

# Temperature and carbonate ion effects on Mg/Ca and Sr/Ca ratios in benthic foraminifera: Aragonitic species *Hoeglundina elegans*

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[1] Core top samples from Atlantic (Little Bahama Banks (LBB)) and Pacific (Hawaii and Indonesia) depth transects have been analyzed in order to assess the influence of bottom water temperature (BWT) and aragonite saturation levels on Mg/Ca and Sr/Ca ratios in the aragonitic benthic foraminifer *Hoeglundina elegans*. Both the Mg/Ca and Sr/Ca ratios in *H. elegans* tests show a general decrease with increasing water depth. Although at each site the decreasing trends are consistent with the in situ temperature profile, Mg/Ca and Sr/Ca ratios in LBB are substantially higher than in Indonesia and Hawaii at comparable water depths with a greater difference observed with increasing water depth. Because we find no significant difference between results obtained on “live” and “dead” specimens, we propose that these differences are due to primary effects on the metal uptake during test formation. Evaluation of the water column properties at each site suggests that in situ CO<sub>3</sub> ion concentrations play an important role in determining the *H. elegans* Mg/Ca and Sr/Ca ratios. The CO<sub>3</sub> ion effect is limited, however, only to aragonite saturation levels ( $[\Delta\text{CO}_3]_{\text{aragonite}}$ ) below 15  $\mu\text{mol kg}^{-1}$ . Above this level, temperature exerts a dominant effect. Accordingly, we propose that Mg/Ca and Sr/Ca in *H. elegans* tests can be used to reconstruct thermocline temperatures only in waters oversaturated with respect to the mineral aragonite using the following relationships:  $\text{Mg/Ca} = (0.034 \pm 0.002)\text{BWT} + (0.96 \pm 0.03)$  and  $\text{Sr/Ca} = (0.060 \pm 0.002)\text{BWT} + (1.53 \pm 0.03)$  (for  $[\Delta\text{CO}_3]_{\text{aragonite}} > 15 \mu\text{mol kg}^{-1}$ ). The standard error associated with these equations is about  $\pm 1.1^\circ\text{C}$ . Reconstruction of deeper water temperatures is complicated because in undersaturated waters, changes in Mg/Ca and Sr/Ca ratios reflect a combination of changes in [CO<sub>3</sub>] and BWT. Overall, we find that Sr/Ca, rather than Mg/Ca, in *H. elegans* may be a more accurate proxy for reconstructing paleotemperatures.

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## 1. Introduction

[2] Mg/Ca paleothermometry in benthic foraminifera is a proxy that potentially allows for salinity-independent reconstruction of bottom water temperatures (BWT) [Rosenthal *et al.*, 1997]. When used in conjunction with foraminiferal  $\delta^{18}\text{O}$ , it may enable quantitative reconstructions of seawater  $\delta^{18}\text{O}$ , and, with judicious assumptions, potentially the estimation of variations in salinity, global ice volume and past ocean circulation [e.g., Billups, 2003; Billups and

Schrag, 2002; Lear *et al.*, 2000, 2003, 2004; Keigwin *et al.*, 2003; Martin *et al.*, 2002].

[3] To date, BWT reconstructions are based only on the Mg/Ca of calcitic benthic foraminifera [Lear *et al.*, 2002; Martin *et al.*, 2002]. In this manuscript we assess the potential use of both Mg/Ca and Sr/Ca in the aragonitic benthic foraminifer *Hoeglundina elegans* for reconstructing seawater temperature. This species has a widespread distribution, occurring in the Atlantic, Pacific and Indian oceans [Morkhoven *et al.*, 1986]. Although most abundant on the outer shelf and slope, it has been observed at depths up to 4,330 m [Phleger and Parker, 1951] and is generally considered a cosmopolitan, oligotrophic taxon, which lives close to the sediment-water interface. This form evolved in the Eocene [Morkhoven *et al.*, 1986], but because of its high dissolution susceptibility does not often occur continuously through the geological record. Nevertheless, it is a favored species for trace element (cadmium/calcium)-based intermediate-depth nutrient reconstructions because its tests are smooth and glassy, making it less susceptible to contamination by sedimentary-derived authigenic phases than many calcitic species [Boyle *et al.*, 1995; Marchitto *et al.*, 1998].

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**Table 1.** Core Top Locations

Core	Latitude	Longitude	Depth, m	BWT, °C	Core Type <sup>a</sup>
<i>Bahamas</i>					
OC205-2 BC79	26.23°N	77.65°W	301	18.4	BC
OC205-2 BC77	26.23°N	77.66°W	433	16.6	BC
OC205-2 BC76	26.23°N	77.66°W	529	14.2	BC
OC205-2 BC48	26.24°N	77.68°W	580	13.3	BC
OC205-2 BC52	26.24°N	77.69°W	668	11.5	BC
OC205-2 BC69	26.23°N	77.69°W	735	9.9	BC
OC205-2 BC51	26.23°N	77.70°W	830	8.2	BC
OC205-2 BC54	26.19°N	77.71°W	1043	5.5	BC
OC205-2 BC57	26.16°N	77.72°W	1243	4.5	BC
OC205-2 BC60	26.14°N	77.74°W	1312	4.4	BC
OC205-2 BC59	26.15°N	77.73°W	1477	4.2	BC
OC205-2 BC61	26.12°N	77.75°W	1585	4.1	BC
<i>Hawaii</i>					
MW98-13 MC47	20.78°N	157.10°W	194	17.3	MC
MW98-13 MC32	20.92°N	157.10°W	320	12.0	MC
MW98-13 MC46	20.80°N	157.05°W	402	8.7	MC
MW98-13 MC39	20.88°N	159.15°W	715	5.0	MC
MW98-13 MC28	20.81°N	157.12°W	797	4.6	MC
MW98-13 MC138	20.87°N	157.33°W	1775	2.4	MC
MW98-13 MC137	20.77°N	157.32°W	2578	1.8	MC
MW98-13 MC42	20.77°N	157.32°W	2583	1.8	MC
MW98-13 MC135	20.72°N	157.32°W	2682	1.8	MC
<i>Indonesia</i>					
BJ8-03MC37	3.86°S	119.48°E	179	15.7	MC
BJ8-03MC40	3.91°S	119.50°E	251	11.5	MC
BJ8-03MC63	3.87°S	119.47°E	252	11.7	MC
BJ8-03MC45	2.87°N	118.39°E	332	10.0	MC
BJ8-03MC65	3.57°S	119.04°E	334	9.8	MC
BJ8-03MC58	3.87°S	119.46°E	347	9.7	MC
BJ8-03MC67	3.57°S	119.40°E	401	8.9	MC
BJ8-03MC56	3.88°S	119.46°E	405	8.8	MC
BJ8-03MC129	5.85°S	120.28°E	406	8.7	MC
BJ8-03MC31	3.88°S	119.45°E	459	8.0	MC
BJ8-03MC33	3.89°S	119.45°E	505	7.5	MC
BJ8-03MC77	1.74°S	117.41°E	525	7.2	MC
BJ8-03MC35	3.89°S	119.44°E	565	7.0	MC
BJ8-03MC49	3.89°S	119.41°E	676	6.4	MC
BJ8-03MC140	6.08°S	120.14°E	755	5.9	MC
BJ8-03MC138	6.15°S	120.09°E	827	5.6	MC
BJ8-03MC24	5.06°S	117.45°E	832	5.5	MC
BJ8-03MC53	3.89°S	119.39°E	868	5.3	MC
BJ8-03MC22	3.89°S	119.50°E	1189	4.0	MC
BJ8-03MC72	2.02°S	117.59°E	1552	3.8	MC

<sup>a</sup>MC indicates multicore; BC indicates box core.

[4] Although it has been proposed recently that variations in Mg and Sr content of *H. elegans* tests can be used to reconstruct bottom water temperatures [Reichart et al., 2003], no rigorous examination of the environmental factors potentially affecting their chemical composition has been carried out so far. Here we use core top samples collected along three depth transects in the Atlantic and Pacific oceans to unravel and quantify the effects of temperature and CO<sub>3</sub> ion concentrations (hereinafter referred to as [CO<sub>3</sub>]) on Mg/Ca and Sr/Ca in *H. elegans*. Taking advantage of the different bottom water carbonate chemistries of these sites, we show that both temperature and [CO<sub>3</sub>] exert significant influence on the Mg and Sr content of the aragonite shells of *H. elegans*. The [CO<sub>3</sub>] ion effect is, however, limited to waters that are undersaturated with respect to aragonite. Furthermore, by comparing data obtained on “live” and “dead” tests, we show that this

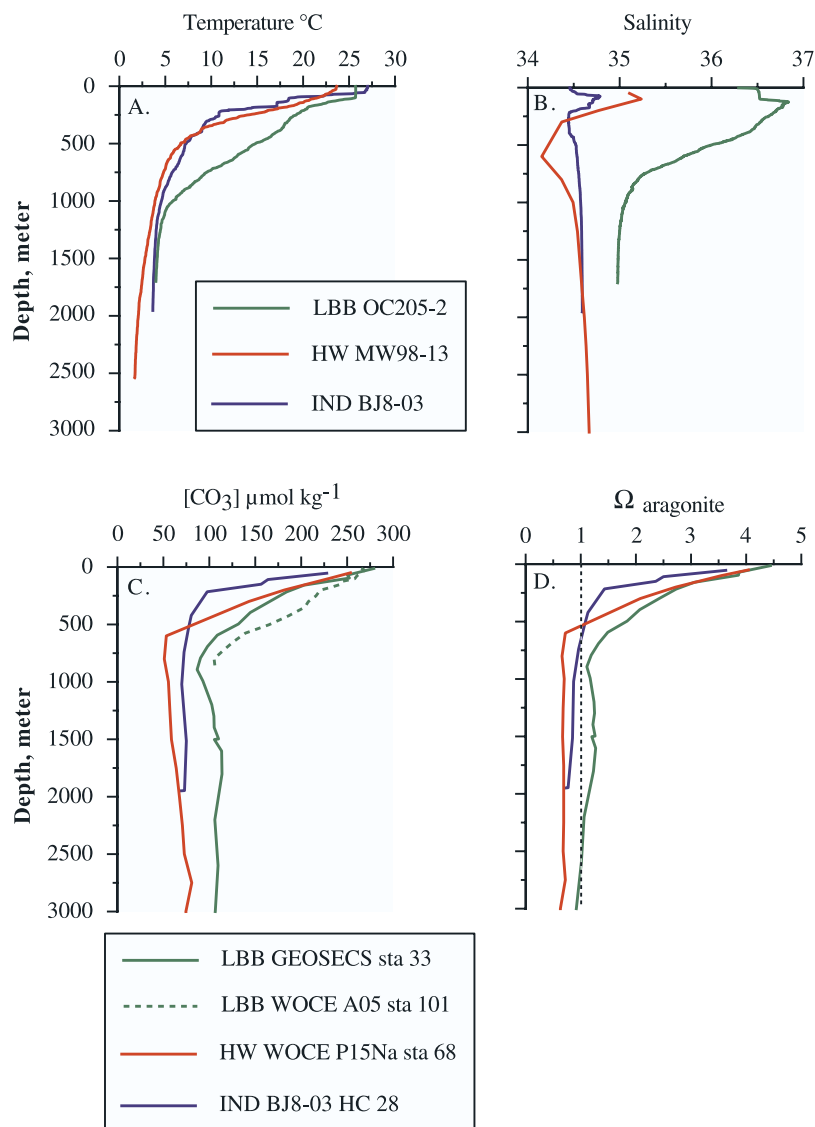
[CO<sub>3</sub>] ion effect is primarily due to saturation effect on the metals uptake during shell formation and not due to post-mortem alteration of the tests by preferential dissolution.

