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Mg/Ca temperature calibration for the benthic foraminifer *Cibicidoides pachyderma*

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[1] The recent development of foraminiferal Mg/Ca as a paleotemperature proxy has enabled the extraction of global ice volume and local salinity from the more traditional paleotemperature proxy δ^{18}O. The benthic foraminiferal genus *Cibicidoides* is widely used in paleoceanographic reconstructions because of its epifaunal habitat and cosmopolitan distribution, and it has received early attention in Mg/Ca work. However, existing temperature calibrations for *Cibicidoides* rely heavily on *C. pachyderma* core top data from one location, Little Bahamas Bank, where authigenic processes and/or reworking may result in elevated warm water Mg/Ca values. Here we present new *C. pachyderma* Mg/Ca data from a series of 29 high-quality multicore tops collected in the Florida Straits, spanning a temperature range of 5.8–18.6°C. In contrast to previous calibrations, we find no evidence for a strongly exponential response to temperature. The data are best explained by a linear relationship, with a sensitivity of 0.12 mmol mol^{-1} per °C.

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1. Introduction

[2] Over the past several years, foraminiferal Mg/Ca has emerged as a valuable and widely applied paleotemperature proxy. It has also been used to separate the temperature and seawater δ^{18}O components of foraminiferal δ^{18}O records, allowing for improved reconstructions of global ice volume and local salinity. Most paleoceanographic work thus far has focused on planktonic foraminifera [e.g., *Lea et al.*, 2000; *Koutavas et al.*, 2002; *Rosenthal et al.*, 2003; *Barker et al.*, 2005]. Numerous planktonic Mg/Ca calibrations have been performed using core top, sediment trap, and cultured foraminifera, and it is well established that Mg/Ca increases exponentially at ~9–10% per degree Celsius in most species [*Nurnberg et al.*, 1996; *Lea et al.*, 1999; *Elderfield and Ganssen*, 2000; *Anand et al.*, 2003].

[3] Benthic foraminiferal Mg/Ca applications have been more limited, but some important paleoclimate problems have been investigated, including glacial-interglacial deep sea temperature change [*Martin et al.*, 2002] and the Cenozoic evolution of global ice volume [*Lear et al.*, 2000]. In contrast to planktonic foraminifera, the behavior of Mg/Ca in benthic foraminifera remains rather poorly constrained. Early work with *Cassidulina* [*Izuka*, 1988] and *Cibicides* (cf. *Cibicidoides*) [*Rathburn and De Deckker*, 1997] suggested promising relationships between Mg/Ca and temperature. *Rosenthal et al.* [1997] calibrated *Cibicidoides pachyderma* (cf. *C. floridanus*) versus temperature and proposed an exponential relationship. Exponential equations have since been reported for several different genera and species [*Lear et al.*, 2002; *Rathmann et al.*, 2004]. In contrast, *Toyofuku et al.* [2000] found strong linear relationships in two species of cultured high-Mg shallow water benthic foraminifera, though these data can alternately be fit with weak exponentials [*Lea*, 2004].

[4] The current state of the art for *Cibicidoides* Mg/Ca calibration relies heavily on *C. pachyderma* from nine Little Bahamas Bank core tops studied by *Rosenthal et al.* [1997]. *Lear et al.* [2002] reanalyzed these samples and reported values ~30% lower than *Rosenthal et al.* [1997]. *Lear et al.* [2002] then applied a multiplier offset to the earlier data and to cold water (<5°C) *C. wuellerstorfi* data from the same study. Combining these data sets with additional new measurements on *C. pachyderma*, *C. wuellerstorfi*, *C. compressus*, and *Cibicidoides* sp., yielded the exponential equation [*Lear et al.*, 2002]:

$$\mathrm{Mg/Ca} = 0.867e^{0.109T}. \tag{1}$$

Martin et al. [2002] combined the *Rosenthal et al.* [1997] *C. pachyderma* and *C. wuellerstorfi* data with additional *C. wuellerstorfi* measurements by *Russell et al.* [1994] to yield an exponential equation with the same temperature sensitivity as *Lear et al.* [2002]. *Martin et al.* [2002] then adjusted the preexponential constant of this equation to reflect the apparent analytical bias in both of the earlier studies, yielding

$$\mathrm{Mg/Ca} = 0.85e^{0.11T}. \tag{2}$$

The reliance on biased data is less than ideal, especially since the source of the bias is not obvious. *Rosenthal et al.* [1997] used neither oxidative nor reductive chemical cleaning, while *Russell et al.* [1994], *Lear et al.* [2002],

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and *Martin et al.* [2002] performed both. *Lear et al.* [2002] suggested that the bias is analytical, since the two earlier studies analyzed samples by AAS while the later studies used ICP-MS. Equations (1) and (2) also combine species of *Cibicidoides* that might behave differently. Benthic Mg/Ca differences have been documented at both the genus [*Rosenthal et al.*, 1997; *Lear et al.*, 2002] and species [*Rosenthal et al.*, 1997; *Elderfield et al.*, 2006] levels.

