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Testing the utility of paleonutrient proxies Cd/Ca and Zn/Ca in benthic foraminifera from thermocline waters

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[1] Reconstruction of oceanic nutrient concentrations in the past provides information about nutrient cycling and physical circulation and the role these processes have played in past climate changes. The Cd/Ca and Zn/Ca of benthic foraminifera have been used successfully to reconstruct past deep ocean nutrient concentrations. In this study we test the ability of benthic foraminiferal Cd/Ca and Zn/Ca to detect changes in thermocline nutrient concentrations using a set of 31 multicores collected in the Florida Straits. Multicore sites span depths of 173–751 m, estimated seawater Cd concentrations of 0.02–0.42 nmol kg^{-1}, and estimated seawater Zn concentrations of 0.3–3.1 nmol kg^{-1}. Cd/Ca in several taxa of benthic foraminifera captures the regional differences and general shape of the nutricline on either side of the Florida Straits, indicating that it is capable of resolving small changes in upper ocean nutrient concentrations in the past. We estimate that the upper ocean partition coefficient for calcitic Cd/Ca may be slightly higher than the established value. Low seawater Zn concentrations combined with low partition coefficients and slight laboratory contamination severely complicated the evaluation of benthic foraminiferal Zn/Ca. However, at least one species, *C. pachyderma*, incorporates Zn with a relatively high partition coefficient (~22), minimizing these complications. *C. pachyderma* Zn/Ca reflects the regional differences and general shape of the nutricline on either side of the Florida Straits and demonstrates potential for thermocline paleoceanography.

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1. Introduction

[2] Reconstructing marine nutrient concentrations and patterns in the past is an important objective of paleoceanographers. Paleonutrient reconstructions provide insights into the operation of the biological pump, as well as changes in the physical circulation of the ocean on a variety of time scales. These reconstructions are derived from a variety of geochemical proxies recorded in marine sediments. Three of these proxies involve the concentrations of trace metals incorporated into the calcium carbonate shells of benthic foraminifera: Cd/Ca, Zn/Ca, and Ba/Ca. Cadmium displays a labile nutrient-type distribution in seawater, and is well correlated with phosphate [*Boyle et al.*, 1976; *Boyle*, 1988;

Elderfield and Rickaby, 2000]. Zinc displays a refractory nutrient-type distribution with a deeper regeneration cycle than phosphate; zinc is well correlated with silica in the ocean [*Bruland et al.*, 1978; *Bruland and Franks*, 1983; *Martin et al.*, 1993]. Barium also displays a refractory nutrient-type distribution but with a lesser surface depletion than Zn, and is therefore well correlated with alkalinity [*Lea and Boyle*, 1989; *Lea*, 1993]. Cd, Zn and Ba are incorporated into the calcium carbonate tests of benthic foraminifera in proportion to seawater Cd, Zn and Ba concentrations, respectively [*Hester and Boyle*, 1982; *Lea and Boyle*, 1989; *Marchitto et al.*, 2000]. In this study we focus on Cd/Ca and Zn/Ca.

[3] Cd/Ca of benthic foraminifera has been used extensively to investigate patterns of past deep ocean circulation [e.g., *Bertram et al.*, 1995; *Beveridge et al.*, 1995; *Boyle*, 1992; *Boyle and Keigwin*, 1982, 1985; *Marchitto and Broecker*, 2006; *Rosenthal et al.*, 1997a]. More recently, benthic foraminiferal Cd/Ca has been used to reconstruct changes in upper ocean circulation [*Came et al.*, 2008; *Marchitto et al.*, 1998; *van Geen et al.*, 1996; *Willamowski and Zahn*, 2000; *Zahn and Stuber*, 2002]. Cd/Ca in planktonic foraminifera has also been used to reconstruct sea surface nutrient concentrations [*Elderfield and Rickaby*, 2000; *Rickaby et al.*, 2000; *Rosenthal et al.*, 1997a]. Zn/Ca is a less established paleonutrient proxy, but it has been used to investigate deep ocean circulation and carbonate saturation [*Marchitto et al.*, 2002, 2005]. *Boyle et al.* [1995] and *Rosenthal et al.* [1997b] first demonstrated that Cd/Ca in benthic foraminifera can measure the increase in [Cd] with water depth in the nutricline, using core tops from the Bahama Banks. Waters within the thermocline reflect conditions at the higher-latitude sea surface where corresponding isopycnals outcrop, as well as the strength of the thermocline ventilation and the biological recycling of nutrients [*Luyten et al.*, 1983; *Slowey and Curry*, 1995]. In this study we test the ability of benthic foraminiferal Cd/Ca to record small changes in regional nutricline concentrations using a set of sediment core tops from both sides of the Florida Straits. We also present the first benthic foraminiferal Zn/Ca measurements from the upper ocean and demonstrate the potential of Zn/Ca for thermocline paleoceanography.

2. Materials and Methods

[4] Samples for these calibrations were collected during R/V *Knorr* cruise 166-2, January 2002, in the Florida Straits. Sediments were collected from three regions: the western side of the Florida Current near Dry Tortugas; the eastern side of the Florida and Santaren Currents near Great Bahama Bank; and the western side of the Santaren Current near Cay Sal Bank (Figure 1 and Table 1). Thirty-eight multicore casts were recovered, each consisting of eight short cores (30–40 cm long, 12 cm diameter). The 0–1 cm slice of one short core from 31 of those multicore casts was used for this study.

[5] Sloping of isopycnals associated with the Florida Current causes the eastern side of the Florida Straits to have higher temperature, salinity, [CO_3^{2-}] and lower nutrient concentrations at a given depth than the western side of the Straits [see *Lynch-Stieglitz et al.*, 1999]. Fifty-five conductivity-temperature-depth (CTD) casts were made during the course of the cruise. Bottom water samples from the multicore sites were collected using a Niskin bottle attached to the multicorer frame, which was rigged to close when the multicorer hit the seafloor. Aliquots of the Niskin seawater were sampled for salinity, $\delta^{18}O$, alkalinity and ΣCO_2. In situ temperatures at the multicore sites were determined from nearby CTD casts as described by *Bryan and Marchitto* [2008]. Multicore sites cover depth, in situ temperature, and salinity ranges of 173–751 m, 5.8–18.6°C, and 34.9–36.8 psu, respectively (Table 1 and Figure 2).