## 2. Methods

### 2.1. Sample Locations

[5] Samples were obtained from three depth transects: (1) Little Bahama Bank (LBB); (2) Hawaiian Islands (HW); and (3) Sulawesi margins in Indonesia (IND) (Table 1). The three transects cover a similar range in bottom water temperature (BWT), although there is a significant difference in the thermocline structure between the Atlantic and Pacific sites (Figure 1). Temperature and salinity profiles are based on conductivity-temperature-depth (CTD) data collected near the coring sites during each cruise [Slowey, 1990]. Total dissolved inorganic carbon (TCO<sub>2</sub>) and total alkalinity (TALK) data for LBB and HW come from the nearest GEOSECS [Bainbridge, 1981; Broecker et al., 1982] and WOCE stations (A05 station 101: [http://cdiac.esd.ornl.gov/oceans/ndp\\_074/ndp074.html](http://cdiac.esd.ornl.gov/oceans/ndp_074/ndp074.html) and station P15Na 68: <http://cdiac.ornl.gov/ftp/oceans/p15nabwoce/>) to the core locations. During our BJ8-03 cruise to Indonesia, we collected water samples for TCO<sub>2</sub> and TALK analyses. These samples were measured by Chris Sabine, at the NOAA/Pacific Marine Environmental Laboratory (Seattle, Washington) following the WOCE protocols. Carbonate ion concentrations and the degree of aragonite saturation ( $\Omega_{\text{aragonite}}$ ) were calculated using a program available online [Lewis and Wallace, 1998].

[6] The carbonate-rich slopes of LBB intersect the North Atlantic subtropical gyre thermocline and reach down into the upper layer of the North Atlantic Deep Water (NADW). Core tops from the LBB span a depth range of ~300 to 1600 m associated with BWT, salinity and [CO<sub>3</sub>] change of ~18 to 4°C, 36.7 to 35.0 and ~210 to 100  $\mu\text{mol kg}^{-1}$ , respectively. These samples were collected using a box corer during the OC205-2 cruise in 1986. Along the southwestern slope of LBB, Holocene sedimentation rates are high (tens of centimeters per kiloyear) and there is little downslope reworking [Slowey, 1990]. The Hawaiian transect, collected using a multicorer during the MW98-13 cruise in 1998 intersects the North Pacific subtropical gyre thermocline, the North Pacific Intermediate Water (NPIW) and reaches down into the North Pacific Deep Water (NPDW). Hawaiian core tops span a depth range of ~200 to 2700 m associated with BWT, salinity and [CO<sub>3</sub>] change of ~17 to 2°C, 35.2 to 34.2 and ~180 to 50  $\mu\text{mol kg}^{-1}$ , respectively. Sedimentation rates are relatively low (<10 cm kyr<sup>-1</sup>). The Indonesian samples come from two transects, one on the southwestern Sulawesi margin in the Makassar Strait and the other from the southern Sulawesi margin in the Flores Sea. All the samples were collected using a multicorer during the BJ8-03 cruise in 2003. Nearly all of the thermocline water in the Makassar Strait derives from North Pacific Intermediate Water (NPIW) and North Pacific Subtropical Water [Gordon and Fine, 1996]. Combined, the two Indonesian transects span a depth range of ~200 to 1600 m associated with BWT, salinity and [CO<sub>3</sub>] change of ~16 to 4°C, 34.7 to 34.4 and ~140 to 70  $\mu\text{mol kg}^{-1}$ ,



**Figure 1.** Hydrographic profiles from the three sites studied here, Little Bahama Bank (LBB), Hawaii (HW), and Sulawesi margins in Indonesia (IND). Profiles include (a) temperature (b) salinity (c)  $\text{CO}_3$  ion concentration, and (d) degree of saturation for aragonite ( $\Omega_{\text{aragonite}}$ ). Conductivity-temperature-depth (CTD) profiles were collected near the coring sites during the individual cruises (see Table 1 for locations). Total dissolved inorganic carbon ( $\text{TCO}_2$ ) and total alkalinity (TALK) data come from Geochemical Ocean Sections Study (GEOSECS) station 33 and World Ocean Circulation Experiment (WOCE) A05 station 101 for LBB; WOCE P015Na station 68 and BJ8-03 station HC28 for Indonesia.  $\text{TCO}_2$  and TALK data from the BJ8-03 cruise to Indonesia were measured at Chris Sabine’s laboratory (NOAA/Pacific Marine Environmental Laboratory, Seattle, Washington).  $\text{CO}_3$  ion concentrations and aragonite saturation levels were calculated using a program available online [Lewis and Wallace, 1998].

respectively. Sedimentation rates are high in this region ( $10\text{--}100\text{ cm kyr}^{-1}$ ), because of the large input of terrigenous sediment delivered by rivers.

## 2.2. Analytical Protocols

[7] Samples from the Hawaiian and Indonesian cruises were Rose Bengal stained to identify protoplasm in the tests and hence to separate “live” (stained) and “dead” (unstained) individuals [Corliss and Emerson, 1990]. The

Hawaiian samples were preserved on board with 3.8% formalin solution, buffered with Borax to  $\text{pH} \approx 8$ , and later stained in the laboratory, whereas the Indonesian samples were kept at  $\sim 4^\circ\text{C}$  until they were processed by the same protocol in the laboratory. In both cases, the samples were left shaking in the staining solution for at least one week. The stained sediments were wet sieved through  $60\text{ }\mu\text{m}$  mesh sieves, and the stained samples were picked from the wet coarse fraction. After the stained specimens were picked,

the residual sediments were washed in deionized water and dried in the oven at 60°C before the picking of “dead” specimens. Between 6 and 20 stained (“live”) and unstained (“dead”) samples were picked from the >150 μm size fraction of each sample. The foraminiferal tests were cleaned using a protocol to remove clays, organic matter and metal oxides [Boyle and Keigwin, 1985] and modified after Barker *et al.* [2003]. The foraminifera were gradually dissolved in trace metal clean 0.065N HNO<sub>3</sub> (OPTIMA<sup>®</sup>) and 100 μL of this solution was diluted with 300 μL trace metal clean 0.5N HNO<sub>3</sub> to obtain a Ca concentration of 3 ± 1 mmol L<sup>-1</sup>. Samples were analyzed by Finnigan MAT Element Sector Field Inductively Coupled Plasma Mass Spectrometer (ICP-MS) operated in low resolution ( $m/\Delta m = 300$ ) following the method outlined by Rosenthal *et al.* [1999]. Direct determination of elemental ratios from intensity ratios requires control of the sample Ca concentration; in each run six standard solutions with identical elemental ratios but variable Ca concentrations, which covered the range of Ca concentrations of the samples, were included. These standard solutions allow us to quantify and correct for the effects of variable Ca concentrations in sample solutions on the accuracy of Mg/Ca and Sr/Ca measurements (so-called matrix effects) [Rosenthal *et al.*, 1999]. The corrections are typically <0.1 mmol mol<sup>-1</sup> Mg/Ca. A discussion of matrix effects on the accuracy of Mg/Ca and Sr/Ca measurements in foraminifera is given by Lear *et al.* [2002].

[8] Instrument precision was determined by repeated analysis of three consistency standards over the course of this study. The long-term precision of the consistency standard with Mg/Ca of 1.10 mmol mol<sup>-1</sup> was ±1.6% (r.s.d.), the precisions of the consistency standards with Mg/Ca of 2.40 mmol mol<sup>-1</sup> and 6.10 mmol mol<sup>-1</sup> was ±1.2%. The precision of the consistency standard with Sr/Ca of 0.46 mmol mol<sup>-1</sup> was ±1.0%, the precisions of the consistency standards with Sr/Ca of 0.92 mmol mol<sup>-1</sup> and 1.84 mmol mol<sup>-1</sup> was ±0.8%. We also include in this paper data of Hall and Chan [2004] from LBB. We corrected the Mg/Ca data of Hall and Chan [2004] for a +15% offset from our data. The correction is based on the fact that although Hall and Chan [2004] analyzed the same solutions of planktonic foraminifera as used by Rosenthal and Lohmann [2002], their ratios are about 15% higher than reported in the latter study (note that the solution was provided by Y. Rosenthal). As our data are generally consistent with other laboratories [Rosenthal *et al.*, 2004], we attribute this to a bias in their standards. No correction was required for their Sr/Ca data.

[9] Core top Mg/Ca and Sr/Ca data from the three transects are given in Tables 2–4. Several of the LBB samples were separated into various size fractions, to assess whether size may introduce significant variability in the results. The data do not show significant differences in Mg/Ca and Sr/Ca among the different size fractions (Table 2).

### 3. Results

[10] Mg/Ca ratios in *H. elegans* tests show a general decrease with increasing water depth; however, the trends

differ among the three sites (Figure 2). Mg/Ca ratios in LBB are substantially higher than in Indonesia and Hawaii for a given water depth. Sr/Ca ratios behave similarly to Mg/Ca, showing both the decrease with depth and the interbasinal difference (Figure 3). Although at each site the decreasing trends in Mg/Ca and Sr/Ca seem consistent with the local temperature profile, there are some distinct differences among the sites. Most noticeably, bottom water temperatures in the main thermocline (0–1000 m) are substantially warmer at LBB than at Hawaii and Indonesia, whereas below the main thermocline (below ~1200 m) the temperature at all three sites are very similar. In fact, below 1200 m BWT at LBB are identical to those in Indonesia and both are about 1°C warmer than in Hawaii. In contrast, Mg/Ca and Sr/Ca profiles from the LBB and Pacific sites diverge downward and show the greatest difference (0.5 mmol mol<sup>-1</sup> and 1 mmol mol<sup>-1</sup>, respectively), in the deep, cold waters below the main thermocline. These differences are significantly larger than the analytical uncertainties. Because of these large differences, when fitting the Mg/Ca and Sr/Ca data to the vertical water temperature profile, the Mg/Ca-BWT and Sr/Ca-BWT scaling at LBB (Figures 2 and 3, insets) requires a significantly different scale than those used for the Pacific locations. Mg/Ca and Sr/Ca ratios in Hawaiian samples are about 0.3 and 0.5 mmol mol<sup>-1</sup>, respectively, lower than in Indonesian samples. The differences between IND and HW samples, although small, are also significantly larger than our analytical uncertainties.

