



## Mg/Ca–temperature proxy in benthic foraminifera: New calibrations from the Florida Straits and a hypothesis regarding Mg/Li

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[1] Over the past decade, the ratio of Mg to Ca in foraminiferal tests has emerged as a valuable paleotemperature proxy. However, large uncertainties remain in the relationships between benthic foraminiferal Mg/Ca and temperature. Mg/Ca was measured in benthic foraminifera from 31 high-quality multicore tops collected in the Florida Straits, spanning a temperature range of 5.8° to 18.6°C. New calibrations are presented for *Uvigerina peregrina*, *Planulina ariminensis*, *Planulina foveolata*, and *Hoeglundina elegans*. The Mg/Ca values and temperature sensitivities vary among species, but all species exhibit a positive correlation that decreases in slope at higher temperatures. The decrease in the sensitivity of Mg/Ca to temperature may potentially be explained by Mg/Ca suppression at high carbonate ion concentrations. It is suggested that a carbonate ion influence on Mg/Ca may be adjusted for by dividing Mg/Ca by Li/Ca. The Mg/Li ratio displays stronger correlations to temperature, with up to 90% of variance explained, than Mg/Ca alone. These new calibrations are tested on several Last Glacial Maximum (LGM) samples from the Florida Straits. LGM temperatures reconstructed from Mg/Ca and Mg/Li are generally more scattered than core top measurements and may be contaminated by high-Mg overgrowths. The potential for Mg/Ca and Mg/Li as temperature proxies warrants further testing.

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### 1. Introduction

[2] Over the past decade, the magnesium to calcium ratio (Mg/Ca) in foraminifera has been developed as a proxy for the temperature of the seawater in which the foraminifer calcified. Foraminiferal Mg/Ca has the potential to provide independent temperature reconstructions, which combined with shell  $\delta^{18}\text{O}$  allow the reconstruction of seawater  $\delta^{18}\text{O}$  [Mashiotto *et al.*, 1999; Elderfield and Ganssen, 2000]. Mg/Ca in planktonic foraminifera has been used to investigate variations in sea surface temperatures [e.g., Hastings *et al.*, 1998; Mashiotto *et al.*, 1999; Lea *et al.*, 2000; Koutavas *et al.*, 2002; Stott *et al.*, 2002; Barker *et al.*, 2005], sea surface salinity [e.g., Gussone *et al.*, 2004; Schmidt *et al.*, 2004; Benway *et al.*, 2006; Newton *et al.*, 2006; Schmidt *et al.*, 2006], and sea level [Lea *et al.*, 2002]. Although its application has been more limited, Mg/Ca in benthic foraminifera has been used to investigate deep sea temperatures and global ice volume over Quaternary and Cenozoic timescales [Lea *et al.*, 2000; Billups and Schrag, 2002, 2003; Martin *et al.*, 2002; Lear *et al.*, 2003; Marchitto and deMenocal, 2003; Skinner *et al.*, 2003].

[3] The incorporation of Mg into foraminiferal shells is likely related to temperature through both thermodynamics and physiological processes [Rosenthal *et al.*, 1997; Lea *et al.*, 1999; Erez, 2003; Bentov and Erez, 2006]. The ther-

modynamics of solid-solution substitution of Mg for Ca in calcite predicts that Mg/Ca should increase by  $\sim 3\%$  per °C increase in temperature [Lea *et al.*, 1999]. This prediction is generally supported by inorganic precipitation experiments [e.g., Katz, 1973; Mucci, 1987; Oomori *et al.*, 1987]. However, the low-Mg calcite tests of planktonic and deep sea benthic foraminifera contain about an order of magnitude less Mg than inorganic calcite, and the response of Mg/Ca in foraminifera to temperature is 2–3 times greater than thermodynamics predict [e.g., Rosenthal *et al.*, 1997; Lea *et al.*, 1999; Lear *et al.*, 2002]. There is increasing evidence that foraminifera exert a strong biological control on the biomineralization process. Foraminifera likely calcify from seawater that is encapsulated within an internal calcification pool, and the composition of the calcification pool may be altered by the removal of Mg through selective channels and pumps [Erez, 2003; Bentov and Erez, 2006]. Interspecies differences in shell Mg/Ca have been observed in planktonic [Lea *et al.*, 1999; Anand *et al.*, 2003] and benthic foraminifera [Rosenthal *et al.*, 1997; Lear *et al.*, 2002; Elderfield *et al.*, 2006]. Variations in trace metal concentrations within individual shells have been observed in association with organic membranes [Kunioka *et al.*, 2006]. These observations suggest that physiological processes and manipulation of the parent solution (“vital effects”) are likely important controls on the eventual shell Mg/Ca ratio.

[4] Empirical calibration and understanding of influential parameters other than temperature are vital to the application of Mg/Ca as a paleotemperature proxy. Planktonic foraminifera have been calibrated by core top [Nurnberg, 1995; Elderfield and Ganssen, 2000; Lea *et al.*, 2000; Dekens *et*

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**Table 1.** Benthic Foraminiferal Mg/Ca–Temperature Calibrations From This Study and Literature

Species	Mg/Ca =	Location	Temperature Range (°C)	Cleaning Method <sup>a</sup>	Reference
<i>C. pachyderma</i>	0.116T + 1.20	Florida Straits	5.8–18.6	R	Marchitto et al. [2007]
<i>C. pachyderma</i>	1.36 * 10 <sup>0.044T</sup>	Little Bahama Bank	0.8–18.4	L	Rosenthal et al. [1997]
<i>Cibicides</i> spp.	0.867e <sup>0.109T</sup>	multiple regions	0.8–18.4	R	Lear et al. [2002]
<i>C. pachyderma</i> / <i>C. wuellerstorfi</i>	0.85e <sup>0.11T</sup>	multiple regions	–1–18	L/R	Martin et al. [2002]
<i>Cibicides</i> spp.	0.90e <sup>0.11T</sup>	multiple regions	–0.6–18.4	O/R	Elderfield et al. [2006]
<i>C. kullenbergi</i>	0.11T + 0.88	off Somalia	2.6–11.8	O	Elderfield et al. [2006]
<i>C. wuellerstorfi</i>	0.342T + 1.39	Coral Sea/Prydz Bay	2–6	S	Rathburn and DeDeckker [1997]
<i>C. wuellerstorfi</i> / <i>C. refulgens</i>	0.277T + 1.73	Coral Sea/Prydz Bay	–2–6	S	Rathburn and DeDeckker [1997]
<i>U. peregrina</i>	0.079T + 0.77	Florida Straits	5.8–17.2	R	this study
<i>U. peregrina</i>	0.065T + 0.91	off Somalia	1.5–11.8	O	Elderfield et al. [2006]
<i>Uvigerina</i> spp.	0.075T + 0.87	Arabian Sea	1.7–20	R	Elderfield et al. [2006]
<i>Uvigerina</i> spp.	0.924e <sup>0.061T</sup>	multiple regions	1.8–18.4	R	Lear et al. [2002]
<i>P. ariminensis</i>	0.17T + 0.5	Florida Straits	7.0–12.1	R	this study
<i>P. ariminensis</i>	0.911e <sup>0.062T</sup>	multiple regions	3.0–14.5	R	Lear et al. [2002]
<i>P. foveolata</i>	0.04T + 2.1	Florida Straits	11.0–17.8	R	this study
<i>Planulina</i> spp.	0.788e <sup>0.119T</sup>	multiple regions	2.3–12.0	R	Lear et al. [2002]
<i>H. elegans</i>	0.030T + 1.01	Florida Straits	5.8–19.0	R	this study
<i>H. elegans</i>	0.034T + 0.96	multiple regions	1.7–18.4	R	Rosenthal et al. [2006]
<i>O. umbonatus</i>	1.008e <sup>0.114T</sup>	multiple regions	0.8–9.9	R	Lear et al. [2002]
<i>O. umbonatus</i>	1.528e <sup>0.09T</sup>	off Namibia	2.9–10.4	N	Rathmann et al. [2004]
<i>G. affinis</i>	2.91e <sup>0.080T</sup>	Iberian Margin	–1.8–3.28	O	Skinner et al. [2003]
<i>M. barleeanus</i> / <i>M. pompilioides</i>	0.982e <sup>0.101T</sup>	multiple regions	0.8–18.4	R	Lear et al. [2002]
<i>M. barleeanus</i>	0.658e <sup>0.137T</sup>	near Iceland	0.19–6.99	R	Kristjansdottir et al. [2007]
<i>I. norcorossi</i> / <i>I. helenae</i>	1.051e <sup>0.060T</sup>	near Iceland	0.21–5.25	R	Kristjansdottir et al. [2007]
<i>C. neoteretis</i>	0.864e <sup>0.082T</sup>	near Iceland	0.96–5.47	R	Kristjansdottir et al. [2007]

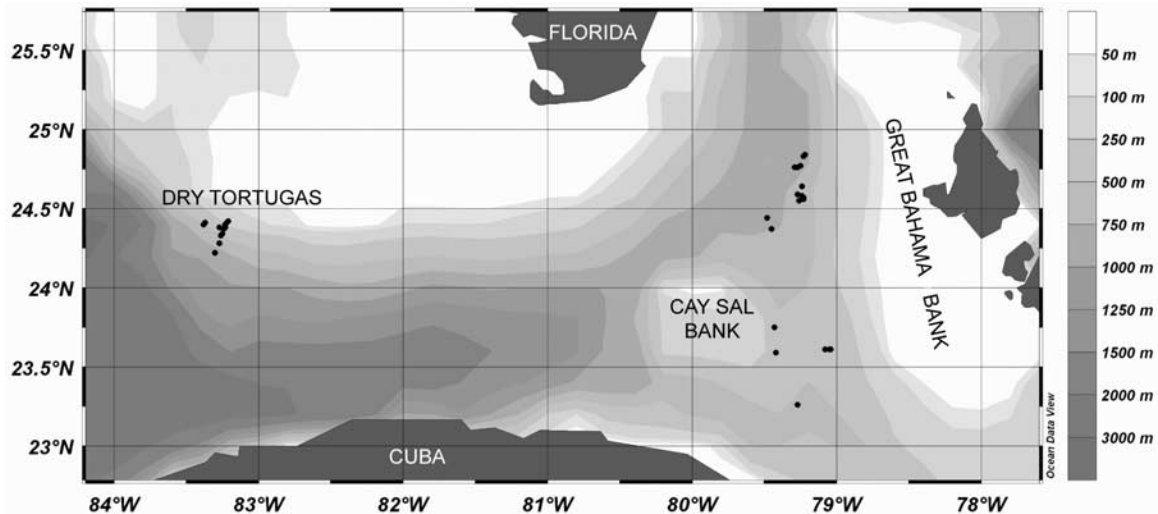
<sup>a</sup>Cleaning methods are as follows: R, full trace metal cleaning method with a reductive step; O, the “Mg cleaning method” without the reductive step; L, acid leach; S, sonicated in methanol; and N, no cleaning (laser ablation).

