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## Temperature control on the incorporation of magnesium, strontium, fluorine, and cadmium into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline paleoceanography

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**Abstract**—Surface sediments from Little Bahama Bank (LBB), intersecting the subtropical thermocline, were used to assess the influence of temperature on the incorporation of Mg, Sr, F, and Cd into shells of benthic foraminifera. Samples were obtained from twelve box cores along the southern slope of LBB, covering a temperature range of 18–4.5°C between 301 and 1585 m. We studied the composition of ten calcitic and one aragonitic species, which are often used in paleochemical reconstructions. Mg/Ca ratios decrease with increasing water depth in all benthic species, both with calcitic and aragonitic mineralogy, showing a strong correlation with water temperature. Similar decrease is seen in Sr/Ca but with no correlation with temperature. None of the benthic species studied here exhibits a depth or temperature related change in F/Ca. Similar trends are observed when using an ocean-wide dataset, which includes shallow and deep core tops (300–5000 m). We suggest that temperature is the primary control on the Mg content of benthic foraminifera. Based on inorganic precipitation experiments and thermodynamic considerations, presented here, a 30–40% decrease in the Mg distribution coefficient in calcite may be expected as a result of a temperature change from 25°C to 5°C, which is about half the observed change in LBB. A calibration curve applied to *C. pachyderma* data from core tops along the slope of Little Bahama Bank suggests that water temperature may be inferred from Mg/Ca ratios with an uncertainty of about  $\pm 0.8^\circ\text{C}$ . Therefore, the Mg content of benthic foraminifera may provide a new, independent temperature proxy for studying shallow waters paleoceanography. The linear decrease in Sr/Ca with increasing depth is not correlated with temperature; the trend is constant from the ocean surface down to 5 km, suggesting that pressure related effects on the calcification process are a more likely explanation than post-depositional dissolution. Mg/Ca ratios in aragonitic shells of *H. elegans* covary with temperature, in accord with recent observations from corals. In contrast, the Sr and F chemistry of *H. elegans* is very different than that of corals and inorganically precipitated aragonites. The disparities between the elemental composition of biogenic and inorganic phases and the large intergeneric and interspecific differences observed both in planktonic and benthic foraminifera implicate temperature related physiological processes in regulating the coprecipitation of elements in foraminiferal shells. Our work demonstrates that Cd/Ca ratios of shallow calcitic species reflect the vertical distribution of nutrients; no significant influence of temperature on the partitioning of Cd into the shells was found. Our data extend the previous deep water calibration (Boyle, 1992), thereby allowing for the reconstruction of the nutrient chemistry of shallow thermocline waters. Copyright © 1997 Elsevier Science Ltd

### 1. INTRODUCTION

Variations in sea-surface temperature (SST) occur in association with changes in the Earth's climate. Therefore, understanding the temporal variability of SST has been the focus of many paleoclimate studies. However, despite a large effort, the glacial record of SST is still controversial, especially in the tropics. The problem stems from two, apparently contradictory, datasets: based on marine faunal assemblages (CLIMAP, 1981), isotopic measurements of foraminifera (Broecker, 1986), and unsaturated alkenone data (Rostek et al., 1993; Sikes and Keigwin, 1994), it was suggested that there was only slight cooling ( $<2^\circ\text{C}$ ) of tropical sea-surface temperatures during the last glacial maximum (LGM). On the other hand, evidence of glacial snowline depression (Broecker and Denton, 1989) and ice-core records from equatorial mountains (Thompson et al., 1995), as well as measurements of noble gases in groundwaters (Stute et al.,

1995), suggest that tropical temperatures were about 4–5°C cooler during the LGM. These estimates are supported by recent coralline Sr/Ca records suggesting a similar cooling of tropical SST (Beck et al., 1992; Guilderson et al., 1994) as well as by new  $\delta^{18}\text{O}$  records of foraminifera from the tropical Atlantic Ocean (Slowey and Curry, 1995; Curry and Oppo, 1997). The new studies call into question the long held conclusions of CLIMAP.

Different proxies of paleotemperature have their own advantages and drawbacks. For example, because foraminiferal  $\delta^{18}\text{O}$  depends both on temperature and the isotopic composition of seawater, oxygen isotope based reconstructions of SST require some assumptions about variations in ice volume and salinity. Therefore, developing an independent proxy for paleotemperature will be of great utility in paleoceanography. This is especially important in subtropical seas where corals are absent. The strong correlation between Mg/Ca and temperature, found in inorganically precipitated

calcites (Katz, 1973; Mucci, 1987; Oomori et al., 1987), suggested that variations in the Mg content of biogenic calcites may be driven by temperature. Likewise, studies of foraminifera demonstrated that the interspecific variability in Mg/Ca ratios of planktonic shells is strongly correlated with water temperature at the estimated calcification depth (Savin and Douglas, 1973; Bender et al., 1975; Rosenthal and Boyle, 1993). Similar correlations were also observed for Sr/Ca and F/Ca (Opdyke et al., 1993; Rosenthal and Boyle, 1993) possibly suggesting an important role for temperature on the elemental composition of foraminifera. Until recently, calibration efforts of single species chemistry found no strong correlation between Mg/Ca (Bender et al., 1975; Delaney et al., 1985) and F/Ca (Rosenthal and Boyle, 1993) and temperature. However, a recent culture study of living foraminifera demonstrated a strong covariance between Mg/Ca ratios in *G. sacculifer* shells and ambient temperatures suggesting that, with careful calibration, Mg may provide a new proxy for seawater temperature (Nürnberg et al., 1996). Similarly encouraging results were obtained in a study of core tops from the Ontong Java Plateau, showing a correlation between Mg/Ca ratios in benthic shells of *Cassidulina subglobosa* and bottom water temperature (Izuka, 1988).