[6] In order to estimate seawater [Cd] at the multicore sites, a regional relationship between salinity and phosphate concentrations was developed using a least squares linear regression with data from 100 to 1000 m water depth at 26 Florida Straits WOCE stations (AT109LG3 stations 236–261) [*Schlitzer*, 2000] as well as three sites in the Gulf of Mexico [*Boyle et al.*, 1984] (Figure 3):

$$PO_4 = -1.0243^*S + 37.654,\ R^2 = 0.96,\ n = 162 \quad (1)$$

The residual standard error for this regression is 0.14 μmol kg^{-1}. Seawater cadmium concentrations were then calculated using the Atlantic Ocean Cd:PO_4 relationship of *Elderfield and Rickaby* [2000]:

$$Cd = 1.2/(\alpha^*(3.3/PO_4 - 1) + 1) \quad (2)$$

where α = 2.5 for the Atlantic Ocean, giving a range of 0.02 to 0.42 nmol kg^{-1} at our core sites. *Boyle et al.* [1984] also measured seawater [Cd] at the three Gulf of Mexico stations, which can be used to test our method for estimating seawater [Cd]. The measured [Cd] and [Cd] estimated using

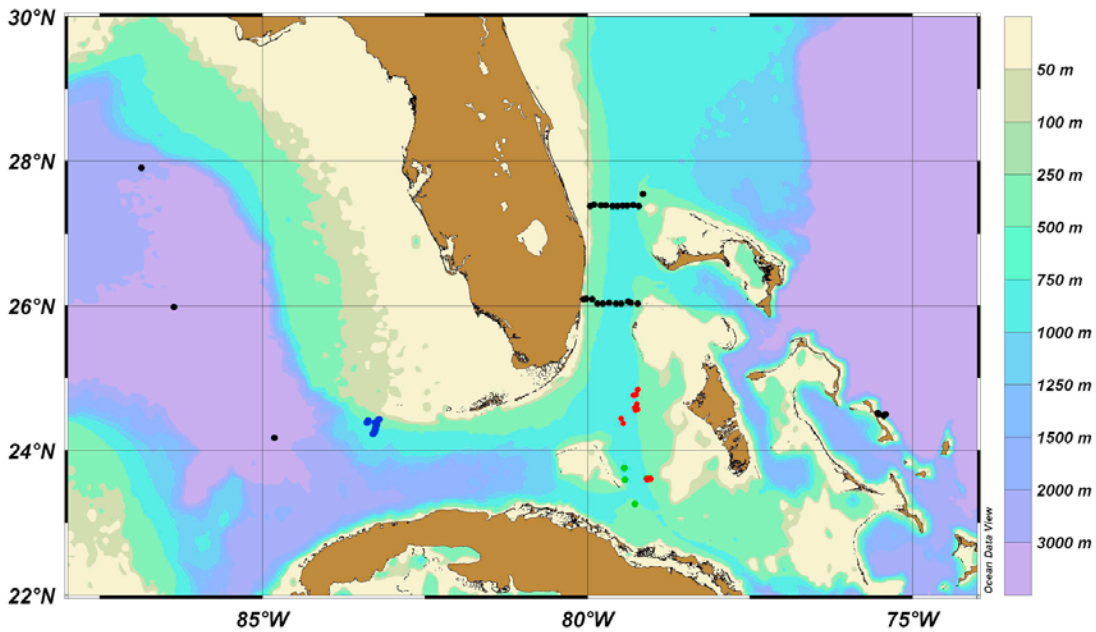

Figure 1. Map of KNR166-2 multicore sites used in this study. Multicore sites are indicated by red (Great Bahama Bank), green (Cay Sal Bank), and blue (Dry Tortugas) dots. Black dots indicate WOCE and *Boyle et al.* [1984] seawater sites used to develop salinity-PO_4 and salinity-Si relationships. Color scale indicates water depth; note that contour intervals increase with depth. The Florida Current flows from the southwest to the northeast in between Dry Tortugas and the Bahama Banks. Map was created using Ocean Data View software (R. Schlitzer, 2008, available at http://odv.awi.de).

the salinity-PO_4 relationship and the PO_4-Cd relationship agree well (R^2 = 0.99). The average difference between the estimated [Cd] values and the measured [Cd] values is -0.0005 ± 0.020 nmol kg^{-1}. We estimated the error on our seawater [Cd] values by taking the 1σ standard error from the salinity-PO_4 regression (equation (1)) and propagating it through the PO_4-Cd relationship (equation (2)) using an α value of 2 on the high-end PO_4 estimates and an α value of 3 on the low-end PO_4 estimates. The estimated error in seawater [Cd] varies from ~±24% at core sites where [Cd] is >0.4 nmol kg^{-1} to ~±76% at core sites where [Cd] is <0.1 nmol kg^{-1}.

[7] Seawater silica was estimated from the same 26 Florida Straits WOCE stations and three Gulf of Mexico stations using a second-order polynomial relationship between silica and salinity (Figure 4a):

$$\mathrm{Si} = 5.640^* \mathrm{S}^2 - 415.6^* \mathrm{S} + 7658,\ R^2 = 0.97,\ n = 172 \quad (3)$$

The residual standard error of this regression is 1.4 μmol kg^{-1}. Seawater [Zn] was then calculated using a linear relationship between [Si] and [Zn] determined from measurements from water depths less than or equal to 1000 m in the Atlantic Ocean [*Bruland and Franks*, 1983; *Ellwood and Van den Berg*, 2000; *Martin et al.*, 1993] (Figure 4b).

$$\mathrm{Zn} = 0.132^* \mathrm{Si} + 0.096,\ R^2 = 0.81,\ n = 44 \quad (4)$$

which has a residual standard error of 0.22 nmol kg^{-1}. This produces a [Zn] range of 0.3 to 3.1 nmol kg^{-1} at our core sites. The slope of the upper Atlantic Ocean Zn-Si relationship is greater than twice the slope of the deep water (>1000 m) global relationship of *Marchitto et al.* [2000]. The slope difference indicates that the Zn-Si relationship is not entirely linear; however it is unclear at what point and how rapidly the slope decreases, and whether it might vary between ocean basins. Estimated [Zn] at 15 of the Florida Straits multicore sites exceeds 2 nmol kg^{-1}; if the slope decreases rapidly above 2 nmol kg^{-1}, then [Zn] estimates at the deeper Dry Tortugas sites may be too high. We estimate the error on our seawater [Zn] estimates using the 1σ standard error on the salinity-Si regression (equation (3)) propagated through the Si-Zn regression (equation (4)) along with the 1σ standard error from the Si-Zn regression. The resulting 1σ error is ±0.4 nmol kg^{-1}. For both Cd/Ca and Zn/Ca, we follow the convention of *Boyle* [1992] and take seawater [Ca] to be constant

Table 1. KNR 166-2 Multicore Locations, Hydrographic Data, Seawater Cd and Zn Concentrations, and Radiocarbon Ages

