McCorkle et al., 1997). Likewise, *Ammonia beccarii* is reported to be infaunal (Frankel, 1975). It is more difficult to assign *Bulimina marginata* to a habitat because it has been described as both epifaunal and infaunal (see Murray, 1991), with its location dependent on the surrounding microenvironment (Barmawidjaja et al., 1992).

It is possible that the cadmium in the pore water varied relative to the overlying water, depending on the chemistry of the sediment at a particular horizon (Klinkhammer et al., 1982; McCorkle and Klinkhammer, 1991). The sampled overlying water may not accurately reflect the cadmium levels encountered by some calcifying foraminifera, particularly those with an infaunal habitat. *Cibicidoides* is generally thought to be free from pore water influences on its shell chemistry (e.g., McCorkle et al., 1990; 1995). However, differences in the Cd content between *Cibicidoides*, *Bulimina*, and *Uvigerina* in the deep-sea cultures may be related to their positions in the sediment culture. Barium concentrations from overlying to pore water are not expected to be as variable in these oxic sediments, and probably do not account for the difference between the D_{Ba} for *Cibicidoides* and remaining species (Dymond et al., 1992). We cannot negate the possibility that species variability is a result of differences in uptake mechanisms, or biological effects. However, isotopic equilibrium with bottom water is

known to vary with species due to microhabitat preferences (e.g., Grossman, 1987; McCorkle et al., 1990; Rathburn et al., 1996).

It is noteworthy that *Ammonia* partition coefficients are very similar to those for deep-sea species. *Ammonia* juveniles reach adequate calcite mass in approximately 2 weeks, while the deep-sea juveniles take at least five times that long (G. T. Chandler, personal communication). This suggests that the faster rate with which *Ammonia* calcifies after release from the adult does not greatly affect metal uptake. Lea and Spero (1992) made a similar conclusion after culturing planktonic foraminifera under conditions of low and high light. Although individuals grown under low light had smaller, more fragile shells, there was no significant difference in Ba/Ca values compared to their high-light counterparts, suggesting that the expected slower calcification taking place under low light was not an important factor in metal uptake kinetics (Lea and Spero, 1992).

3.2.2. The role of pressure effects on partition coefficients

It has previously been observed that the D_{Ba} for planktonic foraminifera is about one-half that for benthic foraminifera. This divergence has been attributed to differences in environmental factors. In addition to the low/high-light study of 1992, Lea and Spero (1994) found that culturing planktonic foraminifera over a 7°C temperature and 3 ppt salinity range did not significantly change Ba/Ca shell values. While these were relatively small ranges compared to ocean water column changes, the lack of any temperature or salinity effect might suggest that these parameters are not strong influences on barium uptake. An untested factor influencing benthic foraminifera is the effect of pressure on metal incorporation. Several studies have observed variability in D_{TE} with depth (see Tables 1 and 2 for comparison of published results). Boyle (1992) could not explain the depth-dependent incorporation of Cd in his study but suggested it may be more likely related to pressure than to temperature. McCorkle et al. (1995) attributed their depth dependence of Ba, Cd, and Sr to preferential dissolution of those trace elements from foraminiferal calcite. The aragonitic foraminifer *Hoeglundina elegans* did not exhibit any clear depth dependence in the Boyle et al. (1995) study, perhaps due to differences in the aragonitic calcium carbonate structure. Our benthic foraminifera are calcifying at atmospheric pressure, yet have D_{Ba} similar to field samples from both shallow and deep cores. Our results indicate that pressure effects do not have a strong influence on benthic foraminiferal trace element uptake. These results support the McCorkle et al. (1995) hypothesis of depth dependent dissolution.