When using planktonic foraminifera to study variations in SST, there are relatively large uncertainties associated with the difficulty of sorting out depth habitats of planktonic species (Fairbanks et al., 1982). As well, post-depositional dissolution of planktonic foraminifera may modify both the faunal assemblages and alter the chemical composition of the shells, primarily in cores below the lysocline (Berger, 1970; Rosenthal and Boyle, 1993; Russell et al., 1994). A different approach for studying ocean surface conditions was applied by Slowey and Curry (1987, 1992, 1995) who reconstructed the glacial hydrography of the North Atlantic thermocline using the isotopic composition ( $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  as proxies of temperature and nutrients, respectively) of benthic foraminifera from Little Bahama Bank. As they note, the distribution of water properties in the thermocline reflects the conditions at the ocean surface where the deep water masses originated (Slowey and Curry, 1995). This approach avoids many of the limitations associated with studies of planktonic foraminifera. Nonetheless, isotopic studies of benthic foraminifera are not free of uncertainties. As mentioned above, a knowledge of the oxygen isotopic composition of the water is required in order to constrain paleotemperature estimates. Likewise, climate related variations in gas exchange and the carbon isotopic composition of the atmosphere may affect the  $\delta^{13}\text{C}$  composition of surface waters, independent of the cycling and vertical distribution of organic matter (Broecker and Maier-Reimer, 1993). In this study we examine the possibility of using Mg/Ca, Sr/Ca, and F/Ca ratios of benthic foraminifera for seawater thermometry. We also study the applicability of Cd/Ca ratios in shallow species as a nutrient proxy in thermocline waters. The response of benthic foraminiferal cadmium to deep water Cd concentrations and its applicability for paleo-nutrient studies has already been established (Boyle, 1988, 1992). This study extends the calibration of Cd as a paleo-nutrient tracer into shallow water. Further, Boyle (1992) showed a depth related change in the partition coefficient of Cd in

calcitic foraminifera and suggested as possible causes for this variability temperature, pressure, or depth-dependent biological processes. The current settings allow us to assess the effect that temperature might have on the partitioning of Cd into benthic shells.

The carbonate rich slopes of Little Bahama Bank (Fig. 1) intersect the subtropical gyre thermocline and reach down into the upper layer of the North Atlantic Deep Water (NADW). Water temperature in this region decreases from about 25°C at the base of the mixed layer to about 4.0°C at 1400 m (Fig. 2) while salinity changes from 36.75 to 35.00 over the same depth range (with a subsurface maximum of 36.84 at 125 m below the sea surface). The mixed layer depth changes from about 100 m during the winter to <75 m during the summer while changes in the seasonal thermocline reach as deep as 150 m (Levitus and Boyer, 1994). Surface sediments consist of terropod and foraminifera rich aragonite ooze (Slowey, 1990). Along the southwestern slope of Little Bahama Bank (LBB), Holocene sedimentation rates are high (10's of cm/kyr), and there is little down-slope reworking (Slowey, 1990). The strong hydrographic gradients make this region an ideal setting for calibrating the composition of benthic shells against environmental factors. The results from the LBB are compared with our ocean wide measurements of core top foraminifera, spanning a depth range of 300–5000 m. The comparison demonstrates that the results observed in LBB are general, reflecting global rather than local trends.

## 2. METHODS

Samples were obtained from twelve box cores along the southern slope of LBB, covering a temperature range of 18–4.5°C between 301 and 1585 m (Table 1). Benthic foraminifera are very abundant though not all the species are present throughout the entire depth range. Samples from other ocean regions were picked from core-tops with documented late-Holocene surface sediments (Table 2). We focused on benthic species that are often used in paleoceanographic studies, including *Cibicides pachyderma* (*floridanus*), *C. cicatricosus*, *C. robertsonianus*, *Planulina wuellerstorfi*, *C. kulenbergi*, *Melonis barleeanum*, *Nutallides umbenifera*, *Planulina foveolata*, *P. arimenesis*, *Uvigerina* species. In addition to the calcitic species, we studied the chemistry of *Hoeglandina elegans*, a benthic foraminifer with an aragonitic shell. In light of recent findings of a strong correlation between the elemental composition (e.g., Sr, Mg,

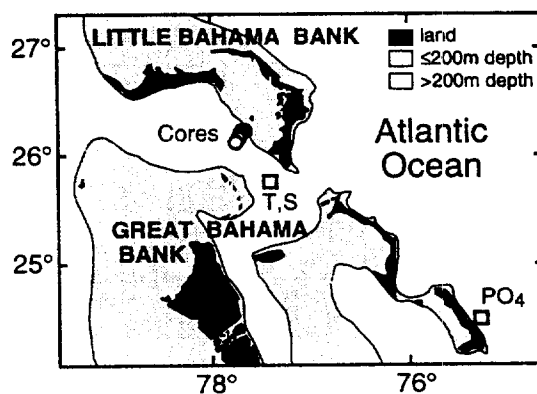


Fig. 1. A regional map of the Bahamas region. Core sites (circles) and hydrographic stations (squares) are marked on the map.

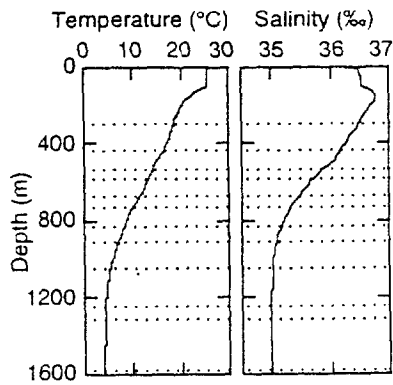


Fig. 2. Temperature and salinity data from the Bahamas region (station OC205-89 24.47°N 75.44°W); (Slowey and Curry, 1995). The stippled marks indicate the depth of cores from which foraminifera were picked.

and F) of corals and sea surface temperatures (Beck et al., 1992; Hart and Cohen, 1996; Mitsuguchi et al., 1996), it was interesting to examine the chemical response of *H. elegans* shells to the strong temperature gradient in LBB. Note that the Mg, Sr, and F data will be archived at NGDC/WDC-A.

Foraminifera shells were hand-picked from disaggregated sediments. Samples visibly contaminated with ferromanganese-oxides were excluded. A typical sample, weighing 0.5 mg contained between ten and twenty-five shells. For Mg, Sr, and F analysis, gently crushed samples were ultrasonically cleaned, first in distilled water and then in weak acid to remove any adhered sediment. This cleaning protocol proved sufficient for the analysis of minor-elements in foraminifera. Cleaned samples were dissolved with weak HNO<sub>3</sub>, calculated to result in approximately constant calcium concentrations, in order to minimize potential interferences from calcium (Ca = 0.017 M using 0.038 N HNO<sub>3</sub>). Fluoride was analyzed by the spectrophotometric technique of Greenhalgh and Riley (1961) for determination of fluoride in seawater, modified, and scaled down to run small samples (Rosenthal and Boyle, 1993). Calcium and magnesium were analyzed on a Perkin-Elmer model 403 flame atomic absorption spectrophotometer. All samples were diluted with lanthanum solution (400 ppm La in a 0.05 N HCl and a 0.002 N HNO<sub>3</sub> solution) to eliminate suppression of the Ca signal due to phosphine in the acetylene. Strontium concentrations were analyzed by isotope dilution using a spike enriched with the <sup>87</sup>Sr isotope. The <sup>87</sup>Sr/<sup>86</sup>Sr

ratio was measured on ICP-MS (VG PlasmaQuad-I). The long-term analytical precision of F/Ca, Mg/Ca, and Sr/Ca measurements was about ±2% as determined from replicate measurements of representative solutions. In general, at least three replicate samples were analyzed at each depth.