[5] *Lear et al.* [2002] noted that they found no statistical evidence to support an exponential fit to the *Cibicidoides* data. Only a single core, the warmest one in the equation (1) calibration, could be said to imply an exponential relationship, and this core is believed to be impacted by high-Mg calcite overgrowths and/or downslope transport [*Lear et al.*, 2002] (see their Figure 8b and our Figure 3b). In fact, we know of no calibration data from any benthic foraminiferal species that statistically support an exponential response to temperature. The incorporation of Mg into foraminiferal calcite is likely related to temperature through both thermodynamics (expected to be exponential) and physiological processes [*Rosenthal et al.*, 1997; *Bentov and Erez*, 2006]. Mg/Ca ratios in planktonic foraminifera and many benthic foraminifera are about an order of magnitude lower than expected from inorganic precipitation [*Mucci*, 1987], implying active exclusion of Mg during biomineralization [*Bentov and Erez*, 2006]. It is therefore possible that thermodynamics and biology could combine to produce benthic foraminiferal temperature relationships that are not strongly exponential.

[6] The main obstacle to clarifying the response of *Cibicidoides* Mg/Ca to temperature is the lack of data from warm waters. There are only three core tops >15°C included in equation (1) (two from Little Bahamas Bank and one from Hawaii) and only two in equation (2) (Little Bahamas Bank). Here we report 48 new *C. pachyderma* Mg/Ca measurements from 29 core tops collected in the Florida Straits, including nine sites from waters warmer than 15°C.

2. Study Area and Methods

[7] R/V *Knorr* cruise 166-2 operated in the Florida Straits in January 2002 with the goal of collecting rapidly accumulating sediments for paleoceanographic study. Sediments were collected from three main regions: on the western side of the Florida Current, near Dry Tortugas; on the eastern side of the current, near Great Bahamas Bank; and on the western side of the Santaren Current, near Cay Sal Bank (Figure 1). As part of this effort, a multicorer was deployed at each site to recover short cores (~30–40 cm long, 12 cm diameter) with undisturbed sediment-water interfaces. For this study, we used the 0–1 cm slice from 29 of the multicore sites (Table 1).

[8] AMS radiocarbon ages were measured on *Globigerinoides ruber* (>250 μm) from the 0–1 or 0–2 cm slices from 14 of the KNR166-2 multicores [*Lund and Curry*, 2004, 2006; *Lund*, 2005] (Table 1). Five core tops contained significant levels of "bomb" radiocarbon (fraction modern >1), 3 gave ages between 200 and 400 yr, and 6 ranged from ~1000–3000 yr. KNR166-2 gravity and piston cores exhibit sedimentation rates commonly between 10 and 50 cm kyr^{-1} near Dry Tortugas and up to several hundred cm kyr^{-1} on Great Bahamas Bank.

[9] *C. pachyderma* (cf. *C. floridanus* [*Poag*, 1981]) was picked from the >250 μm size fraction for Mg/Ca analysis. Each sample contained at least 4 to 7 individuals, and where abundance allowed, 8 to 14 individuals were crushed, homogenized, and split into replicate samples. Crushed samples were cleaned reductively (using anhydrous hydrazine) and oxidatively (using H_2O_2) in a Class-1000 clean lab following the methods of *Boyle and Keigwin* [1985] as modified by *Boyle and Rosenthal* [1996]. Multiple trace elements were measured by magnetic-sector single-collector ICP-MS, on a Thermo-Finnigan Element2, using methods adapted from *Rosenthal et al.* [1999] [*Marchitto*, 2006]. Long-term 1σ precision for Mg/Ca, based on analysis of four consistency standard solutions, is 0.54% across a wide range of Mg/Ca values and sample sizes.

[10] Water depths for the multicores used here span 173–751 m near Dry Tortugas and 259–694 m near Great Bahamas and Cay Sal Banks. Because of the sloping of isopycnals associated with Florida Current flow, the three regions have very different seawater properties at a given water depth (Figure 2). Seawater samples were collected using a Niskin bottle mounted directly on the multicorer frame, rigged to trip as the multicorer hit the seafloor. Aliquots of this water were analyzed for salinity so that each multicore site could be matched to the nearest of 55 CTD casts, providing precise bottom water temperatures. For 12 sites this method was not possible because either the bottle failed to trip (3 sites), the bottle tripped early (7 sites), or the salinity profile was too invariant to provide an unambiguous match to a CTD (2 sites). In these cases salinity and temperature were derived from nearby CTDs assuming a multicore-CTD depth offset characteristic for each region: +15 m near Dry Tortugas and −15 m near Great Bahamas Bank. These slight offsets presumably reflect increased sloping of isopycnals very close to the seafloor.

