

## Foraminiferal magnesium in *Globeriginoides sacculifer* as a paleotemperature proxy

David W. Hastings

Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia, Canada

Ann D. Russell

Department of Geology, University of California, Davis

Steven R. Emerson

School of Oceanography, University of Washington, Seattle

**Abstract.** Foraminiferal magnesium shows increasing promise as a paleothermometer, but the accuracy and precision are limited by biases introduced by partial dissolution, salinity variations, Mg-rich gametogenic calcite, and contaminant phases. We improved cleaning methods and reduced errors introduced by partial dissolution by sampling from well-preserved cores in the equatorial Atlantic and the Caribbean Sea with different dissolution histories. All cores reveal a synchronous 25% increase in Mg/Ca from the stage 2/3 boundary to the Holocene core top, indicating that dissolution is not a controlling factor. Modern temperatures estimated from core top Mg/Ca are 24.5°-25.0°C, equal to mean annual water temperatures at 50-100 m. We estimate that sea surface temperature increased by 2.6°C ( $\pm 1.3$ ) from the last glacial maximum to the Holocene. Holocene values were comparable to those during isotope stage 5e. Our data indicate that biases from contaminant phases and partial dissolution can be reduced. This paleothermometer holds promise if uncertainties introduced by salinity variations and gametogenic calcite can be constrained.

### 1. Introduction

Reconstruction of past sea surface temperatures (SSTs) is essential for understanding processes that control climate change throughout Earth's history. Tropical SST estimates during the last glacial period using different proxies vary by several degrees, severely limiting our ability to understand past climates and the role of oceanic heat transport in climate change. Faunal transfer functions, one of the primary tools for determining paleocean temperatures, indicate that tropical SST increased 1°-2°C from the last glacial maximum to the present [CLIMAP, 1981; McIntyre *et al.*, 1989; Thunell *et al.*, 1994; Stott and Tang, 1996]. Tropical SST derived from the oxygen isotope record in planktonic foraminifera also suggests a 2.0° - 2.6°C temperature drop during peak glacial time in the Atlantic, consistent with the original CLIMAP estimates [Billups and Spero, 1996]. Additional support for a small change in tropical SST comes from down-core  $U^{k}_{37}$  measurements which indicate a glacial cooling of 1.8°C in the tropical Atlantic [Sikes and Keigwin, 1994] and 1.5° - 2.5°C in the equatorial Indian Ocean [Rostek *et al.*, 1993].

Other proxies indicate significantly larger temperature differences in the tropics, including coralline Sr data which suggest that mean temperatures were 5°C cooler during peak glacial in tropical Vanuatu [Beck *et al.*, 1992] and Barbados [Guilderson *et al.*, 1994]. Many continental temperature

proxies also indicate a glacial cooling of ~5°C [Rind and Peteet, 1985] including noble gases dissolved in Brazilian aquifers [Stute *et al.*, 1995], pollen data [Piperno *et al.*, 1990], and mountain snowline data [Broecker and Denton, 1989]. Recent  $\delta^{18}O$  data in *Globeriginoides sacculifer* from the equatorial Atlantic point to a higher glacial-interglacial amplitude in equatorial SST of at least 4°C [Curry and Oppo, 1997]. Since each of these paleothermometers has its own advantages and drawbacks, development of new proxies for SST is critical.

Several decades of research suggest that foraminiferal Mg may become a reliable paleotemperature proxy. Chave [1954] first reported that Mg in biologically precipitated calcite is a function of water temperature in which the marine organisms live. Calcification temperature and magnesium content are correlated for data from all species considered together [Savin and Douglas, 1973] but not for data from a single species (*G. sacculifer*) [Bender *et al.*, 1975]. Magnesium in *Globigerina bulloides* and *Globorotalia inflata* from deep-sea sediment cores showed fluctuations in phase with oscillations in paleoclimatic indices [Cronblad and Malmgren, 1981]. A limited data set of core top benthic foraminifera shows that both bottom water temperature and Mg/Ca of *Cassidulina subglobosa* decrease with increasing water depth [Izuka, 1988]. Recently, a study of Mg in *Neogloboquadrina pachyderma* (sinistral) in modern core tops showed that Mg covaried with surface water temperature [Nürnberg, 1995]. The Mg content of foraminiferal calcite also affects its dissolution susceptibility and can alter the saturation horizon for Mg-rich parts of the test by several hundred meters [Brown and Elderfield, 1996]. Magnesium incorporation in other carbonate shells including benthic ostracods [Chivas *et al.*, 1986; Correge and De

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Deckker, 1995; Dwyer et al., 1995], mussels [Klein et al., 1996] and barnacles [Smith et al., 1988] has been used as a paleotemperature proxy.

Physiological control of magnesium in the calcitic test of foraminifera is probable because the distribution coefficient is 50-200 times less than in inorganically precipitated calcite [Katz, 1973; Mucci and Morse, 1990]. Our working hypothesis is that the physiological processes responsible for Mg incorporation in foraminiferal calcite [Robertson, 1989] are temperature-related, and thus Mg incorporated into the test is an indicator of SST when the organism was alive. A significant advantage of this paleotemperature proxy is that Mg is a conservative element with a residence time of  $13 \times 10^6$  years with respect to river input [Broecker and Peng, 1982], so that temporal and spatial changes in dissolved Mg in the world ocean are not expected to be significant over timescales of  $10^4$ - $10^5$  years.