Core	Latitude (°N)	Longitude (°W)	Water Depth (m)	Temperature[a] (°C)	Salinity (psu)	Estimated Seawater Cd[b] (nmol kg^{-1})	Estimated Seawater Zn[b] (nmol kg^{-1})	Conventional ^{14}C Age[c] (years B.P.)	NOSAMS Number[d]
5MC[e]	24.40	83.38	447	8.5	35.02	0.381	2.74		
11MC[e]	24.22	83.30	751	5.8	34.91	0.424	3.10	355 ± 35	OS-39958 (2)
13MC[e]	24.37	83.24	348	9.7	35.17	0.337	2.37	3040 ± 35	OS-46032 (4)
16MC[e]	24.40	83.23	248	10.8	35.32	0.293	2.02	960 ± 30	OS-44554 (4)
19MC[e]	24.42	83.21	173	12.7	35.60	0.218	1.42	1320 ± 50	OS-39967 (4)
22MC[e]	24.41	83.37	398	9.0	35.08	0.365	2.61		
24MC[e]	24.34	83.25	494	7.8	34.95	0.406	2.95		
28MC[e]	24.28	83.27	648	6.3	34.91	0.424	3.10	2980 ± 40	OS-46037 (2)
50MC[e]	24.41	83.22	198	12.1	35.51	0.243	1.61	1080 ± 45	OS-41646 (4)
53MC[e]	24.38	83.23	302	10.0	35.21	0.325	2.28	1800 ± 30	OS-39969 (2)
55MC[e]	24.38	83.27	359	9.1	35.10	0.358	2.55		
62MC[e]	24.33	83.26	547	7.0	34.91	0.421	3.08	Fm > 1	OS-39971 (1)
66MC[f]	23.61	79.05	302	19.0	36.62	0.021	0.31		
68MC[f]	23.61	79.08	431	16.6	36.24	0.086	0.55		
72MC[g]	23.75	79.43	542	10.8	35.31	0.296	2.04		
76MC[g]	23.59	79.42	539	11.0	35.33	0.291	1.99		
79MC[g]	23.26	79.27	486	12.1	35.50	0.246	1.63		
84MC[f]	24.37	79.45	638	10.5	35.27	0.308	2.13		
89MC[f]	24.56	79.24	353	17.8	36.48	0.044	0.38	2280 ± 35	OS-40243 (2)
92MC[f]	24.55	79.26	478	15.7	36.13	0.107	0.66		
94MC[f]	24.57	79.23	259	18.5	36.57	0.030	0.33	215 ± 35	OS-40244 (4)
97MC[f]	24.56	79.23	303	18.6	36.58	0.028	0.33		
103MC[f]	24.44	79.48	683	9.3	35.11	0.355	2.53		
110MC[f]	24.58	79.24	390	17.3	36.39	0.059	0.43	Fm > 1	OS-46039 (2)
112MC[f]	24.64	79.24	404	17.1	36.35	0.066	0.46		
118MC[f]	24.59	79.27	531	14.5	35.91	0.151	0.93	Fm > 1	OS-39973 (3)
121MC[f]	24.77	79.25	578	11.9	35.48	0.251	1.67		
123MC[f]	24.76	79.27	632	10.6	35.30	0.299	2.06		
125MC[f]	24.76	79.29	694	9.4	35.13	0.349	2.48	Fm > 1	OS-39975 (3)
134MC[f]	24.84	79.22	441	17.2	36.37	0.063	0.45	Fm > 1	OS-46043 (4)
138MC[f]	24.83	79.23	484	16.8	36.29	0.077	0.51		

[a] Bottom water temperatures were estimated by matching Niskin bottle salinities to nearby CTDs. See *Bryan and Marchitto* [2008] for a detailed description.
[b] Estimated from salinity as described in section 2.
[c] Fm > 1 refers to fraction modern greater than one, indicating the presence of ^{14}C for nuclear weapons testing.
[d] Sources of radiocarbon ages are indicated by numbers in parentheses with the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) sample numbers: 1, *Lund and Curry* [2004]; 2, *Lund* [2005]; 3, *Lund and Curry* [2006]; and 4, *Lund et al.* [2006].
[e] Dry Tortugas sites.
[f] Great Bahama Bank sites.
[g] Cay Sal Bank sites.

at 0.01 mol kg^{-1}. Basing [Ca] on measured salinities would result in a [Ca] range of about 5%.

[8] Five species of benthic foraminifera, *Cibicidoides pachyderma, Uvigerina peregrina, Planulina ariminensis, Planulina foveolata* and *Hoeglundina elegans,* were picked from the 250–600 μm size fraction of the 0–1 cm slice of each core. Samples for trace element analysis contained 4–7 individuals (*C. pachyderma*), 9–10 individuals (*U. peregrina*), 13–15 individuals (*P. ariminensis*), 18–20 individuals (*P. foveolata*), and 9–10 individuals (*H. elegans*). Where abundances allowed, the number of individuals was doubled and samples were crushed, homogenized and split for replicate analysis. Crushed samples were cleaned reductively (using anhydrous hydrazine) and oxidatively (using hydrogen peroxide) in a Class-1000 clean lab, following the methods of *Boyle and Keigwin* [1985] as modified by *Boyle and Rosenthal* [1996]. Samples were analyzed for Cd/Ca and Zn/Ca by magnetic sector single-collector ICP-MS, on a Thermo-Finnigan Element2, using methods adapted from *Rosenthal et al.* [1999] [*Marchitto*, 2006]. Long-term 1σ precisions (relative standard deviations of liquid consistency standards) are: Cd/Ca = 1.8%, Zn/Ca = 3.2% [*Marchitto*, 2006]. Mn/Ca and Fe/Ca were also measured to screen against contamination from diagenetic coatings or detrital material; values were almost always below 30 μmol mol^{-1} and did not exceed 60 μmol mol^{-1} in any sample, well below

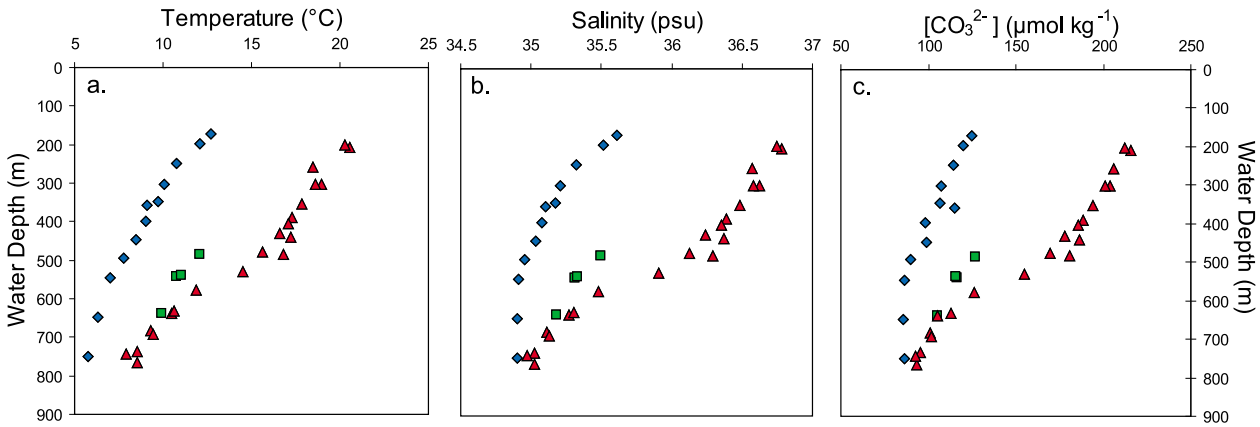

Figure 2. (a) Temperature, (b) salinity, (c) and $[CO_3^{2-}]$ estimates for the KNR166-2 multicore sites plotted versus water depth. Each symbol represents one multicore site: blue diamonds represent sites near Dry Tortugas, green squares represent sites near Cay Sal Bank, and red triangles represent sites near Great Bahamas Bank.

thresholds for likely trace metal contamination (>100 μmol mol^{-1}) [*Barker et al.*, 2003; *Boyle*, 1983].

[9] AMS radiocarbon ages were measured on *Globigerinoides ruber* (>250 μm) from the 0–1 or 0–2 cm slices from 14 of the KNR166-2 multicores [*Lund*, 2005; *Lund et al.*, 2006; *Lund and Curry*, 2004, 2006]. Seven of the core tops contained significant levels of "bomb" radiocarbon (either fraction modern >1 or conventional radiocarbon age <400 years), and seven ranged from ~1000–3000 years (mostly from the Dry Tortugas region). Sedimentation rates in KNR166-2 cores range between 11 and 66 cm kyr^{-1} near Dry Tortugas and 20 to 350 cm kyr^{-1} on Great Bahama Bank [*Lund et al.*, 2006]. Although not all of the core tops are modern, calcification temperatures calculated from δ^{18}O in *C. pachyderma* [*Bryan and Marchitto*, 2008] indicate that modern bottom water temperatures are not significantly different from those in which the foraminifera calcified. Given that nutrient concentrations are strongly correlated with temperature in the modern Florida Straits, we believe that any changes in the Florida Current strength over the past several thousand years did not greatly affect the nutrient concentrations at the core sites.