al., 2002], sediment trap [Anand et al., 2003; McConnell and Thunell, 2005] and laboratory culture studies [Nurnberg et al., 1996; Lea et al., 1999; Mashiotta et al., 1999] (see Barker et al. [2005] for a review); and most of these studies have demonstrated a ~9–10% exponential increase in Mg/Ca per degree Celsius in most species. The response of benthic Mg/Ca to temperature is less well constrained. With the exception of recent progress in culturing benthic foraminifera [Hintz et al., 2006a, 2006b], benthic foraminiferal Mg/Ca has been calibrated exclusively by the comparison of core top samples to bottom water temperatures. Early studies of Mg/Ca in benthic foraminifera demonstrated a strong correlation with seawater temperature [Chave, 1954; Izuka, 1988; Rathburn and DeDeckker, 1997]. Rosenthal et al. [1997] proposed an exponential temperature response of ~11% per °C for *Cibicides pachyderma* (cf. *C. floridanus*) using core tops from the Little Bahama Bank. Lear et al. [2002] confirmed the ~11% per °C response for *C. pachyderma* by reanalyzing the samples of Rosenthal et al. [1997], but noted that several other species such as *Uvigerina* spp. and *P. ariminensis* had lower temperature sensitivities (~6% per °C). Marchitto et al. [2007] recently found that warm water *C. pachyderma* Mg/Ca values from the Florida Straits are much lower than those from the Little Bahama Bank, suggesting that some Bahamas measurements may be affected by authigenic contamination. Marchitto et al. [2007] proposed that the Mg/Ca–temperature relationship of *C. pachyderma* is best described by a straight line. In the past

several years core top calibrations have been presented for several other benthic species [Rathmann et al., 2004; Elderfield et al., 2006; Rosenthal et al., 2006; Kristjansdottir et al., 2007], although questions about the use of exponential relationships and differences in temperature sensitivities between species still remain. A compilation of published calibrations for deep-sea benthic species is given in Table 1.

[5] Mg/Ca in benthic foraminifera may also be significantly influenced by variables other than temperature. Recent studies have focused on the influence of carbonate ion concentration [Elderfield et al., 2006; Rosenthal et al., 2006]; these studies concluded that Mg/Ca is reduced at low carbonate ion saturation ( $\Delta\text{CO}_3^{2-} = [\text{CO}_3^{2-}]_{\text{in situ}} - [\text{CO}_3^{2-}]_{\text{saturation}}$ ), similar to other trace elements (Cd/Ca, Ba/Ca and Zn/Ca) [McCorkle et al., 1995; Marchitto et al., 2000, 2005]. The evidence presented thus far suggests that a carbonate ion effect is limited to waters near or below saturation, although more analyses are needed from super-saturated waters.

[6] This study adds species-specific Mg/Ca–temperature calibrations for *Uvigerina peregrina*, *Planulina ariminensis*, *Planulina foveolata*, and the aragonitic *Hoeglundina elegans* using a set of core top samples from the Florida Straits. The Florida Straits measurements agree well with published data, and we suggest that linear calibrations of these data are more useful approximations than exponential ones. However, Mg/Ca in benthic foraminifera appears to be suppressed at high carbonate ion concentrations. We



**Figure 1.** Map of KNR166-2 multicore sites used in this study. Multicore sites are indicated by black dots. Gray scale indicates water depth; note that contour intervals increase with depth. The Florida Current flows from the southwest to the northeast in between Dry Tortugas and the Bahama Banks. Map was created using Ocean Data View software (R. Schlitzer, 2008, available at <http://odv.awi.de>).

explore a method to correct for Mg/Ca suppression using Li/Ca. Our new Mg/Ca calibrations and this new method are then tested on several samples from the Last Glacial Maximum.

## 2. Materials and Methods

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

[8] Multicore sites cover depth, in situ temperature, salinity, and  $\Delta\text{CO}_3^{2-}\text{-calcite}$  ranges of 173–751 m, 5.8–18.6°C, 34.9–36.8 psu, and 46–161  $\mu\text{mol kg}^{-1}$  respectively (Figure 2). Sloping of isopycnals associated with the Florida Current causes the eastern side of the Florida Straits to have higher temperature, salinity and  $[\text{CO}_3^{2-}]$  at a given depth than the western side of the Straits [see Lynch-Stieglitz *et al.*, 1999]. Fifty-five conductivity-temperature-depth profile (CTD) casts were made during the course of the cruise, and bottom water samples from the multicore sites were also collected using a Niskin bottle attached to the multicorer frame. Aliquots of the Niskin seawater were sampled for salinity,  $\delta^{18}\text{O}$ , alkalinity and  $\Sigma\text{CO}_2$ . Owing to the sloping of isopycnals, simply using CTD temperatures at the same depths as the multicores would be slightly inaccurate. Instead, bottom water temperatures were determined by, in effect, tracing isopycnals from the multicore sites to the CTD sites. This was done by matching the salinity measurement of the Niskin water from each multicore site to the salinity of

a nearby CTD cast, and then applying the corresponding CTD temperature to the multicore site. On the east side of the Florida Current the matching CTD depths were on average 15 m shallower than the depths of the multicores, and on the west side of the Florida Current the CTD depths were on average 15 m deeper than the multicore depths. At 12 of the multicore sites the salinity-matching method was not possible because of either Niskin bottle malfunction or because salinity was too constant with depth to provide a clear match. At these 12 sites salinity and temperature were derived from nearby CTDs using the average CTD-multicore depth offset described above. That is, at Dry Tortugas 15 m was added to the depth of the multicore site and the CTD temperature and salinity at that depth was used. Likewise, at Great Bahama Bank 15 m was subtracted from the multicore depth and the CTD measurements at that depth were used.

[9] Carbonate ion concentrations for 13 of the multicore sites were calculated from alkalinity and  $\Sigma\text{CO}_2$  measurements with the CO2SYS program v. 1.05 [Lewis and Wallace, 1998], using the first and second dissociation constants of carbonic acid from Hansson [1973] and Mehrbach *et al.* [1973] as refit by Dickson and Millero [1987] [Marchitto *et al.*, 2007].  $\Delta\text{CO}_3^{2-}$  with respect to both calcite and aragonite was calculated using CO2SYS [Lewis and Wallace, 1998]. For the other sites,  $\Delta\text{CO}_3^{2-}$  with respect to calcite and aragonite were inferred from second-order polynomial relationships with salinity ( $\Delta\text{CO}_3^{2-}\text{-calcite} = 13.590*S^2 - 904.76*S + 15069.4$ ,  $R^2 = 0.99$ ;  $\Delta\text{CO}_3^{2-}\text{-aragonite} = 12.729*S^2 - 841.17*S + 13872.0$ ,  $R^2 = 0.99$ ).

[10] AMS radiocarbon ages were measured on *Globigerinoides ruber* (>250  $\mu\text{m}$ ) from the 0–1 or 0–2 cm slices from 14 of the KNR166-2 multicores [Lund and Curry, 2004, 2006; Lund, 2005; Lund *et al.*, 2006]. Seven of the core tops contained significant levels of “bomb” radiocarbon (core fraction modern >1 or conventional radiocarbon age <400 years), and seven ranged from ~1000 to 3000 years

**Table 2.** KNR 166-2 Multicore Locations, Hydrographic Data, and Radiocarbon Ages

Core <sup>a</sup>	Latitude (°N)	Longitude (°W)	Depth (m)	Temperature (°C) <sup>b</sup>	Salinity (psu)	$\Delta\text{CO}_3^{2-}\text{calcite}$ ( $\mu\text{mol kg}^{-1}$ )	$\Delta\text{CO}_3^{2-}\text{aragonite}$ ( $\mu\text{mol kg}^{-1}$ )	Conventional <sup>14</sup> C Age (years B.P.) <sup>c</sup>	NOSAMS Number <sup>d</sup>
5MC (1)	24.4	83.38	447	8.5	35.02	54	28		
11MC (1)	24.22	83.30	751	5.8	34.91	55	28	355 ± 35	OS-39958 (2)
13MC (1)	24.37	83.24	348	9.7	35.17	62	27	3040 ± 35	OS-46032 (4)
16MC (1)	24.4	83.23	248	10.8	35.32	66	40	960 ± 30	OS-44554 (4)
19MC (1)	24.42	83.21	173	12.7	35.60	82	57	1320 ± 50	OS-39967 (4)
22MC (1)	24.41	83.37	398	9.0	35.08	54	57		
24MC (1)	24.34	83.25	494	7.8	34.95	48	28		
28MC (1)	24.28	83.27	648	6.3	34.91	50	22	2980 ± 40	OS-46037 (2)
50MC (1)	24.41	83.22	198	12.1	35.51	76	22	1080 ± 45	OS-41646 (4)
53MC (1)	24.38	83.23	302	10.0	35.21	61	22	1800 ± 30	OS-39969 (2)
55MC (1)	24.38	83.27	359	9.1	35.10	55	52		
62MC (1)	24.33	83.26	547	7.0	34.91	46	35	Fm > 1	OS-39971 (1)
66MC (3)	23.61	79.05	302	19.0	36.62	160	136		
68MC (3)	23.61	79.08	431	16.6	36.24	129	105		
72MC (2)	23.75	79.43	542	10.8	35.31	70	44		
76MC (2)	23.59	79.42	539	11.0	35.33	67	42		
79MC (2)	23.26	79.27	486	12.1	35.50	77	51		
84MC (3)	24.37	79.45	638	10.5	35.27	58	31		
89MC (3)	24.56	79.24	353	17.8	36.48	149	125	2280 ± 35	OS-40243 (2)
92MC (3)	24.55	79.26	478	15.7	36.13	124	99		
94MC (3)	24.57	79.23	259	18.5	36.57	161	138	215 ± 35	OS-40244 (4)
97MC (3)	24.56	79.23	303	18.6	36.58	158	134		
103MC (3)	24.44	79.48	683	9.3	35.11	53	27		
110MC (3)	24.58	79.24	390	17.3	36.39	141	117	Fm > 1	OS-46039 (2)
112MC (3)	24.64	79.24	404	17.1	36.35	138	114		
118MC (3)	24.59	79.27	531	14.5	35.91	104	79	Fm > 1	OS-39973 (3)
121MC (3)	24.77	79.25	578	11.9	35.48	76	51		
123MC (3)	24.76	79.27	632	10.6	35.30	65	39		
125MC (3)	24.76	79.29	694	9.4	35.13	57	30	Fm > 1	OS-39975 (3)
134MC (3)	24.84	79.22	441	17.2	36.37	139	115	Fm > 1	OS-46043 (4)
138MC (3)	24.83	79.23	484	16.8	36.29	135	110		

<sup>a</sup>Numbers in parentheses with cores indicate 1, Dry Tortugas sites; 2, Cay Sal Bank sites; and 3, Great Bahama Bank sites.