The Cd content of the shells was determined on separate splits according to the protocol outlined in Boyle and Keigwin (1985), with a small modification: the reduction step was performed before the oxidation step. This recently modified procedure was devised in order to eliminate potential CdS contamination which occurs primarily in suboxic sediments (Rosenthal, 1994). However, CdS contamination is not a problem in the highly oxic Bahama Banks sediments. The long-term precision was about 3.5% (at Cd/Ca ratios < 0.060 μmol mol<sup>-1</sup>).

### 3. RESULTS

Depth transects showing changes in the chemical composition of benthic foraminiferal shells as a function of water depth in Little Bahama Bank are shown in Figs. 3–6. Mg/Ca ratios in calcitic species from LBB decrease by a factor of 3–4 with increasing calcification depth (Fig. 3a–c), showing a strong covariance with water temperature. The Mg/Ca ratios in aragonitic shells of *H. elegans* decrease by a similar magnitude (about ×4) between the shallowest and deepest cores but are generally lower than in calcitic species, as expected from their aragonitic mineralogy (Fig. 3d). Calcitic shells of *Uvigerina spp.* deviate from this general behavior showing very low Mg/Ca ratios; not only lower than in other calcitic species but also than in shells of *H. elegans*. Note that shallow aragonitic samples from cores at 301 and 433 m show poor reproducibility which is not seen in the F and Sr data. Therefore, we suspect that contamination by high-Mg calcite led to some of the high values; high-Mg calcite does not contain unusually high levels of F and Sr and, therefore, such contamination should affect only the Mg/Ca ratio (Rude and Aller, 1991). In addition to the intergeneric variability among calcitic foraminifera, there is also significant interspecific variability, particularly among *Cibicidoides* species which is larger than our analytical precision and the natural intraspecific variability.

Sr/Ca ratios of calcitic shells show a smaller decrease

Table 1. Box cores from Little Bahama Bank with corresponding temperature, salinity, PO<sub>4</sub> and estimated Cd profiles. The Cd data was computed from phosphate data using Bruland and Franks (1983) and Sakamoto-Arnold et al. (1987) Sargasso Sea Cd-PO<sub>4</sub> relationship.

Core	Latitude °N	Longitude °W	Depth m	Temp. °C	Sal. psu	PO <sub>4</sub> μmol/kg	Cd nmol/kg
OC205-2 BC79	26.23	77.65	301	18.38	36.53	0.196	0.065
OC205-2 BC77	26.23	77.66	433	16.55	36.27	0.397	0.131
OC205-2 BC76	26.23	77.66	529	14.20	35.90	0.708	0.199
OC205-2 BC48	26.24	77.68	580	13.31	35.76	0.874	0.227
OC205-2 BC52	26.24	77.69	668	11.49	35.50	1.247	0.288
OC205-2 BC69	26.23	77.69	735	9.86	35.31	1.461	0.324
OC205-2 BC51	26.23	77.70	830	8.20	35.17	1.583	0.344
OC205-2 BC72	26.22	77.71	908	7.04	35.12	1.535	0.336
OC205-2 BC54	26.19	77.71	1043	5.34	35.04	1.357	0.306
OC205-2 BC57	26.16	77.72	1243	4.50	35.00	1.263	0.291
OC205-2 BC60	26.14	77.74	1312	4.35	34.99	1.248	0.288
OC205-2 BC61	26.12	77.75	1585	4.05	34.98	1.212	0.282

Note: temperature and salinity were measured at station OC205-89 and dissolved PO<sub>4</sub> concentrations measured at station AT109-237 (see Fig. 1).

Table 2. Location, depth, and bottom-water temperatures of deep Atlantic and Pacific core tops used in this study.

Core	Latitude	Longitude	Depth, m	Temp, °C
Equatorial Pacific				
ERDC 77 BC	04 55N	156 04W	3585	1.51
ERDC 79 BC	02 47N	156 14W	2767	1.79
ERDC 83 BC	01 24N	157 19W	2342	1.98
ERDC 84 BC	01 20N	157 19W	2339	1.98
ERDC 88 BC	00 03S	155 52W	1924	2.30
ERDC 89 P	00 00S	155 52W	4407	1.48
ERDC 92 BC	02 14S	157 00W	1598	2.71
ERDC 112 BC	01 38S	159 14W	2168	2.09
ERDC 113 P	01 38S	159 13W	2163	2.10
ERDC 120 BC	00 01S	158 42W	2247	2.03
ERDC 123 BC	00 01N	160 25W	2948	1.74
ERDC 125 BC	00 00S	161 00W	3368	1.58
ERDC 128 BC	00 00S	161 26W	3732	1.46
ERDC 135 BC	00 52S	160 59W	3509	1.52
ERDC 136 BC	01 06N	161 36W	3848	1.45
PLDS 66 BC	00 57N	104 06E	3496	1.48
PLDS 68 BC	01 02N	105 30E	3650	1.41
PLDS 70 BC	01 04N	107 13E	3694	1.39
PLDS 72 BC	01 01N	109 16E	3626	1.42
PLDS 77 BC	01 04N	119 56E	4366	1.47
PLDS 79 BC	01 05N	122 15E	4542	1.49
PLDS 89 BC	00 58N	131 39E	4407	1.48
Sierra Leone Rise				
EN66 10 GGC	06 39N	21 54W	3527	2.46
EN66 16 GGC	05 28N	21 08W	3152	2.62
EN66 21 GGC	04 14N	20 38W	3995	2.42
EN66 26 GGC	03 05N	20 01W	4745	2.27
EN66 29 GGC	02 28N	19 46W	5104	2.20
EN66 32 GGC	02 28N	19 44W	5003	2.19
EN66 38 GGC	04 55N	20 30W	2931	2.64
EN66 44 GGC	05 16N	21 43W	3428	2.53
Ceara Rise				
KNR 110 84 BC	04 22N	43 31W	2947	2.75
KNR 110 86 BC	04 27N	43 29W	3320	2.56
KNR 110 88 BC	04 38N	43 39W	2952	2.75
KNR 110 90 BC	04 43N	43 25W	3654	2.45
KNR 110 92 BC	04 46N	43 17W	3882	2.40
KNR 110 94 BC	04 53N	43 05W	4107	1.52
KNR 110 96 BC	05 09N	43 59W	4427	0.91
KNR 110 99 BC	04 22N	43 44W	4643	1.05