[11] Total alkalinity and ΣCO_2 were measured on Niskin waters from 18 of the multicore sites used here. Seawater aliquots were poisoned with $HgCl_2$ immediately after collection. Alkalinity and ΣCO_2 concentrations were determined on ~100 mL samples using an automated closed-vessel titration system, with equivalence points located using a nonlinear curve fitting approach [*Bradshaw et al.*, 1981; *Brewer et al.*, 1986; *Dickson and Goyet*, 1994]. Titrations were standardized using a Certified Reference Material obtained from A. Dickson at Scripps Institution of Oceanography. The KNR166-2 water samples were not replicated, but the standard deviation of two sets of replicate analyses of seawater consistency standards run with these samples was 2 μeq kg^{-1} for alkalinity and 3 μmol kg^{-1} for ΣCO_2 (n = 4 for each set of standards). ΔCO_3^{2-} with respect to calcite ($\Delta CO_3^{2-} = [CO_3^{2-}]_{measured} - [CO_3^{2-}]_{saturation}$) (Figure 2c) was calculated 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]. Measurements from six of the multicore sites were rejected owing to Niskin pretripping as

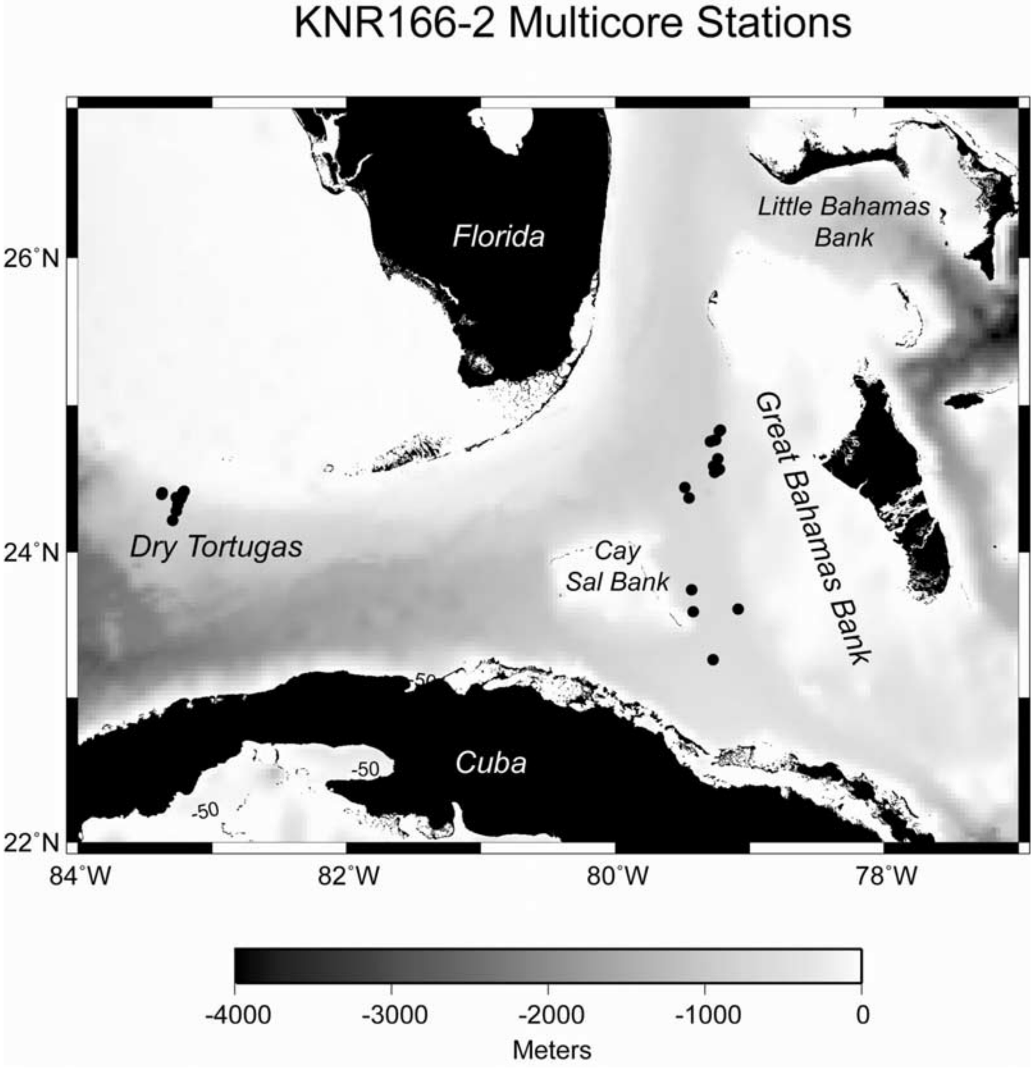

Figure 1. Map of the study area. Dots indicate locations of KNR166-2 multicores used here.

noted above for salinity. For these sites and for sites where waters were not collected, ΔCO_3^{2-} was inferred using our observed second-order polynomial relationship with salinity ($r^2 = 0.99$), which includes measurements from six additional KNR166-2 multicore sites not used for *C. pachyderma* analysis.

3. Results and Discussion

3.1. Mg/Ca Calibration to Temperature

[12] *C. pachyderma* Mg/Ca ranges from 1.34 to 3.44 mmol mol^{-1} in the KNR166-2 multicore tops (Figure 3a). Average reproducibility of sample splits was 0.097 mmol mol^{-1} (pooled standard deviation, dof = 19) or ~3.7%, which is about seven times larger than analytical precision. Mn/Ca and Fe/Ca, used to monitor possible diagenetic overgrowths [*Boyle*, 1983] and detrital contamination [*Barker et al.*, 2003], were almost always below 30 μmol mol^{-1} and did not exceed 60 μmol mol^{-1} in any sample, well below thresholds for likely trace metal contamination (>100 μmol mol^{-1}).