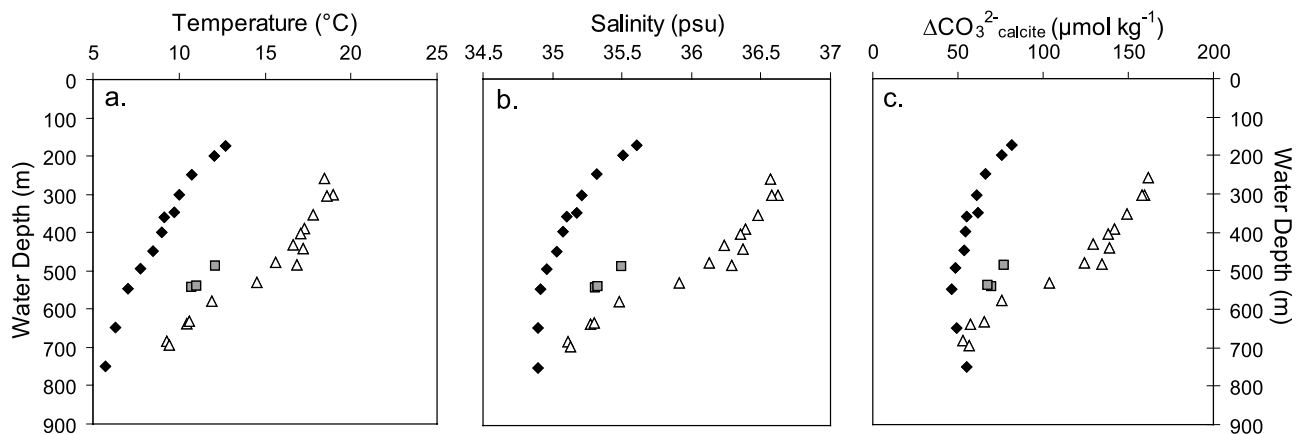
<sup>b</sup>Bottom water temperatures were estimated by matching Niskin bottle salinities to nearby CTDs. Italicized salinities and  $\Delta\text{CO}_3^{2-}$  values were estimated as described in text.

<sup>c</sup>Fm > 1 refers to fraction modern greater than one, indicating the presence of <sup>14</sup>C from nuclear weapons testing.

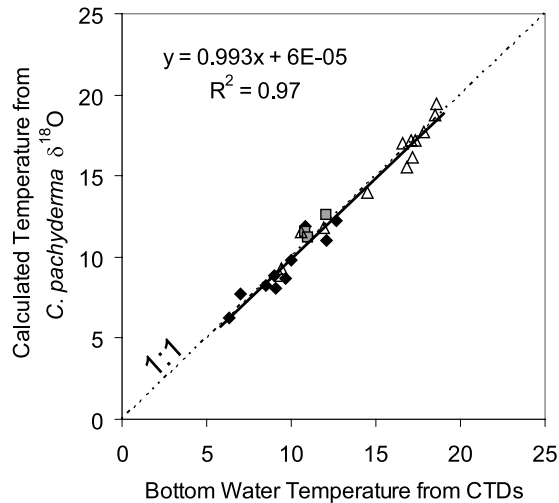
<sup>d</sup>Sources of radiocarbon ages are indicated by numbers in parentheses with the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) sample numbers: 1, *Lund and Curry* [2004]; 2, *Lund* [2005]; 3, *Lund and Curry* [2006]; and 4, *Lund et al.* [2006].

(mostly from the Dry Tortugas region). Sedimentation rates in KNR166-2 cores range between 11 and 66 cm ka<sup>-1</sup> near Dry Tortugas and 20 and 350 cm ka<sup>-1</sup> on Great Bahama Bank [*Lund et al.*, 2006].

[11] Given that bottom water temperature at the multicore sites is sensitive to the sloping of isopycnals associated with the Florida Current, variability in current strength over the past few millennia may introduce some error into our



**Figure 2.** (a) Temperature, (b) salinity, and (c)  $\Delta\text{CO}_3^{2-}$  with respect to calcite estimates for the KNR166-2 multicore sites plotted versus water depth. Each symbol represents one multicore site: diamonds represent sites near Dry Tortugas; squares represent sites near Cay Sal Bank; and triangles represent sites near Great Bahama Bank.



**Figure 3.** Comparison of bottom water temperatures at the multicore sites derived from CTD measurements (as described in text) to calcification temperatures derived from *C. pachyderma*  $\delta^{18}\text{O}$ . Diamonds are multicore sites near Dry Tortugas; squares are sites near Cay Sal Bank, and triangles are sites near Great Bahama Bank. The 1:1 relationship and strong correlation indicate that bottom water temperature estimates are good approximations of the temperature at which the foraminifera calcified.

calcification temperature estimates for core tops with non-modern ages. Gulf Stream transport through the Florida Straits appears to have varied by  $\sim 10\%$  over the past 1000 years [Lund *et al.*, 2006]. Our temperature estimates may be verified by comparison to calcification temperatures derived from benthic foraminiferal  $\delta^{18}\text{O}$ . We calculate calcification temperatures for *C. pachyderma* using splits of the Knorr 166-2 trace metal samples measured by Marchitto *et al.* [2007] and the *Cibicides* and *Planulina* paleotemperature equation of Lynch-Stieglitz *et al.* [1999], with seawater  $\delta^{18}\text{O}$  determined from measurements on Niskin waters (T. M. Marchitto, manuscript in preparation, 2008). Calcification temperatures agree very well with our

temperature estimates (Figure 3), indicating that bottom water temperatures have not changed significantly over the time period represented by the core tops and that there are no systematic biases between the different regions.

[12] Benthic foraminifera *U. peregrina*, *P. ariminensis*, *P. foveolata* and *H. elegans* were picked from the 250–600  $\mu\text{m}$  size fraction of each core top. Samples for trace element analysis contained about 9–10 individuals (*U. peregrina*), 13–15 individuals (*P. ariminensis*), 18–20 individuals (*P. foveolata*), and 9–10 individuals (*H. elegans*). Where abundances allowed, the number of individuals was doubled and samples were crushed, homogenized and split for replicate analysis. Crushed samples were cleaned reductively (using anhydrous hydrazine) and oxidatively (using  $\text{H}_2\text{O}_2$ ) in a Class-1000 clean lab, following the methods of Boyle and Keigwin [1985] as modified by Boyle and Rosenthal [1996]. Samples were analyzed for Mg/Ca, Sr/Ca, Cd/Ca, Zn/Ca, Li/Ca, U/Ca, Mn/Ca and Fe/Ca by magnetic-sector single-collector ICP-MS, on a Thermo-Finnigan Element2, using methods adapted from Rosenthal *et al.* [1999] [Marchitto, 2006]. Long-term  $1\sigma$  precisions are: Mg/Ca = 0.54%, Sr/Ca = 0.57%, Cd/Ca = 1.8%, Zn/Ca = 3.2%, Li/Ca = 0.88%, U/Ca = 1.9%, Mn/Ca = 0.97% and Fe/Ca = 1.4% [Marchitto, 2006]. Mn/Ca and Fe/Ca were measured to screen against contamination from diagenetic coatings or detrital material; values were almost always below 30  $\mu\text{mol mol}^{-1}$  and did not exceed 50  $\mu\text{mol mol}^{-1}$  in any sample, well below thresholds for likely trace metal contamination ( $>100 \mu\text{mol mol}^{-1}$ ) [Boyle, 1983; Barker *et al.*, 2003].

### 3. Results

[13] Core top Mg/Ca values range from 1.02 to 2.15  $\text{mmol mol}^{-1}$  for *U. peregrina*, 1.74 to 2.73  $\text{mmol mol}^{-1}$  for *P. ariminensis*, 2.31 to 2.84  $\text{mmol mol}^{-1}$  for *P. foveolata*, and 1.03 to 1.69  $\text{mmol mol}^{-1}$  for *H. elegans* (Table 3). *H. elegans* Mg/Ca measurements from two multicores were much higher than measurements from nearby cores and are suspected to be contaminated (Table 3). These measurements are excluded from the Figures 4–6 and 8–10 and regressions. The source of the contamination

**Table 3.** Benthic Foraminiferal Mg/Ca and Li/Ca Measurements<sup>a</sup>

Core	<i>U. peregrina</i>		<i>P. ariminensis</i>		<i>P. foveolata</i>		<i>H. elegans</i>		<i>C. pachyderma</i>	
	Mg/Ca	Li/Ca	Mg/Ca	Li/Ca	Mg/Ca	Li/Ca	Mg/Ca	Li/Ca	Mg/Ca <sup>b</sup>	Li/Ca
	<i>Core Top</i>									
5MC	1.48	17.37	2.09	12.93			1.55	3.90	2.09	13.04
5MC	1.46	17.42	2.04	12.87			1.19	3.75	2.00	8.76 <sup>c</sup>
11MC	1.07	16.96					1.03	3.86	1.34	12.38
11MC	1.02	17.27								
13MC	1.52	16.50	2.36	12.66			1.31	3.89	2.33	12.82
13MC	1.53	16.52	2.25	12.39			1.26	3.83	2.44	13.09
16MC									2.40	12.20
16MC									2.27	12.12
19MC					2.58	12.48	1.49	3.77	2.09	12.22
19MC							1.53	3.79	2.73	12.61
22MC	1.48	16.97					1.38	4.20	2.63	15.93 <sup>c</sup>
22MC	1.43	16.91							2.49	13.43
24MC	1.69	17.77					1.12	3.62		
28MC	1.13	16.90					1.07	3.79	1.42	13.31
28MC	1.15	16.90					1.03	3.74	1.54	13.36

Table 3. (continued)