3. Results and Discussion

3.1. Cd/Ca

[10] Cd/Ca values (Table 2) range from 0.016 to 0.084 μmol mol^{-1} for *C. pachyderma*, 0.020 to 0.095 μmol mol^{-1} for *U. peregrina*, 0.047 to 0.073 μmol mol^{-1} for *P. ariminensis*, 0.016 to 0.086 μmol mol^{-1} for *P. foveolata*, and 0.0061 to 0.057 μmol mol^{-1} for *H. elegans*. These ranges exclude one *U. peregrina* value that was much higher than all other measurements and is suspected of contamination. The pooled standard deviation of sample splits [*McNaught and Wilkinson*, 1997], excluding the one *U. peregrina* measurement, is 0.0070 μmol mol^{-1} (dof = 48). An additional three measurements (one *C. pachyderma* and two *U. peregrina*) were >0.014 μmol mol^{-1} (2σ) higher than sample splits and are excluded from

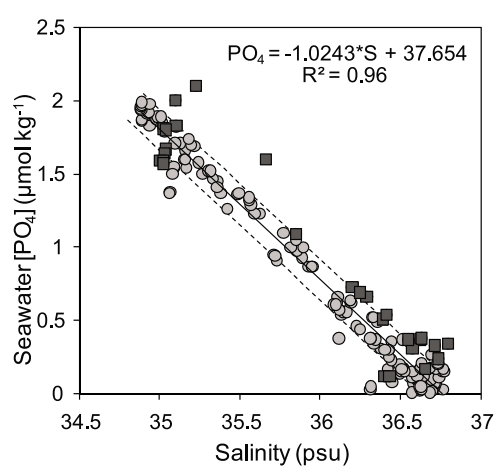

Figure 3. Paired salinity and seawater $[PO_4]$ data used to derive an empirical relationship from which we estimate seawater $[PO_4]$ at the KNR166-2 multicore sites. Circles represent data from 26 Florida Straits WOCE stations (AT109LG3 stations 236–261) [*Schlitzer*, 2000], and squares represent data from three Gulf of Mexico sites [*Boyle et al.*, 1984]. All measurements are from water depths between 100 and 1000 m. The dashed lines indicate the 1σ standard error on the linear regression (solid line).

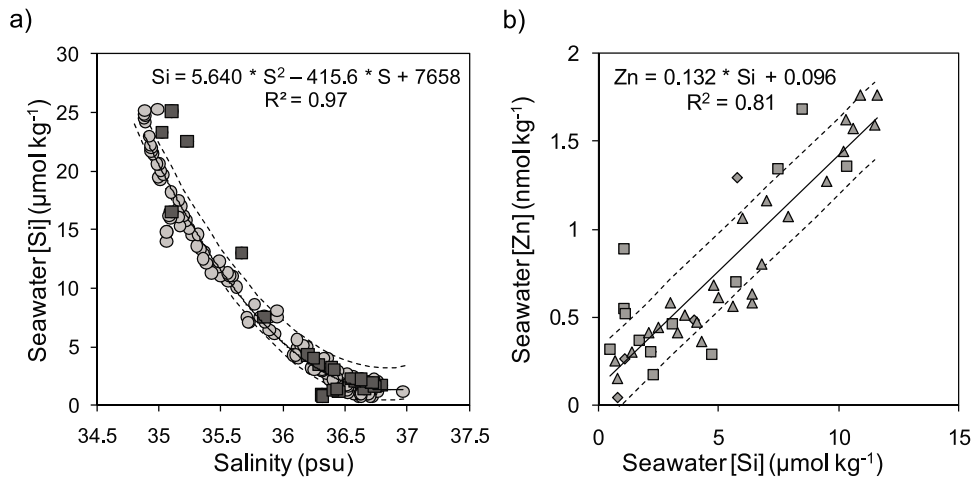

Figure 4. (a) Paired salinity and seawater [Si] data used to derive an empirical relationship from which we estimate seawater [Si] at the KNR166-2 multicore sites. Circles represent data from 26 Florida Straits WOCE stations (AT109LG3 stations 236–261) [*Schlitzer*, 2000], and squares represent data from three Gulf of Mexico sites [*Boyle et al.*, 1984]. All measurements are from water depths between 100 and 1000 m. The dashed lines indicate the 1σ standard error on the second-order polynomial regression (solid line). (b) Paired seawater [Si] and [Zn] measurements from *Bruland and Franks* [1983] (diamonds), *Ellwood and Van den Berg* [2000] (squares), and *Martin et al.* [1993] (triangles). All measurements are from $\leq$1000 m water depth in the Atlantic Ocean. The dashed lines indicate the 1σ standard error on the linear regression (solid line). This linear regression was used to estimate seawater [Zn] at the KNR166-2 multicore sites.

the following analysis. The four excluded measurements (out of 147 total) are italicized in Table 2.

[11] In all of the species analyzed, Cd/Ca increases with water depth (Figure 5). For similar depths, Dry Tortugas multicore sites have the highest Cd/Ca values and Great Bahama Bank sites have the lowest, with Cay Sal Bank sites falling in between. The regional differences in the depth profiles are consistent with the expected sloping of isopycnals associated with the Florida Current, with denser waters containing higher nutrient concentrations. There are no consistent offsets in Cd/Ca between the different calcitic species. Cd/Ca in the aragonitic species *H. elegans* is lower than in the calcitic species but displays similar profiles with water depth. The foraminiferal Cd/Ca data are well correlated to the estimated seawater [Cd], R^2 = 0.77 for calcitic foraminifera and 0.76 for *H. elegans*.

[12] Calcitic foraminiferal Cd/Ca measurements are consistently higher than would be expected from the estimated seawater Cd/Ca assuming a partition coefficient of 1.3 [*Boyle*, 1992]. For the most part, however, the Cd/Ca values fall within the error bars of the seawater Cd/Ca estimates. The difference between the calcitic foraminiferal Cd/Ca and the expected Cd/Ca is greatest at the shallowest core sites (especially on the Great Bahama Bank side of the Florida Current) and decreases with increasing water. *H. elegans* Cd/Ca generally agrees with the expected Cd/Ca at core sites deeper than ~500 m water depth; however, above that depth, *H. elegans* Cd/Ca is elevated relative to the expected values, similar to the pattern seen in the calcitic foraminifera. The discrepancies between the foraminiferal Cd/Ca measurements and the values expected from estimated seawater [Cd] can be explained by a combination of the established Cd/Ca partition coefficient for the calcitic foraminifera being too low and/or inaccuracies in the estimates of seawater [Cd]. The consistency of the elevated calcitic Cd/Ca measurements at all water depths suggests that the partition coefficient for calcitic foraminifera is slightly higher than 1.3. This possibility is discussed further in section 3.2. There are also a couple of reasons to believe that there are inaccuracies in our seawater Cd/Ca estimates, particularly at the shallow core sites. First, the discrepancies are consistent between the different calcitic species as well as in the aragonitic *H. elegans*. The consistency between species makes it is unlikely that the differences can be explained by laboratory contamination or contamination from diagenetic carbonate overgrowths. *H. elegans* is thought to be immune to problems from overgrowths [*Boyle et al.*, 1995]. Second, the estimates of seawater Cd/Ca rely on both the relationship between salinity and phosphate and the relationship between phosphate and cadmium being applicable