[13] Mg/Ca is strongly correlated with bottom water temperature, and the data are well fit by a straight line ($r^2 = 0.73$, $p < 0.0001$):

$$\mathrm{Mg/Ca} = 0.116 \pm 0.014\,\mathrm{T} + 1.20 \pm 0.18. \qquad (3)$$

There is no hint of an exponential increase of Mg/Ca with temperature, and an exponential fit to the data ($r^2 = 0.70$, $p < 0.0001$) is not significantly better or worse than the linear one:

$$\mathrm{Mg/Ca} = 1.55 \pm 0.12\,e^{0.042 \pm 0.005\,\mathrm{T}}. \qquad (4)$$

The standard error of estimate for equation (3) is 0.28 mmol mol^{-1}, equivalent to 2.4°C, and for equation (4) it is 0.30 mmol mol^{-1}. For comparison, *Lear et al.* [2002] reported a standard error of 1.7°C on *Cibicidoides* (equation (1)). Although it is unlikely that the combined thermodynamic-physiological factors influencing benthic foraminiferal Mg/Ca are purely linear with temperature, we suggest that

Table 1. KNR166-2 Multicore Locations, Hydrographic Data, *C. Pachyderma* Mg/Ca, and *G. Ruber* Radiocarbon Ages[a]

Core	Latitude, °N	Longitude, °W	Depth, m	Temperature, °C	Salinity, psu	ΔCO_3^{2-}, μmol kg^{-1}	Mg/Ca, mmol mol^{-1}	Conventional ^{14}C Age, yr BP	NOSAMS Number
5	24.40	83.38	447	8.5	35.02	54	2.05 ± 0.06		
11	24.22	83.30	751	5.8	34.91	55	1.34	355 ± 35	OS-39958[2]
13	24.37	83.24	348	9.7	35.17	62	2.39 ± 0.08	3040 ± 35	OS-46032[2]
16	24.40	83.23	248	10.8	*35.32*	*66*	2.34 ± 0.09		
19	24.42	83.21	173	12.7	35.60	82	2.41 ± 0.45	1320 ± 50	OS-39967[2]
22	24.41	83.37	398	9.0	*35.08*	*54*	2.56 ± 0.10		
28	24.28	83.27	648	6.3	34.91	50	1.48 ± 0.09	2980 ± 40	OS-46037[2]
50	24.41	83.22	198	12.1	35.51	76	2.43 ± 0.06	1080 ± 45	OS-41646[2]
53	24.38	83.23	302	10.0	*35.21*	*61*	2.28 ± 0.12	1800 ± 30	OS-39969[2]
55	24.38	83.27	359	9.1	*35.10*	*55*	2.29 ± 0.06		
62	24.33	83.26	547	7.0	*34.91*	*46*	2.19	Fm > 1	OS-39971[1]
68	23.61	79.08	431	16.6	36.24	*129*	3.34 ± 0.07		
72	23.75	79.43	542	10.8	35.31	70	2.85 ± 0.03		
76	23.59	79.42	539	11.0	35.33	*67*	2.83 ± 0.06		
79	23.26	79.27	486	12.1	*35.50*	*77*	3.25 ± 0.14		
84	24.37	79.45	638	10.5	35.27	58	2.48		
89	24.56	79.24	353	17.8	*36.48*	*149*	3.44	2280 ± 35	OS-40243[2]
92	24.55	79.26	478	15.7	36.13	124	3.19		
94	24.57	79.23	259	18.5	36.57	161	3.41 ± 0.09	215 ± 35	OS-40244[2]
97	24.56	79.23	303	18.6	*36.58*	*158*	3.26 ± 0.02		
103	24.44	79.48	683	9.3	35.11	53	2.32 ± 0.02		
110	24.58	79.24	390	17.3	*36.39*	*141*	3.31	Fm > 1	OS-46039[2]
112	24.64	79.24	404	17.1	*36.35*	*138*	2.92		
118	24.59	79.27	531	14.5	35.91	*104*	2.68	Fm > 1	OS-39973[3]
121	24.77	79.25	578	11.9	35.48	*76*	2.58 ± 0.13		
123	24.76	79.27	632	10.6	35.30	*65*	2.54 ± 0.15		
125	24.76	79.29	694	9.4	35.13	*57*	2.48	Fm > 1	OS-39975[3]
134	24.84	79.22	441	17.2	36.37	*139*	3.04 ± 0.14	Fm > 1	OS-46043[2]
138	24.83	79.23	484	16.8	36.29	135	2.56		

[a] Bottom temperatures were estimated by matching bottle (or estimated) salinities to nearby CTD casts. Italicized salinity and ΔCO_3^{2-} data were estimated as described in text. Superscripts on National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) sample numbers indicate source of radiocarbon ages: 1, *Lund and Curry* [2004]; 2, *Lund* [2005]; and 3, *Lund and Curry* [2006]. Fm > 1 refers to fraction modern >1, indicating the presence of ^{14}C from nuclear weapons testing.