Recent culture experiments with living foraminifera demonstrate temperature control on the Mg content of *G. sacculifer* showing a 130% increase in Mg for a 10°C change in water temperature [Nürnberg et al., 1996a]. Applying this calibration curve to three down-core records with opposite dissolution histories, we estimate sea surface temperature changes based on changes in foraminiferal Mg. Several other variables known to affect the Mg content must also be evaluated including salinity changes, amount of gametogenic calcite, and postdepositional dissolution of the test.

## 2. Methods

Foraminifera were obtained by washing and sieving (>63 µm) bulk ocean sediment in 5% (NaPO<sub>3</sub>)<sub>6</sub> buffered to pH 8 with NaOH to remove clays and fines. The dried sediment was sieved into different size fractions, and single specimens of *G. sacculifer* were hand-picked from the 355-425 µm size fraction. Those individuals visibly contaminated by black specks, assumed to be ferromanganese oxide, were discarded.

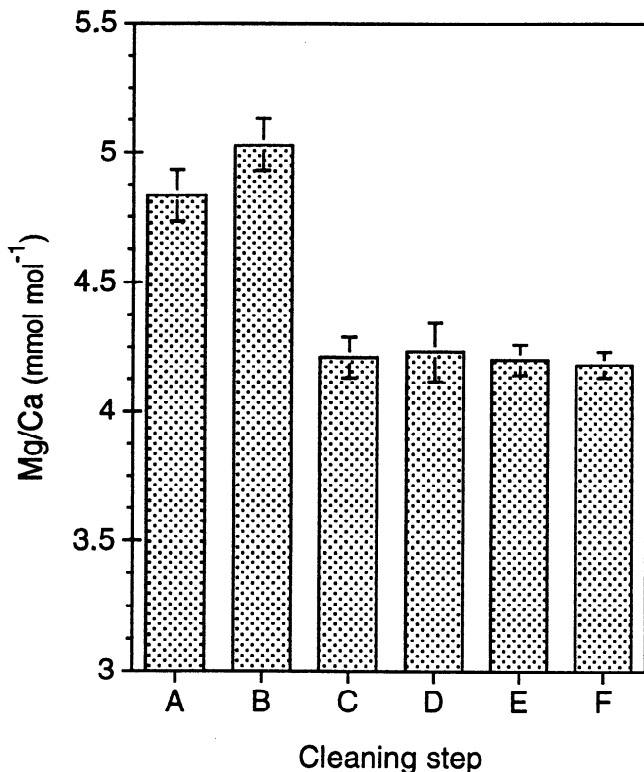
*G. sacculifer* is a tropical species that lives in the photic zone, bears dinoflagellate symbionts, and tolerates salinities in the range of 24-47 and temperatures from 14° to 31°C [Hemleben et al., 1989]. A final sac-like chamber may be added in the terminal stage of development in *G. sacculifer* [Bé et al., 1983; Hemleben et al., 1989]. Our analyses showed that those with the final chamber did not have a significantly different Mg content compared to phenotypes without, confirming results by Nürnberg [1996a]. Both variants were picked for this study.

These samples were also used to determine foraminiferal vanadium or uranium levels, so they were rigorously cleaned using modifications [Russell et al., 1994; Hastings et al., 1996c] of previously developed cleaning methods [Boyle, 1981; Boyle and Keigwin, 1985/1986]. Briefly, 5-15 mg of foraminiferal tests were gently crushed to open the chambers, subjected to a strongly reducing solution of hot (90°C) hydrazine, and then an oxidizing solution of alkaline H<sub>2</sub>O<sub>2</sub> followed by several rinses with hot distilled deionized water (DDI H<sub>2</sub>O). Samples are rinsed several (3-5) times with DDI H<sub>2</sub>O between steps. For details regarding the cleaning procedure see Hastings et al. [1996a].

Magnesium, calcium, and manganese were measured simultaneously by inductively coupled plasma mass spectrometry (ICPMS) or by flame atomic absorption spectroscopy (FAAS). For ICPMS analysis, 25 µl of the cleaned, dissolved sample were diluted into 2 ml of 0.1 N HNO<sub>3</sub> and introduced into a Perkin Elmer Sciex ELAN 5000 ICPMS via a Meinhardt glass nebulizer with a Perkin Elmer AS-90 autosampler. Dwell times of 400 ms were used at mass to charge ratios (*m/z*) 24, 43, 55, and 45 for a total measurement time of 50 s. The ion optics were optimized for Mg and Mn at *m/z* 24 and 55 to give equal response for those two elements. To normalize for both short-term variability and long-term drift in the mass spectrometer, samples and standards were spiked with a Sc internal standard [Vanhaecke et al., 1992]. Some Mg and Ca analyses were determined using a Perkin Elmer model 5000 flame atomic absorption spectrophotometer. Subsamples (50 µl) of the dissolved sample were diluted into 25 ml of La solution (400 ppm La in 0.05 N HCl and 0.002 N HNO<sub>3</sub>). Measurement precision of Mg/Ca was ±3% (1σ) for both FAAS and ICPMS. Mg/Ca values determined by ICPMS were always within 6% of the value determined by FAAS. If isotope dilution were used for the ICPMS Mg analyses, the precision and accuracy could be greatly improved.