Core	<i>U. peregrina</i>		<i>P. ariminensis</i>		<i>P. foveolata</i>		<i>H. elegans</i>		<i>C. pachyderma</i>	
	Mg/Ca	Li/Ca	Mg/Ca	Li/Ca	Mg/Ca	Li/Ca	Mg/Ca	Li/Ca	Mg/Ca <sup>b</sup>	Li/Ca
50MC			2.73	12.37	2.72	12.33	1.49	3.85	2.39	12.05
50MC									2.47	12.02
53MC	1.46	16.34	2.38	12.44			2.12 <sup>d</sup>	8.48 <sup>d</sup>	2.37	12.61
53MC	1.41	16.27	2.36	12.55			2.19 <sup>d</sup>	9.32 <sup>d</sup>	2.20	12.47
55MC	1.64	16.79	2.24	14.17			5.63 <sup>d</sup>	5.64 <sup>d</sup>	2.34	13.07
55MC	1.69	17.25	2.20	13.82			4.53 <sup>d</sup>	5.12 <sup>d</sup>	2.24	13.22
62MC	1.36	17.24	1.74	13.40			1.07	3.56	2.19	13.27
62MC	1.43	17.07								
66MC							1.56	3.28		
68MC					2.84	11.53	1.64	3.65	3.29	11.19
68MC							1.49	3.36	3.39	11.43
72MC	1.63	17.14			2.31	16.80	1.47	4.56	2.88	13.14
72MC	1.61	16.94							2.83	13.25
76MC	1.71	16.79	2.23	12.43	2.43	12.55			2.87	12.94
76MC									2.78	12.90
79MC	1.89	16.07			2.59	11.76	1.48	3.87	3.35	13.12
79MC	1.88	16.23							3.15	12.93
84MC									2.48	13.73
89MC					2.64	11.33			3.44	11.32
92MC	2.00	16.28					1.64	3.78	3.19	12.86
94MC							1.30	2.69	3.34	10.88
94MC							1.30	4.21	3.47	11.04
97MC							1.51	3.27	3.27	11.02
97MC							1.42	3.02	3.25	11.00
103MC	1.45	16.96	1.84	13.20					2.31	13.01
103MC									2.34	13.25
110MC	2.15	14.98			2.75	11.61	1.69	3.65	3.31	12.47
110MC	2.14	15.28			2.75	11.46	1.46	3.24		
112MC							1.48	3.23	2.92	11.93
112MC							1.55	3.41		
118MC	1.85	16.26			2.41	12.26	1.54	4.02	2.68	13.28
118MC	1.84	16.24					1.50	3.98		
121MC	1.86	16.27					1.60	4.33	2.48	12.66
121MC									2.67	12.45
123MC									2.44	12.73
123MC									2.65	12.77
125MC			1.84	15.19					2.48	13.26
134MC					2.69	12.09	1.61	3.65	2.94	11.51
134MC							1.52	3.51	3.14	11.66
138MC	1.88	15.86			2.59	11.91	1.59	3.87	2.56	11.92
138MC					2.69	11.87	1.51	3.68		
					<i>LGM</i>					
2JPC	1.92	15.17	2.49	15.43			1.21	4.16	3.00	12.90
2JPC	1.80	14.77								
29JPC	2.29	24.33								
59JPC			2.82	15.12			1.32	4.30	2.43	11.53
59JPC									2.56	11.55
73GGC	3.90	21.25	2.90	16.52					2.96	17.04
73GGC									3.07	17.24
83GGC			3.67	16.44			1.35	5.70	4.76	16.11

<sup>a</sup>Mg/Ca units are mmol mol<sup>-1</sup>; Li/Ca units are μmol mol<sup>-1</sup>.

<sup>b</sup>*C. pachyderma* Mg/Ca measurements were presented by Marchitto *et al.* [2007].

<sup>c</sup>Value is from samples that were too small for reliable Li measurement ([Ca] < 0.05 mM) and are also excluded.

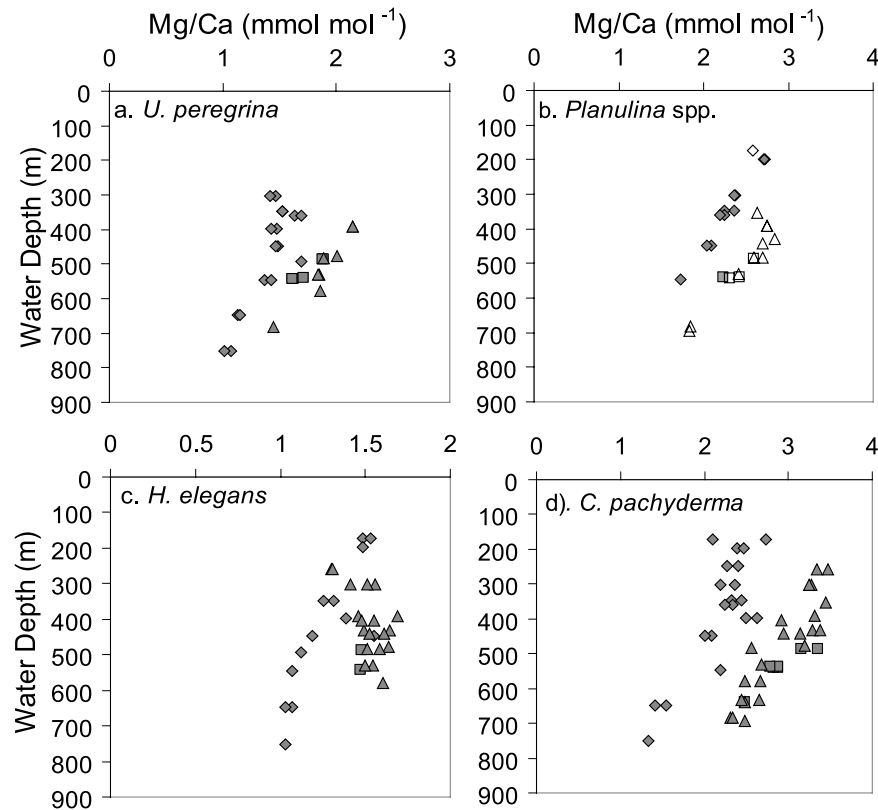
<sup>d</sup>Value was excluded from Figures 4–10 and regressions because of suspected contamination.

is unclear; it is possible that these samples were affected by diagenetic overgrowths. However, *H. elegans* is thought to be less susceptible to overgrowths than many other foraminifera because of its glassy aragonitic test [Boyle *et al.*, 1995].

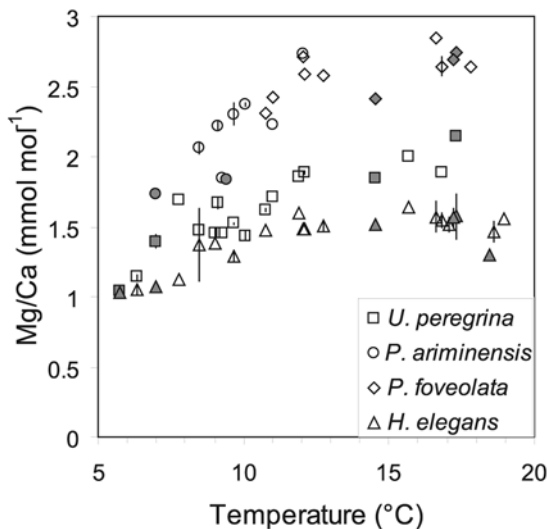
[14] In all species, Mg/Ca decreases with increasing depth, and depth profiles are distinct between regions, with generally lower values on the western (colder) side of the Florida Current (Figure 4). The standard deviation of sample splits is several times larger than the analytical uncertainty (pooled standard deviation = 0.049 mmol mol<sup>-1</sup>, degrees of freedom = 30), indicating variability within a sample

and some inadequate homogenization. Some of the scatter in the replicates may be due to individual foraminifera representing a range in ages of up to several thousand years, especially in the Dry Tortugas samples.

[15] Core top Li/Ca ranges from 14.98 to 17.77 μmol mol<sup>-1</sup> in *U. peregrina*, 12.37 to 15.19 μmol mol<sup>-1</sup> in *P. ariminensis*, 11.33 to 16.80 μmol mol<sup>-1</sup> in *P. foveolata*, 2.69 to 4.57 μmol mol<sup>-1</sup> in *H. elegans*, and 10.88 to 13.73 μmol mol<sup>-1</sup> in *C. pachyderma* (Table 3). Li/Ca in *C. pachyderma* was measured on the same samples as the Mg/Ca presented by Marchitto *et al.* [2007]. The pooled



**Figure 4.** Individual Mg/Ca measurements plotted versus water depth: (a) *U. peregrina*, (b) *Planulina* spp. (*P. ariminensis* measurements are gray symbols, and *P. foveolata* measurements are open symbols), (c) *H. elegans*, and (d) *C. pachyderma* measurements from Marchitto *et al.* [2007]. Measurements from Dry Tortugas sites are indicated by diamonds; Cay Sal Bank sites are squares; and Great Bahama Bank sites are triangles. Note the differing Mg/Ca scales.



**Figure 5.** Average Mg/Ca plotted against bottom water temperature for each species. Error bars are one standard deviation of sample splits, where applicable. Shaded symbols indicate multicores determined to be modern by the presence of “bomb”  $^{14}\text{C}$  (<400 years).

standard deviation of sample splits is  $0.15 \mu\text{mol mol}^{-1}$  (degrees of freedom = 47). Li/Ca in *H. elegans* is elevated in the two cores with elevated Mg/Ca. There are large interspecies differences in Li/Ca, and Li/Ca in *H. elegans* is much lower than in the calcitic species. Li/Ca increases with increasing water depth for all species.

## 4. Discussion

### 4.1. Mg/Ca–Temperature Regressions

[16] The Mg/Ca of all the species analyzed in this study is positively correlated with bottom water temperature (Figure 5). Below are linear and exponential regressions fit to the individual measurements for each species. The errors are the standard errors ( $1\sigma$ ) of the regression coefficients, and  $n$  is the number of Mg/Ca measurements included in the regressions.