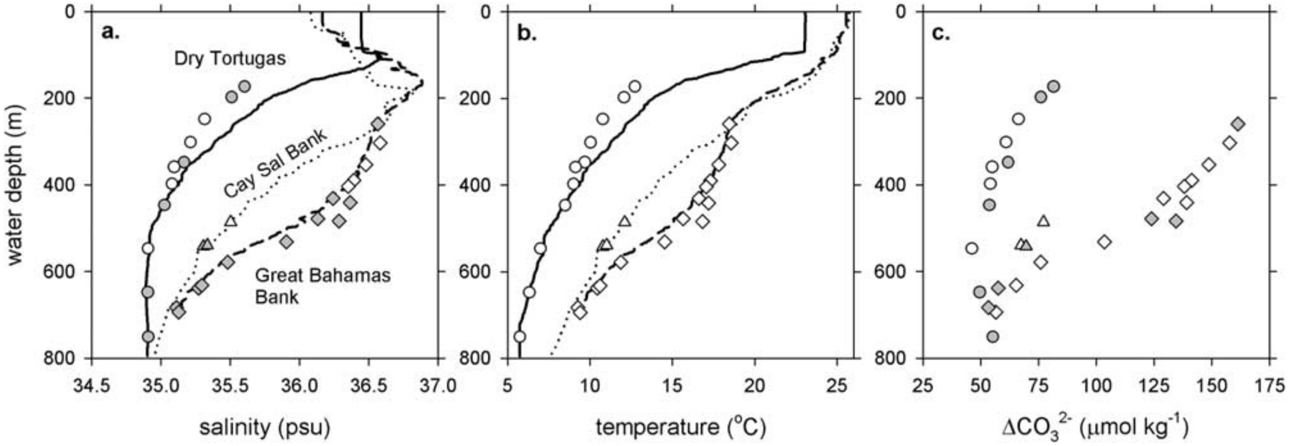

Figure 2. (a) Salinity at multicore sites (symbols) either measured directly from Niskin bottle mounted to the multicorer (shaded) or estimated from nearby conductivity-temperature-depth (CTD) casts as described in text (open). Sites are divided into three regions: Dry Tortugas (circles), Cay Sal Bank (triangles), and Great Bahamas Bank (diamonds). Representative deep CTD casts from each region are also shown (lines). Note that casts from shallower waters are better fits to the shallower multicore data, owing to sloping isopycnals. (b) Temperatures at each multicore site estimated by matching salinities in Figure 2a to nearest CTD casts. (c) ΔCO_3^{2-} with respect to calcite calculated from measured total alkalinity and ΣCO_2 (shaded) or estimated using the strong local correlation between ΔCO_3^{2-} and salinity (open).

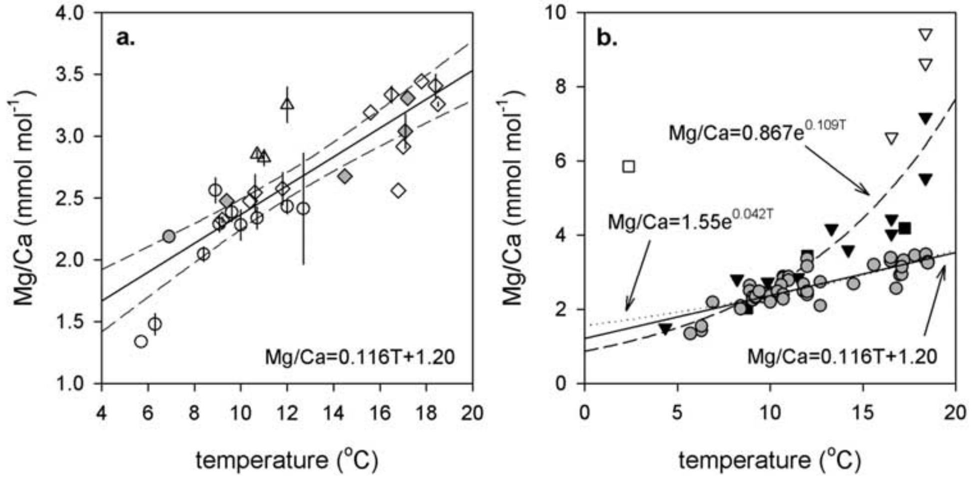

Figure 3. (a) Florida Straits *C. pachyderma* Mg/Ca plotted versus temperature, with best fit linear regression (equation (3)) and 95% confidence intervals. Multicores are from Dry Tortugas (circles), Cay Sal Bank (triangles), and Great Bahamas Bank (diamonds). Shaded symbols indicate those multicore tops with modern (bomb) radiocarbon ages. Error bars indicate $\pm 1\sigma$ of sample splits where available. (b) Individual measurements (shaded circles) of the data shown in Figure 3a, compared to *Lear et al.*'s [2002] new *C. pachyderma* measurements from Little Bahamas Bank (triangles) and Hawaii (squares). Open symbols were rejected by *Lear et al.* [2002] owing to suspected authigenic overgrowths and/or downslope transport. Equations (1) (dashed, *Lear et al.* [2002]), (3) (solid), and (4) (dotted) are also shown.

the linear fit is a more useful approximation than the exponential. The exponential curve results in large exaggerations of inferred temperature at the cold extreme of the calibration, as discussed in Section 3.3.