In order to assess the necessity and efficacy of various cleaning procedures for foraminiferal Mg and to develop a suitable protocol, we subjected core top samples of *G. sacculifer* (355-425 µm) from the Ontong Java Plateau in the eastern equatorial Pacific (0°00' N, 158°54' W; 2301 m depth) to sequentially more rigorous cleaning. From previous work it is known that the presence of detrital clays, organic material, Mn carbonate, and ferromanganese oxyhydroxides affects the trace metal content of foraminifera, including Cd [Boyle, 1981], Ba [Lea and Boyle, 1993], V [Hastings et al., 1996a], U [Russell et al., 1994], and rare earth elements [Palmer, 1985]. Different methods have been developed to reduce or eliminate these phases and are shown in Figure 1. Sample A shows the Mg content of washed and sieved foraminiferal tests. Multiple (3-5) distilled deionized water rinses with sonication (sample B) did not change the Mg content within the measurement error. Cleaning the sample with hot alkaline peroxide for 30 min (0.15% H<sub>2</sub>O<sub>2</sub> in 0.1 N NaOH immersed in a 90°C water bath with periodic sonication; sample C), decreased the Mg content by 15% compared to the original untreated sample. Neither one or two reducing steps with hot hydrazine reagent for 30 min (16 M NH<sub>4</sub>OH, 0.25 M citric acid and 1 M NH<sub>2</sub>NH<sub>2</sub> at 90° C, referred to as samples D and E, respectively) nor a dilute 0.005N HNO<sub>3</sub> rinse (sample F) had a significant effect on the Mg content. Thus the oxidation step, as indicated by sample C, significantly lowered the Mg/Ca ratio, but foraminiferal Mg remained relatively constant following the subsequent chemical cleaning methods.

Previous paleotemperature reconstructions using foraminiferal Mg [Brown, 1996; Nürnberg et al., 1996a] have used an electron microprobe to determine the Mg content of the test. Being able to determine the Mg content of different parts of the test is advantageous for studies examining heterogeneity of the Mg distribution and postdepositional diagenetic influences. For paleotemperature reconstructions, determining the average Mg/Ca value of the entire assemblage is



**Figure 1.** Results of cleaning experiment using sequentially more rigorous cleaning methods. Cleaning steps used for each sample, detailed in the text, are summarized as follows: A, washed, sieved, and picked foraminifera with no additional chemical cleaning; B, performed multiple (4 - 6) distilled water rinses with sonication; C, performed distilled water rinses followed by oxidation with hot alkaline  $H_2O_2$ ; D, same as C, followed by a reducing step with hot hydrazine; E, same as C, followed by two reducing steps with hot hydrazine; F, same as E followed by one dilute acid (0.005 N  $HNO_3$ ) rinse.

preferable because it inherently averages sample differences both within the individual test and within the assemblage. Furthermore, it enables the analyst to clean the sample chemically and remove contaminant phases before analysis.

### 3. Site Description and Chronology

#### 3.1. Eastern Equatorial Atlantic

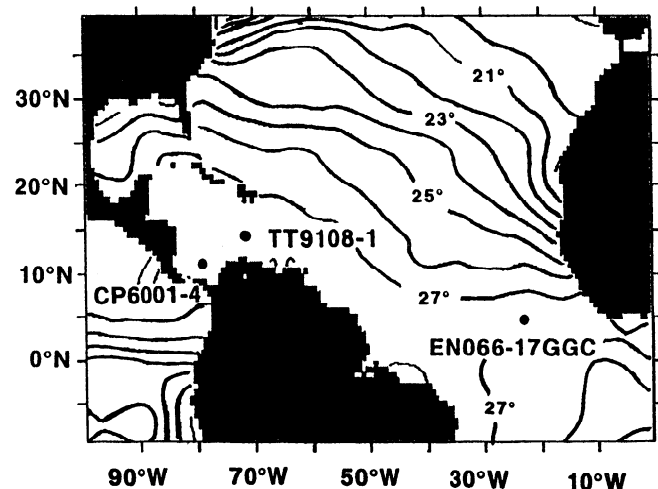
Relatively shallow cores taken substantially above the foraminiferal lysocline in the eastern equatorial Atlantic and the Caribbean were chosen to avoid effects related to partial dissolution of the foraminiferal calcite (Figure 2). Gravity core EN066-17GGC (5°22'N, 21°5'W [Curry and Lohmann, 1986]) was raised from 3050 m water depth on the Sierra Leone Rise where the calcite lysocline is estimated to be 4800 m [Thunell, 1982]. Fragmentation and carbonate accumulation data in the eastern basin indicated a shoaling of the lysocline by 1000 m during glacial stages [Curry and Lohmann, 1986] which implies that the foraminiferal lysocline was at ~3700 m during the last glacial period.

The chronology is based on  $\delta^{18}O$  measurements on *Cibicides wuellerstorfi* (Table 1 and Figure 3) [Curry and Lohmann, 1986, 1990]. Isotope stage boundaries are located at the midpoint between  $\delta^{18}O$  maxima and minima; the ages associated with these boundaries are from the stacked SPECMAP curve [Imbrie et al., 1984; Martinson et al., 1987]. The ages are the same as those given by Curry and Lohmann [1986; 1990] except that the stage 2/3 boundary was estimated to be at 50 cm. All ages are given in calendar years using a multilinear algorithm [Keigwin and Jones, 1994] based on the original linear equation [Bard et al., 1993] to make the correction to calendar years. Holocene sedimentation rates averaged 1.4 cm kyr<sup>-1</sup> compared to 2.7 cm kyr<sup>-1</sup> during the last glacial period.