(about 10%) throughout the depth interval between 300 and 1300 m with no obvious correlation with temperature (Fig. 4a-c). The observed Sr partition coefficient ( $D_{Sr}$ ) in *Cibicides* spp. and *M. barleeanum* decreases from 0.18 in shallow samples to about 0.15 in the deepest ones. The generally high  $D_{Sr}$  values are consistent with values expected at fast precipitation rates (Lorens, 1981), characteristic of foraminiferal calcite (Carpenter and Lohmann, 1992). Shells of *Uvigerina* spp. have significantly lower Sr content than in other calcitic species. There is no significant interspecific variability in the Sr content of *Cibicides* species. The Sr/Ca ratios in *H. elegans* are 20–40% higher than in calcitic shells (Fig. 4d). Sr/Ca ratios in the aragonitic shells decrease from about 2.5 to 1.7 mmol mol<sup>-1</sup> between 301 and 1585 m. These values are about three to four times higher than Sr/Ca ratios observed in shells from deeper sites

(>2000 m) (Elderfield et al., 1996), suggesting a continuous decrease of  $D_{Sr}$  with increasing water depth as is also seen in calcitic species.

F/Ca ratios of benthic foraminifera are generally constant, showing no change with increasing calcification depth, regardless of species or mineralogy (Fig. 5). There are significant differences, however, among species: the F/Ca ratio in *Cibicides* species and *M. barleeanum* from the shallowest core (301 m) is about 3.5 mmol mol<sup>-1</sup>, which is significantly higher than observed in planktonic species (Rosenthal and Boyle, 1993). F/Ca ratios in *M. barleeanum* decrease from 3.5 to about 1 mmol mol<sup>-1</sup> between 301 and 1312 m. However, this change is relatively abrupt, and the F/Ca profile shows no visual similarity to any hydrographic property. As seen for Mg and Sr, F/Ca ratios in *Uvigerina* shells are also anomalously low (mean F/Ca = 0.35 mmol mol<sup>-1</sup>), as low as F/Ca ratios in the aragonitic shells of *H. elegans* (F/Ca = 0.37 mmol mol<sup>-1</sup>; Fig. 5d). The absence of any discernible change in F/Ca despite a 14°C temperature gradient and a salinity change of about 1.5‰ between 301 and 1585 m suggests that neither parameter has a significant influence on the uptake of F by benthic foraminifera. Likewise, the records show no correlation with carbonate ion activity; a decrease in the CO<sub>3</sub><sup>2-</sup> content with depth should have resulted in increasing solid phase fluoride (Rosenthal and Boyle, 1993). The new data support our previous conclusions that F/Ca of foraminifera is governed primarily by biological processes.

The effect of temperature on the partitioning of Cd into calcitic shells was also tested in this study. The foraminiferal data represent an average value of eight benthic species (Table 3). From a total of sixty samples, six samples were suspected of being contaminated and were, therefore, rejected from the discussion. A comparison between Cd/Ca observed in calcitic shells and ratios predicted from dissolved phosphate (Fig. 6) suggests that foraminiferal Cd/Ca in LBB samples records the general features of the nutricline. Samples from cores deeper than 900 m are consistently higher than predicted by the above mentioned relationship. These deviations are smaller than 0.020 μmol kg<sup>-1</sup> and, therefore, may be explained by small sedimentary contamination; the low nutrient concentrations of the Atlantic thermocline water (PO<sub>4</sub> < 1.5 μmol kg<sup>-1</sup>) may potentially lead to a relatively large analytical error, due to even a very small contamination from the sediments. For example, a contamination of the order of 0.010 μmol mol<sup>-1</sup> in Cd/Ca may result in errors of 5 and 10% in deep Pacific and deep Atlantic samples, respectively, but may cause a 50–100% increase in the Cd/Ca ratios of samples from the Bahama Banks. Alternatively, it is possible that the increase in the Cd partition coefficient suggested by Boyle (1992) starts at water depth shallower than 1150 m.

The chemical composition of *Uvigerina* is quite puzzling. The Mg/Ca, Sr/Ca, and F/Ca ratios in *Uvigerina* shells are very different than in other calcitic foraminifera and, in fact, more similar to ratios obtained in aragonitic shells of *H. elegans*. In contrast, Cd/Ca ratios are the same in all calcitic shells and very different than in aragonitic shells. These differences reflect the important role that biological pro-

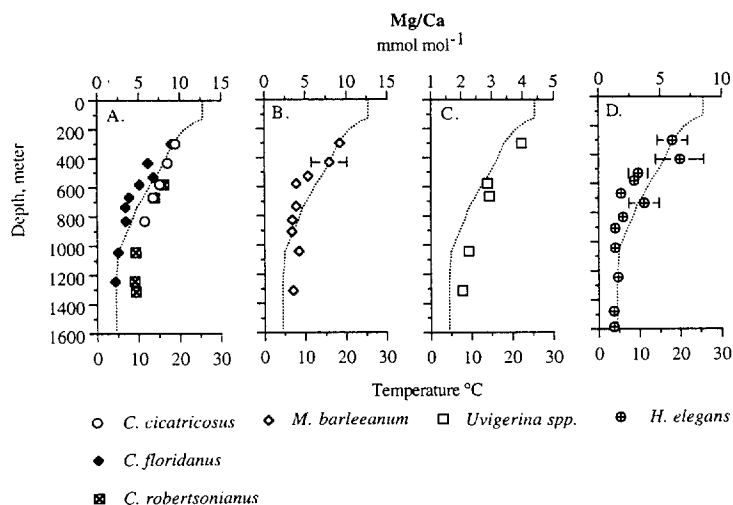


Fig. 3. Mg/Ca ratios in benthic foraminifera from Little Bahama Bank: (a) *Cibicidoides* species; (b) *M. barleeianum*; (c) *Uvigerina spp.*; and (d) *H. elegans*. Note the change in scale. The dotted line represents the in situ temperature profile. Figures 3–5 show mean and one standard error ( $n \geq 2$ ) for each sample (note that in many cases the error bar is smaller than the symbol size).

cesses have on the chemistry of foraminiferal shells, which sometimes dominate over mineralogical differences.