## 4. Discussion

### 4.1. Mineralogical Consideration

[11] The benthic species *Hoeglundina elegans* is one of a few living foraminifera with aragonitic tests. Strictly on the basis of structural considerations the chemical composition of aragonitic tests should be significantly different than that of calcitic tests. Because SrCO<sub>3</sub> is isostructural with the aragonite crystal cell (orthorhombic), one expects higher concentrations of strontium in aragonite than in calcite, which has a tighter rhombohedral structure. The situation is the opposite for Mg, which has a better fit in the calcitic lattice, than in aragonite. Strontium concentrations in *H. elegans* vary from about 3 mmol mol<sup>-1</sup> in the surface to 0.4 mmol mol<sup>-1</sup> in the deep Pacific (i.e., the partition coefficient  $K_{Sr}$  varies between about 0.3 and 0.04, respectively, where  $K_{Sr} = (Sr/Ca)_{test}/(Sr/Ca)_{seawater}$ ). These values are about 5 times lower than those obtained in corals [Smith *et al.*, 1979] and inorganically precipitated aragonites [Kinsman and Holland, 1969], and only about 20–40% higher than in calcitic foraminiferal shells [Rosenthal *et al.*, 1997]. The values are similar to partition coefficients in aragonitic mollusks suggesting a strong biological regulation on their Sr incorporation process [Lorens and Bender, 1980; Rosenthal and Katz, 1989]. The Mg content of aragonitic tests of *H. elegans* varies between about 1.7 mmol mol<sup>-1</sup> in warm surface water and 0.3 mmol mol<sup>-1</sup> in the deep cold Pacific waters (i.e., the partition coefficient  $K_{Mg}$  varies between  $3 \times 10^{-4}$  and  $0.4 \times 10^{-4}$ , respectively, where  $K_{Mg} = (Mg/Ca)_{test}/(Mg/Ca)_{seawater}$ ). These values are about half of that found in the calcitic

t2.1 **Table 2.** Results From Little Bahama Banks

t2.2	Sample	Size, $\mu\text{m}$	Water Depth, m	BWT, $^{\circ}\text{C}$	$[\text{CO}_3]$ , $\mu\text{mol kg}^{-1}$	$[\Delta\text{CO}_3]_{\text{aragonite}}$ , $\mu\text{mol kg}^{-1}$	Mg/Ca <sup>a</sup>	Sr/Ca <sup>a</sup>
t2.3	OC205-2 BC79	>150	301	18.4	208.0	141.6	1.55	2.53
t2.4	OC205-2 BC79	>150	301	18.4	208.0	141.6	1.56	2.60
t2.5	OC205-2 BC79	>150	301	18.4	208.0	141.6		2.48
t2.6	OC205-2 BC79	>150	301	18.4	208.0	141.6		2.47
t2.7	OC205-2 BC79	>150	301	18.4	208.0	141.6		2.50
t2.8	OC205-2 BC79	>150	301	18.4	208.0	141.6		2.53
t2.9	OC205-2 BC79	>150	301	18.4	208.0	141.6		2.65
t2.10	OC205-2 BC79	>425	301	18.4	208.0	141.6	1.40	2.69
t2.11	OC205-2 BC79	250–355	301	18.4	208.0	141.6	1.55	2.49
t2.12	OC205-2 BC79	150–250	301	18.4	208.0	141.6	1.53	2.58
t2.13	OC205-2 BC77	>150	433	16.6	180.0	112.2	1.50	2.67
t2.14	OC205-2 BC77	>150	433	16.6	180.0	112.2	1.53	2.72
t2.15	OC205-2 BC77	>150	433	16.6	180.0	112.2		2.53
t2.16	OC205-2 BC77	>150	433	16.6	180.0	112.2		2.23
t2.17	OC205-2 BC77	>150	433	16.6	180.0	112.2		2.55
t2.18	OC205-2 BC77	>425	433	16.6	180.0	112.2	1.50	2.67
t2.19	OC205-2 BC77	355–425	433	16.6	180.0	112.2	1.71	2.55
t2.20	OC205-2 BC77	250–355	433	16.6	180.0	112.2	1.54	2.52
t2.21	OC205-2 BC76	>150	529	14.2	142.4	73.5	1.46	2.43
t2.22	OC205-2 BC76	>150	529	14.2	142.4	73.5		2.22
t2.23	OC205-2 BC76	>150	529	14.2	142.4	73.5		
t2.24	OC205-2 BC76	>150	529	14.2	142.4	73.5		2.13
t2.25	OC205-2 BC48	>150	580	13.3	133.5	64.1	1.41	2.36
t2.26	OC205-2 BC48	>150	580	13.3	133.5	64.1		2.26
t2.27	OC205-2 BC48	>150	580	13.3	133.5	64.1		2.36
t2.28	OC205-2 BC48	>150	580	13.3	133.5	64.1		2.47
t2.29	OC205-2 BC48	>425	580	13.3	133.5	64.1	1.33	2.46
t2.30	OC205-2 BC48	355–425	580	13.3	133.5	64.1	1.43	2.49
t2.31	OC205-2 BC48	250–355	580	13.3	133.5	64.1	1.67	2.26
t2.32	OC205-2 BC48	150–250	580	13.3	133.5	64.1	1.38	2.38
t2.33	OC205-2 BC52	>150	668	11.5	114.4	44.0	1.95	2.31
t2.34	OC205-2 BC52	>150	668	11.5	114.4	44.0		2.25
t2.35	OC205-2 BC52	>150	668	11.5	114.4	44.0		2.22
t2.36	OC205-2 BC52	>425	668	11.5	114.4	44.0	1.29	2.41
t2.37	OC205-2 BC52	355–425	668	11.5	114.4	44.0	1.28	2.33
t2.38	OC205-2 BC52	250–355	668	11.5	114.4	44.0	1.57	2.31
t2.39	OC205-2 BC69	>150	735	9.9	105.0	33.8	1.23	2.21
t2.40	OC205-2 BC69	>150	735	9.9	105.0	33.8		2.09
t2.41	OC205-2 BC69	>150	735	9.9	105.0	33.8		2.21
t2.42	OC205-2 BC69	>425	735	9.9	105.0	33.8	1.38	2.29
t2.43	OC205-2 BC69	>425	735	9.9	105.0	33.8	1.23	2.27
t2.44	OC205-2 BC51	>150	830	8.2	95.0	22.7	1.15	2.14
t2.45	OC205-2 BC51	>150	830	8.2	95.0	22.7		1.95
t2.46	OC205-2 BC51	>150	830	8.2	95.0	22.7		2.12
t2.47	OC205-2 BC54	>150	1043	5.5	90.0	15.2		1.96
t2.48	OC205-2 BC54	>250	1043	5.5	90.0	15.2		1.85
t2.49	OC205-2 BC57	>250	1243	4.5	100.0	22.8	1.21	1.66
t2.50	OC205-2 BC57	>250	1243	4.5	100.0	22.8		1.72
t2.51	OC205-2 BC57	>250	1243	4.5	100.0	22.8		1.79
t2.52	OC205-2 BC57	>425	1243	4.5	100.0	22.8	1.15	1.84
t2.53	OC205-2 BC57	355–425	1243	4.5	100.0	22.8	1.13	1.75
t2.54	OC205-2 BC57	250–355	1243	4.5	100.0	22.8	1.14	1.79
t2.55	OC205-2 BC60	>250	1312	4.4	105.0	26.9	1.13	1.73
t2.56	OC205-2 BC60	>250	1312	4.4	105.0	26.9		1.80
t2.57	OC205-2 BC60	>250	1312	4.4	105.0	26.9		1.75
t2.58	OC205-2 BC60	>250	1312	4.4	105.0	26.9		1.75
t2.59	OC205-2 BC60	>250	1312	4.4	105.0	26.9	1.11	1.86
t2.60	OC205-2 BC60	355–425	1312	4.4	105.0	26.9	1.14	1.84
t2.61	OC205-2 BC60	250–355	1312	4.4	105.0	26.9	1.10	1.71
t2.62	OC205-2 BC59	>250	1477	4.2	104.0	23.9		1.85
t2.63	OC205-2 BC59	>250	1477	4.2	104.0	23.9		1.85
t2.64	OC205-2 BC61	>250	1585	4.2	102.1	20.6	1.01	1.67
t2.65	OC205-2 BC61	>250	1585	4.2	102.1	20.6		1.66
t2.66	OC205-2 149JPC <sup>b</sup>	>150	423	16.5	180	112.3	1.63	2.52
t2.67	OC205-2 149JPC <sup>b</sup>	>150	423	16.5	180	112.3	1.71	2.55
t2.68	OC205-2 108GGC <sup>b</sup>	>150	743	9.8	105	33.7	1.27	2.12
t2.69	OC205-2 108GGC <sup>b</sup>	>150	743	9.8	105	33.7	1.27	2.12
t2.70	OC205-2 103GGC <sup>b</sup>	>150	965	6.3	90	16.2	1.17	2.03
t2.71	OC205-2 103GGC <sup>b</sup>	>150	965	6.3	90	16.2	1.17	2.17
t2.72	OC205-2 100GGC <sup>b</sup>	>150	1057	5.5	90	15.1	1.11	1.76
t2.73	OC205-2 97JPC <sup>b</sup>	>150	1183	4.7	95	18.5	1.11	1.78

Table 2. (continued)

t2.74	Sample	Size, $\mu\text{m}$	Water Depth, m	BWT, $^{\circ}\text{C}$	$[\text{CO}_3]$ , $\mu\text{mol kg}^{-1}$	$[\Delta\text{CO}_3]_{\text{aragonite}}$ , $\mu\text{mol kg}^{-1}$	Mg/Ca <sup>a</sup>	Sr/Ca <sup>a</sup>
t2.75	OC205-2 97JPC <sup>b</sup>	>150	1183	4.7	95	18.5	1.06	1.74
t2.76	OC205-2 7JPC <sup>b</sup>	>150	1320	4.40	105	26.8	1.11	1.77
t2.77	OC205-2 7JPC <sup>b</sup>	>150	1320	4.40	105	26.8	1.12	1.68
t2.78	OC205-2 7JPC <sup>b</sup>	>150	1320	4.40	105	26.8	1.05	1.79
t2.79	OC205-2 7JPC <sup>b</sup>	>150	1320	4.40	105	26.8	1.09	1.70
t2.80	OC205-2 7JPC <sup>b</sup>	>150	1320	4.40	105	26.8	1.05	1.79
t2.81	OC205-2 7JPC <sup>b</sup>	>150	1320	4.40	105	26.8	1.11	1.67
t2.82	OC205-2 117JPC <sup>b</sup>	>150	1535	4.20	102.7	21.8	1.28	1.63

t2.83 <sup>a</sup>Mg/Ca and Sr/Ca are given in  $\text{mmol mol}^{-1}$ .

t2.84 <sup>b</sup>Mg/Ca from the *Hall and Chan* [2004] data set was corrected by 15% for interlaboratory offset (see text).

species [*Rosenthal et al.*, 1997], as expected from aragonitic mineralogy. Despite their different fit with aragonitic crystallography, variations in Mg/Ca and Sr/Ca ratios in *H. elegans* tests are positively correlated (Figure 4), suggesting that similar factors control the uptake of Mg and Sr in the aragonitic shells of *H. elegans*. Although the Atlantic and Pacific trends are similar, the LBB samples are offset toward higher Mg/Ca relative to the Pacific samples. Below, we suggest that temperature and the degree of saturation with respect to aragonite exert dominant control on the coprecipitation of Mg and Sr in *H. elegans*.