Table 2. Benthic Foram Cd/Ca and Zn/Ca Measurements for Each Species by Core[a]

	C. pachyderma		*U. peregrina*		*P. ariminensis*		*P. foveolata*		*H. elegans*	
Core	Cd/Ca	Zn/Ca	Cd/Ca	Zn/Ca	Cd/Ca	Zn/Ca	Cd/Ca	Zn/Ca	Cd/Ca	Zn/Ca
5MC	0.059	5.65	0.056	1.00	0.060	1.32			0.035	0.83
5MC			0.053	0.95	0.061	3.06			0.034	0.43
11MC	0.068	7.00	*0.162*	4.95					0.033	0.40
11MC			0.062	1.47						
13MC	0.065	4.79	0.054	0.56	0.058	1.43			0.040	0.35
13MC	0.065	4.22	0.059	0.58	0.056	1.17			0.043	0.69
16MC	0.048	3.63	0.033	0.76	0.037	6.45			0.037	0.78
16MC	0.048	2.98								
19MC	0.050	1.99					0.040	0.44	0.038	2.80
19MC	*0.075*	2.12							0.034	1.50
22MC			0.053	0.85					0.046	1.60
22MC	0.059	7.70	0.053	0.97						
24MC			0.057	1.47					0.039	1.07
28MC	0.058	4.40	0.073	1.21					0.042	0.17
28MC	0.058	4.74	0.073	1.29					0.049	1.21
50MC	0.049	2.30			0.047	1.74	0.044	29.67	0.039	1.60
50MC	0.048	2.59								
53MC	0.053	3.07	0.048	1.21	0.056	1.11			0.053	1.17
53MC	0.055	*9.89*	0.054	3.00	0.064	1.99			0.047	0.44
55MC	0.063	3.65	0.057	0.80	0.059	2.00			0.057	0.82
55MC	0.061	3.63	*0.095*	12.72	0.065	9.73			0.051	1.63
62MC	0.056	5.46	0.058	1.07	0.062	1.85			0.035	0.41
62MC			0.073	13.48						
66MC									0.009	0.90
68MC	0.028	*6.89*					0.017	0.52	0.010	0.22
68MC	0.021	0.45							0.014	0.86
72MC	0.044	5.39	*0.086*	8.84			0.044	1.75	0.032	3.24
72MC	0.045	5.07	0.044	0.74						
76MC	0.047	4.72	0.045	3.38	0.073	11.46	0.086	9.38	0.028	0.45
76MC	0.049	5.40								
79MC	0.055	4.88	0.042	1.50			0.041	15.48	0.023	0.24
79MC	0.054	5.64	0.037	0.69						
84MC	0.082	6.81								
89MC	0.016	0.19					0.016	4.58	0.009	6.43
92MC	0.031	2.18	0.028	4.36					0.016	0.61
94MC	0.016	0.10							0.016	3.79
94MC	0.019	0.13							0.010	2.33
97MC	0.019	0.23							0.012	7.78
97MC	0.018	0.12							0.006	0.21
103MC	0.084	8.99	0.074	2.25	0.061	1.29				
103MC	0.078	7.15								
110MC	0.020	0.68	0.020	0.61			0.019	2.65	0.013	1.61
110MC			0.026	1.44			0.019	1.57	0.009	1.11
112MC	0.021	0.82							0.009	0.30
112MC									0.009	0.51
118MC	0.038	1.67	0.037	1.65			0.027	0.53	0.018	0.20
118MC			0.032	0.55					0.021	0.81
121MC	0.036	2.94	0.039	2.25					0.024	0.39
121MC	0.038	4.40								
123MC	0.043	4.14							0.020	0.29
123MC	0.040	4.80								
125MC	0.055	5.57			0.051	1.70				
134MC	0.024	2.49					0.016	1.43	0.011	0.77
134MC	0.020	0.81							0.011	0.33
138MC	0.026	1.60	0.021	0.66			0.037	1.84	0.018	0.98
138MC							0.033	2.77	0.023	3.02

[a] All units are μmol mol^{-1}. Measurements excluded because of suspected contamination are italicized. A number of additional Zn/Ca measurements from *U. peregrina*, *P. ariminensis*, *P. foveolata*, and *H. elegans* are also likely contaminated.