#### 3.2. Caribbean Sea

Two relatively shallow cores were selected from the Caribbean Sea. Core TT9108-1GC (11°39.83'N, 79°35.52'W, 2540 m; Figure 4) was taken from the southwestern region of the Colombia Basin [see Hastings et al., 1996b]. Visual inspection of the core suggested that the top 50 cm was sampled twice in coring, with the gravity core penetrating the sediment and withdrawing briefly before repenetrating. Measurements of  $\delta^{18}O$  on *C. wuellerstorfi* carried out in the laboratory of A. Mix support this interpretation. These additional 50 cm are not included in data shown for this core. The chronology was developed by assigning the stage 1/2 boundary to 26 cm and the  $\delta^{18}O$  minimum at 41 cm to the last glacial maximum (LGM). We assume a constant sedimentation rate of 6.0 cm kyr<sup>-1</sup> below this depth (Figure 4 and Table 2).

Core CP6001-4PC, TC (14° 55'N, 71° 50'W; Figure 5) was recovered at a water depth of 3645 m from the Beata Ridge that separates the Colombia and Venezuela Basins [see Hastings et al., 1996b]. The data shown are a composite of the trigger



**Figure 2.** Location of cores used in this study. Specific locations and water depths for these cores are EN066-17GGC, 5°22'N, 21°5'W, 3050 m; CP6001-4PC, 14°55'N, 71°50'W, 3645 m; and TT9108-1GC, 11°39.83'N, 79°35.52'W, 2540 m. Isotherms of modern mean annual sea surface temperatures (SSTs) are from Levitus and Boyer [1994].

**Table 1.** Depths, Ages, and Mg/Ca Values for Cleaned *Globeriginoides sacculifer* from Eastern Equatorial Atlantic Core ENO66-17GGC

Depth, cm	Age, ka	Mg/Ca, mmol mol <sup>-1</sup>	Estimated Temperature, °C	Temperature Difference, °C
1	0.7	3.74	24.6	0.0
1	0.7	3.66	24.4	-0.2
3.5	2.5	3.66	24.4	-0.2
3.5	2.5	3.73	24.6	-0.0
10	7.7	3.82	24.8	0.2
10	7.7	3.64	24.3	-0.3
20	15.4	3.37	23.5	-1.1
20	15.4	3.48	23.9	-0.8
24	17.2	3.11	22.8	-1.8
24	17.2	3.10	22.7	-1.9
30	19.8	3.22	23.1	-1.5
30	19.8	3.12	22.8	-1.8
37	22.8	2.93	22.3	-2.4
37	22.8	2.99	22.4	-2.2
50	28.2	2.91	22.2	-2.4
70	45.1	3.03	22.5	-2.1
70	45.1	3.00	22.5	-2.1
90	58.7	3.09	22.7	-1.9
90	58.7	3.21	23.1	-1.5
110	68.8	3.51	23.9	-0.7
130	82.7	3.49	23.9	-0.7
130	82.7	3.48	23.9	-0.8
150	97.3	3.70	24.5	-0.1
150	97.3	3.76	24.7	0.0
170	111.9	3.75	24.6	0.0
190	126.5	3.73	24.6	-0.0
190	126.5	3.93	25.2	0.6
200	133.4	3.88	25.0	0.4
200	133.4	3.52	24.0	-0.6
210	140.2	3.38	23.6	-1.0
210	140.2	3.57	24.1	-0.5
220	147.0	3.44	23.7	-0.9
220	147.0	3.45	23.8	-0.8

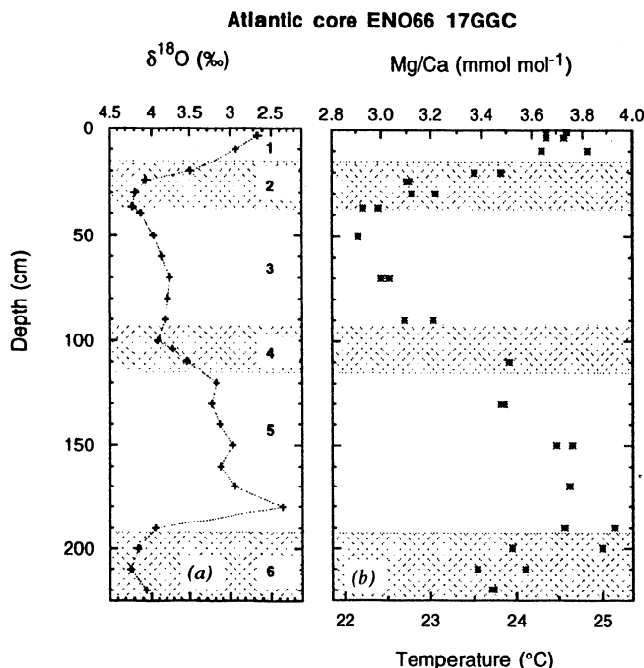
Ages are in calendar years. Estimated temperatures and temperature differences from core top values are based on the calibration for this species [Nürnberg, 1996a] given in the text.

weight core and the piston core (Figure 5 and Table 3). On the basis of the  $\delta^{18}\text{O}$  profile provided by L. Peterson, and by comparison to other nearby Caribbean cores [Emiliani, 1966], we determined that the top 20 cm of the trigger weight core was missing. The gradients in  $\delta^{18}\text{O}$ , Mg/Ca and V/Ca [Hastings et al., 1996b] in the top of the piston core indicate that an additional 25 cm were missing for the piston core top. A turbidite from 107 to 162 cm (relative to the core top) was indicated by isotopically light  $\delta^{18}\text{O}$  and by the presence of *G. menardii* [Russell et al., 1996]. This interval is shown in Figure 5 by a hatched area. Sample ages were estimated by as-