3.2.3. Variability resulting from the culture system design

We experienced higher variability in the seawater element concentrations than expected due to the reservoir size of the culturing system and reactivity of Cd with the culture components. All cultures were open to atmosphere and circulated through a double carbon-filter water-polishing system. Periodically, deionized water or Instant Ocean was added to maintain the correct salinity and a calcium carbonate and borate buffer was added to elevate the pH to at least 8 when necessary. These

small fluctuations in chemistry may account for some of the variability of foraminiferal Ba/Ca ratios due to preferential trace element dissolution as described in McCorkle et al. (1995). In addition, D_{TE} variance may have been caused by the use of a natural sediment substrate for foraminiferal culture. A natural sediment culturing approach was not ideal for D_{Cd} studies because cadmium was scavenged from the overlying culture seawater, and was likely at a different concentration in the pore water. The loss of Cd to the sediments/carbon filter system and addition of Cd with fresh Instant Ocean account for most of the reported uncertainty in the D_{Cd} . Fortunately, the frequency of variation was relatively short compared to the calcification period of the juvenile foraminifera.

4. CONCLUSIONS

This preliminary work on trace metal uptake by cultured deep-sea benthic foraminifera yields partition coefficients that fall within the range of field data for D_{Ba} , and D_{Cd} . We determined D_{Ba} s for *Cibicidoides pachyderma* of 0.5 ± 0.1 , for *Bulimina marginata* of 0.24 ± 0.07 , for *Uvigerina peregrina* of 0.24 ± 0.06 , and for the shallow water species *Ammonia beccarii* of 0.20 ± 0.04 . We determined a D_{Cd} for *Cibicidoides* of 4 ± 2 , for *Bulimina* of 3 ± 1 , for *Uvigerina* 2 ± 1 and for *Ammonia* of 1.0 ± 0.5 . We observed species variability in Cd/Ca in the cultured foraminiferal calcite that may reflect either real differences in uptake mechanisms or possible habitat effects. The concentration of Cd in this natural sediment culture system was difficult to maintain resulting in a high level of uncertainty in our D_{Cd} results. Our D_{TE} results for cultures at atmospheric pressure indicate no consistent variation from deep ocean core top results that would indicate any significant pressure effect on TE uptake. The variability of replicate D_{TE} will improve, as metal concentrations in the culture system are better constrained.

Acknowledgements—We thank the captain and crew of the R/V Cape Hatteras for their help and support during numerous collection cruises. We thank Ed Boyle for helpful input on our (his) cleaning procedure, our analytical techniques, experimental design, and his insightful review of this paper. This paper also benefited from the helpful comments of Harry Elderfield, David Lea, and Chris German. We also acknowledge support from NSF Grant No. 95047933.