#### 4.2. Temperature Versus Carbonate Ion Effects

[12] The strong covariance between the depth-related decreases in LBB *H. elegans*' Mg/Ca, Sr/Ca and water temperature has already been noted [*Hall and Chan*, 2004; *Rosenthal et al.*, 1997]. More recently, on the basis of similar behavior in samples from the Arabian Sea and Bay of Biscay, *Reichert et al.* [2003] proposed that variations in the Mg and Sr content of *H. elegans* tests can be used to reconstruct bottom water temperatures. These authors proposed a paleotemperature equation for *H. elegans*, where the temperature dependence can be described as a function of both Mg and Sr content of the test. The positive covariance between *H. elegans*' Sr/Ca and temperature observed in the above studies, however, is in apparent contrast with results from laboratory experiments [*Kinsman and*

*Holland*, 1969] and with thermodynamic expectations [*Rosenthal et al.*, 1997], both suggesting an inverse correlation between the Sr<sup>2+</sup> uptake and temperature. It is also at odds with the relationship observed in corals [*Beck et al.*, 1992; *De Villiers et al.*, 1994], thus raising concerns that the positive covariance between Mg/Ca, Sr/Ca and temperature in *H. elegans* is coincidental, and does not necessarily reflect a mechanistic dependency.

[13] The possibility that the differences in the relationships of Mg/Ca and Sr/Ca to temperature at the LBB and Pacific are caused by diagenetic processes needs to be addressed. First, we consider the possibility that the relatively high Mg/Ca and Sr/Ca values of the LBB samples reflect contamination by inorganic coatings on the foraminifera tests. Studies in the Bahama Banks show that dissolution and recrystallization of metastable aragonite and high-Mg biogenic calcites occur during the earliest stages of sedimentation in some shallow marine carbonate platforms [*Hover et al.*, 2001]. In the oversaturated pore waters, these processes can result in secondary precipitation of high-Mg and high-Sr coatings on foraminiferal tests, thus offsetting their primary composition toward higher values. There are three lines of evidence, however, suggesting that such processes cannot account for the observed differences: (1) The effect of secondary coatings should be the strongest in shallow sediments and decrease with depth. In contrast, the LBB-Pacific difference for both Mg/Ca and Sr/Ca is the

Table 3. Results From Hawaii

Sample	Water Depth, m	BWT, $^{\circ}\text{C}$	$[\text{CO}_3]$ , $\mu\text{mol kg}^{-1}$	$[\Delta\text{CO}_3]_{\text{aragonite}}$ , $\mu\text{mol kg}^{-1}$	Mg/Ca <sup>a</sup>		Sr/Ca <sup>a</sup>	
					"Unstained"	"Stained"	"Unstained"	"Stained"
MC 047	194	17.3	180	114.7	1.30	1.24	2.88	3.04
MC 047	194	17.3	180	114.7	1.24	1.17	3.11	2.89
MC 032	320	11.0	135	68.4		1.32		2.67
MC 046	402	8.7	110	42.5	0.99	1.03	1.78	2.28
MC 046	402	8.7	110	42.5	0.91	0.78	2.02	2.05
MC 039	715	5.0	60	-10.9	0.52	1.12	0.91	0.86
MC 039	715	5.0	60	-10.9		0.52		1.11
MC 028	797	4.6	60	-11.9		0.43		0.79
MC 028	797	4.6	60	-11.9		0.52		1.00
MC 138	1775	2.4	64	-20.1	0.47	0.29	0.59	0.35
MC 138	1775	2.4	64	-20.1	0.50	0.34	0.82	0.31
MC 137	2578	1.8	73	-22.6	0.26	0.24	0.35	0.26
MC 137	2578	1.8	73	-22.6	0.32	0.24	0.38	0.29
MC 137	2578	1.8	73	-22.6	0.29	0.26	0.33	0.31
MC 042	2583	1.8	73	-22.7	0.25		0.28	
MC 042	2583	1.8	73	-22.7	0.25		0.47	
MC 135	2682	1.7	77	-20.2	0.37	0.29	0.28	0.35
MC 135	2682	1.7	77	-20.2	0.27	0.29	0.33	0.35

<sup>a</sup>Mg/Ca and Sr/Ca are given in  $\text{mmol mol}^{-1}$ .

**Table 4.** Results From Indonesia

Sample	Water Depth, m	BWT, °C	[CO <sub>3</sub> ], μmol kg <sup>-1</sup>	[ΔCO <sub>3</sub> ] <sub>laragonite</sub> , μmol kg <sup>-1</sup>	Mg/Ca <sup>a</sup>		Sr/Ca <sup>a</sup>	
					“Unstained”	“Stained”	“Unstained”	“Stained”
MC 37	179	15.7	140	74.9		0.80		1.31
MC 40	251	11.5	95.0	29.1	1.55	1.05	2.32	2.24
MC 63	252	11.7	95	29.1		1.01		2.19
MC 45	332	10.0	88.0	21.3	1.02	0.86	2.04	1.88
MC 65	334	9.8	88	21.3		1.15		1.80
MC 58	347	9.7	88	21.1		0.77		1.79
MC 67	401	8.9	80	12.5		1.05		2.13
MC 67	401	8.9	80	12.5		0.90		1.74
MC 56	405	8.8	80	12.5		0.84		1.58
MC 129	406	8.7	80	12.5		1.26		1.96
MC 31	459	8.0	78.0	9.9	0.82		1.85	
MC 33	505	7.5	78.0	9.4	0.74	0.78	1.68	1.47
MC 77	525	7.2	76	7.2		1.00		1.90
MC 35	565	7.0	75.0	5.7	0.77	0.79	1.55	1.72
MC 49	676	6.4	75	4.5	0.72	0.78	1.35	1.40
MC 140	755	5.9	74	2.6		0.81		1.51
MC 138	827	5.6	72	-0.2		0.77		1.25
MC 24	832	5.5	72.7	0.4	0.67	0.64	1.33	1.45
MC 24	832	5.6	72	-0.3				
MC 53	868	5.3	72	-0.7		0.56		1.41
MC 22	1189	4.0	72.0	-4.5	0.57		0.78	
MC 72	1552	3.8	75.0	-6.1	0.52		0.72	

<sup>a</sup>Mg/Ca and Sr/Ca are given in mmol mol<sup>-1</sup>.

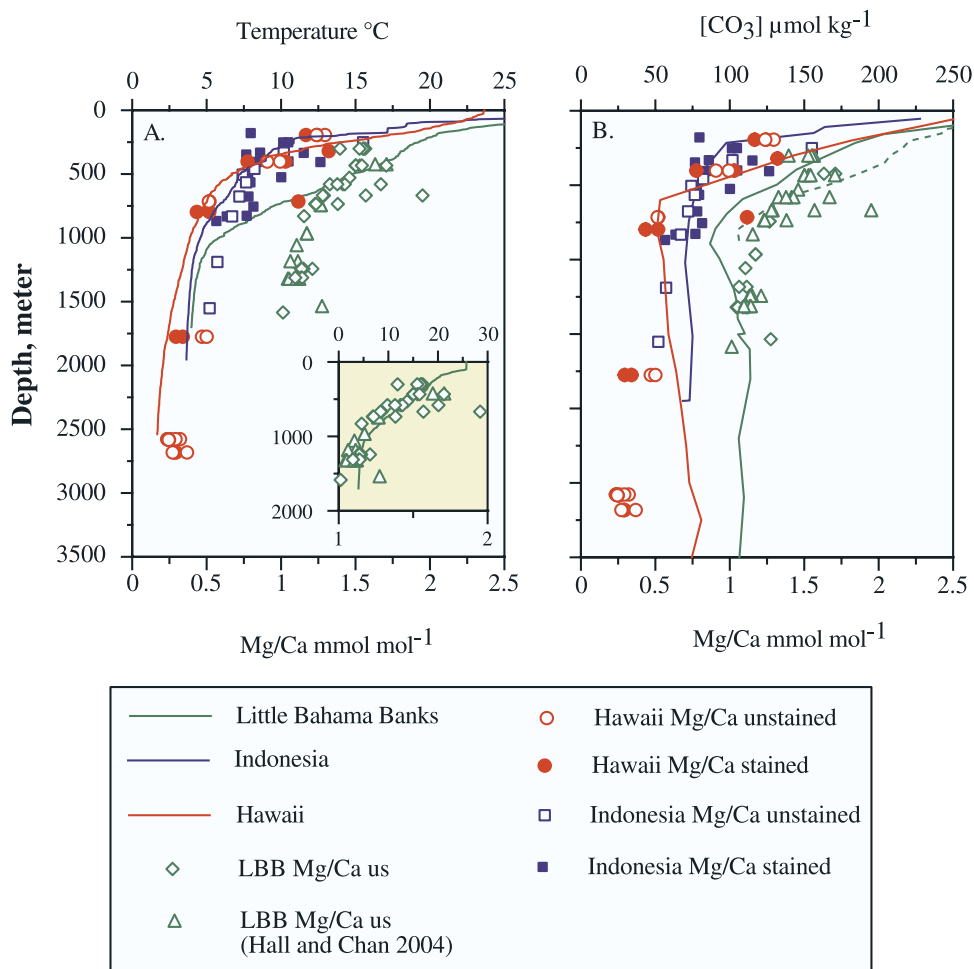
largest in deep waters (>1000 m). Furthermore, contamination of shallow samples should have led to an apparent increase of the Mg/Ca and Sr/Ca versus temperature slopes in LBB samples, whereas we find steeper slopes in Pacific samples. (2) A study of surface sediments from LBB suggests that secondary coatings have negligible effect on the Mg/Ca of the planktonic foraminifer *G. ruber* [Lear *et al.*, 2002]. (3) Studies suggest that diagenetic contamination by sedimentary-derived authigenic phases are minimal in *H. elegans* relative to many calcitic species because of the test's smooth and glassy surface [Boyle *et al.*, 1995; Marchitto *et al.*, 1998]. In summary, while we cannot rule out the possibility that the LBB samples are affected by diagenetic contamination, it seems more likely that the observed trends reflect the primary composition of the tests.

[14] A second possibility is that the Pacific samples were altered by dissolution. The comparison between results obtained on Rose Bengal stained (“live”) and unstained (“dead”) specimens allows us to assess whether the difference between Atlantic and Pacific tests is caused by postburial dissolution, which may preferentially remove metal-rich and dissolution-prone parts of the tests, or by the effects of depth-dependent parameters (e.g., temperature and Δ[CO<sub>3</sub>]) on metal uptake during the foraminiferal test's precipitation. In the Hawaiian and Indonesian transects, we analyzed both stained and unstained shells at various depths (see Tables 3 and 4). In all cases, there is no statistically significant difference between results obtained on stained and unstained specimens. In fact, both the stained and unstained samples show the same depth-related trend, and interocean biases in Mg/Ca and Sr/Ca (Figures 2 and 3). These observations strongly suggest that differences in elemental ratios of *H. elegans* between the LBB and our two Pacific sites (Figure 2) are due to primary effects on metals uptake during test formation, although additional

second-order postmortem diagenetic alteration of the test's composition cannot completely be ruled out.