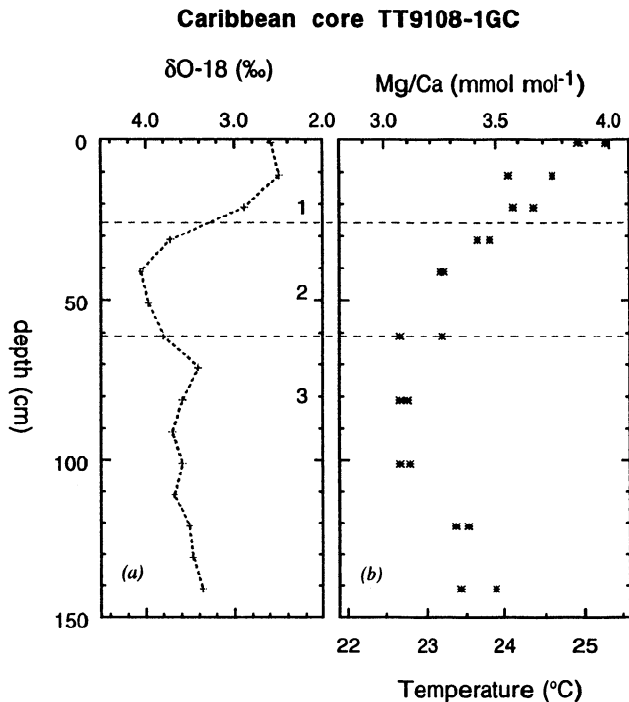
signing the isotope stage 1/2 boundary to the depth at which *Globorotalia menardii* appears (55 cm) and assuming a constant sedimentation rate (4.55 cm kyr<sup>-1</sup>) through stage 1. The LGM was assigned to 172 cm on the basis of the  $\delta^{18}\text{O}$  values. Ages for stage 2 and early stage 3 samples were estimated on the basis of a constant sedimentation rate of 6 cm kyr<sup>-1</sup>, as for the other Caribbean core. Ages for the deepest samples were based on assigning the stage 5e (123.8 ka) at 567 cm and a constant sedimentation rate of 4.1 cm kyr<sup>-1</sup> for stages 3-6.

#### 4. Results

In all three cores, consistent glacial-interglacial changes are revealed by an increase in Mg/Ca from a minimum value of 2.9-3.1 centered at the stage 2/3 boundary to a core top Holocene value of 3.7-3.9 mmol mol<sup>-1</sup> (Figures 3, 4, and 5). Using the temperature calibration developed for foraminiferal Mg in *G. sacculifer* [Nürnberg et al., 1996a], this corresponds to a warming of 2.2°C (Figure 6). In Caribbean core CP6001-4 a sharp secondary minimum centered at 56.5 cm (14.4 kyr) was observed, possibly a reflection of meltwater pulse 1A [Fairbanks, 1989]. In the Atlantic core, Mg/Ca values increased from 3.4 mmol mol<sup>-1</sup> during glacial stage 6 to values of 3.85 mmol mol<sup>-1</sup> at stage 5e, which is similar to core top values. This indicates that sea surface temperatures during stage 5e were similar to modern values. Two deep samples from Caribbean core CP6001-4 at stages 5e and 6 (Figure 6) confirm the temperature trends seen in the Atlantic core.



**Figure 3.** Eastern equatorial Atlantic core ENO66-17GGC. (a) Isotope  $\delta^{18}\text{O}$  from *Cibicidoides wuellerstorfi* [Curry and Lohmann, 1986]; glacial stages are indicated on the right-hand side of the  $\delta^{18}\text{O}$  profile and separated by dashed lines. (b) Mg/Ca variations with depth in cleaned *Globeriginoides sacculifer*. Temperatures estimated from Mg/Ca values are shown on the bottom axis.



**Figure 4.** Caribbean core TT9108-1GC. (a) Isotope  $\delta^{18}\text{O}$  from *C. wuellerstorfi*; glacial stages are indicated on the right hand side of the  $\delta^{18}\text{O}$  profile and separated by dashed lines. (b) Mg/Ca variations with depth in cleaned *G. sacculifer*. Temperatures estimated from Mg/Ca values are shown on the bottom axis.

Modern temperatures based on core top samples from each site are estimated to be 24.5° and 25.0°C for the Atlantic and Caribbean cores, respectively (Tables 1, 2 and 3). This corresponds to the observed temperatures at 50-100 m at these stations [Levitus and Boyer, 1994] and is slightly deeper than the depth habitat of 25-75 m for *G. sacculifer* based on both abundance and isotopic temperatures [Fairbanks *et al.*, 1980; Erez and Honjo, 1981; Fairbanks *et al.*, 1982; Billups and Spero, 1996]. A somewhat greater depth would be predicted since one quarter of the weight of the test is laid down during gametogenesis [Bé, 1980] which for most individuals occurs around 100 m, but some *G. sacculifer* sink to the deep, cold ocean before crusting [Lohmann, 1995].

For the temperature calibration we used a linear fit of the molar Mg/Ca ratios [Nürnberg *et al.*, 1996b, revised Table 4] for single species *G. sacculifer* [Nürnberg *et al.*, 1996a, Figure 5]. We have chosen a linear fit (temperature = 2.898 Mg/Ca + 13.76;  $r^2 = 0.92$ ) which matches the data as well as an exponential fit. The error in the inferred temperature was estimated by combining the analytical error in the Mg/Ca measurement ( $\pm 0.08 \text{ mmol mol}^{-1}$ ) with the error associated with the calibration curve. At the 95% confidence interval the error in the temperature estimate is  $\pm 1.3^\circ\text{C}$  from 22-26°C. This error is only a partial estimate of the total uncertainty since the temperature calibration is based on electron microprobe data, not total dissolution, and because probe data for carbonates are difficult to calibrate. Furthermore, the calibration via microprobe avoids gametogenic calcite whereas our analysis by dis-

solution includes the entire foraminifer. Improving the calibration curve and using total dissolution to measure Mg would increase the accuracy and precision of the estimated temperature.