Associate editor: C. R. German

REFERENCES

- Barmawidjaja D. M., Jorissen F. J., Puskaric S., and Van Der Zwaan G. J. (1992) Microhabitat selection by benthic foraminifera in the northern Adriatic Sea. *J. Foram. Res.* **22**, 297–317.
- Boyle E. A. (1981) Cadmium, zinc, copper, and barium in foraminifera tests. *Earth Planet. Sci. Lett.* **53**, 11–35.
- Boyle E. A. (1986) Paired carbon isotope and cadmium data from benthic foraminifera: Implications for changes in oceanic phosphorus, oceanic circulation, and atmospheric carbon dioxide. *Geochim. Cosmochim. Acta* **50**, 265–276.
- Boyle E. A. (1988) Cadmium: Chemical tracer of deepwater paleoceanography. *Paleoceanography* **3**, 471–89.
- Boyle E. A. (1992) Cadmium and $\delta^{13}C$ paleochemical ocean distributions during the stage 2 glacial maximum. *Annu. Rev. Earth Planet. Sci. Lett.* **20**, 245–87.
- Boyle E. A. and Keigwin L. D. (1982) Deep circulation of the North Atlantic over the last 200,000 years: Geochemical evidence. *Science* **218**, 784–787.
- Boyle E. A. and Keigwin L. D. (1985/86) Comparison of Atlantic and Pacific paleochemical records for the last 215,000 years: Changes in deep ocean circulation and chemical inventories. *Earth Planet. Sci. Lett.* **76**, 135–150.
- Boyle E. A., Sclatter F., and Edmond J. M. (1976) On the marine geochemistry of cadmium. *Nature* **263**, 42–44.
- Boyle E. A., Labeyrie L., and Duplessy J. (1995) Calcitic foraminiferal data confirmed by cadmium in aragonitic *Hoeglundina*: Application to the last glacial maximum in the northern Indian Ocean. *Paleoceanography* **10**, 881–900.
- Broecker W. S. (1982) Ocean chemistry during glacial time. *Geochim. Cosmochim. Acta* **46**, 1689–1705.
- Chan L. H., Drummond D., Edmond J. M., and Grant B. (1977) On the barium data from the Atlantic GEOSECS Expedition. *Deep-Sea Res.* **24**, 613–649.
- Chandler G. T. (1986) High density culture of meiobenthic harpacticoid copepods within a muddy sediment substrate. *Can. J. Fish. Aquat. Sci.* **43**, 53–59.
- Corliss B. H. (1985) Microhabitats of benthic foraminifera within deep-sea sediments. *Nature* **314**, 435–438.
- Corliss B. H. (1991) Morphology and microhabitat preferences of benthic foraminifera from the northwest Atlantic Ocean. *Marine Micropaleontology* **17**, 195–236.
- Delaney M. L. (1989) Uptake of cadmium into calcite shells by planktonic foraminifera. *Chem. Geology* **78**, 159–165.
- Delaney M. L. and Boyle E. A. (1987) Cd/Ca in late Miocene benthic foraminifera and changes in the global organic carbon budget. *Nature* **330**, 156–159.
- Dymond J., Suess E., and Lyle M. (1992) Barium in deep-sea sediment: A geochemical proxy for paleoproductivity. *Paleoceanography* **7**, 163–181.
- Emiliani C. (1955) Pleistocene temperatures. *J. Geology* **63**, 538–578.
- Frankel L. (1975) Subsurface feeding in foraminifera. *J. Paleontology* **49**, 563–565.
- Grossman E. L. (1984) Carbon isotope fractionation in live benthic foraminifera—comparison with inorganic precipitation studies. *Geochim. Cosmochim. Acta* **48**, 1505–1512.
- Grossman E. L. (1987) Stable isotopes in modern benthic foraminifera: A study of vital effect. *J. Foram. Res.* **17**, 48–61.
- Hester K. and Boyle E. A. (1982) Water chemistry control of the Cd content of benthic foraminifera. *Nature* **298**, 260–261.
- Klinkhammer G., Heggge D. T., and Graham D. W. (1982) Metal diagenesis in oxic marine sediments. *Earth Planet. Sci. Lett.* **61**, 211–219.
- Klinkhammer G. P. and Chan L. H. (1990) Determination of barium in marine waters by isotope dilution inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* **232**, 323–329.
- Lea D. W. (1995) A trace metal perspective on the evolution of Antarctic Circumpolar Deep Water chemistry. *Paleoceanography* **10**, 733–747.
- Lea D. W. and Boyle E. A. (1989) Barium content of benthic foraminifera controlled by bottom-water composition. *Nature* **338**, 751–753.
- Lea D. W. and Boyle E. A. (1990a) A 210,000-year record of barium variability in the deep northwest Atlantic Ocean. *Nature* **347**, 269–272.
- Lea D. W. and Boyle E. A. (1990b) Foraminiferal reconstructions of barium distributions in water masses of the glacial oceans. *Paleoceanography* **5**, 719–742.
- Lea D. W. and Boyle E. A. (1993) Determination of carbonate-bound barium in foraminifera and corals by isotope dilution plasma-mass spectrometry. *Chem. Geol.* **103**, 73–84.
- Lea D. W. and Spero H. J. (1992) Experimental determination of barium uptake in shells of the planktonic foraminifera *Orbulina universa* at 22°C. *Geochim. Cosmochim. Acta* **56**, 2673–2680.
- Lea D. W. and Spero H. J. (1994) Assessing the reliability of paleochemical tracers: Barium uptake in the shells of planktonic foraminifera. *Paleoceanography* **9**, 445–452.
- Lea D. W. and Martin P. A. (1996) A rapid mass spectrometric method for the simultaneous analysis of barium, cadmium, and strontium in foraminifera shells. *Geochim. Cosmochim. Acta* **60**, 3143–3149.
- Lynch-Steglitz J. and Fairbanks R. G. (1994) A conservative tracer for glacial ocean circulation from carbon isotope and paleo-nutrient measurements in benthic foraminifera. *Nature* **369**, 308–310.