[15] Separating the effects of bottom water temperature and CO<sub>3</sub> ion concentration on Mg/Ca and Sr/Ca is not straightforward, as the two parameters are positively correlated in the ocean. To demonstrate this relationship, we plot data from several GEOSECS and WOCE stations in the Atlantic and Pacific oceans (Figure 5). This correlation reflects the dependence of [CO<sub>3</sub>] on both the biogeochemical cycling of organic matter and temperature. Among the specific processes that lead to this covariance are the following: (1) The depth-related decrease in [CO<sub>3</sub>] reflects the fact that surface water pH is relatively high, because of photosynthetic uptake of inorganic carbon at the surface but decreases with depth because of particle regeneration and the release of metabolic CO<sub>2</sub>. These processes are partly responsible for the relatively high (low) CO<sub>3</sub> concentrations in surface (deep) waters. (2) The latitudinal decrease in surface water concentrations of CO<sub>3</sub> is partly driven by the tendency of surface water to reach equilibrium with the atmosphere, which depends on temperature. The increased solubility of CO<sub>2</sub> at colder temperatures lowers the pH and thus CO<sub>3</sub> ion concentration of cold relative to warm surface waters. This preformed relationship is maintained as a water parcel is advected to the deep ocean and is largely conserved, although some modification occurs because of the dependence of the carbonate system constants on temperature and pressure.

[16] Two properties of this relationship allow us to distinguish between the effects of BWT versus the effects of [CO<sub>3</sub>] on Mg/Ca and Sr/Ca in benthic foraminifera (Figure 5): (1) The positive correlation between BWT and [CO<sub>3</sub>] is strongest in the main thermocline. Below that, changes in deepwater [CO<sub>3</sub>] are small, and often do not covary with temperature. (2) There is a substantial



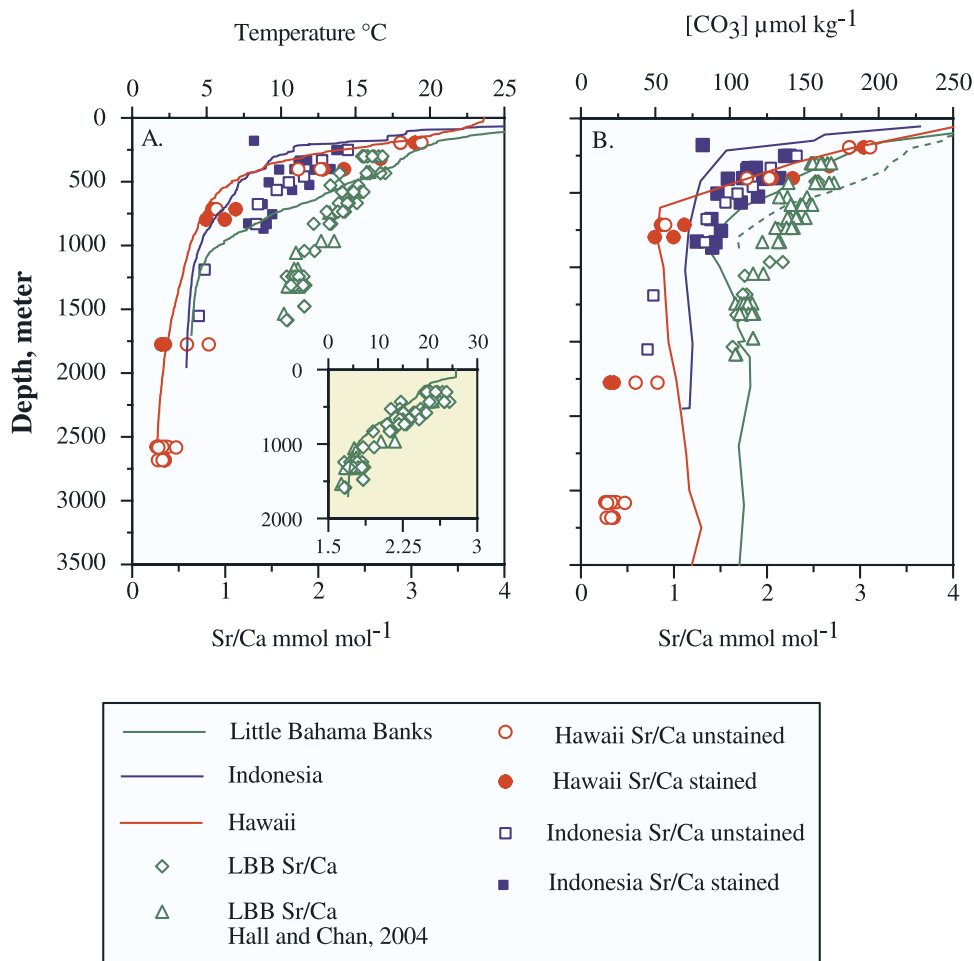
**Figure 2.** Depth profiles of Mg/Ca ratios in *H. elegans* shells from LBB, Hawaii, and Indonesian sites plotted with in situ temperature (a) and (b) CO<sub>3</sub> ion concentrations. Open and solid symbols denote unstained (“dead”) and stained (“live”) specimens, respectively. Note the strong similarity between the Mg/Ca and temperature profiles at each site (inset shows a close-up of the profiles in LBB) and the large difference between the deep Pacific and Atlantic sites.

offset in deep water CO<sub>3</sub> ion content (on average about 35 μmol kg<sup>-1</sup>) between the Atlantic and Pacific oceans, although the BWTs are similar. These two properties are also reflected in the degree of saturation with respect to aragonite. The aragonite saturation levels are significantly higher in the Atlantic relative to the Pacific Ocean. Below, we take advantage of these properties, and attempt to separate the relative effects of [CO<sub>3</sub>] and temperature on the elemental composition of the foraminiferal tests. To account for the fact that some of the samples represent the same BWT and [CO<sub>3</sub>] yet come from different depths, we chose to use the aragonite saturation level, [ΔCO<sub>3</sub>]<sub>aragonite</sub>, rather than [CO<sub>3</sub>] as a primary variable in the discussion that follows. We follow *Broecker and Peng* [1982], where [ΔCO<sub>3</sub>] = [CO<sub>3</sub>]<sub>in situ</sub> - [CO<sub>3</sub>]<sub>saturation</sub> and for aragonite [CO<sub>3</sub>]<sub>saturation</sub> = 120exp[0.16(Z - 4)], where Z is depth in kilometers.

[17] The influence of [ΔCO<sub>3</sub>]<sub>aragonite</sub> on the test composition is clearly evident when plotting Mg/Ca and Sr/Ca against bottom water temperature; in both cases the LBB

data fall on distinctly different trends than the Pacific data, suggesting that temperature alone cannot account for the observed depth-related variations in these elemental ratios (Figures 6a and 6b). Plots of Mg/Ca and Sr/Ca against [ΔCO<sub>3</sub>]<sub>aragonite</sub> show a logarithmic-like behavior, with strong dependence at low [ΔCO<sub>3</sub>]<sub>aragonite</sub>, and no dependence at levels higher than ~15 μmol kg<sup>-1</sup> (Figures 6c and 6d). Combined, these relationships suggest that in the deep ocean, where temperature variability is small, Mg/Ca and Sr/Ca in *H. elegans* tests are mainly dependent on [ΔCO<sub>3</sub>]<sub>aragonite</sub>. However, in shallow and saturated waters, temperature exerts the main control on these elemental ratios. In the following discussion, we start with two basic assumptions: (1) The difference in Mg/Ca and Sr/Ca between deep LBB and Pacific samples is linearly related to the difference in bottom water [CO<sub>3</sub>] content. The fact that in both cases the Pacific and LBB trends converge in shallow waters suggests that the [CO<sub>3</sub>] effect depends on the degree of aragonite saturation and not simply on [CO<sub>3</sub>], a corollary that leads to our second assumption. (2) As most





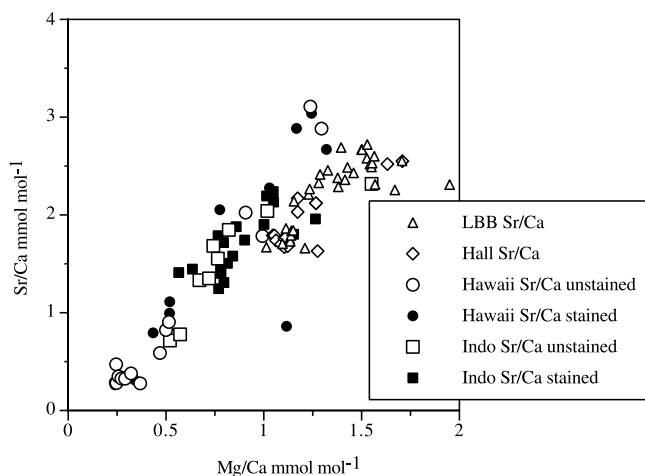
**Figure 3.** Depth profiles of Sr/Ca ratios in *H. elegans* shells from LBB, Hawaii, and Indonesian sites plotted with in situ temperature (a) and (b) CO<sub>3</sub> ion concentrations. Open and solid symbols denote unstained (“dead”) and stained (“live”) specimens, respectively. Note the strong similarity between the Sr/Ca and temperature profiles in each site (inset shows a close-up of the profiles in LBB) and the large difference between the deep Pacific and Atlantic sites.

of the LBB sites are overlain with water that is oversaturated with respect to aragonite, we assume that the LBB Mg/Ca and Sr/Ca trends are driven primarily by temperature. In support of this, a visual examination of the depth-related Mg/Ca and Sr/Ca profiles from the LBB suggests a close resemblance to the temperature profile (Figures 2 and 3 insets). Most notably, Mg/Ca, Sr/Ca and BWT start to increase with decreasing depth below 1000 m, whereas the increase in [CO<sub>3</sub>] occurs shallower, suggesting that [CO<sub>3</sub>] is not the primary control on the distribution of these ratios in LBB samples. In contrast, the Pacific trends reflect the combined effects of both [CO<sub>3</sub>] (as many of the Pacific sites are overlain by undersaturated waters with respect to aragonite) and temperature. The combined effects of temperature and [CO<sub>3</sub>] explain the steeper trends observed in the Pacific samples. These assumptions are further examined below.

[18] First, we apply the temperature dependencies calculated from the LBB samples shown in Figure 6a and 6b to the entire data set, correcting Mg/Ca and Sr/Ca ratios to a reference temperature of 18°C (Figures 7a and 7b). Plotting

the Mg/Ca and Sr/Ca results against  $[\Delta\text{CO}_3]_{\text{aragonite}}$  highlights two conspicuous features: (1) Both Mg/Ca and Sr/Ca data from the LBB are relatively constant, exhibiting no significant dependence on  $[\Delta\text{CO}_3]_{\text{aragonite}}$ . (2) In contrast, the Pacific data show a clear dependence on  $[\Delta\text{CO}_3]_{\text{aragonite}}$ , increasing linearly up to 15 µmol kg<sup>-1</sup> and then flattening out at a relatively constant value above 15 µmol kg<sup>-1</sup> (Figures 7a and 7b). These observations support the assumption that LBB depth-related trends in Mg/Ca and Sr/Ca reflect primarily a temperature effect, with the corollary that the degree of aragonite saturation influences the uptake of Mg and Sr only at low saturation levels. On the basis of the results shown in Figures 7a and 7b, we propose  $[\Delta\text{CO}_3]_{\text{aragonite}} = 15 \mu\text{mol kg}^{-1}$  as the “threshold” value for [CO<sub>3</sub>] correction, as above this level there is no discernible effect for carbonate ion effect.