[14] Our Mg/Ca values overlap with the Little Bahamas Bank *C. pachyderma* data of *Lear et al.* [2002] up to ~12°C (Figure 3b). In warmer waters, our data are significantly lower than even the lowest Little Bahamas Bank measurements. Both data sets were cleaned using the same methods, and we do not suspect that the offset is analytical. The warm-water values presented here have been reproduced using an entirely different analytical method, Secondary Ionization Mass Spectrometry (SIMS) on polished cross sections of foraminiferal tests (without chemical cleaning) [*Bice et al.*, 2005], and the agreement is excellent [*Curry and Marchitto*, 2005]. Also, several Little Bahamas Bank *C. pachyderma* Mg/Ca measurements by *Hall and Chan* [2004], including one warmer than 15°C, agree with *Lear et al.*'s [2002] values. Therefore we conclude that the offset between regions is related to some natural process affecting *C. pachyderma* Mg/Ca.

[15] Large *C. pachyderma* Mg/Ca scatter in the warmest cores at Little Bahamas Bank was initially observed by *Rosenthal et al.* [1997]. *Lear et al.* [2002] rejected three of seven individual measurements from their two cores warmer than 15°C because of suspected high-Mg calcite overgrowths and/or downslope transport (open triangles in Figure 3b). One of two *G. ruber* Mg/Ca measurements from their warmest core was very elevated (>12 mmol mol^{-1}), suggestive of overgrowths. Carbonate diagenesis in the form of "hardground" is well known in surface and downcore sediments at the Bahamas [e.g., *Neumann et al.*, 1977; *Mullins et al.*, 1985]. It has been observed in surface sediments along the western margin of Little Bahamas Bank at depths of about 600 m during DSRV *Alvin* dives, and at shallow depths in some but not all locations within Northwest Providence Channel [*Neumann et al.*, 1977]. It has also been found in subsurface sediments often concentrated at glacial-interglacial transitions [*Slowey et al.*, 1989]. High-Mg calcites are a common component of the diagenetic cements, and these phases may affect core top benthic foraminiferal chemistry at Little Bahamas Bank. We have measured Mg/Ca values of ~150 mmol mol^{-1} (3.6% of $CaCO_3$ by weight) in chemically cleaned carbonate hardground from the deglacial section of core OCE205-2-149JPC from 423 m on Little Bahamas Bank. These Mg contents are indistinguishable from measurements made on cements from glacial-age sections of shallow-water Great Bahamas Bank sediment cores [*Malone et al.*, 2001]. If characteristic of the hypothesized overgrowths on Little Bahamas Bank core top foraminifera, a contribution of <1% by mass would elevate Mg/Ca by 1 mmol mol^{-1}. We suggest that all of the warm (>12°C) Little Bahamas Bank *C. pachyderma* Mg/Ca data may be biased toward high values owing to overgrowths.

[16] If we are correct about high-Mg overgrowths on Little Bahamas Bank, it is not obvious why such diagenesis is not apparent in our data from the Florida Straits near Great Bahamas Bank, since the seawater carbonate chemistry is comparable [*Rosenthal et al.*, 2006]. Additional factors such as high sedimentation rates, limited pore water flushing, and organic matter composition may act to inhibit cement formation in surface sediments [*Morse*, 2003]. We also cannot eliminate the possibility that high *C. pachyderma* Mg/Ca at Little Bahamas Bank is a primary feature of shell chemistry. Potentially high concentrations of pore

water Mg are unlikely to blame because *C. pachyderma* is an epifaunal taxon and should not be significantly affected by pore waters. Alternatively, *C. pachyderma* from warm-water sites on Little Bahamas Bank might incorporate high Mg owing to some unidentified physiological effect. We note that *Uvigerina* from warm Little Bahamas Bank sites exhibit much lower Mg/Ca values than *C. pachyderma* [*Lear et al.*, 2002].

[17] It is also possible that downslope reworking is more prevalent along Little Bahamas Bank than at our Great Bahamas Bank core sites, although there is no evidence to support this speculation and it is unlikely to be the cause of the high Mg/Ca values at Little Bahamas Bank. If our new linear temperature calibration is correct, then the highest *C. pachyderma* Mg/Ca values at Little Bahamas Bank (>8 mmol mol^{-1}) require the presence of impossibly high sea water temperatures, exceeding 50°C at shallow locations. Thus we reject downslope reworking as the main cause of the observed high Mg/Ca scatter at Little Bahamas Bank.