- Mashiotta T. A., Lea D. W., and Spero H. J. (1997) Experimental determination of cadmium uptake in shells of the planktonic foraminifera *Orbulina universa* and *Globigerina bulloides*: Implications for surface water paleoreconstructions. *Geochim. Cosmochim. Acta* **61**, 4053–4065.
- McCorkle D. C. and Klinkhammer G. P. (1991) Porewater cadmium geochemistry and the porewater cadmium $\delta^{13}\text{C}$ relationship. *Geochim. Cosmochim. Acta* **55**, 161–168.
- McCorkle D. C., Corliss B. N., and Emerson S. R. (1990) The influence of microhabitats on the carbon isotope composition of deep-sea benthic foraminifera. *Paleoceanography* **5**, 161–185.
- McCorkle D. C., Corliss B. H., and Farnham C. A. (1997) Vertical distributions and stable isotopic compositions of live (stained) benthic foraminifera from the North Carolina and California continental margins. *Deep Sea Res. I* **44**, 983–1024.
- McCorkle D. C., Martin P. A., Lea D. W., and Klinkhammer G. P. (1995) Evidence of a dissolution effect on benthic foraminiferal shell chemistry: $\delta^{13}\text{C}$, Cd/Ca, Ba/Ca, and Sr/Ca results from the Ontong Java Plateau. *Paleoceanography* **10**, 699–714.
- McIntyre K., Ravelo A. C., Delaney M. L., Anderson L. D., and Johannessen T. (1997) Ground truthing the Cd/Ca-carbon isotope relationship in foraminifera of the Greenland-Iceland-Norwegian Seas. *Mar. Geol.* **140**, 61–73.
- Murray J. W. (1991) *Ecology and Palaeoecology of Benthic Foraminifera*. Addison-Wesley.
- Ohkouchi N., Kawahata H., Okada M., Murayama M., Matsumoto E., Nakamura T., and Taira A. (1995) Benthic foraminifera cadmium record from the western equatorial Pacific. *Mar. Geol.* **127**, 167–180.
- Paytan A. and Kastner M. (1996) Benthic Ba fluxes in the central equatorial Pacific, implications for the oceanic Ba cycle. *Earth Planet. Sci. Lett.* **142**, 439–450.
- Rathburn A. E., Corliss B. H., Tappa K. D., and Lohmann K. C. (1996) Comparisons of the ecology and stable isotopic compositions of living (stained) benthic foraminifera from the Sulu and South China Seas. *Deep-Sea Res. I* **43**, 1617–1646.
- Rosenthal Y., Boyle E. A., and Labeyrie L. (1997) Last glacial maximum paleochemistry and deepwater circulation in the Southern Ocean: Evidence from foraminiferal cadmium. *Paleoceanography* **12**, 787–796.
- Sejrup H. P. and Kundsén K. L. (1993) Paleoenvironments and correlations of interglacial sediments in the North Sea. *Boreas* **22**, 223–235.
- Shaw T. J., Gieskes J. M., and Jahnke R. A. (1990) Early diagenesis in differing depositional environments: The response of transition metals in pore water. *Geochim. Cosmochim. Acta* **54**, 1233–1246.
- Stumm W. and Morgan J. J. (1995) *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*. Wiley.
- Vanhaecke F., Moens L., Dams R., Papadakis I., and Taylor P. (1997) Applicability of high-resolution ICP-mass spectrometry for isotope ratio measurements. *Anal. Chem.* **69**, 268–273.
- Webster R. K. (1960) Mass spectrometric isotope dilution analysis. In *Methods of Geochemistry* (eds. A. A. Smales and L. R. Wagner), pp. 202–246. Interscience.
- Wilson-Finelli A., Chandler G. T., and Spero H. J. (1998) Reliability of benthic foraminiferal calcite as proxy for paleoceanographic conditions: Results from Microcosm culture experiments. *J. Foram. Res.* **28**, 52–60.