#### 4. DISCUSSION

##### 4.1. Magnesium in Calcitic Foraminifera

Plotting *Cibicidoides* data from Little Bahama Bank and from deeper sites in the Atlantic (Sierra Leone Rise and Ceara Rise) and Equatorial Pacific (Ontong Java Plateau) Oceans accentuates the trends observed above (Fig. 7); there is a remarkable similarity between the global Mg/Ca and temperature profiles (estimated from GEOSECS and Levitus Atlas data), suggesting that temperature is most

likely the primary control on the Mg content of calcitic foraminifera. A temperature regulation on the coprecipitation of Mg in foraminiferal shells probably involves both a thermodynamic response of the inorganic distribution coefficient ( $k_{Mg}^c$ ), and a temperature effect on physiological processes regulating the uptake of Mg into the cell. The effect of temperature on the coprecipitation of Mg in inorganic calcites has been investigated by several researchers (Katz, 1973; Mucci, 1987; Oomori et al., 1987). The experimentally derived Mg distribution coefficients obtained in these studies were positively correlated with temperature although there were significant differences in the absolute values obtained in each study (see reviews by: Morse and Bender,

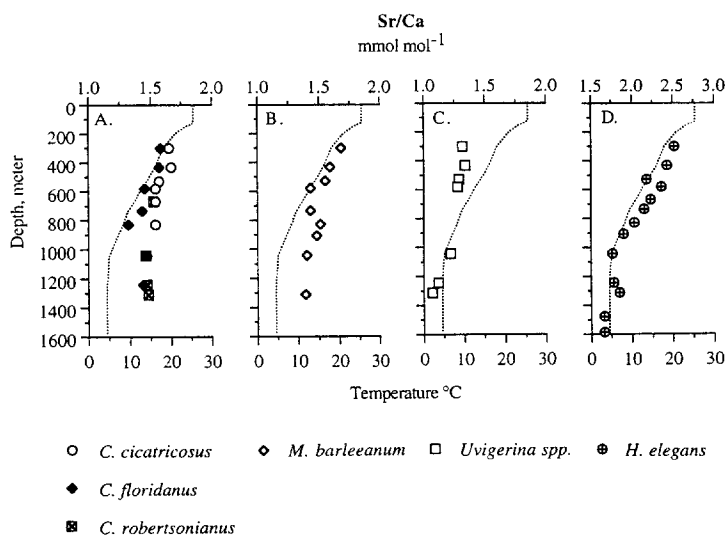


Fig. 4. Sr/Ca ratios in benthic foraminifera from Little Bahama Bank: (a) *Cibicidoides* species; (b) *M. barleeianum*; (c) *Uvigerina spp.*; and (d) *H. elegans*. Note the change in scale. The dotted line represents the in situ temperature profile.

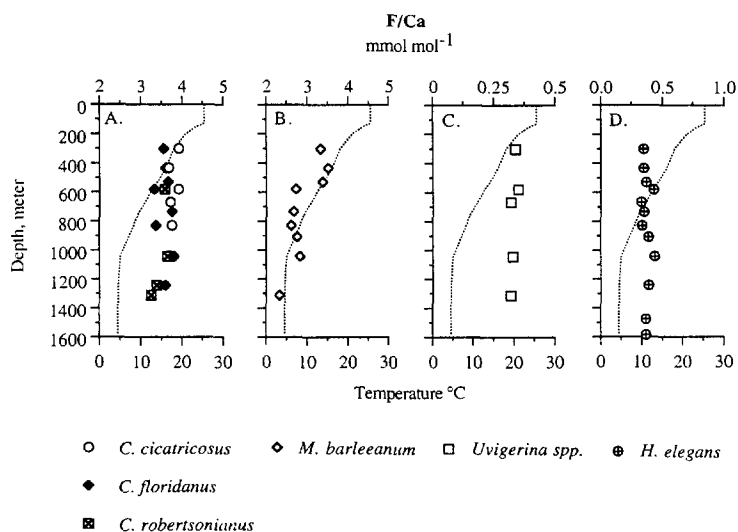


Fig. 5. F/Ca ratios in benthic foraminifera from Little Bahama Bank: (a) *Cibicidoides* species; (b) *M. barleeaanum*; (c) *Uvigerina* spp.; and (d) *H. elegans*. Note the change in scale. The dotted line represents the in situ temperature profile.

1990; Mucci and Morse, 1990). Based on inorganic precipitation experiments, a 30–40% decrease in  $k_{Mg}$  may be expected due to a temperature change from 25°C to 5°C which is consistent with our estimate from thermodynamic consid-

erations (Table 4). The field data show about 70% decrease in Mg/Ca ratios of benthic foraminifera, along a similar temperature gradient (i.e., 20°C). Evidently, temperature related physiological processes have a dominant role in regu-

Table 3. Cd/Ca ratios in benthic foraminifera from Little Bahama Bank. Also shown are the average ratios, standard error, and number of samples (in parentheses is the number of rejected values marked with "r").