## 5. Discussion

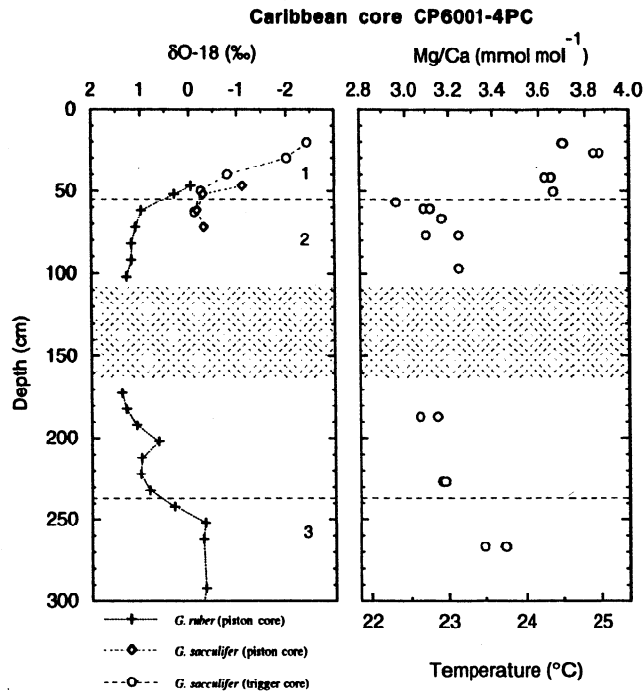
### 5.1. Dissolution Effects

Use of biogenic Mg in calcite as a paleotemperature proxy is complicated by several factors including (1) postdepositional dissolution, which can alter the original shell composition, (2) the composition and amount of gametogenic calcite, and (3) salinity effects. Since Mg distribution is heterogeneous in many foraminiferal species [Bender *et al.*, 1975; Duckworth, 1977; Brown and Elderfield, 1996], preferential dissolution of the Mg-rich parts of the foraminiferal test can change the Mg/Ca ratio by up to 25% [Rosenthal and Boyle, 1993; Russell *et al.*, 1994; Hastings *et al.*, 1996a]. The Mg content of *G. sacculifer* is less affected by partial dissolution than in another planktonic species *Globorotalia tumida* [Brown and Elderfield, 1996]. In order to confidently interpret a foraminiferal Mg record as a paleotemperature proxy it is critical to use samples that have not been subjected to postdepositional dissolution.

**Table 2.** Depths, Ages, and Mg/Ca Values for Cleaned *G. sacculifer* from Caribbean Core TT9108-1GC

Corrected Depth, cm	Age, ka	Mg/Ca, mmol mol <sup>-1</sup>	Estimated Temperature, °C	Temperature Difference, °C
1	0.7	3.87	25.0	-0.2
1	0.7	3.98	25.3	0.2
10	5.1	3.75	24.6	-0.5
10	5.1	3.56	24.1	-1.0
20	11.1	3.66	24.4	-0.8
20	11.1	3.58	24.1	-1.0
30	16.5	3.41	23.7	-1.5
30	16.5	3.47	23.8	-1.3
40	21.3	3.27	23.2	-1.9
40	21.3	3.25	23.2	-2.0
60	25.2	3.07	22.7	-2.5
60	25.2	3.26	23.2	-1.9
80	29.0	3.1	22.7	-2.4
80	29.0	3.07	22.7	-2.5
100	32.5	3.11	22.8	-2.4
100	32.5	3.07	22.7	-2.5
120	36.0	3.37	23.5	-1.6
120	36.0	3.32	23.4	-1.7
140	39.4	3.5	23.9	-1.2
140	39.4	3.34	23.4	-1.7

Ages are in calendar years. Estimated temperatures and temperature differences from core top values are based on the calibration for this species [Nürnberg, 1996a] given in the text.



**Figure 5.** Caribbean core CP6001-4PC, TC. (a) Isotope  $\delta^{18}\text{O}$  from *G. sacculifer* in the piston core (diamonds) and trigger weight core (open circles) combined with  $\delta^{18}\text{O}$  from *Globeriginoides ruber* in the piston core (crosses); glacial stages are indicated on the right hand side of the  $\delta^{18}\text{O}$  profile and separated by dashed lines. (b) Mg/Ca variations with depth in cleaned *G. sacculifer*. Temperatures estimated from Mg/Ca values are shown on the bottom axis. A turbidite indicated by the hatched area appears from 107 to 162 cm (see text)

The most compelling line of evidence that the Mg record is not being controlled by dissolution in these records is that carbonate dissolution cycles in the Caribbean and Atlantic are out of phase while the Mg values are synchronous. Because of the 1800 m sill separating the Caribbean from the Atlantic, deep Caribbean waters reflect the chemistry of Atlantic intermediate waters, and sediments from the Caribbean reflect dissolution cycles that are opposite in sense to the dissolution cycles of the deep Atlantic. Glacial sediments in the Atlantic are more dissolved than those during interglacial periods [Crowley, 1985; Curry and Lohmann, 1990], while glacial Caribbean sediments reflect enhanced carbonate preservation compared to those in the interglacial [Chen, 1968; Peterson, 1990; Haddad and Drozler, 1996]. This was confirmed in our work by the observation of abundant aragonitic pteropods in stage 2 and the upper part of stage 3 and by the presence of *G. sacculifer* tests with dissolution prone spines in glacial Caribbean sediments which indicated a deepening of the aragonite compensation depth during this interval.