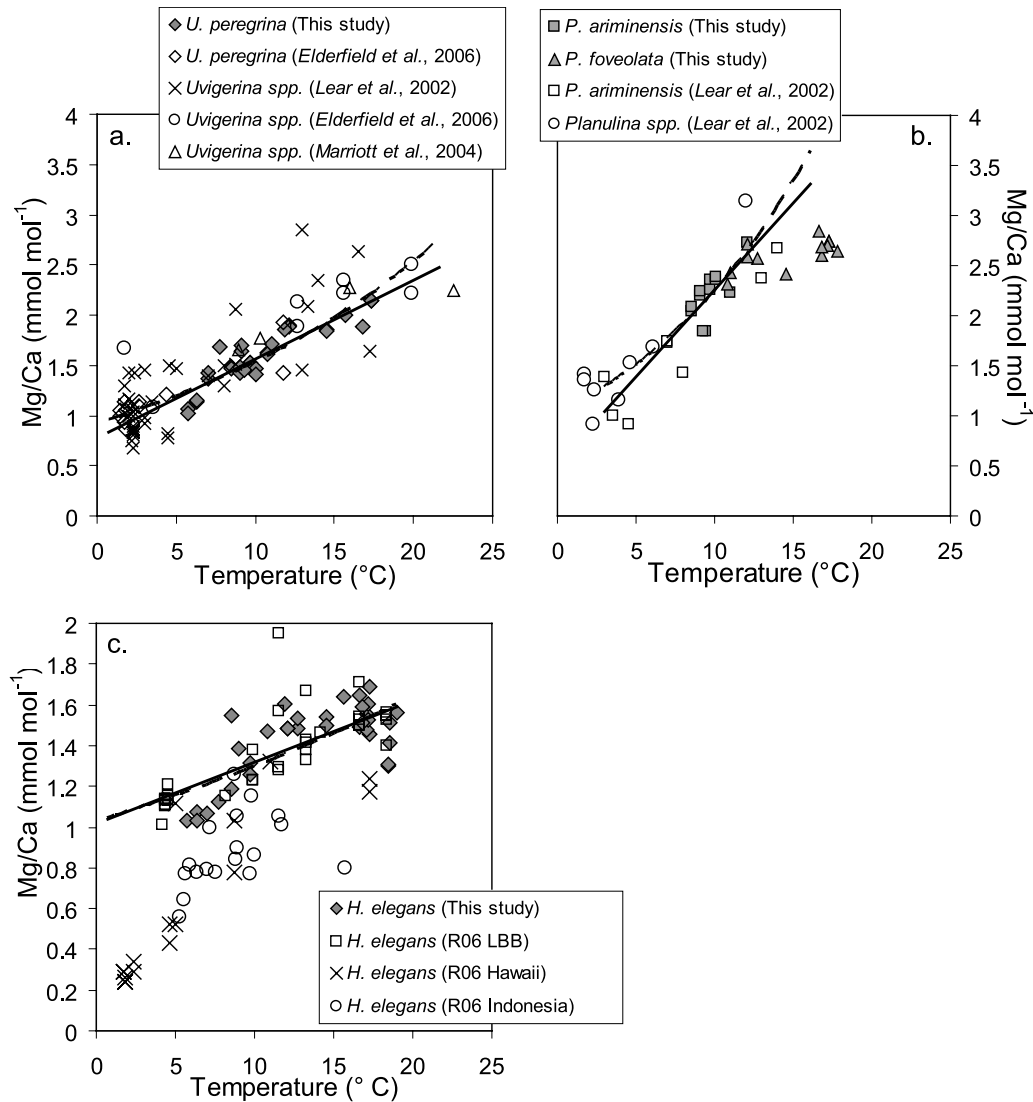
*U. peregrina*

$$\text{Mg/Ca} = 0.079 \pm 0.007 T + 0.77 \pm 0.08$$

$$(R^2 = 0.82, p < 0.0001, n = 30) \quad (1)$$

$$\text{Mg/Ca} = 0.98 \pm 0.05 e^{0.045 \pm 0.004 T}$$

$$(R^2 = 0.79, p < 0.0001, n = 30) \quad (2)$$



**Figure 6.** Comparison of the Florida Straits individual measurements with published data. Regressions shown are (a) *U. peregrina* equations (1) (solid curve) and (2) (dashed curve); (b) *P. ariminensis* equations (3) (solid curve) and (4) (dashed curve); and (c) *H. elegans* equations (7) (solid curve) and (8) (dashed curve). The regressions shown were derived from the Florida Straits data only. The Rosenthal et al. [2006] (*R06*) *H. elegans* measurements have been subdivided by region (LBB stands for Little Bahama Bank) to illustrate the apparent influence of carbonate ion. Note the different Mg/Ca scale for *H. elegans* (Figure 6c).

*P. ariminensis*

$$\text{Mg/Ca} = 0.174 \pm 0.040 T + 0.52 \pm 0.39$$

$$(R^2 = 0.63, p = 0.0012, n = 13) \quad (3)$$

$$\text{Mg/Ca} = 1.0 \pm 0.2 e^{0.080 \pm 0.019 T}$$

$$(R^2 = 0.63, p = 0.0016, n = 13) \quad (4)$$

$$\text{Mg/Ca} = 2.1 \pm 0.2 e^{0.014 \pm 0.005 T}$$

$$(R^2 = 0.44, p = 0.013, n = 13) \quad (6)$$

*H. elegans*

$$\text{Mg/Ca} = 0.030 \pm 0.006 T + 1.01 \pm 0.08$$

$$(R^2 = 0.49, p < 0.0001, n = 34) \quad (7)$$

*P. foveolata*

$$\text{Mg/Ca} = 0.037 \pm 0.013 T + 2.06 \pm 0.19$$

$$(R^2 = 0.44, p = 0.0014, n = 13) \quad (5)$$

$$\text{Mg/Ca} = 1.07 \pm 0.07 e^{0.021 \pm 0.004 T}$$

$$(R^2 = 0.46, p < 0.0001, n = 34) \quad (8)$$

[17] Exponential fits have traditionally been used to describe the Mg/Ca–temperature relationship because of, in part, the expected thermodynamic influence on Mg incorporation [Rosenthal *et al.*, 1997; Lea *et al.*, 1999]. As the strong biological control exerted on the biomineralization process by foraminifera has become increasingly evident [e.g., Bentov and Erez, 2006], it is not clear that the Mg/Ca response to temperature should be dominated by thermodynamics. Exponential fits to the data presented here are not significantly better or worse than the linear ones. However, there is no hint at an exponential increase of Mg/Ca with temperature, and these data suggest that the sensitivity of Mg/Ca to temperature may actually decrease at higher temperatures rather than increase, as observed for *C. pachyderma* by Marchitto *et al.* [2007]. This behavior is especially apparent in *H. elegans*. While it is unlikely that the combined influences of temperature-dependent physiological processes and thermodynamics on test Mg/Ca are truly linear, the linear fits are more useful approximations than the exponential ones given the data presented here. However, as will be discussed in section 4.3, these data likely do not solely represent a temperature signal, but may be affected by high carbonate ion concentrations.

#### 4.2. Comparison to Published Data

[18] Our *U. peregrina* data agree well with the *U. peregrina* measurements from core tops near Somalia presented by Elderfield *et al.* [2006] (Figure 6a). The addition of the Elderfield *et al.* [2006] *U. peregrina* data to our linear regression extends the calibration down to 1.5°C and does not significantly change the regression:

$$\text{Mg/Ca} = 0.071 \pm 0.005 T + 0.86 \pm 0.04$$

$$(R^2 = 0.86, p < 0.0001, n = 41) \quad (9)$$

[19] It is important to note that the *U. peregrina* samples of Elderfield *et al.* [2006] were not cleaned using a reductive step. Elderfield *et al.* [2006] found that Mg/Ca measured in foraminifera cleaned using a reductive step (the “Cd cleaning method”) is slightly lower (by  $\sim 0.2 \text{ mmol mol}^{-1}$ ) than in those cleaned without the reduction step (the “Mg cleaning method”). Other studies have also found slight offsets between the cleaning methods [Martin and Lea, 2002; Barker *et al.*, 2003; Yu *et al.*, 2007]. If a  $-0.2 \text{ mmol mol}^{-1}$  adjustment is applied to the Elderfield *et al.* [2006] *U. peregrina* measurements, the combined equation is altered slightly but is still not significantly different than equation (1):

$$\text{Mg/Ca} = 0.084 \pm 0.005 T + 0.70 \pm 0.05$$

$$(R^2 = 0.89, p < 0.0001, n = 41) \quad (10)$$

[20] The data also overlap with the *Uvigerina* spp. data of Lear *et al.* [2002], Marriott *et al.* [2004], and Elderfield *et al.* [2006] (Figure 6a), indicating that there may not be significant interspecific differences within the genus *Uvigerina*, such as those that have been observed between *Cibicides* species [Elderfield *et al.*, 2006]. However, a more thorough examination of other *Uvigerina*

species is suggested before this calibration is applied to species other than *U. peregrina*.

[21] There is little direct temperature overlap between the *P. ariminensis* data of this study and those of Lear *et al.* [2002] (Figure 6b). However, the *P. ariminensis* Mg/Ca measurements of Lear *et al.* [2002] do not deviate markedly from our linear regression. If the Lear *et al.* [2002] *P. ariminensis* data are added to our regression, the calibration is extended down to 3°C; the combined *P. ariminensis* linear regression has a higher  $R^2$  value than equation (3), although the standard error of the regression is slightly higher than that of equation (3) (1.47°C versus 0.98°C).

$$\text{Mg/Ca} = 0.158 \pm 0.019 T + 0.60 \pm 0.17$$

$$(R^2 = 0.80, p < 0.0001, n = 20) \quad (11)$$

[22] To our best knowledge there are no other published core top Mg/Ca measurements of *P. foveolata*. The regression presented here has a much lower slope than that of the other calcitic species; however, *P. foveolata* was only found in the warmest Florida Straits multicore sites. *C. pachyderma* [Marchitto *et al.*, 2007], *U. peregrina*, and *H. elegans* also show a decrease in slope at the warm end of the calibration. *P. foveolata* and *P. ariminensis* only overlap in sufficient quantities in two multicore sites, so direct comparison is difficult. Interestingly though, if the two *Planulina* species are combined, the linear regression is indistinguishable from the *C. pachyderma* calibration of Marchitto *et al.* [2007]:

$$\text{Mg/Ca} = 0.112 \pm 0.009 T + 1.0 \pm 0.1$$

$$(R^2 = 0.67, p < 0.0001, n = 26) \quad (12)$$

[23] The new *H. elegans* data agree well with Rosenthal *et al.* [2006] data from the Little Bahama Bank, but their samples from Hawaii and Indonesia have lower Mg/Ca values for the same temperatures (Figure 6c). Rosenthal *et al.* [2006] explain the low Mg/Ca at the Hawaii and Indonesia sites through reduced Mg uptake due to low  $\Delta\text{CO}_3^{2-}$ . The Florida Straits and Little Bahama Bank have similar carbonate chemistry, with much higher saturation than at the Hawaii and Indonesia sites. While Florida Straits *H. elegans* Mg/Ca does seem to be influenced by temperature, the linear temperature regression (equation (7)) can only explain about half of the variance in our Mg/Ca data, and the standard error of the regression is very high (equivalent to 4.5°C). This suggests that *H. elegans* Mg/Ca is a less reliable recorder of seawater temperature than other species [Rosenthal *et al.*, 2006], perhaps because of its aragonitic mineralogy and/or the possibility that the carbonate ion influence is not limited to low saturation states.

#### 4.3. Influence of Carbonate Saturation State

[24] It has been proposed that Mg/Ca may be suppressed during calcification because of low  $\Delta\text{CO}_3^{2-}$  [Martin *et al.*, 2002; Elderfield *et al.*, 2006; Rosenthal *et al.*, 2006]. Martin *et al.* [2002] noted that abyssal *C. wuellerstorfi* had a steeper Mg/Ca–temperature slope than that of *C. pachyderma* found

at warmer temperatures; the steeper slope was attributed to decreased saturation at the colder sites. After removing the apparent temperature effect on Mg/Ca (by assuming that *Cibicides* Mg/Ca is not significantly affected by  $\Delta\text{CO}_3^{2-}$  at temperatures greater than  $\sim 2^\circ\text{C}$ – $3^\circ\text{C}$ ), *Elderfield et al.* [2006] determined that *C. wuellerstorfi* Mg/Ca decreases by  $\sim 0.0086$  mmol mol<sup>-1</sup> per  $\mu\text{mol kg}^{-1}$  decrease in  $\Delta\text{CO}_3^{2-}$  over a  $\Delta\text{CO}_3^{2-}$  range of  $-20$  to  $80$   $\mu\text{mol kg}^{-1}$ . *Elderfield et al.* [2006] noted that the Mg/Ca data from temperatures higher than  $2^\circ\text{C}$  likely contain some  $\Delta\text{CO}_3^{2-}$  influence. *Rosenthal et al.* [2006] similarly determined that Mg/Ca of the aragonitic foraminifer *H. elegans* decreases by  $\sim 0.017$  mmol mol<sup>-1</sup> per  $\mu\text{mol kg}^{-1}$  decrease in  $\Delta\text{CO}_3^{2-}$  below  $15$   $\mu\text{mol kg}^{-1}$  with respect to aragonite.