3.2. Possible Impact of Calcite Saturation State

[18] Partial dissolution of various species of planktonic foraminifera is known to result in lowered Mg/Ca [*Brown and Elderfield*, 1996; *Rosenthal et al.*, 2000; *Dekens et al.*, 2002]. This preferential loss of Mg has been attributed to the fact that calcite formed in warmer waters (with higher Mg/Ca) tends to be more susceptible to dissolution. Bathyal benthic foraminifera are generally not expected to suffer from this bias because their entire life is spent at a relatively constant temperature. Uptake of Mg during growth, however, may be affected by bottom water saturation state with respect to calcite. *Martin et al.* [2002] found that abyssal *C. wuellerstorfi* Mg/Ca exhibits a steeper apparent response to temperature than *C. pachyderma* from warmer waters, and attributed the enhanced slope to decreased saturation at the colder sites. *Elderfield et al.* [2006] recently quantified this effect, concluding that *C. wuellerstorfi* Mg/Ca decreases by ~0.01 mmol mol^{-1} per μmol kg^{-1} decrease in ΔCO_3^{2-}. Both studies assume that *C. wuellerstorfi* should exhibit the same temperature sensitivity as *C. pachyderma*, but this assumption has not been explicitly tested. *Rosenthal et al.* [2006] have demonstrated a similar effect in the aragonitic benthic foraminifer *Hoeglundina elegans*. Undersaturation has also been implicated in reducing benthic foraminiferal incorporation of Cd, Ba, and Zn [*McCorkle et al.*, 1995; *Marchitto et al.*, 2000, 2005], possibly through a physiological response to the difficulty of precipitating calcite in low-ΔCO_3^{2-} waters [*Elderfield et al.*, 1996]. Foraminifera may actively exclude Mg because it inhibits calcite precipitation [*Davis et al.*, 2000], so perhaps they exclude Mg more rigorously in undersaturated waters [*Elderfield et al.*, 2006].

[19] The effects of temperature and ΔCO_3^{2-} on Mg/Ca are difficult to separate because the two properties are often well correlated in the ocean, especially regionally, and the Florida Straits are no exception. ΔCO_3^{2-} values at our core sites range from 46 to 161 μmol kg^{-1}, which is similar to the range found on Little Bahamas Bank [*Rosenthal et al.*, 2006] and much higher than at most of the deep sea sites where *Elderfield et al.* [2006] reported a ΔCO_3^{2-} influence on *C. wuellerstorfi*. Florida Straits ΔCO_3^{2-} is strongly correlated to temperature ($r^2 = 0.94$) so it is not surprising that *C. pachyderma* Mg/Ca is strongly correlated to ΔCO_3^{2-} ($r^2 = 0.59$). The only hint that Mg/Ca may be reduced at low ΔCO_3^{2-} is that our two coldest sites ($\Delta\text{CO}_3^{2-} = 50-55$ μmol kg^{-1}) fall well below equation (3). Clearly, we cannot draw any conclusions without a larger data set extending into less saturated waters.

[20] Alternatively, one might argue that the Mg/Ca:temperature data are best fit by a second-order polynomial ($r^2 = 0.77$) that actually flattens at high temperatures owing to reduced Mg uptake in more saturated waters. This suggestion appears contrary to the arguments summarized in the preceding paragraphs, but it is interesting to note that high CO_3^{2-} (or high pH) has been shown to suppress planktonic foraminiferal Mg/Ca in culture experiments [*Lea et al.*, 1999; *Russell et al.*, 2004]. It is conceivable that benthic foraminifera incorporate less Mg when calcifying in both undersaturated and very supersaturated conditions. The CO_3^{2-} impact on planktonic foraminifera can be expressed in several ways, but one method of quantification is as percent Mg/Ca decrease per 100 μmol kg^{-1} CO_3^{2-} increase, estimated at 23 ± 18% in *Orbulina universa* and 63 ± 9% in *Globigerina bulloides* [*Russell et al.*, 2004]. Applying a hypothetical correction of 20% per 100 μmol kg^{-1} to our *C. pachyderma* data would remove the apparent Mg/Ca flattening in high ΔCO_3^{2-} waters, and a 60% correction would result in a strongly exponential increase of Mg/Ca with temperature. Again, the strong correlation between temperature and ΔCO_3^{2-} in the Florida Straits prevents us from adequately testing the hypothesis of Mg suppression at high levels of supersaturation.

3.3. Implications for Paleotemperature Reconstruction

[21] It is important to stress that the calibration presented here is directly applicable to only one species, *C. pachyderma*. This species is epifaunal and rather cosmopolitan in waters shallower than ~2500 m, making it one of only several benthic taxa routinely used in both Cd/Ca and δ^{13}C reconstructions [*Boyle*, 1992]. The other most widely used *Cibicidoides* species, *C. wuellerstorfi*, may well exhibit a distinct Mg/Ca temperature response. Indeed, the steeper slope observed by *Martin et al.* [2002] and *Elderfield et al.* [2006] for *C. wuellerstorfi* could be due to a combination of calcite saturation effects and a greater response to temperature. Until more calibration data are collected, caution should be exercised in applying genus-level equations to multiple species.