If preservation differences were controlling the Mg concentration, a maximum in Mg/Ca would be expected at glacial intervals in the Caribbean cores. Instead, a distinct minimum is observed, synchronous with the profile seen in the Atlantic core. Additional evidence that the dissolution signal is not significant for the Caribbean cores comes from the obser-

vation that Mg values for core top Holocene samples, which would be more affected by dissolution compared to glacial samples, show a good match to modern SST.

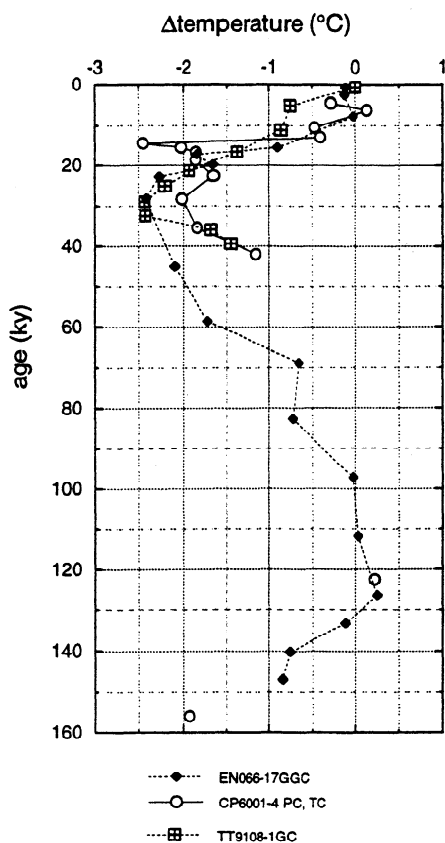
Foraminiferal fragmentation is a function of the intensity of dissolution for a given assemblage. For Caribbean core CP6001-4 (3645 m), fragmentation was <10% throughout the core to stage 6, reflecting good preservation (L. Peterson, personal communication, 1994). The presence of *Globeriginoides ruber* throughout the core, which is the most dissolution susceptible of 15 common planktonic species [Berger, 1968], was additional evidence that partial dissolution was minimal in this depositional environment. Sediments from Caribbean core TT9108-1, which is 1100 m shallower than CP6001-4, should also be well preserved. Foraminiferal fragmentation in the Atlantic core was 10% or lower for stages 1, 2, and 5 [Curry and Lohmann, 1986] and revealed that dissolution was not likely to be important for these intervals.

The effect of partial dissolution on estimated temperatures is observed at 40 ka where the Atlantic and Caribbean records diverge by  $\sim 1^\circ\text{C}$ . Foraminiferal fragmentation increases from

**Table 3.** Depths, Ages, and Mg/Ca values for cleaned *G. sacculifer* from Caribbean Core CP6001-4 PC, TC

Corrected Depth, cm	Age, ka	Mg/Ca, mmol mol <sup>-1</sup>	Estimated Temperature, °C	Temperature Difference, °C
21	4.5	(4.32)	(26.3)	(1.49)
21	4.5	3.71	24.5	-0.28
27	6.2	3.84	24.9	0.10
27	6.2	3.87	25.0	0.18
42	10.5	3.63	24.3	-0.51
42	10.5	3.66	24.4	-0.43
50.5	12.9	3.67	24.4	-0.40
56.5	14.4	2.96	22.3	-2.45
61	15.4	3.12	22.8	-1.99
61	15.4	3.09	22.7	-2.08
67	16.6	3.17	22.9	-1.85
77	18.7	3.10	22.7	-2.05
77	18.7	3.24	23.1	-1.64
97	22.6	3.24	23.1	-1.64
167	28.3	3.07	22.7	-2.13
167	28.3	3.15	22.9	-1.90
227	35.5	3.17	22.9	-1.85
227	35.5	3.18	23.0	-1.82
267	42.0	3.36	23.5	-1.29
267	42.0	3.45	23.8	-1.03
567	122.6	3.86	24.9	0.15
567	122.6	3.91	25.1	0.30
707	156.0	3.12	22.8	-1.99
707	156.0	3.16	22.9	-1.87

Ages are in calendar years. Estimated temperatures and temperature differences from core top values are based on the calibration for this species [Nürnberg, 1996a] given in the text. Values in parentheses are not plotted.



**Figure 6.** Sea surface temperature changes from the modern core top value estimated from foraminiferal magnesium values of *G. sacculifer* in eastern equatorial Atlantic core EN066-17GGC (diamonds) and Caribbean cores TT9108-1GC (open circles) and CP6001-4PC, TC (boxed crosses). Ages are in calendar years. Possible effects of salinity on temperature estimates have not been included in this figure; assuming a salinity decrease of 1 during the deglaciation, temperature estimates during the glacial would be underestimated by  $\sim 0.4^{\circ}\text{C}$ .

stage 2 to stage 4 in the Atlantic core [Curry and Lohmann, 1986], indicating increasingly more corrosive conditions. Partial dissolution producing lower Mg/Ca values and lower inferred temperatures would be predicted. Rather than an indication of temperature differences between the two basins, this difference is likely an artifact associated with the preferential dissolution of calcite with a higher Mg content in the Atlantic and demonstrates the potential influence of postdepositional dissolution.