[25]  $\Delta\text{CO}_3^{2-}$  at the Florida Straits multicore sites range from  $46$  to  $161$   $\mu\text{mol kg}^{-1}$  with respect to calcite and  $22$  to  $138$   $\mu\text{mol kg}^{-1}$  with respect to aragonite. Some of the Florida Straits sites are within the range where *Elderfield et al.* [2006] reported a  $\Delta\text{CO}_3^{2-}$  influence on *C. wuellerstorfi* ( $<80$   $\mu\text{mol kg}^{-1}$ ), although all of the sites are warmer than the  $\sim 2^\circ\text{C}$ – $3^\circ\text{C}$  threshold above which *Elderfield et al.* [2006] suspected that the temperature signal should dominate. *Rosenthal et al.* [2006] concluded that  $\Delta\text{CO}_3^{2-}$  does not significantly affect *H. elegans* above  $\sim 15$   $\mu\text{mol kg}^{-1}$ , lower than the lowest saturation state observed at the Florida Straits multicore sites. However, we do observe a change in slope of the Mg/Ca–temperature relationships in multiple taxa over the range of the calibration, suggesting that some factor other than temperature influences Mg/Ca in the Florida Straits samples. The Mg/Ca–temperature slope is steeper at low temperatures and less steep at higher temperatures; for example, the slope for *U. peregrina*  $<11^\circ\text{C}$  is  $0.096$  and  $>11^\circ\text{C}$  it is  $0.044$ . The slope for *H. elegans*  $<11^\circ\text{C}$  is  $0.089$ , while the slope  $>11^\circ\text{C}$  is not significantly different from zero ( $-0.0078 \pm 0.0087$ ). As was noted above, *P. ariminensis* found at colder multicore sites has a steeper slope ( $0.174$ ) than *P. foveolata* ( $0.037$ ), which was predominantly found at the warmer sites. A similar decrease in slope of the *C. pachyderma* calibration from the Florida Straits was previously noted by *Marchitto et al.* [2007].

[26] Perhaps the  $\Delta\text{CO}_3^{2-}$  effect has a more significant influence above  $2^\circ\text{C}$  than originally thought [*Elderfield et al.*, 2006], decreasing the Mg/Ca of the Florida Straits samples at the lower end of the calibration. This would imply, however, that the temperature influence on Mg/Ca is quite small, being characterized by the slopes at the warm and supersaturated end of the calibration. Alternatively, it is possible that Mg/Ca is reduced at the higher end of the calibration because of very supersaturated conditions. Culturing studies of planktonic [*Lea et al.*, 1999; *Russell et al.*, 2004] and benthic [*Hintz et al.*, 2006c] foraminifera have shown decreases in Mg/Ca with increasing pH, carbonate ion concentration, and/or alkalinity.

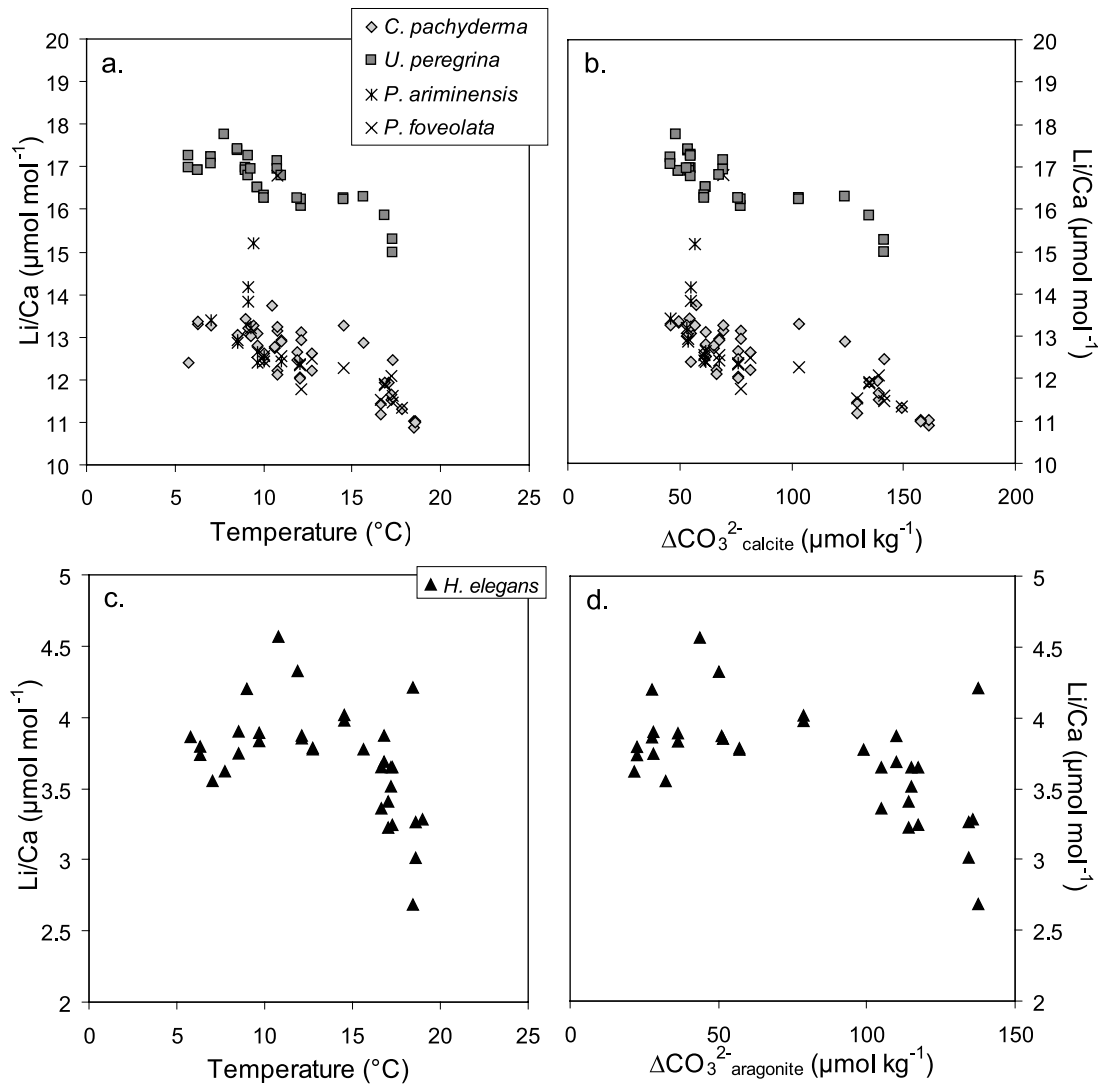
[27] It is very difficult to separate the effects of  $\Delta\text{CO}_3^{2-}$  and temperature in this data set because of their strong correlation in the Florida Straits ( $R^2 = 0.96$ ), but core top measurements from the western Mediterranean are consistent with a decrease in Mg/Ca because of high  $\Delta\text{CO}_3^{2-}$ . *Cacho et al.* [2006] report an average core top

*C. pachyderma* Mg/Ca of  $1.96$  mmol mol<sup>-1</sup> at eight sites with modern bottom water temperatures of  $12.7^\circ\text{C}$  and  $\Delta\text{CO}_3^{2-}$  of  $149$   $\mu\text{mol kg}^{-1}$ . The Mediterranean Mg/Ca is  $\sim 0.7$  mmol mol<sup>-1</sup> lower than would be predicted by the calibration of *Marchitto et al.* [2007] at  $12.7^\circ\text{C}$ .  $\Delta\text{CO}_3^{2-}$  at the Mediterranean sites is  $\sim 70$   $\mu\text{mol kg}^{-1}$  higher than  $\Delta\text{CO}_3^{2-}$  at similar temperatures in the Florida Straits. If the Mg/Ca value for  $12.7^\circ\text{C}$  should be  $\sim 2.7$  mmol mol<sup>-1</sup> (as determined from equation (4) of *Marchitto et al.* [2007]) and the difference is solely due to  $\Delta\text{CO}_3^{2-}$ , then the sensitivity of Mg/Ca to  $\Delta\text{CO}_3^{2-}$  would be roughly  $-0.01$  mmol mol<sup>-1</sup> per  $1$   $\mu\text{mol kg}^{-1}$ . This is similar to the sensitivity determined by *Elderfield et al.* [2006], except in the opposite direction. If the slope of the *Marchitto et al.* [2007] temperature calibration is too low because of reduced Mg/Ca at the warm (high  $\Delta\text{CO}_3^{2-}$ ) Florida Straits multicore sites, then the sensitivity of Mg/Ca to high  $\Delta\text{CO}_3^{2-}$  would be even greater.

#### 4.4. A Working Hypothesis Concerning Mg/Li

[28] One possible mechanism for the suppression of Mg/Ca at high carbonate ion saturation is related to alteration of the internal calcification pool by physiological processes that are sensitive to changes in saturation state. *Elderfield et al.* [1996] described a Rayleigh distillation model whereby foraminiferal trace element concentrations were determined by the fraction of Ca remaining (*f*) in the biomineralization reservoir. *Elderfield et al.* [1996] proposed that *f* would primarily be controlled by the size and flushing rate of the internal reservoir, and that the flushing rate may be influenced by calcification rate and therefore by  $\Delta\text{CO}_3^{2-}$ . This model is similar to the idea of “precipitation efficiency” used by *Gaetani and Cohen* [2006] to explain seasonal variations in Mg/Ca, Sr/Ca and Ba/Ca in coralline aragonite. The idea behind each model is that trace elements are fractionated during calcification because thermodynamically they are either preferentially incorporated into (distribution coefficient  $D > 1$ ) or excluded from ( $D < 1$ ) the calcium carbonate. As calcification progresses the composition of the calcification solution will evolve: the calcification solution will become enriched in trace elements that are preferentially excluded from the calcium carbonate and depleted in trace elements that are preferentially incorporated. As the composition of the calcification solution evolves, so will the composition of the calcium carbonate that is precipitated. Therefore, the final concentration of a trace element in the calcium carbonate will be at least partially controlled by the fraction of the calcification solution that is used (the precipitation efficiency). If higher carbonate saturation states cause increased flushing of the calcification reservoir or decreased precipitation efficiency, then Mg incorporation would theoretically be suppressed since Mg is preferentially excluded from calcite ( $D \ll 1$ ) [*Rimstidt et al.*, 1998].