Depth m	Cd/Ca, $\mu\text{mol/mol}$				
	<i>C. floridanus</i>	<i>C. kulenbergi</i>	<i>P. wuellerstorfi</i>	<i>Uvigerina</i>	<i>M. barleeaanum</i>
301	0.020; 0.017	0.015		0.003	0.016; 0.095r
433	0.014; 0.020			0.021	0.023
529	0.062r			0.025	0.032
580	0.030; 0.045; 0.028			0.037; 0.045; 0.031	0.033
668	0.042			0.049	0.068
735	0.071	0.041			0.059
830	0.088; 0.036	0.080			0.045
908	0.080; 0.087		0.099		0.056
1043	0.047	0.045		0.058	
1243	0.047	0.128r	0.056	0.067	
1312		0.062; 0.052	0.089	0.035	
1585	0.091	0.039			

Depth m	Cd/Ca, $\mu\text{mol/mol}$			Average $\mu\text{mol/mol}$	SE	n (r)
	<i>P. arimenensis</i>	<i>P. foveolata</i>	<i>N. umbonifera</i>			
301	0.071r			0.014	0.003	7 (2)
433	0.016			0.019	0.002	5
529				0.029	0.003	3 (1)
580	0.037	0.044	0.030; 0.030; 0.026	0.035	0.002	12
668				0.053	0.008	3
735	0.047			0.054	0.007	4
830				0.062	0.014	4
908	0.066			0.078	0.008	5
1043	0.047		0.124r	0.049	0.003	5 (1)
1243				0.057	0.006	4 (1)
1312				0.060	0.011	4
1585			0.152r; 0.057	0.062	0.015	4 (1)

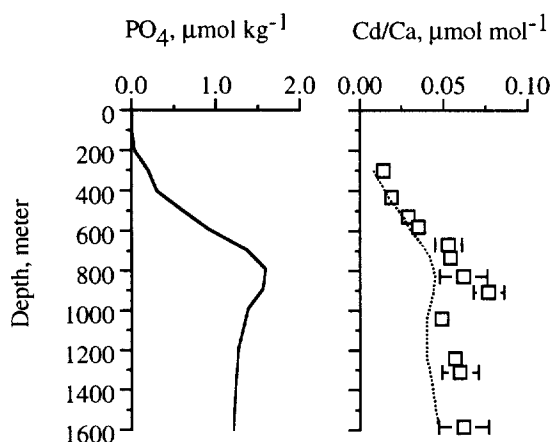


Fig. 6. (a) Dissolved  $\text{PO}_4$  profile from station AT109-237 (25.76°N 77.41°W) (Roemmich and Wunsch, 1985); (b) Cd/Ca concentrations ( $\mu\text{mol mol}^{-1}$ ) in calcitic foraminifera. Plotted are mixed species average values and one standard error. The dotted line represents predicted foraminiferal Cd/Ca ratios calculated from seawater Cd concentrations using Boyle (1992) Cd partition coefficient for calcitic foraminifera: for core depth < 1150 m,  $D_{\text{Cd}} = 1.3$ ; and for core depth = 1150–3000 m,  $D_{\text{Cd}} = 1.3 + (\text{depth} - 1150) (1.6/1850)$ . Seawater Cd concentrations were estimated from dissolved phosphate using Sargasso Sea data (Bruland and Franks, 1983; Sakamoto-Arnold et al., 1987) in preference to the global Cd- $\text{PO}_4$  relationship (Boyle, 1988) because shallow waters are not as uniform in Cd-P as are deep waters.

lating the coprecipitation of Mg in foraminiferal shells, as is also inferred from the large intergeneric and interspecific differences observed in both planktonic and benthic foraminifera.

Can we use Mg/Ca ratios of benthic foraminifera for seawater paleothermometry? The relatively large interspecific variability among benthic species suggests that using a single species calibration may yield the best precision. The calcitic foraminifer, *C. floridanus* (*pachyderma*), has the largest depth range and is abundant in both Holocene and glacial sediments which makes it a prime candidate for paleoceanographic studies in this region. A scatter graph of Mg/Ca ratios in *C. floridanus* from LBB against bottomwater temperature is shown in Fig. 8 (Table 5). Theoretically, one expects the partition coefficient to be exponentially dependent on temperature in proportion to the enthalpy or activation energy of the reactions involved with the calcification process. Therefore, we chose to apply an exponential model to the observed data. The following dependence between seawater temperature and Mg/Ca ratios in shells of *C. floridanus* was obtained:

$$T(^{\circ}\text{C}) = 22.7 \log (\text{Mg/Ca}) - 3.05$$

Adopting the exponential rather than linear fit implies that the sensitivity of foraminiferal Mg to temperature ( $\Delta\text{Mg}/\Delta T$ ) increases with temperature. For instance, using our calibration, a 1°C change between 5 and 6°C leads to a 0.24  $\text{mmol mol}^{-1}$  change in Mg/Ca while a temperature change between 15 and 16°C results in Mg/Ca increase of 0.66  $\text{mmol mol}^{-1}$ . Therefore, Mg/Ca should be a better paleothermometer in thermocline waters where its sensitivity is

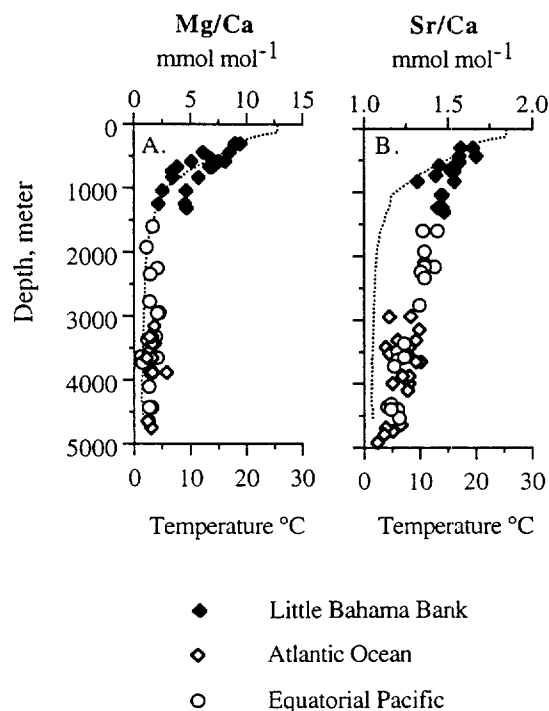
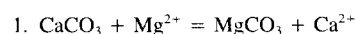


Fig. 7. Ocean wide *Cibicidoides* Mg/Ca (a) and Sr/Ca (b) data from Little Bahama Bank, Sierra Leone Rise, and Ceara Rise in the Atlantic Ocean and from the Ontong Java Plateau in the Pacific Ocean.