[19] To quantify the [CO<sub>3</sub>] ion effect we take advantage of the fact that between 1200 and 1800 m, BWT in LBB and Indonesia are almost identical (4.3° and 4.0°C, respectively). Therefore the difference of ~0.5 mmol mol<sup>-1</sup> in



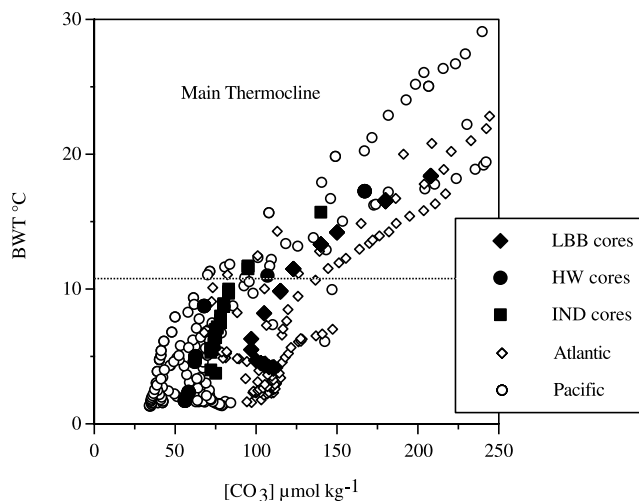
**Figure 4.** A scatterplot of Mg/Ca versus Sr/Ca in *H. elegans* shells from all three sites showing the strong correlation between these ratios. Open and solid symbols denote unstained (“dead”) and stained (“live”) specimens, respectively.

Mg/Ca and 1.0 mmol mol<sup>-1</sup> in Sr/Ca ratios between Indonesian and LBB samples from this depth interval are most probably related to the  $\sim 30 \mu\text{mol kg}^{-1}$  difference in  $[\text{CO}_3]$  between the two sites, which determines the critical aragonite saturation concentration of bottom waters from these sites. In Figures 7c and 7d we calculate the relationships between *H. elegans* Mg/Ca, Sr/Ca and bottom water  $[\Delta\text{CO}_3]_{\text{aragonite}}$  levels below 1200 m in Indonesia and LBB. We do not include results from the Hawaiian transect as both BWT and  $[\text{CO}_3]$  are significantly different there than in Indonesia or LBB. The regression lines shown in Figures 7c and 7d provide the Mg/Ca and Sr/Ca dependence on  $[\Delta\text{CO}_3]_{\text{aragonite}}$  for concentrations below  $15 \mu\text{mol kg}^{-1}$ .

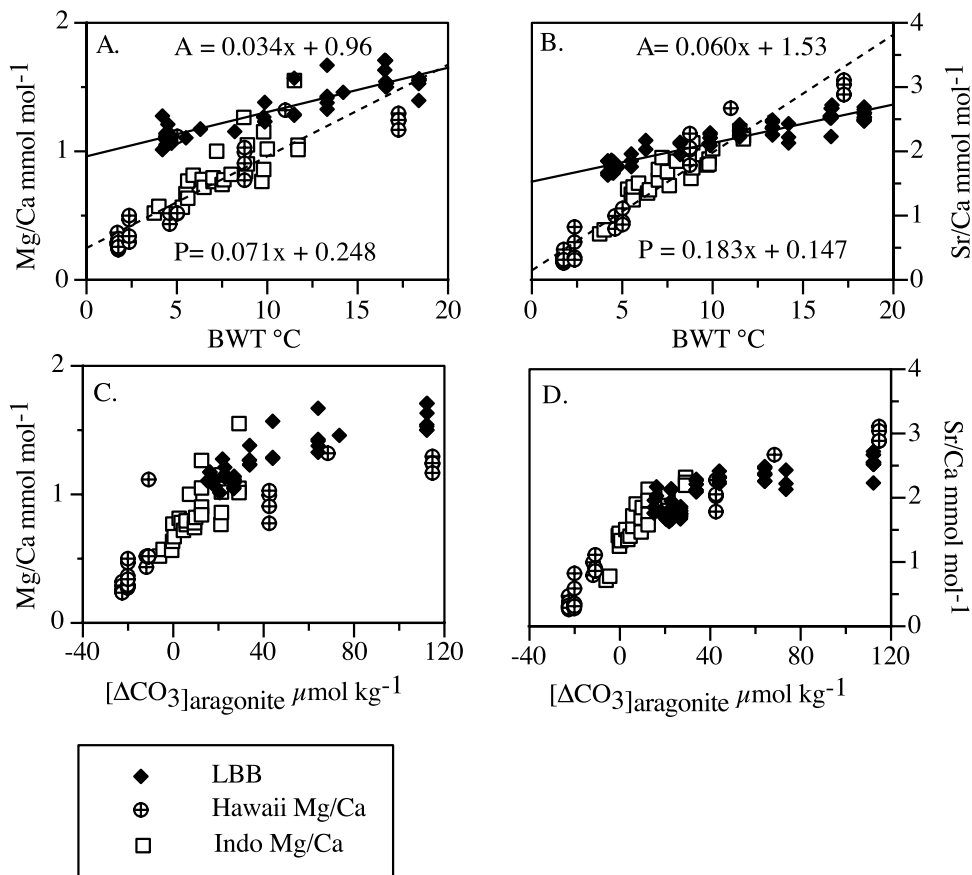
[20] Next, we apply the relationships obtained in Figures 7c and 7d to the Pacific Mg/Ca and Sr/Ca data, in order to correct for the  $[\Delta\text{CO}_3]_{\text{aragonite}}$  difference between Atlantic and Pacific samples and plot the results against BWT (Figures 7e and 7f). Note that this correction is only applied to samples where bottom water  $[\Delta\text{CO}_3]_{\text{aragonite}} < 15 \mu\text{mol kg}^{-1}$ . The  $[\text{CO}_3]$ -corrected Sr/Ca values fall along a much more constrained temperature-related trend than shown in Figures 6a and 6b. The Pacific  $[\text{CO}_3]$ -corrected Sr/Ca versus temperature trend is similar to the one from LBB, though the LBB and Pacific calibrations yield significantly different regressions at the 95% confidence interval (Figure 7f). For both data sets, however, there is clear dependence of Sr/Ca on temperature.

[21] The results for Mg/Ca appear less robust. The Pacific  $[\text{CO}_3]$ -corrected Mg/Ca regression shows a significantly lower slope than the LBB calibration (at the 95% confidence interval Figure 7e), associated with lower correlation coefficient. In fact, the correction of the Pacific Mg/Ca data seems to significantly diminish the temperature dependence that is very clear in the uncorrected data (Figure 6a). Does that mean that our underlying assumption about the effect of  $[\text{CO}_3]$  on Mg/Ca is wrong? We think that there are other

factors that can artificially affect the trend. First, it is important to note that both the LBB and Pacific slopes of Mg/Ca versus BWT are very small and thus any anomalous data could significantly change the regression. In fact, we also note that the problem is not with the corrected values (below  $15 \mu\text{mol kg}^{-1}$ ) but rather with samples from shallow waters. Mg/Ca ratios of shallow samples from Indonesia and Hawaii are low relative to samples representing the same BWT from the LBB (Figure 7a). On the basis of the water column  $[\text{CO}_3]$  data we assume that these samples formed in oversaturated waters ( $> 15 \mu\text{mol kg}^{-1}$ ) and therefore applied no correction to the data. However, the samples came from sediments with high organic carbon inputs, and it is possible that the  $[\text{CO}_3]$  concentrations at the sediment interface, where the foraminifera live, are significantly lower, which would have required a correction. Such a correction would move the shallow Pacific data upward toward the Atlantic data set in Figure 7e, and would yield higher slope. As the organic rain rate typically decreases with depth, the largest effect occurs in shallow sediments. Alternatively, it is possible that Mg/Ca ratios in shallow



**Figure 5.** Bottom water temperature (BWT) versus  $\text{CO}_3$  profiles in Atlantic (diamonds) and Pacific (circles) stations. Note the strong correlations between  $\text{CO}_3$  and BWT in the main thermocline. This relationship, however, breaks down below the thermocline (at temperatures less than about  $7^\circ\text{C}$ ). Also note the offset between Atlantic and Pacific stations. The latter are generally characterized by lower  $\text{CO}_3$  concentrations than the Atlantic stations at similar temperatures. Hydrographic data come from GEOSECS and WOCE stations including the Arctic Ocean: Transient Tracers in the Ocean (TTO) station 143; Atlantic Ocean: WOCE A24 stations 1 and 91, A05 station 101, GEOSECS stations 33, 39, and 113; Pacific Ocean: WOCE P08s station 26, P13 station 81, P15Na stations 13 and 68, P15Nb station 72, P16c station 274, and P16s station 16; data are obtained from the Carbon Dioxide Information Analysis Center (<http://cdiac.esd.ornl.gov/oceans/datmet.html>). These stations cover high-latitude and equatorial regions in both oceans. Our LBB, HW, and IND core top transects are marked with solid symbols.



**Figure 6.** (a) Mg/Ca and (b) Sr/Ca versus bottom water temperature. The Atlantic (LBB, diamonds) and Pacific (Hawaii, crossed circles; Indonesia, squares) data fall along different trends with respect to temperature. Also note that these trends converge in shallow, warm waters. Regressions against temperature for the Atlantic and Pacific data are also shown. A and P represent the Atlantic (solid line) and Pacific (dashed line) regressions, respectively. (c) Mg/Ca and (d) Sr/Ca versus  $[\Delta\text{CO}_3]_{\text{aragonite}}$  showing strong dependence only at low  $\text{CO}_3$  levels.