[29] The situation with Mg is likely more complicated because of its active removal from the internal reservoir [*Bentov and Erez*, 2006]. It is therefore possible that test Mg/Ca reflects the combined influences of precipitation efficiency and Mg pumping. Regardless of the exact mechanisms that affect the composition of the internal



**Figure 7.** Individual Li/Ca measurements plotted against (a and c) temperature and (b and d)  $\Delta\text{CO}_3^{2-}$ . Figure 7b shows  $\Delta\text{CO}_3^{2-}$  with respect to calcite, and Figure 7d shows  $\Delta\text{CO}_3^{2-}$  with respect to aragonite. Note the large difference in Li/Ca values between the calcitic species (Figures 7a and 7b) and the aragonitic *H. elegans* (Figures 7c and 7d).

calcification pool, other trace elements may hypothetically become depleted in tandem with Mg. If this is true, perhaps we can correct for the Mg/Ca suppression at high  $\Delta\text{CO}_3^{2-}$  by using another element that is also preferentially excluded from calcite. We propose that lithium may fill this role.

[30] Li occurs in seawater as a monovalent cation with a conservative distribution and a long residence time ( $\sim 1.5$  Ma) [Huh *et al.*, 1998]. Its distribution coefficient into inorganically precipitated calcite and aragonite is  $\ll 1$ , comparable to that for Mg [Marriott *et al.*, 2004]. Benthic foraminiferal Li/Ca in the Florida Straits multicores

increases with increasing depth, and Great Bahama Bank sites have lower Li/Ca than Dry Tortugas sites at similar depths (Table 3). Li/Ca for all species is negatively correlated with temperature (Figures 7a and 7c) and  $\Delta\text{CO}_3^{2-}$  (Figures 7b and 7d). Li/Ca therefore decreases at the high- $\Delta\text{CO}_3^{2-}$  sites where we infer a suppression of Mg/Ca. This is especially apparent for *H. elegans*, where Li/Ca plunges and Mg/Ca flattens above  $\sim 100 \mu\text{mol kg}^{-1}$ . The anticorrelation of Li/Ca with both temperature and  $\Delta\text{CO}_3^{2-}$  is consistent with observations of core top benthic foraminifera from Little Bahama Bank [Hall and Chan, 2004] and the Arabian Sea [Marriott *et al.*, 2004]. Lear and

**Figure 8.** Individual Mg/Ca and Mg/Li measurements versus temperature for (a and b) *C. pachyderma*, (c and d) *U. peregrina*, (e and f) *Planulina* spp., and (g and h) *H. elegans*. Regressions shown are linear calibrations calculated using only the Florida Straits measurements: equation (3) of Marchitto *et al.* [2007] and our equations (13), (1), (14), (12), (17), (7), and (18) for Figures 8a, 8b, 8c, 8d, 8f, 8g, and 8h, respectively.

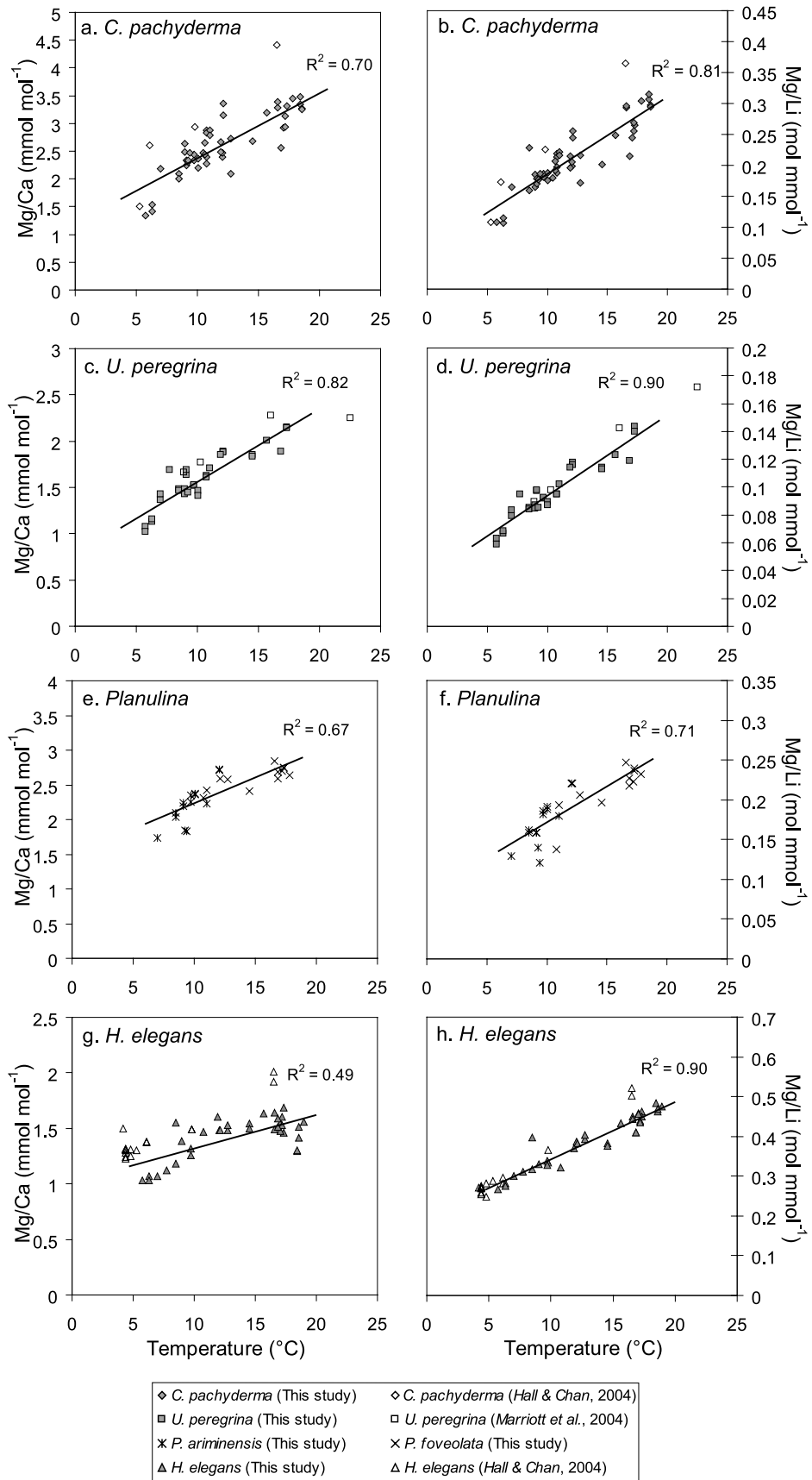


Figure 8

**Table 4.** Comparison of Mg/Ca–Temperature and Mg/Li–Temperature Linear Regressions

Species	Mg/Ca		Mg/Li	
	R <sup>2</sup>	SE <sup>a</sup> (°C)	R <sup>2</sup>	SE <sup>a</sup> (°C)
<i>C. pachyderma</i> <sup>b</sup>	0.73	2.4	0.81	1.8
<i>U. peregrina</i>	0.82	1.6	0.90	1.1
<i>P. ariminensis</i>	0.63	1.0	0.59	1.1
<i>P. foveolata</i>	0.44	3.2	0.52	2.7
Combined <i>Planulina</i>	0.67	2.5	0.71	2.2
<i>H. elegans</i>	0.49	4.5	0.90	1.4

<sup>a</sup>SE is the temperature equivalent of the standard error of the estimate.

<sup>b</sup>*C. pachyderma* Mg/Ca statistics are from Marchitto *et al.* [2007].

Rosenthal [2006] reported a positive correlation between Li/Ca and  $\Delta\text{CO}_3^{2-}$  at low saturation states ( $<50 \mu\text{mol kg}^{-1}$ ) from a holothermal depth profile. It is therefore possible that Li/Ca increases with  $\Delta\text{CO}_3^{2-}$  and decreases with temperature and that the Florida Straits data are dominated by the temperature influence.

[31] However, if Li/Ca is not mechanistically related to  $\Delta\text{CO}_3^{2-}$  but rather indirectly related through changes in the internal calcification pool, it may be possible for Li/Ca (and Mg/Ca) to have differing responses at low- and high-saturation states. In that case Li/Ca may be useful in correcting Mg/Ca suppression at both low and high

**Table 5.** Last Glacial Maximum Samples From KNR166-2 Cores

Core <sup>a</sup>	Depth in Core <sup>b</sup> (cm)	Latitude (°N)	Longitude (°W)	Water Depth <sup>c</sup> (m)
2JPC (1)	749.5	24.38	83.34	446
29JPC (1)	195.5	24.28	83.27	648
59JPC (1)	553.5	24.42	83.37	358
73GGC (2)	233.5	23.75	79.43	542
83GGC (2)	208.5	24.37	79.45	638

<sup>a</sup>Numbers in parentheses indicate 1, Dry Tortugas sites; and 2, Cay Sal Bank sites.

<sup>b</sup>Depth in core is the midpoint of a 1 cm sample.

<sup>c</sup>Water depth indicates the modern water depth at the core site.

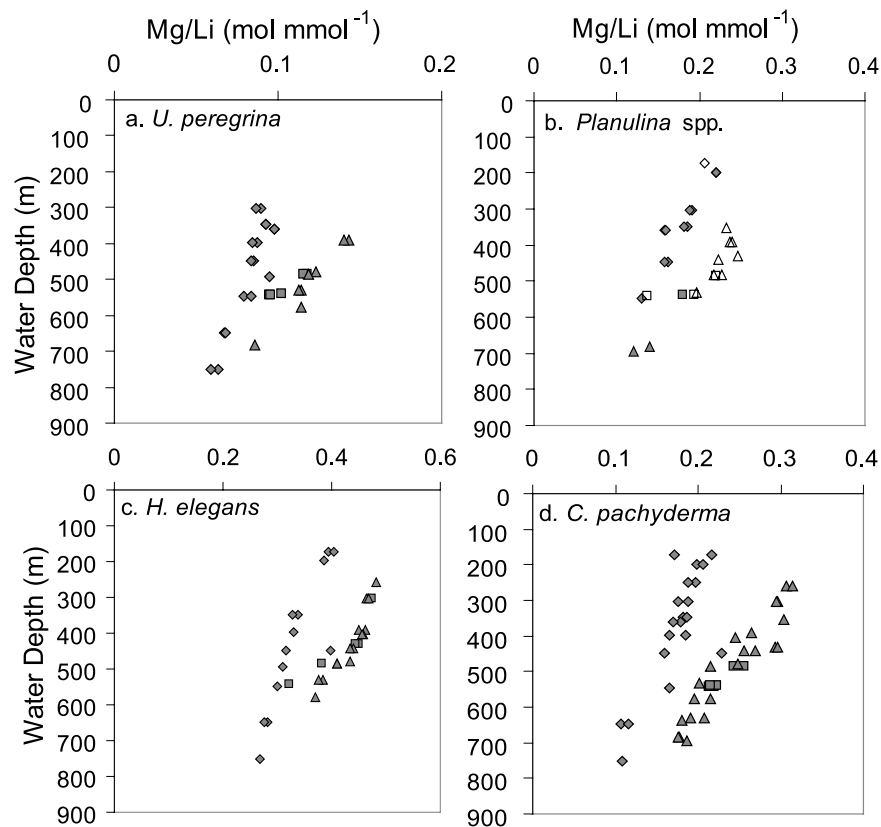
saturation, or indeed under other environmental or physiological conditions that may affect the composition of the calcification pool.