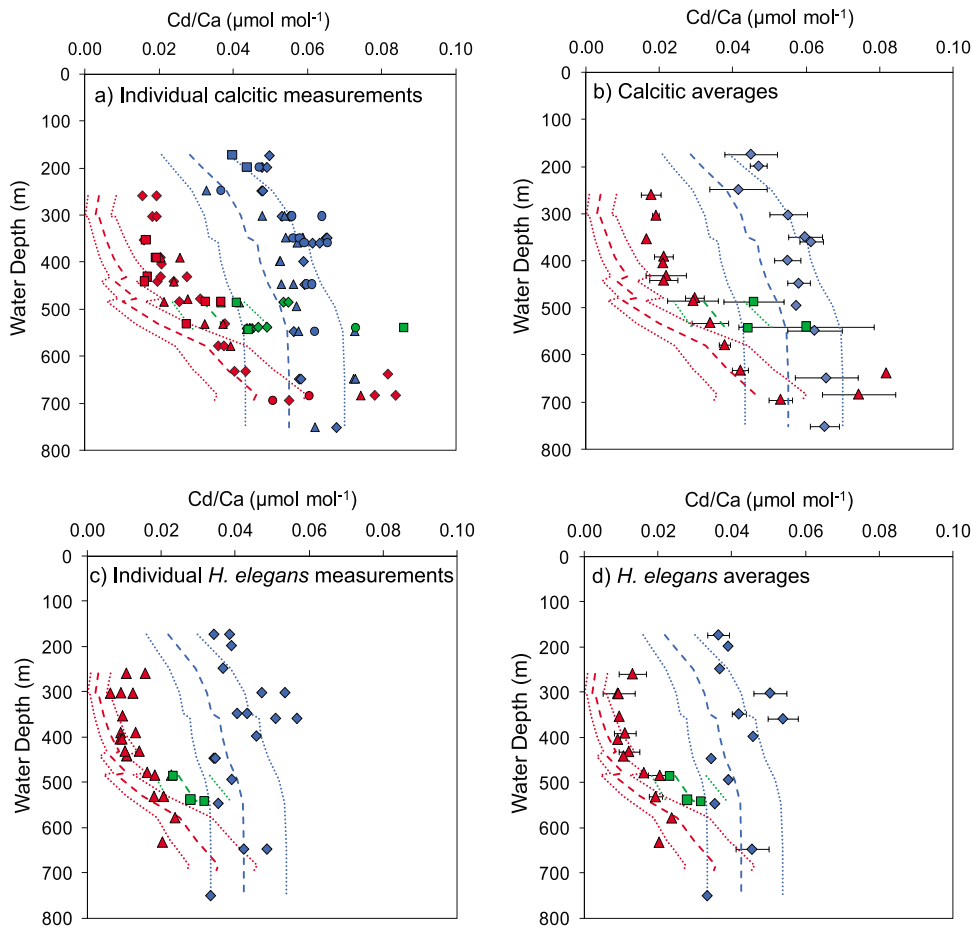

Figure 5. (a) Individual calcitic benthic foraminiferal Cd/Ca measurements plotted versus water depth; diamonds are *C. pachyderma*, triangles are *U. peregrina*, circles are *P. ariminensis*, and squares are *P. foveolata*. Red symbols are from Great Bahama Bank multicore sites, green symbols are from Cal Sal Bank sites, and blue symbols are from Dry Tortugas sites. The dashed lines indicate estimated seawater Cd/Ca for the Great Bahama Bank (red), Cay Sal (green), and Dry Tortugas (blue) core sites. The estimated seawater Cd/Ca is scaled assuming a partition coefficient of 1.3 [*Boyle*, 1992]. The dotted lines are the estimated error for the seawater Cd/Ca estimates described in section 2. (b) Same as Figure 5a except symbols are average values of all calcitic Cd/Ca measurements for each core with 1σ error bars. (c) Individual *H. elegans* Cd/Ca measurements plotted versus water depth for Great Bahama Bank (red triangles), Cay Sal (green squares), and Dry Tortugas (blue diamonds) multicore sites. Estimated seawater Cd/Ca profiles are the same as in Figures 5a and 5b except they have been scaled assuming a partition coefficient of 1.0 [*Boyle et al.*, 1995]. (d) Average *H. elegans* Cd/Ca for each multicore with 1σ error bars. Estimated seawater Cd/Ca profiles are the same as in Figure 5c.

to all of the multicore sites. While we believe that the two relationships for the most part do a good job of estimating the seawater [Cd], in waters with very low [Cd] small departures from the regional relationships can lead to significant inaccuracies.

[13] The difference in Cd/Ca depth profiles between the Dry Tortugas and the Great Bahama Bank indicate that small changes in bottom water [Cd] can be detected using Cd/Ca in benthic foraminifera and allow us to put a constraint on the precision of Cd/Ca in benthic foraminifera. Such an evaluation was not possible in previous calibration studies of thermocline waters [*Boyle et al.*, 1995; *Rosenthal et al.*, 1997b; *Marchitto*, 2004] because only a single nutrient profile was examined. The pooled standard deviation of all of the calcitic Cd/Ca measurements for each Florida Straits core top is 0.0061 μmol mol^{-1} (dof = 71). Visually, the difference between the Dry Tortugas and Great Bahama Bank depth profiles of calcitic Cd/Ca is clearly distinguishable down to ~600 m where the difference in Cd/Ca approaches 0.02 μmol mol^{-1}, or greater than three times the pooled standard deviation. We would therefore suggest that calcitic benthic foraminiferal Cd/Ca can easily resolve

changes in bottom water [Cd] of 0.15 nmol kg^{-1} (assuming a partition coefficient of 1.3 [*Boyle*, 1992]). The precision of Cd/Ca in *H. elegans* may be even higher. The pooled standard deviation of *H. elegans* sample splits is 0.0031 μmol mol^{-1} (dof = 14), suggesting that [Cd] changes of <0.1 nmol kg^{-1} may be resolvable. The precision we describe here should be thought of as an estimate of the underlying precision of the foraminiferal Cd/Ca proxy under favorable depositional conditions. In low sedimentation rate settings, bioturbation may smooth or distort the record by mixing together foraminifera of different ages, thereby limiting the extent to which small seawater changes may be resolved [*Boyle*, 1995].

3.2. D_{Cd}

[14] In order to quantitatively reconstruct the nutrient concentrations in the past we need to know how much Cd is incorporated in to the shell relative to the seawater Cd concentration. This ratio is known as the empirical partition coefficient (D), where

$$D_{Cd} = Cd/Ca_{foram}/Cd/Ca_{seawater} \quad (5)$$

The original calibration of Cd/Ca for the upper ocean (<1150 m) by *Boyle* [1992] was based on eight core tops and established a partition coefficient (D_{Cd}) of ~1.3 for calcitic benthic foraminifera. However, later core top calibrations from the Little Bahama Bank hinted that D_{Cd} may be slightly higher than 1.3 [*Marchitto*, 2004; *Rosenthal et al.*, 1997b].

[15] The equation for the empirical partition coefficient can be rearranged so that

$$Cd/Ca_{foram} = D_{Cd} * Cd/Ca_{seawater} \quad (6)$$

The partition coefficient is therefore the slope of the linear regression of Cd/Ca_{foram} versus $Cd/Ca_{seawater}$, forced through the origin assuming that foraminifera incorporate no Cd if it is absent from seawater. We have made an estimate of the partition coefficient (D_{Cd}) using standardized major axis regression on our Florida Straits results. Standardized major axis regression (SMA) is preferred to ordinary least squares regression in this case since SMA takes into account variance in both the x and y data. However, if ordinary least squares regression is used, the results are not significantly different. For the purpose of estimating the partition coefficient, all of the calcitic species were combined. *Tachikawa and Elderfield* [2002] proposed that infaunal species (such as *U. peregrina*) calcify from pore waters with a constant partition coefficient of ~1, and that the typically similar Cd/Ca measurements of *U. peregrina* and epifaunal *Cibicidoides* sp. are due to elevated pore water [Cd]. We find no consistent offsets between *U. peregrina* and the other calcitic species in the Florida Straits samples. The data presented here do not preclude a different partition coefficient for *U. peregrina*; however, pore water [Cd] measurements would be necessary to investigate this possibility.

[16] D_{Cd} estimated from the Florida Straits core tops using the SMA regression is 1.74 (Figure 6a and Table 3). If D_{Cd} is calculated for each individual measurement, the median of individual measurements agrees well with the regression. In contrast, the mean of individual measurements is higher (2.2), and is likely biased by the measurements at the shallow (very low seawater [Cd]) Great Bahama Bank sites, where either seawater [Cd] is underestimated or very slight foraminiferal Cd/Ca contamination becomes important. If we include the published core top calcitic Cd/Ca measurements for water depths less than 1150 m [*Boyle*, 1988, 1992; *Marchitto*, 2004; *Rosenthal et al.*, 1997b] with the Florida Straits data (Figure 6b), our estimate for the calcitic D_{Cd} is 1.75. Our estimate of D_{Cd} for calcitic benthic foraminifera in the upper ocean of 1.75 is substantially higher than the value of 1.3 originally proposed by *Boyle* [1992]. A portion of the difference can be explained by the method used to estimate seawater [Cd]. Our use of the *Elderfield and Rickaby* [2000] (hereafter ER00) Atlantic $Cd:PO_4$ relationship results in slightly lower estimated seawater [Cd] when compared to the ER00 global relationship or the *Boyle* [1988] global $Cd:PO_4$ relationship. As such, the calculated partition coefficients will be slightly higher than they would be if the other $Cd:PO_4$ relationships were used. If we recalculate our seawater [Cd] estimates using the ER00 global relationship, the resulting estimates of D_{Cd} are 1.49 and 1.58 for the Florida Straits core tops and the combined published data, respectively. The rest of the difference may be taken as a refinement of the estimate due to the addition of more core top data. While the Florida Straits calcitic Cd/Ca data suggest that the true partition coefficient for Cd/Ca at water depths <1150 is slightly higher than 1.3, there is considerable uncertainty in our seawater [Cd] estimates, preventing us from confidently stating what value should be used for calcitic D_{Cd}. As additional core top Cd/Ca data is produced, the D_{Cd} should be further refined. We