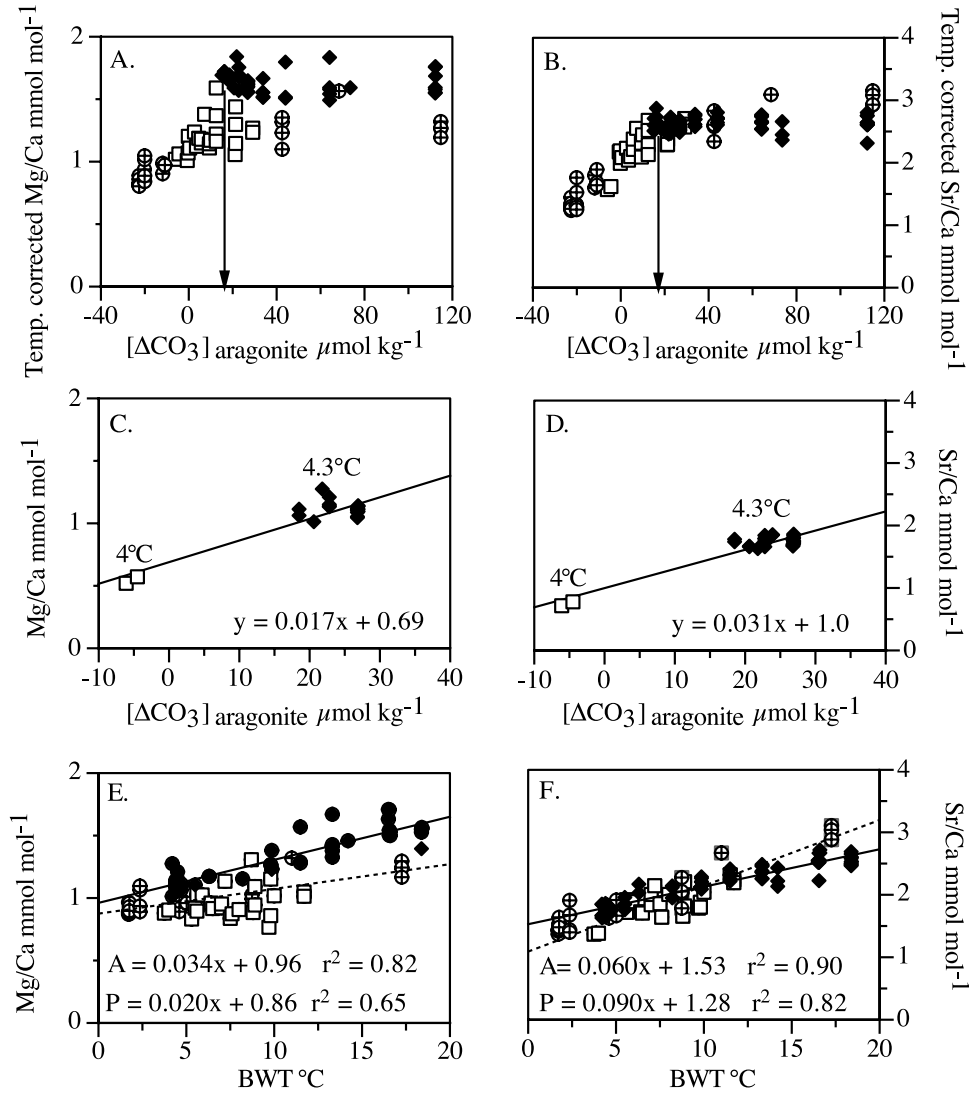
LBB samples are affected by secondary high-Mg coatings, and the Atlantic slope is therefore artificially high. If the former is the case, then we can use the Atlantic regression for estimating bottom water temperatures from Mg/Ca. However, if the latter is the case, our data suggest that Mg/Ca ratios in *H. elegans* tests may not be as precise a proxy as Sr/Ca for paleothermometry. While the reason for the difference in the behavior of Sr/Ca and Mg/Ca is yet unknown, it might be related to the difference in compatibility of  $\text{Mg}^{2+}$  and  $\text{Sr}^{2+}$  ions in the aragonite crystal lattice. As it affects both stained and unstained shells, it is more likely a primary rather than diagenetic effect.

[22] Evidence given here suggests that the effect of  $[\text{CO}_3]$  ion concentration is limited only to the deep ocean in waters that are either undersaturated or only slightly saturated with respect to aragonite. This behavior is consistent with studies of Zn/Ca in calcitic benthic foraminifera, where a strong  $[\text{CO}_3]$  ion effect was observed at bottom waters, which are under-saturated to slightly saturated with respect to calcite ( $[\Delta\text{CO}_3]_{\text{calcite}} < 25 \mu\text{mol kg}^{-1}$  [Marchitto *et al.*, 2000]). The importance of the  $\text{CO}_3$  ion effect on the calcification of benthic foraminifera should not come as a surprise given the unfavorable conditions for calcification in the deep ocean. It

is well documented that benthic foraminifera (calcitic and aragonitic alike) live and even flourish in undersaturated waters. This requires them to manipulate the calcifying solution in order to initiate and maintain shell precipitation. The observation that the “threshold” values exceed the saturation level (i.e.,  $[\Delta\text{CO}_3] = 0$ ) can be explained in two ways. One, the “threshold” values suggested here and elsewhere [Marchitto *et al.*, 2000] represent the concentration in the overlying bottom water, whereas foraminifera are more likely influenced by the conditions at the sediment-water interface. The latter might be significantly different, and often less saturated, than the overlying water because of the release of  $\text{CO}_2$  by decaying organic matter. This is very likely the case in our Indonesian samples, as they come from continental margin sediments with relatively high organic matter. A second, not mutually exclusive, explanation is that the calcification of benthic foraminifera shells commences only at slightly oversaturated levels.

### 4.3. Paleoceanographic Implications

[23] Our data suggest that both temperature and  $[\text{CO}_3]$  exert significant influence on the Mg and Sr content of the aragonite shells of *H. elegans*. The  $[\text{CO}_3]$  ion effect is



**Figure 7.** Temperature-corrected (a) Mg/Ca and (b) Sr/Ca ratios versus  $[\Delta\text{CO}_3]_{\text{aragonite}}$ . The correction is based on the regression obtained from the LBB data in Figures 6a and 6b and was applied to all the data to a reference of 18°C. The arrows mark the concentration at which the elemental ratios flatten out, about  $15 \mu\text{mol kg}^{-1}$   $[\Delta\text{CO}_3]_{\text{aragonite}}$ . Comparison of (c) Mg/Ca and (d) Sr/Ca ratios versus  $[\Delta\text{CO}_3]_{\text{aragonite}}$  in *H. elegans* shells from deep cores (1200–1750 m) in LBB and Indonesia. BWT along this depth interval is identical in both sites, but  $[\text{CO}_3]$  levels are substantially different. The  $[\text{CO}_3]$ -corrected (e) Mg/Ca and (f) Sr/Ca versus BWT. The correction is based on the regression obtained in Figures 6c and 6d and is only applied to samples where bottom water  $[\Delta\text{CO}_3]_{\text{aragonite}} < 15 \mu\text{mol kg}^{-1}$ . Symbols are as in Figure 6: LBB, diamonds; Hawaii, crossed circles; and Indonesia, squares. A and P represent the Atlantic and Pacific regressions, respectively.

limited, however, to waters with  $[\Delta\text{CO}_3]_{\text{aragonite}}$  levels below  $15 \mu\text{mol kg}^{-1}$ , whereas above this level the temperature effect dominates. Accordingly, we define the relationships among these parameters as follows:

At  $[\Delta\text{CO}_3]_{\text{aragonite}} > 15 \mu\text{mol kg}^{-1}$

$$\text{Mg/Ca} = (0.034 \pm 0.002)\text{BWT} + (0.96 \pm 0.03) \quad (1)$$

$$\text{Sr/Ca} = (0.060 \pm 0.002)\text{BWT} + (1.53 \pm 0.03). \quad (2)$$

At  $[\Delta\text{CO}_3]_{\text{aragonite}} < 15 \mu\text{mol kg}^{-1}$

$$\text{Mg/Ca} = 0.034\text{BWT} - (0.017 \pm 0.002) \cdot (15 - [\Delta\text{CO}_3]_{\text{aragonite}}) + 0.96 \quad (3)$$

$$\text{Sr/Ca} = 0.060\text{BWT} - (0.031 \pm 0.002) \cdot (15 - [\Delta\text{CO}_3]_{\text{aragonite}}) + 1.53, \quad (4)$$

where BWT is temperature in °C,  $[\Delta\text{CO}_3]_{\text{aragonite}}$  is in  $\mu\text{mol kg}^{-1}$ , Mg/Ca and Sr/Ca in  $\text{mmol mol}^{-1}$ . According to these relationships, the uncertainties associated with reconstructing BWTs based on Mg/Ca and Sr/Ca ratios are about  $\pm 1.1^\circ\text{C}$  and  $0.8^\circ\text{C}$ , respectively. The uncertainties are based on 1 standard error on the regression. These error estimates are based only on the LBB regression, and apply only to samples taken from saturated waters. We do not consider the accuracy and precision of estimates of BWT and  $[\Delta\text{CO}_3]$ , in undersaturated conditions as the regressions presented in Figure 7, are still insufficiently constrained. Furthermore, there is no a priori reason to expect that the dependence on  $[\Delta\text{CO}_3]$  will be as precise as on temperature. It is clear, however, that better temperature estimates can be obtained from measurements of Sr/Ca rather than Mg/Ca in *H. elegans*; measurement of both ratios is recommended, nonetheless.

[24] The implications of this study are that Mg/Ca and Sr/Ca can be used to reconstruct thermocline temperatures where  $[\Delta\text{CO}_3]_{\text{aragonite}} > 15 \mu\text{mol kg}^{-1}$ . These conditions prevail in the Bahama Banks today from intermediate depths to the surface, and likely persisted throughout the Holocene. On longer timescales, the aragonite saturation level shows significant secular variations due to variations in aragonite input from nearby shallow carbonate banks as sea levels go up and down and/or due to changes in carbonate chemistry of the entire water column. Mineralogical records (e.g., percent aragonite), however, provide guidance as to variations in aragonite saturation state through time [Droxler et al., 1990]. In the Pacific Ocean, the application of this potential paleothermometer is likely to be limited to the uppermost thermocline waters, which are restricted today, and likely throughout the Holocene, to depths shallower than 400 m. *H. elegans*, which has a relatively large vertical distribution, might be very useful in shallow, carbonate-rich sediments, such as in the Bahama Banks, where coatings of high-Mg calcite on calcitic foraminifera shells lead to contamination problems that cannot be eliminated by the commonly used cleaning procedures [Curry and Marchitto, 2005]. Furthermore, as it seems that Sr/Ca may provide a more precise and accurate paleothermometer than Mg/Ca, it may completely eliminate the problem of high-Mg calcite contamination.

## 5. Conclusions

[25] The results of this study add to the growing body of evidence for a significant  $[\text{CO}_3]$  ion effect on the incorporation of metals in benthic foraminifera. To date, most of the evidence comes from calcitic benthic species, where it was initially debated whether the depth-related decreasing trends in trace elements are due to dissolution, which preferentially removes metals from calcitic shells [McCorkle et al., 1995], or to the effects of  $[\text{CO}_3]$  on metal uptake during a foraminiferal tests formation [Boyle and Rosenthal, 1996; Elderfield et al., 1996]. The current study focuses on the benthic species, *H. elegans*, which has an aragonitic mineralogy. The results suggest that in

this species, the depth-related decrease in Mg/Ca and Sr/Ca below the aragonite lysocline is primarily due to a  $\text{CO}_3$  ion effect on Mg and Sr coprecipitation in tests that form in deep waters, characterized by low aragonite saturation levels. We find no discernible signs for post-burial alteration of the shell chemistry by dissolution. Studies of Zn/Ca [Marchitto et al., 2000] in calcitic benthic foraminifera reach similar conclusions, thus suggesting that the  $\text{CO}_3$  ion effect on metal uptake by benthic foraminifera is a more fundamental phenomenon than previously thought. Combined, results of these studies suggest that the  $\text{CO}_3$  ion effect occurs both in calcitic and aragonitic mineralogies, and probably affects different species that calcify in deep waters. The fact that these studies suggest that the  $\text{CO}_3$  ion effect is limited mainly to undersaturated water suggests that the mechanisms behind this effect are likely related to biological manipulation of the chemistry of the calcifying solution, as a means of reaching oversaturation with respect to the specific mineral that forms the shell.