## 5.2. Gametogenic Calcite

The gametogenic calcite of *G. sacculifer*, a layer of calcite laid down rapidly at the final stage of its reproductive cycle, has 3 times more Mg compared to primary chamber calcite [Nürnberg *et al.*, 1996a] and adds on average 28% to the weight of the shell [Bé, 1980]. Changes in foraminiferal Mg can also be explained by variability in the amount of gametogenic calcite in the downcore record. If three quarters of the gametogenic calcite ( $\text{Mg/Ca} \sim 8.0 \text{ mmol mol}^{-1}$ ) dissolved and none of the primary calcite ( $\text{Mg/Ca} \sim 2.5 \text{ mmol mol}^{-1}$ ) dis-

solved, the Mg/Ca ratio would decrease by  $0.8 \text{ mmol mol}^{-1}$ , the observed change in the paleoceanographic record. Since the primary calcite is relatively more soluble than the gametogenic crust [Lohmann, 1995], this is an unlikely scenario; nonetheless, it provides some insight into the importance of gametogenic calcite in affecting Mg/Ca values. For this study we are assuming that all tests of this size class preserved in the sediments underwent gametogenesis or that the proportion of non-gametogenic to gametogenic foraminifera preserved in sediments does not change with time. Furthermore, we assume that for individual foraminifera the mass of gametogenic calcite relative to primary calcite is constant over time and is not a controlling factor in the Mg content of foraminifera. These assumptions are key to Mg/Ca thermometry.

## 5.3. Salinity Effects

Existing culture experiments suggest that higher salinity enhances foraminiferal Mg uptake possibly because of increased metabolic activity; a salinity increase of 10 results in a doubling of Mg in *G. sacculifer* [Nürnberg *et al.*, 1996a]. If surface salinity decreased by 1 during the deglaciation, the Mg/Ca ratio would decrease by  $0.14 \text{ mmol mol}^{-1}$ , and consequently, the temperature estimates would be underestimated by  $0.4^{\circ}\text{C}$ . In the NE Atlantic, sea surface salinity variations as great as 3 are estimated to have occurred during the deglaciation, but the aggregate shift in surface salinity from the LGM to the late Holocene is zero in this record [Duplessy *et al.*, 1993]. If both salinity and temperature controls on foraminiferal Mg are included and a surface salinity decrease of 1 is assumed from the last glacial to the present, the measured increase in Mg/Ca reflects a SST increase of  $2.6^{\circ}\text{C}$ , not  $2.2^{\circ}\text{C}$ . This influence needs to be fully considered in any rigorous paleotemperature estimate. Additional culture experiments need to be completed in order to fully understand the salinity-Mg relationship.

## 6. Conclusions

Foraminiferal Mg data from three relatively shallow cores substantially above the foraminiferal lysocline and with opposite dissolution histories reveal the utility of estimating paleotemperatures from Mg/Ca ratios of cleaned foraminifera. At all three sites, there is a synchronous increase in foraminiferal Mg from stage 2 into the present that is equivalent to a glacial cooling of  $2.2^{\circ}\text{C}$ , which is consistent with the CLIMAP,  $\delta^{18}\text{O}$ , and  $U^{k}_{37}$  temperature estimates. Incorporating a surface salinity decrease of 1 during the glacial increases this change to  $2.6^{\circ}\text{C}$ . Estimated temperatures increase from glacial stage 6, and at stage 5e, SST is similar to the Holocene, consistent with the current understanding for these periods. Calculated temperatures from core top Mg data are consistent with observed temperatures for the mixed layer at the stations sampled.

For whole shell analyses it is important to remove Mg-enriched contaminant phases including organic matter that can be removed by hot alkaline peroxide. This organic phase may be an interlamellar organic matrix that has been shown to be greatly enriched in Mg and  $\text{SO}_4$  [Szafranek and Erez, 1993]. Other cleaning procedures including a reducing step with hot hydrazine and dilute acid do not change the Mg/Ca ratio.

In addition to growth temperature, other influences on foraminiferal Mg must be considered, including partial dissolution, salinity variations, and addition of a Mg-rich gametogenic crust, all of which limit the certainty of the temperature estimate. By sampling and by using indicators of dissolution the dissolution effect can be minimized. Our strategy in this work was to compare records with opposite dissolution histories from shallow cores well above the foraminiferal lysocline. The analytical error associated with determining Mg/Ca is small ( $\pm 0.08 \text{ mmol mol}^{-1}$ , corresponding to  $\pm 0.2^\circ\text{C}$ ) and could be improved by using isotope dilution ICPMS. The error associated with the calibration curve,  $\pm 1.3^\circ\text{C}$ , combined with those from salinity variations and possible variability in gametogenic calcite is potentially large enough to make the range of values for glacial cooling overlap those found by coralline Sr and continental estimates.

Since each paleothermometer has its own advantages with different artifacts, the development of a new SST proxy is extremely useful. These data demonstrate the promise and potential utility of foraminiferal Mg as a tool for estimating tem-

peratures in the past and reveal the areas of research necessary to further develop the method. Comparing estimated temperatures using different paleoproxies on the same core at a variety of locations should be the next step in paleotemperature reconstructions. Such a multiproxy approach could lead to a resolution of the discrepancies in temperature estimates during the glacial period.

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S. R. Emerson, School of Oceanography, WB-10, University of Washington, Seattle, WA 98195. (e-mail: emerson@u.washington.edu)

D. W. Hastings, Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z4. (e-mail: hastings@ocgy.ubc.ca)

Ann D. Russell, Department of Geology, University of California, Davis, CA 95616. (e-mail: russell@jade.ucdavis.edu)

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