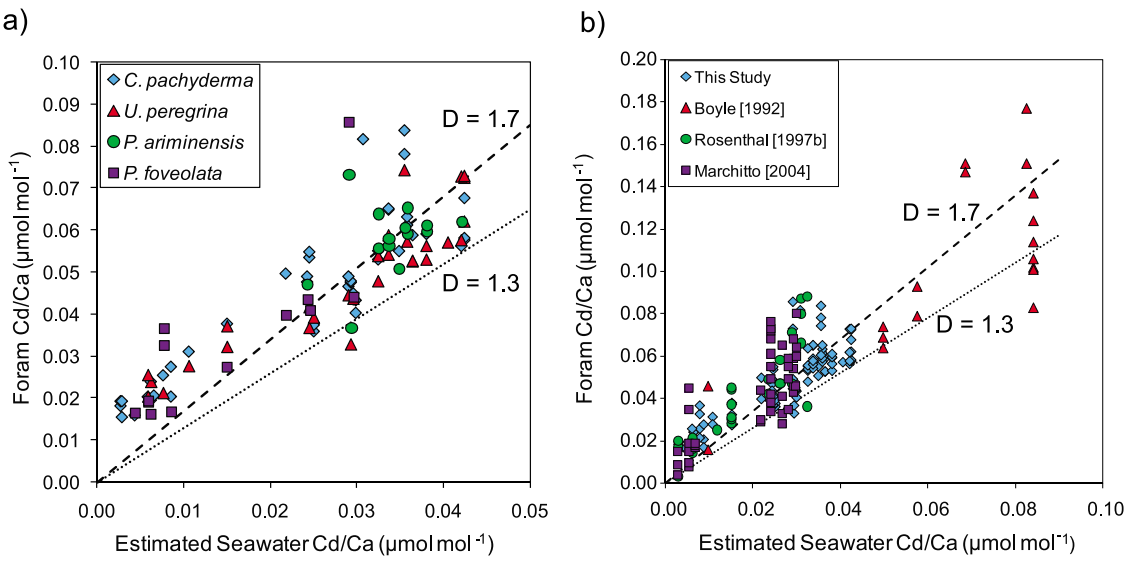

Figure 6. (a) Estimated seawater Cd/Ca versus individual calcitic benthic foraminiferal Cd/Ca measurements. The slope of a standardized major axis regression forced through the origin was used to estimate the partition coefficient (D_{Cd}). Our best estimate for D_{Cd} of 1.7 is shown as a dashed line; D_{Cd} of 1.3 (*Boyle* [1992], dotted line) is also shown for comparison. (b) The Florida Straits calcitic benthic foraminiferal Cd/Ca (light blue diamonds) compared to published core top calcitic Cd/Ca data from water depths <1150 m; published data are from *Boyle* [1988, 1992] (red triangles), *Marchitto* [2004] (purple squares), and *Rosenthal et al.* [1997b] (green circles). All of the seawater Cd/Ca values for the published data were recalculated using the ER00 Atlantic Cd:PO4 relationship for Atlantic data and the ER00 global relationship for Pacific data. D_{Cd} values of 1.3 (dotted line) and 1.7 (dashed line) are shown. *Boyle*'s [1992]D_{Cd} estimate of 1.3 was based on seawater [Cd] derived using the global relationship of *Boyle* [1988], which can account for roughly 0.2 of the slope difference.

suggest that future calibration efforts measure bottom water [Cd] at the core sites. A calibration study at shallow sites in the Pacific would be particularly useful, since seawater [Cd] would be generally higher there.

[17] Previous workers have suggested that calcitic D_{Cd} increases with water depth in the range of 1150–3000 m [*Boyle*, 1992], decreases in waters that are undersaturated with respect to calcite [*McCorkle et al.*, 1995; *Marchitto et al.*, 2005], and is insensitive to temperature [*Marchitto*, 2004]. Unfortunately the uncertainties in Florida Straits seawater [Cd], combined with the covariance of temperature, salinity, and [CO_3^{2-}], preclude us from drawing any new conclusions about the environmental parameters that may affect D_{Cd}.

[18] D_{Cd} was estimated for the aragonitic species *H. elegans* in the same manner as the calcitic species, by calculating the slope of a SMA regression of the estimated seawater Cd/Ca and the foraminiferal Cd/Ca forced through the origin. *Boyle et al.* [1995] demonstrated that *H. elegans* has a depth-independent partition coefficient of 1.0. The D_{Cd} estimate here from the Florida Straits data is 1.2 (Table 3). As with the calcitic species, our estimate is slightly higher (by ~0.2) due to the use of the ER00 Atlantic Cd:P relationship. The

Table 3. Partition Coefficients

Data Set	D Value From SMA Regression	95% CI on Slope	Mean D[a]	Median D[a]	Standard Deviation of D[a]
Florida Straits calcitic Cd/Ca	1.74	1.66–1.81	2.24	1.72	1.14
Including published calcitic Cd/Ca (<1150 m)	1.75	1.68–1.81	2.29	1.86	1.2
Florida Straits *Hoeglundina* Cd/Ca	1.2	1.10–1.30	1.68	1.41	1
Including published *Hoeglundina* Cd/Ca	1.1	1.04–1.16	1.5	1.29	0.91
C. pachyderma Zn/Ca	22.1	20.2–24.2	20	18	10

[a] Mean, median, and standard deviation of D are calculated from D values of individual measurements.

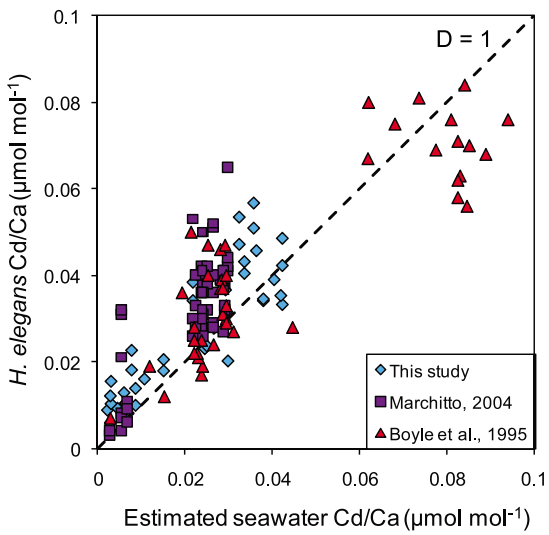

Figure 7. Individual Florida Straits *H. elegans* Cd/Ca measurements (light blue diamonds) plotted against estimated seawater Cd/Ca. Published core top *H. elegans* Cd/Ca data from *Boyle et al.* [1995] (red triangles) and *Marchitto* [2004] (purple squares) are shown for comparison. All of the seawater Cd/Ca values for the published data were recalculated using the ER00 Atlantic Cd:PO4 relationship for Atlantic data and the ER00 global relationship for Pacific and Indian data. The estimated D_{Cd} value for *H. elegans* is 1.0 (dashed line).