[26] For paleoceanographers, our results add another level of complexity to the utility of geochemical proxies in benthic foraminifera. Specifically, we show that Sr/Ca and perhaps Mg/Ca ratios in *H. elegans* shells can be used to reconstruct temperatures only in waters oversaturated with respect to the mineral aragonite (i.e.,  $[\Delta\text{CO}_3]_{\text{aragonite}} > 15 \mu\text{mol kg}^{-1}$ ). Under these conditions the use of Sr/Ca as a paleothermometer is likely to yield better results than Mg/Ca, both because of its higher dependency on temperature and the better fit of the Sr ion in the aragonite crystal. In undersaturated waters, however, changes in Mg/Ca and Sr/Ca ratios reflect a combination of changes in  $[\text{CO}_3]$  and temperature. While the distinction between saturated and undersaturated waters can be made a priori in the modern ocean, it is more complicated when we examine ancient environments. Clearly, the use of this new BWT proxy is limited to shallow depths and to times when the ocean chemistry was not vastly different than today (e.g., the Holocene). In these cases, the use of Mg/Ca, and especially Sr/Ca, in *H. elegans* tests may fill a gap, where the use of Mg/Ca thermometry in calcitic foraminifera has been compromised by contamination issues or where the “right” calcitic species are missing.

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## References

- Bainbridge, A. E. (1981), *GEOSECS Atlantic Expedition*, vol. 1, *Hydrographic Data 1972–1973*, 121 pp., Natl. Sci. Found., Washington, D. C.
- Barker, S., M. Greaves, and H. Elderfield (2003), A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry, *Geochim. Geophys. Geosyst.*, 4(9), 8407, doi:10.1029/2003GC000559.
- Beck, W. J., L. R. Edwards, E. Ito, F. W. Taylor, J. Recy, F. Rougerie, P. Joannot, and C. Henin (1992), Sea-surface temperature from coral skeletal strontium/calcium ratios, *Science*, 257, 644–647.
- Billups, K. (2003), Application of benthic foraminiferal Mg/Ca ratios to questions of early Cenozoic climate change, *Earth Planet. Sci. Lett.*, 209, 181–195.
- Billups, K., and D. P. Schrag (2002), Paleotemperatures and ice volume of the past 27 Myr revisited with paired Mg/Ca and  $^{18}\text{O}/^{16}\text{O}$  measurements on benthic foraminifera, *Paleoceanography*, 17(1), 1003, doi:10.1029/2000PA000567.
- Boyle, E. A., and L. D. Keigwin (1985), Comparison of Atlantic and Pacific paleochemical records for the last 250,000 years: Changes in deep ocean circulation and chemical inventories, *Earth Planet. Sci. Lett.*, 76, 135–150.
- Boyle, E. A., and Y. Rosenthal (1996), Chemical hydrography of the South Atlantic during the last glacial maximum:  $\delta^{13}\text{C}$  vs. Cd, in *The South Atlantic: Present and Past Circulation*, edited by G. Wefer et al., pp. 423–443, Springer, New York.
- Boyle, E. A., L. Labeyrie, and J.-C. Duplessy (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., and T.-H. Peng (1982), *Tracers in the Sea*, 690 pp., Lamont-Doherty Earth Obs., Palisades, N. Y.
- Broecker, W. S., D. W. Spence, and H. Craig (1982), *GEOSECS Pacific Expedition*, vol. 3, *Hydrographic Data 1973–1974*, Natl. Sci. Found., Washington, D. C.
- Corliss, B. H., and S. R. Emerson (1990), Distribution of Rose Bengal stained deep-sea benthic foraminifera from the Nova Scotian continental margin and Gulf of Maine, *Deep Sea Res., Part A*, 37, 381–400.
- Curry, W. B., and T. M. Marchitto (2005), A SIMS calibration of benthic foraminiferal Mg/Ca, *Eos Trans. AGU*, 86(52), Fall Meet. Suppl., Abstract PP51A-0583.
- De Villiers, S., G. T. Shen, and B. K. Nelson (1994), The Sr/Ca-temperature relationship in coralline aragonite: Influence of variability in (Sr/Ca) seawater and skeletal growth parameters, *Geochim. Cosmochim. Acta*, 58, 197–208.
- Droxler, A. W., G. A. Haddad, D. A. Mucciarone, and J. L. Cullen (1990), Pliocene-Pleistocene aragonite cyclic variations in holes 714A and 716B (the Maldives) compared with hole 633A (the Bahamas): Records of climate-induced  $\text{CaCO}_3$  preservation at intermediate water depths, *Proc. Ocean Drill. Program Sci. Results*, 115, 539–577.
- Elderfield, H., C. J. Bertram, and J. Erez (1996), A biomineralization model for the incorporation of trace elements into foraminiferal calcium carbonate, *Earth Planet. Sci. Lett.*, 142, 409–423.
- Gordon, A. L., and R. A. Fine (1996), Pathways of water between the Pacific and Indian oceans in the Indonesian seas, *Nature*, 379, 146–149.
- Hall, J. M., and L. H. Chan (2004), Li/Ca in multiple species of benthic and planktonic foraminifera: Thermocline, latitudinal, and glacial-interglacial variation, *Geochim. Cosmochim. Acta*, 68, 529–545.
- Hover, V. C., L. M. Walter, and D. R. Peacor (2001), Early marine diagenesis of biogenic aragonite and Mg-calcite: New constraints from high-resolution STEM and AEM analyses of modern platform carbonates, *Chem. Geol.*, 175, 221–248.
- Keigwin, L. D., J. P. Sachs, and Y. Rosenthal (2003), A 1600-year history of the Labrador Current off Nova Scotia, *Clim. Dyn.*, 21, 53–62, doi:10.1007/s382-003-0316-6.
- Kinsman, D. J. J., and H. D. Holland (1969), The co-precipitation of cations with  $\text{CaCO}_3$ -IV. The co-precipitation of Sr with aragonite between 16 and 96 degrees, *Geochim. Cosmochim. Acta*, 33, 1–18.
- Lear, C. H., H. Elderfield, and P. A. Wilson (2000), Cenozoic deep-sea temperatures and global ice volumes from Mg/Ca in benthic foraminiferal calcite, *Science*, 287, 269–272.
- Lear, C. H., Y. Rosenthal, and N. C. Slowey (2002), Benthic foraminiferal Mg/Ca-paleothermometry: A revised core-top calibration, *Geochim. Cosmochim. Acta*, 66, 3375–3387.
- Lear, C. H., Y. Rosenthal, and J. D. Wright (2003), The closing of a seaway: Ocean water masses and global climate change, *Earth Planet. Sci. Lett.*, 210, 425–436.
- Lear, C. H., Y. Rosenthal, H. K. Coxall, and P. A. Wilson (2004), Late Eocene to early Miocene ice sheet dynamics and the global carbon cycle, *Paleoceanography*, 19, PA4015, doi:10.1029/2004PA001039.
- Lewis, E., and D. Wallace (1998), Program developed for  $\text{CO}_2$  system calculations, *Rep. ORNL/CDIAC-105*, Carbon Dioxide Inf. Anal. Cent., Oak Ridge Natl. Lab., U.S. Dep. of Energy, Oak Ridge, Tenn. (Available at <http://cdiac.esd.ornl.gov/oceans/co2rprt.html>)
- Lorens, R. B., and M. L. Bender (1980), The impact of solution chemistry on *Mytilus edulis* calcite and aragonite, *Geochim. Cosmochim. Acta*, 44, 1265–1278.
- Marchitto, T. M., W. B. Curry, and D. W. Oppo (1998), Millennial-scale changes in North Atlantic circulation since the last glaciation, *Nature*, 393, 557–561.
- Marchitto, T. M., W. B. Curry, and D. W. Oppo (2000), Zinc concentrations in benthic foraminifera reflect seawater chemistry, *Paleoceanography*, 15, 299–306.
- Martin, P. A., D. W. Lea, Y. Rosenthal, T. P. Papenfuss, and M. Sarnthein (2002), Late Quaternary deep-sea temperatures inferred from benthic foraminiferal magnesium, *Earth Planet. Sci. Lett.*, 198, 193–209.
- McCorkle, D. C., P. A. Martin, D. W. Lea, and G. P. Klinkhammer (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.
- Morkhoven, F. P. C. M. V., W. A. Berggren, and A. S. Edwards (1986), *Cenozoic Cosmopolitan Deep-Water Benthic Foraminifera*, *Cent. Rech. Explor. Prod. ElfAquitaine*, 11, 421 pp.
- Phleger, F. B., and F. L. Parker (1951), Ecology of foraminifera, northwest Gulf of Mexico, part II—Foraminifera species, *Mem. Geol. Soc. Am.*, 46, 1–64.
- Reichert, G.-J., F. Jorissen, P. Anschutz, and P. R. Mason (2003), Single foraminiferal test chemistry records the marine environment, *Geology*, 31, 355–358.
- Rosenthal, Y., and A. Katz (1989), The applicability of trace-elements in freshwater shells for paleochemical studies, *Chem. Geol.*, 78, 65–76.
- Rosenthal, Y., and G. P. Lohmann (2002), Accurate estimation of sea surface temperatures using dissolution-corrected calibrations for Mg/Ca paleothermometry, *Paleoceanography*, 17(3), 1044, doi:10.1029/2001PA000749.
- Rosenthal, Y., E. A. Boyle, and N. Slowey (1997), Environmental controls on the incorporation of Mg, Sr, F and Cd into benthic foraminiferal shells from Little Bahama Bank: Prospects for thermocline paleoceanography, *Geochim. Cosmochim. Acta*, 61, 3633–3643.
- Rosenthal, Y., F. Field, and R. M. Sherrill (1999), Precise determination of element/calcium ratios in calcareous samples using Sector Field Inductively Coupled Plasma Mass Spectrometry, *Anal. Chem.*, 71, 3248–3253.
- Rosenthal, Y., et al. (2004), Laboratory inter-comparison study of Mg/Ca and Sr/Ca measurements in planktonic foraminifera for paleoceanographic research, *Geochem. Geophys. Geosyst.*, 5, Q04D09, doi:10.1029/2003GC000650.
- Slowey, N. C. (1990), The modern and glacial thermoclines along the Bahamas Banks, Ph.D. thesis, Mass. Inst. of Technol./Woods Hole Oceanogr. Inst., Woods Hole, Mass.
- Smith, S. V., R. W. Buddemeier, R. C. Redalje, and J. E. Houck (1979), Strontium-calcium thermometry in coral skeletons, *Science*, 204, 404–407.

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