[22] Compared to *Cibicidoides* exponential equations (1) and (2), our new linear *C. pachyderma* calibration has a similar slope below ~5°C and a shallower slope above (Figure 3b). It is also much shallower than the provisional linear *C. pachyderma* equation proposed by *Marchitto and deMenocal* [2003] to pass through the lower end of *Lear et al.*'s [2002] Mg/Ca data. A shallower slope means that Mg/Ca errors are magnified in terms of reconstructed temperature, so *C. pachyderma* would seem to be less sensitive in thermocline waters than previously suggested [*Rosenthal et al.*, 1997; *Lear et al.*, 2002; *Martin et al.*, 2002], though the

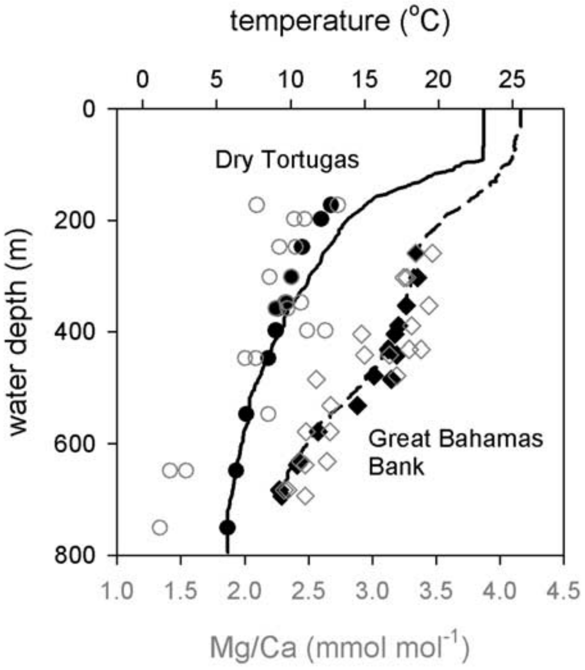

Figure 4. Individual *C. pachyderma* Mg/Ca measurements from the western (Dry Tortugas, gray open circles) and eastern (Great Bahamas Bank, gray open diamonds) sides of the Florida Current. Solid symbols and lines are modern in situ temperatures based on data in Figure 2b. Mg/Ca and temperature are scaled according to equation (3). Core tops on the eastern margin reproduce the shape of the thermocline with reasonable fidelity, but cores from the western margin appear to be more scattered.

troubling warm-water scatter in the earlier calibrations has been eliminated. It is possible that equation (3) is biased by the lack of cold water (<5°C) data, and that such data will increase the slope of this calibration in the future.

[23] Application of linear equation (3) to the Laurentian Slope *C. pachyderma* data of *Marchitto and deMenocal* [2003] produces a temperature range of ~−4 to 0°C, which is both implausibly large and impossibly cold. Exponential equation (4) has such a low slope in cold waters that application to the *Marchitto and deMenocal* [2003] data produces an absurd range of roughly −18 to −6°C. If equation (3) is a reasonably accurate calibration for well-saturated waters, the Laurentian Slope data may be taken as further evidence for a significant low-ΔCO_3^{2-} suppression of *C. pachyderma* Mg/Ca. Modern ΔCO_3^{2-} at the Laurentian Slope site is ~45 μmol kg^{-1}, comparable to our deep Florida Straits sites. Low-Mg/Ca intervals in the Laurentian Slope record might then represent a combination of cooling and reduced seawater CO_3^{2-} related to deep water circulation changes. The alternative scenario of Mg/Ca suppression at high saturation states would allow for a temperature slope closer to that used by *Marchitto and deMenocal* [2003], which resulted in a more reasonable downcore temperature range of ~1.5 to 3.5°C.

[24] Our core top calibration is unusually well-constrained because of extensive seawater sampling, undisturbed multicore tops, high sedimentation rates, and radiocarbon documentation. Nevertheless, the standard error of estimate for equation (3) (0.28 mmol mol^{-1} or 2.4°C) is likely an overestimate because our core tops do represent a span of late Holocene ages that may not always correspond to the modern temperatures used in the calibration. This is especially true on the western side of the Florida Current (Dry Tortugas) where core tops tend to be older and temperatures are more sensitive to changes in geostrophic flow. Even modern temperatures appear to be variable, with *Bryden et al.* [2005] noting a 1 to 2°C warming between 400 and 800 m along the eastern margin of the Bahamas since the 1990s. However, the low slope of equation (3) means that our average reproducibility of sample splits alone is equivalent to ±0.8°C. Although our stated error is discouraging, Figure 4 suggests that *C. pachyderma* can be used to reconstruct past thermocline structure over a large temperature range and thereby support δ^{18}O-based paleogeostrophic flux calculations [*Lynch-Stieglitz et al.*, 1999]. Best results would likely emerge from numerous replicate measurements in each core.

4. Conclusions

[25] In contrast to previous calibrations of *Cibicidoides* Mg/Ca versus temperature, we find no evidence to support a strong exponential relationship. Instead, *C. pachyderma* data from the Florida Straits are well fit by a straight line, with a Mg/Ca sensitivity of 0.12 mmol mol^{-1} per °C over the temperature range 5.8 to 18.6°C. We suggest that previous *Cibicidoides* equations based on samples from Little Bahamas Bank are heavily biased by authigenic contamination of *C. pachyderma*. If our measured high Mg/Ca values of Little Bahamas Bank hardground are representative of local cements, then only small amounts of overgrowths would be required to explain the earlier data. We stress that our new calibration is directly applicable to only one species, though our observations call into question the assumption of strongly exponential behavior in other benthic taxa. It is essential that other benthic species be independently calibrated to establish their Mg/Ca behavior. The possible influence of seawater carbonate chemistry must also be evaluated by comparing sites with similar temperatures but disparate ΔCO_3^{2-} values.

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