Florida Straits Cd/Ca measurements agree well with the Little Bahama Bank measurements of *Marchitto* [2004] and the upper ocean Atlantic measurements of *Boyle et al.* [1995] (Figure 7). It should be noted that *Marchitto* [2004] found a systematic positive offset from measurements of *Boyle et al.* [1995] on the same cores, although the offset was less than *Boyle*'s [1995] average reproducibility of replicate picks (±0.023 μmol mol^{-1}). The D_{Cd} estimated from the Florida Straits data combined with all published data [*Boyle et al.*, 1995; *Marchitto*, 2004] is 1.1. Given the uncertainty in the seawater [Cd] estimates, we believe 1.0 is still the best estimate for *H. elegans* D_{Cd}.

3.3. Zn/Ca

[19] Benthic foraminiferal Zn/Ca values (Table 2) range from 0.10 to 9.89 μmol mol^{-1} for *C. pachyderma*, 0.55 to 13.48 μmol mol^{-1} for *U. peregrina*, 1.11 to 11.46 μmol mol^{-1} for *P. arimi-nensis*, 0.44 to 29.67 μmol mol^{-1} for *P. foveolata*, and 0.17 to 7.78 μmol mol^{-1} for *H. elegans*. Of the five species, only *C. pachyderma* Zn/Ca displays coherent profiles with water depth and is correlated with estimated seawater [Zn] (R^2 = 0.70). Even after removing obviously contaminated values, Zn/Ca in the other four species are extremely scattered when plotted against water depth or estimated seawater Zn/Ca; they are also not correlated with seawater Zn/Ca (R^2 < 0.10). The combination of low seawater [Zn], low benthic foraminiferal partition coefficients, and slight laboratory contamination is the likely explanation for the scatter in the Zn/Ca data. For this reason, we concentrate on *C. pachyderma* Zn/Ca in the following discussion. The pooled standard deviation of *C. pachyderma* sample splits is 1.70 μmol mol^{-1} (dof = 17). We excluded 2 measurements that were >3.4 μmol mol^{-1} (2σ) higher than sample splits. Zn/Ca in *C. pachyderma* reflects the difference in seawater [Zn] between the Dry Tortugas and Great Bahama Banks sides of the Florida Straits expected from the sloping of isopycnals (Figure 8). Zn/Ca is also able to capture the general shape of the nutriclines on either side of the Florida Straits.

3.4. D_{Zn}

[20] The partition coefficient for Zn/Ca (D_{Zn}), where

$$D_{Zn} = Zn/Ca_{foram}/Zn/Ca_{seawater} \quad (7)$$

can be determined in the same manner as D_{Cd}: from the slope of a standardized major axis (SMA)

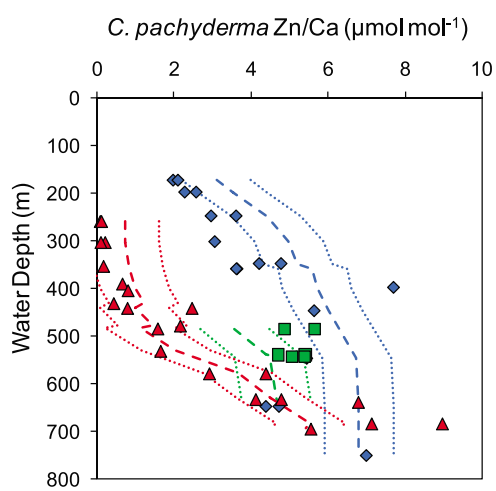

Figure 8. Individual *C. pachyderma* Zn/Ca measurements plotted versus water depth for Dry Tortugas (blue diamonds), Cay Sal Bank (green squares), and Great Bahama Bank (red triangles) multicore sites. The dashed lines are estimated seawater Zn/Ca values for the multicore sites. The seawater Zn/Ca values have been scaled assuming a partition coefficient of 22. The dotted lines are 1σ standard errors on the seawater Zn/Ca estimates.

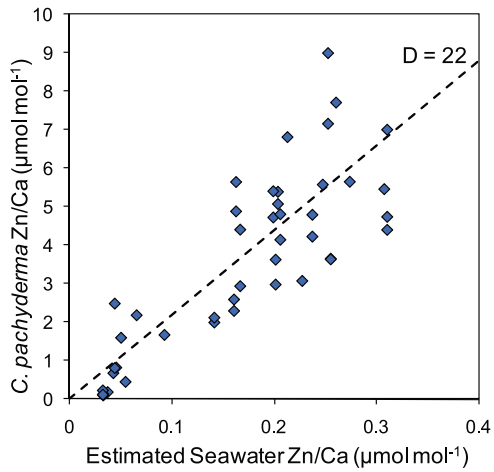

Figure 9. Individual *C. pachyderma* Zn/Ca measurements plotted versus estimated seawater Zn/Ca. The partition coefficient for Zn/Ca (D_{Zn}) was estimated using the slope of a standardized major axis regression forced through the origin. The estimate of the D_{Zn} for *C. pachyderma* is ~22 (dashed line).

regression fit to the Zn/Ca of seawater and the Zn/Ca of the foraminifera forced though the origin (Figure 9). D_{Zn} for *C. pachyderma* calculated using a SMA regression is 22.1. The slope is not significantly different if an ordinary least squares regression is used. The mean of individual D_{Zn} measurements is 20.1 and the median is 18.0. As with D_{Cd} we suggest that the regression estimate is a less biased estimate, but in the case of *C. pachyderma* D_{Zn} it is likely that the mean is biased toward low values due to a slight overestimation of seawater [Zn] in low-nutrient waters. Despite some uncertainty, the D_{Zn} calculated for *C. pachyderma* is clearly much higher than the maximum partition coefficient estimated for *C. wuellerstorfi* and *Uvigerina* (~9) by *Marchitto et al.* [2000], and also much higher than any of the other species analyzed in this study.

4. Conclusions

[21] In this paper we have presented new Cd/Ca and Zn/Ca measurements of core top benthic foraminifera from thermocline depths in the Florida Straits. Cd/Ca in the calcitic benthic foraminifera and in the aragonitic *H. elegans* is able to reconstruct small changes in nutricline Cd concentrations related to the sloping of isopycnals across the Florida Straits. We estimate that the partition coefficient for Cd/Ca in calcitic foraminifera is slightly higher than the value of 1.3 previously determined by *Boyle* [1992]; our best estimate is ~1.7, although uncertainties in our seawater [Cd] make this estimate tentative. We also confirm 1.0 as the best estimate for the Cd/Ca partition coefficient in *H. elegans*.

[22] Zn/Ca measurement is complicated by laboratory contamination, especially in samples from sites with very low seawater Zn concentrations. The contamination problem is minimized in *C. pachyderma* because this species reflects seawater Zn/Ca with a high partition coefficient of ~22. Zn/Ca in *C. pachyderma* is able to reconstruct the general shape of the nutricline and the expected small differences in Zn concentrations across the Florida Straits.

[23] Uncertainties related to the estimation of seawater Cd and Zn concentrations were problematic for the calculation of partition coefficients. While estimation of nutrient concentrations from nearby seawater stations has been adequate for core top calibrations in the deep ocean, in thermocline waters where strong nutrient gradients exist, small inaccuracies become important. We suggest that future calibration efforts measure seawater Cd and Zn concentrations at the core sites and obtain samples from shallow depths in the Pacific. However, regardless of uncertainties in partition coefficients, the data presented in this study demonstrate the potential for benthic foraminiferal Cd/Ca and *C. pachyderma* Zn/Ca to reconstruct small changes in nutrient concentrations in thermocline waters.

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