Table 4. Relative changes in the distribution coefficient of Mg in calcite due to a temperature change from 25°C to 5°C as estimated from inorganic precipitation experiments and from thermodynamic considerations. The thermodynamic coefficient ( $k_{\text{Mg}}^{\text{M}}$ ) is determined by the ratio of the solubility products  $K^{\text{C}}$  and  $K^{\text{M}}$  of pure calcite and magnesite, by the ratio of the effective activity coefficients of  $\text{MgCO}_3$  and  $\text{CaCO}_3$  in the precipitate, and by the ratio of the activity coefficients of  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in seawater (Eqn. 2). Assuming that temperature has only negligible effect on the ratios of the solid and aqueous activity coefficients, then temperature induced changes in the distribution coefficient are controlled largely by changes in the ratio of the solubility products  $K^{\text{C}}/K^{\text{M}}$  which is estimated from equation 3.  $\Delta H_{25^{\circ}\text{C}}^{\circ}$  is the reaction enthalpy (Robie et al., 1978), R the gas constant and T is the temperature in Kelvin. Both the inorganic experiments and the thermodynamic calculation suggest about 30–40% decrease in  $k_{\text{Mg}}^{\text{M}}$  due to temperature change from 25°C to 5°C.



$$2. k_{\text{Mg}}^{\text{C}} = \frac{K^{\text{C}}}{K^{\text{M}}} \cdot \frac{\lambda_{\text{CaCO}_3}}{\lambda_{\text{MgCO}_3}} \cdot \frac{\gamma_{\text{Mg}^{2+}}}{\gamma_{\text{Ca}^{2+}}}$$

$$3. \log \left( \frac{K_{T_2}}{K_{T_1}} \right) = \frac{\Delta H^{\circ}}{2.3R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$(\Delta H_{25^{\circ}\text{C}}^{\circ} = 18.06 \text{ kJ mol}^{-1} \text{ K}^{-1})$$

4. $K_{5^{\circ}\text{C}}/K_{25^{\circ}\text{C}}$ Relative change:	
Katz, 1973:	0.69
Mucci, 1987:	0.70
Oomori et al., 1987:	0.53
Calculated (this study):	0.59

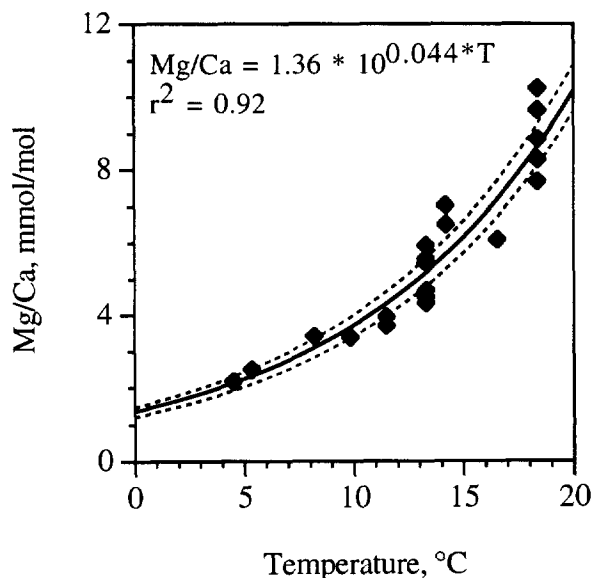


Fig. 8. Mg/Ca ratios in *C. floridanus* as a function of water temperature. Data points represent analysis of a single sample (10–25 shells) rather than an average value. Also included is an exponential regression (solid line) with forecast interval at the 96% confidence level (dashed lines).

high. The forecasting uncertainty varies from about  $\pm 0.60$  to  $0.85^\circ\text{C}$  (at the 95% level) along a temperature gradient from 12 to  $18^\circ\text{C}$ , respectively. A similar relationship, though with slightly larger scatter, is obtained when using the global *Cibicoides* data. An uncertainty of this magnitude may limit the use of Mg/Ca paleothermometry in deep waters, where expected temperature variations are small but can be very useful for thermocline paleoceanography.

#### 4.2. Strontium in Calcitic Foraminifera

The global Sr/Ca data exhibit a linear decrease with increasing water depth with no correlation with temperature (Fig. 7b), suggesting that temperature is not the primary cause for the observed change. This conclusion is supported by inorganic precipitation experiments and thermodynamic considerations which suggest that the distribution coefficient of Sr in calcite is inversely correlated with temperature. Using similar calculations to those presented above for Mg, a  $20^\circ\text{C}$  decrease in temperature should lead to about 30% increase in Sr/Ca, in sharp contrast with the observed records. The only available data from inorganic experiments suggest that temperature has only a negligible effect on the Sr distribution coefficient in calcite (Katz et al., 1972).

The linear decrease in Sr/Ca with increasing water depth suggests that the partition coefficient of Sr ( $D_{\text{Sr}}$ ) in foraminiferal shells (both calcitic and aragonitic) is probably a pressure related phenomenon (Lloyd-Kindstrand et al., 1994; McCorkle et al., 1995; Elderfield et al., 1996). While a pressure dependence of the thermodynamic coefficients is plausible, the large magnitude of the change in Sr/Ca suggests that other processes are very important. Depth related decreases in  $D_{\text{Ca}}$ ,  $D_{\text{Ba}}$ , and  $D_{\text{Sr}}$  were observed in core top

(dead) *P. wuellerstorfi* shells from Ontong Java Plateau (McCorkle et al., 1995). Based on these data McCorkle et al. (1995) concluded that these trends may be explained by post-depositional, inhomogeneous dissolution, or by saturation-state effect on the calcification of benthic foraminifera. The former explanation is apparently at odds with our records from LBB showing that the decrease in  $D_{\text{Sr}}$  already starts in shallow water, well above the lysocline. There is also no evidence in LBB sediments for significant metabolic dissolution. Recently, Elderfield et al. (1996) presented a conceptual model in which the Sr content of foraminiferal shells is determined by the extent of calcification from a closed internal pool which controls the solution Sr/Ca ratio and, consequently, the heterogeneous partition coefficient. The model relies on the proposal of Erez et al. (1994) suggesting that calcitic shells of foraminifera precipitate from an internal calcification pool rather than directly from seawater. Consequently, it was suggested that the depth gradient of  $D_{\text{Sr}}$  reflects a regular change in the calcification rate with increasing depth. However, the cause for the change in calcification rate with increasing water depth is unclear. Clearly, the nature of these effects needs further investigation.