[32] Simply dividing Mg/Ca by Li/Ca removes much of the apparent flattening of the temperature regressions at high temperature (Figure 8). Linear regressions for each species, now including *C. pachyderma*, are as follows:

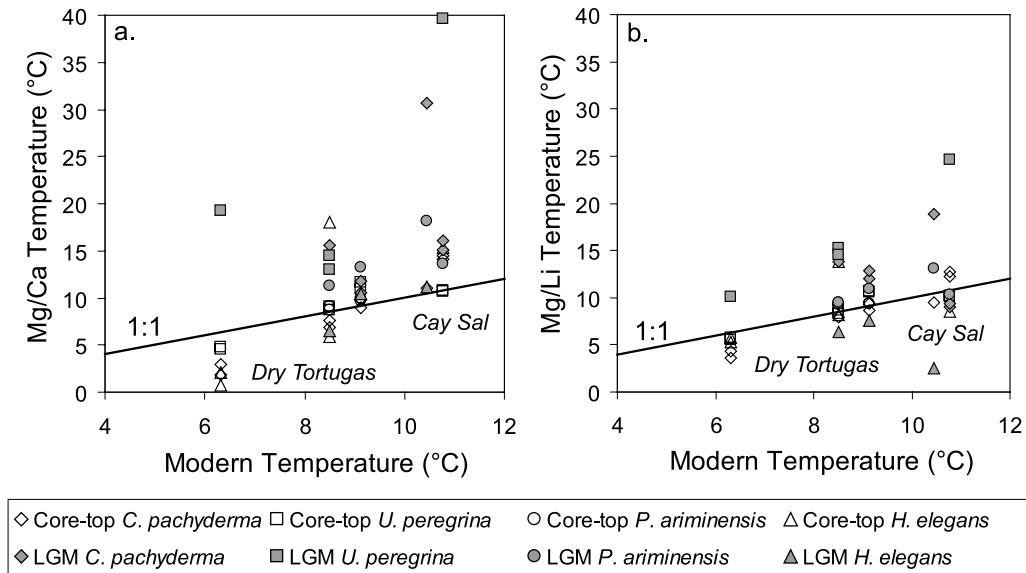
#### *C. pachyderma*

$$\text{Mg/Li} = 0.0124 \pm 0.0009 T + 0.062 \pm 0.01$$

$$(R^2 = 0.81, p < 0.0001, n = 48) \quad (13)$$



**Figure 9.** Individual Mg/Li measurements plotted versus water depth: (a) *U. peregrina*, (b) *Planulina* spp. (*P. ariminensis* measurements are indicated by gray symbols and *P. foveolata* measurements are open symbols), (c) *H. elegans*, and (d) *C. pachyderma* measurements from Marchitto *et al.* [2007]. Measurements from Dry Tortugas sites are indicated by diamonds; Cay Sal Bank sites are squares, and Great Bahama Bank sites are triangles. Note the differing Mg/Li scales. The shape of the thermocline is reproduced with greater fidelity by Mg/Li than by Mg/Ca (Figure 4), especially for *H. elegans*.



**Figure 10.** (a) Core top (open) and LGM (gray) temperatures calculated from Mg/Ca using the species-specific linear calibrations derived in this study (or from *Marchitto et al.* [2007] for *C. pachyderma*) plotted against the modern temperatures at the core sites. The two warmest cores are near Cay Sal Bank; the rest are near Dry Tortugas. Extremely high LGM temperatures are likely a result of contamination from high-Mg calcite overgrowths. (b) As in (Figure 10a) except temperatures are calculated from Mg/Li using the linear calibrations derived in this study. There is slight LGM improvement using Mg/Li, but some Mg contamination is still evident.

#### *U. peregrina*

$$\text{Mg/Li} = 0.0061 \pm 0.0004 T + 0.033 \pm 0.004$$

$$(R^2 = 0.90, p < 0.0001, n = 30) \quad (14)$$

#### *P. ariminensis*

$$\text{Mg/Li} = 0.017 \pm 0.004 T + 0.00 \pm 0.04$$

$$(R^2 = 0.59, p < 0.002, n = 13) \quad (15)$$

#### *P. foveolata*

$$\text{Mg/Li} = 0.008 \pm 0.002 T + 0.10 \pm 0.03$$

$$(R^2 = 0.52, p = 0.005, n = 13) \quad (16)$$

#### Combined

#### *Planulina*

$$\text{Mg/Li} = 0.009 \pm 0.001 T + 0.08 \pm 0.01$$

$$(R^2 = 0.71, p < 0.0001, n = 26) \quad (17)$$

#### *H. elegans*

$$\text{Mg/Li} = 0.0143 \pm 0.0009 T + 0.20 \pm 0.01$$

$$(R^2 = 0.90, p < 0.0001, n = 33) \quad (18)$$

[33] For all species except *P. ariminensis* the Mg/Li–temperature linear regression has a higher  $R^2$  value and

lower standard error than the Mg/Ca–temperature linear regression (Table 4). The *P. ariminensis* statistics are about the same; since *P. ariminensis* was not found at the multi-core sites with the highest  $\Delta\text{CO}_3^{2-}$ , its regression is not expected to be significantly affected. The improvement is especially remarkable for *H. elegans*: the  $R^2$  of the Mg/Ca–temperature calibration is 0.49, while the  $R^2$  of the Mg/Li–temperature calibration is 0.90. The *U. peregrina* Mg/Li regression is equally strong with an  $R^2$  of 0.90. Published *H. elegans* data from Little Bahama Bank [Hall and Chan, 2004] and *U. peregrina* from the Arabian Sea [Marriott et al., 2004] also fall closer to our Florida Straits Mg/Li regressions than to our Mg/Ca regressions (Figure 8). Depth profiles of Florida Straits Mg/Li (Figure 9) reproduce the shape of the thermocline with greater fidelity than Mg/Ca.

[34] While the mechanisms behind Mg/Ca suppression and the connection to Li remain speculative at this point, the strong correlations between Mg/Li and temperature (especially for *H. elegans* and *U. peregrina*) and the agreement with limited data from other regions [Hall and Chan, 2004; Marriott et al., 2004] (Figure 8) are encouraging. An alternative explanation for the improved correlations is that simply combining a proxy that is positively correlated with temperature with a proxy that is negatively correlated with temperature may increase the sensitivity to temperature and improve the regression fits. Our preliminary examination of this possibility using simulated data suggests that there would indeed be a slight improvement ( $R^2$  increases on the order of 0.03), but smaller than what we observe, especially for *H. elegans*. Ultimately the value of Mg/Li as temperature proxy will be determined by

examination of the response to temperature in regions with differing temperature– $\Delta\text{CO}_3^{2-}$  relationships.

#### 4.5. A Test on the Last Glacial Maximum

[35] To test the Mg/Ca and Mg/Li temperature calibrations presented here, Mg/Ca and Li/Ca were measured on several samples of Last Glacial Maximum (LGM) age from the Florida Straits (Tables 3 and 5). The LGM was identified by planktonic  $\delta^{18}\text{O}$  maxima and bracketing  $^{14}\text{C}$  ages (J. Lynch-Stieglitz, personal communication, 2008). Thermocline temperatures in the Bahama Banks region are expected to be  $\sim 2^\circ\text{C}$ – $4^\circ\text{C}$  colder during the LGM [Slowey and Curry, 1992]. However, a given core site is expected to record a smaller cooling because of the downward shift of the thermocline in response to lower sea level. LGM slowdown of the Florida Current would have flattened isopycnals [Lynch-Stieglitz *et al.*, 1999] and reduced cooling or possibly even warmed the Dry Tortugas sites slightly.

[36] Core top and LGM temperatures calculated from Mg/Ca and Mg/Li are compared to modern temperatures in Figure 10. Temperatures calculated from core top Mg/Ca and Mg/Li generally reflect modern temperatures, although the Mg/Ca temperatures show greater bias. LGM temperatures from both Mg/Ca and Mg/Li are highly scattered, and different species from the same core vary widely. As with the core top data, there is greater scatter in the Mg/Ca temperatures than the Mg/Li temperatures. When Mg/Ca values are high, Li/Ca values also tend to be high, lowering the reconstructed Mg/Li temperatures somewhat. However, many of the Mg/Li paleotemperatures remain unrealistically high. It is possible that some of the samples are contaminated by high-Mg diagenetic carbonate. High-Mg calcite hardgrounds and cements have previously been observed in Bahama Bank sediments [e.g., Neumann *et al.*, 1977; Mullins *et al.*, 1985] and are more prevalent in glacial sections [Malone *et al.*, 2001]. Mg/Ca measured in a hardground from the deglacial section of a Little

Bahama Bank core is  $\sim 150$  mmol/mol [Marchitto *et al.*, 2007]. Li/Ca measured in the same hardground ( $\sim 25$ – $30$   $\mu\text{mol mol}^{-1}$ ) is only slightly elevated relative to benthic foraminifera, so the Mg/Li ratio cannot correct for contamination. While interpretations are limited because of the possible presence of diagenetic overgrowths, LGM temperatures derived from Mg/Li from some of the samples are reasonable, and the scatter is reduced relative to Mg/Ca temperatures. However, before Mg/Li can be applied as a temperature proxy, further testing is needed on core top and down-core samples from other regions where diagenetic overgrowths are not an issue.

#### 5. Conclusions

[37] New Mg/Ca–temperature calibrations are presented for four species of benthic foraminifera. The sensitivity of Mg/Ca to temperature decreases at higher temperatures, contrary to the expected increase in sensitivity in an exponential relationship. The decrease in sensitivity may be related to Mg/Ca suppression at high  $\Delta\text{CO}_3^{2-}$  or other undetermined factors. The correlation to temperature is improved by dividing Mg/Ca by Li/Ca in core top samples. LGM temperatures reconstructed from Mg/Li are less scattered than temperatures from Mg/Ca, although some samples appear to be compromised by diagenetic overgrowths. The potential of Mg/Li as a temperature proxy should be tested further with core top and down-core samples from other regions.

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