#### 4.3 Cadmium in Calcitic Foraminifera

The conformity of foraminiferal cadmium with shallow water nutrient composition is very encouraging. First, the Cd record suggests that the effect of temperature on the uptake of Cd by calcitic foraminifera is rather minimal: despite a temperature change of more than  $10^\circ\text{C}$  between 300 and 1150 m, there is no discernible change in the Cd partition coefficient. This conclusion is consistent with Boyle (1992) who showed that  $D_{\text{Cd}}$  more than doubles between the depths of 1150 and 3000 m (from 1.3 to 2.9, respectively) while bottom water temperature changes only slightly. We found no significant difference between the interspecific and intraspecific variability of shallow species, in agreement with previous studies (Boyle, 1992). More importantly, the core tops calibration demonstrates the potential of foraminiferal Cd for reconstructing nutrient concentrations in shallow waters. There, the distribution of carbon isotopes is influenced not only by the cycling of organic matter but also by gas exchange with atmospheric  $\text{CO}_2$ . Cadmium, which does not circulate through the atmosphere, provides an independent proxy for nutrient chemistry. In principle, by using Cd (as  $\text{PO}_4$  proxy) and  $\delta^{13}\text{C}$  data in shallow water foraminifera, the

Table 5. Mg/Ca ratios in calcitic shells of *C. floridanus*. Each sample contained ten to twenty shells.

Depth, m	Temp, °C	Mg/Ca, mmol/mol					
301	18.38	8.28	9.64	8.85	7.68	10.24	
433	16.55	6.09					
529	14.20	6.51	7.03				
580	13.31	4.68	5.94	5.45	4.49	5.56	4.34
668	11.49	3.71	3.95				
735	9.86	3.39					
830	8.20	3.42					
1043	5.34	2.50					
1243	4.50	2.17					



atmospheric signature on the carbon isotopic composition of seawater may be extracted. This approach was applied recently to glacial samples along a depth transect in the Bahama Bank in order to reconstruct the ocean surface chemistry where the water masses originated (Slowey and Curry, 1995; Marchitto et al., 1996).

#### 4.4. *Hoeglandina elegans*

The benthic species *H. elegans* is a living foraminifer with an aragonitic shell. Its global abundance make it a useful species for intermediate depth and upper deepwater paleoceanography (Boyle et al., 1995). Based strictly on structural considerations, the chemical composition of aragonitic shells should be significantly different than that of calcitic shells. Because  $\text{SrCO}_3$  is iso-structural with the aragonite crystal cell (orthorhombic), one may expect higher concentrations of Sr in aragonite than in calcite which has a tighter rhombohedral structure. Similarly, it was suggested that a substitution of  $\text{CO}_3^{2-}$  group with two  $\text{F}^-$  anions is more likely to occur in aragonitic than in calcitic crystal structure (Ichikuni, 1979). The higher F content of corals is consistent with this hypothesis (Carpenter, 1969). In contrast,  $\text{MgCO}_3$  is isostructural with calcite, and, therefore, we expect lower Mg content in aragonitic than in calcitic shells.

The Mg/Ca ratios in aragonitic shells of *H. elegans* are generally lower than in calcitic species, as expected from their aragonitic mineralogy. The ratios obtained in the aragonitic shells and the degree of covariance with temperature are similar to those recently observed in corals (Mitsuguchi et al., 1996) suggesting that the decreasing trend with depth is probably caused by temperature. The temperature sensitivity of *H. elegans* is about a factor of two lower than obtained for *C. floridanus*, and, therefore, we have focused on the latter as a potential paleothermometer. In contrast, the Sr and F chemistry of *H. elegans* is very different than that of corals and inorganically precipitated aragonites. The partition coefficient of strontium in *H. elegans* varies between 0.28 and 0.19 (at 300 and 1585 m, respectively). These values are about five times lower than coefficients obtained in corals and aragonitic algae (Smith et al., 1979) and in inorganically precipitated aragonites (at 20°C) (Kinsman and Holland, 1969). The  $D_{\text{Sr}}$  values are similar to partition coefficients obtained in aragonitic marine mollusks (Lorenz and Bender, 1980; Rosenthal and Katz, 1989). The positive covariance between Sr/Ca and temperature, observed in *H. elegans* samples, is also apparently in contrast with results from laboratory experiments (Kinsman and Holland, 1969) as well as with the trend observed in corals (Beck et al., 1992; De Villiers et al., 1994), suggesting an inverse correlation between Sr uptake and temperature. Therefore, it is likely that, as was discussed for calcitic species, the Sr/Ca decrease in *H. elegans* is related to depth-dependent factors other than temperature. The F/Ca ratios are also substantially lower than observed in aragonitic corals and algae (Carpenter, 1969; Rude and Aller, 1991) as well as in inorganic aragonite (Kitano and Okumura, 1973). The apparent disparities between the chemical composition of *H. elegans* and other biogenic aragonites suggest a strong biological regulation of the calcification process.

## 5. CONCLUSIONS

Surface sediments from Little Bahama Bank, intersecting the subtropical thermocline, were used to assess the influence of temperature on the incorporation of Mg, Sr, F, and Cd into shells of benthic foraminifera. We suggest that the Mg content of shallow water benthic foraminifera can be used as an independent tracer of thermocline paleotemperatures, thereby allowing the reconstruction of the conditions at the ocean surface where the deep water masses originated. This new approach avoids many of the limitations associated with studies of planktonic foraminifera (e.g., uncertainty with respect to calcification depth and post-burial dissolution). The best precision of Mg/Ca thermometry may be achieved by using single species calibrations which avoid the scatter introduced by interspecific variability. In principle, the method should allow for analyzing  $\delta^{18}\text{O}$  and Mg/Ca on the same samples, thus avoiding potential errors introduced by combining measurements on different organisms which could have lived at different depths or during different seasons. This is an important advantage over other approaches because using combined measurements of foraminiferal  $\delta^{18}\text{O}$ , and Mg will allow for the estimation of both paleo-temperature and salinity which may provide the physical dataset necessary for reconstructing surface-water paleohydrography.

This study also demonstrates that Cd/Ca ratios of shallow benthic species reflect the vertical distribution of nutrients in the thermocline. We found no significant influence of temperature on the partitioning of Cd into benthic shells despite 13°C temperature change along the LBB transect. Our data extend the previous deep water calibration (Boyle, 1992), thereby allowing for the reconstruction of the nutrient chemistry of shallow thermocline waters. Consequently, it offers the possibility that, using coupled Cd and  $\delta^{13}\text{C}$  data in shallow waters, the atmospheric signature on the carbon isotopic composition of seawater may be extracted.

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