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### Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series

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[1] Paired Mg/Ca and  $\delta^{18}$ O measurements on planktonic foraminiferal species (G. ruber white, G. ruber pink, G. sacculifer, G. conglobatus, G. aequilateralis, O. universa, N. dutertrei, P. obliquiloculata, G. inflata, G. truncatulinoides, G. hirsuta, and G. crassaformis) from a 6-year sediment trap time series in the Sargasso Sea were used to define the sensitivity of foraminiferal Mg/Ca to calcification temperature. Habitat depths and calcification temperatures were estimated from comparison of  $\delta^{18}$ O of foraminifera with equilibrium calcite, based on historical temperature and salinity data. When considered together, Mg/Ca (mmol/mol) of all species, except two, show a significant (r = 0.93) relationship with temperature (T  $^{\circ}$ C) of the form Mg/Ca = 0.38  $(\pm 0.02) \exp 0.090 \ (\pm 0.003)$ T, equivalent to a 9.0  $\pm 0.3\%$  change in Mg/Ca for a 1°C change in temperature. Small differences exist in calibrations between species and between different size fractions of the same species. O. universa and G. aequilateralis have higher Mg/Ca than other species, and in general, data can be best described with the same temperature sensitivity for all species and pre-exponential constants in the sequence O. universa > G. aequilateralis  $\approx$  G. bulloides > G. ruber  $\approx$  G. sacculifer  $\approx$  other species. This approach gives an accuracy of  $\pm 1.2^{\circ}$ C in the estimation of calcification temperature. The ~9% sensitivity to temperature is similar to published studies from culture and core top calibrations, but differences exist from some literature values of pre-exponential constants. Different cleaning methodologies and artefacts of core top dissolution are probably implicated, and perhaps environmental factors yet understood. Planktonic foraminiferal Mg/Ca temperature estimates can be used for reconstructing surface temperatures and mixed and thermocline temperatures (using G. ruber pink, G. ruber white, G. sacculifer, N. dutertrei, P. obliquiloculata, etc.). The existence of a single Mg thermometry equation is valuable for extinct species, although use of species-specific equations will, where statistically significant, provide more accurate evaluation of Mg/Ca paleotemperature. INDEX TERMS: 1050 Geochemistry: Marine geochemistry (4835, 4850); 4267 Oceanography: General: Paleoceanography; 1065 Geochemistry: Trace elements (3670); KEYWORDS: magnesium, calcium, foraminifera, thermometry, sediment trap, planktonic

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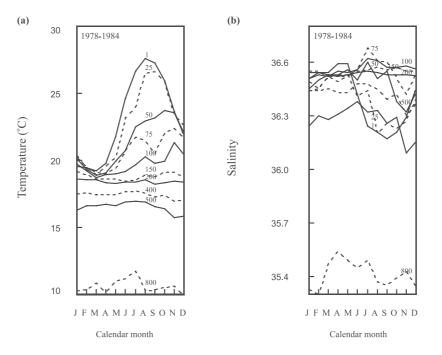
### 1. Introduction

[2] Mg/Ca in foraminiferal calcite is becoming an established paleotemperature proxy. The advantage of foraminiferal Mg/Ca thermometry over other marine paleotemperature proxy methods is that temperature estimates can be obtained from the same foraminiferal sample upon which data on oxygen isotopes, also sensitive to temperature, are obtained. The oxygen isotope composition of foraminiferal calcite is additionally controlled by the oxygen isotopic composition of seawater. Thus the approach of measuring Mg/Ca and  $\delta^{18}$ O in single species of foraminiferal calcite is potentially of great value in estimating both temperature and seawater

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 $\delta^{18}O$  from the same sample and associated with the same parcel of seawater.

[3] Early studies [e.g., *Emiliani*, 1955; *Delaney et al.*, 1985], on planktonic foraminifera showed no correlation between temperature and Mg/Ca because of complicating factors not appreciated at that time. Since then, a dependence of Mg on temperature has been established in foraminifera from core tops [*Nuernberg*, 1995; *Rosenthal et al.*, 1997; *Elderfield and Ganssen*, 2000; *Lea et al.*, 2000; *Rosenthal et al.*, 2000; *Rosenthal and Lohman*, 2002; *Dekens et al.*, 2002; *Lear et al.*, 2002] and in cultures of three species: *G. sacculifer, G. bulloides* and *O. universa* [*Nuernberg et al.*, 1996; *Lea et al.*, 1999; *Mashiotta et al.*, 1999]. Calibrations based on culture and core tops are invaluable but both have disadvantages. Culture calibrations have the great advantage that foraminifera calcify under prescribed and accurately known temperatures but the



**Figure 1.** Average annual cycles of temperature and salinity at station S in the Sargasso Sea, during the sediment trap deployments, April 1978 to May 1984. (a) Temperature ( $^{\circ}$ C). (b) Salinity, 0–800 m [*Deuser and Ross*, 1989]. Numbers on the plot are water depths in meters.

disadvantage that the controlled environment may not reproduce natural growth fully and that a limited number of species can be studied. Core-top calibrations have the great advantage that they reflect the material that is buried to form the paleoceanographic record but the disadvantage of potential artefacts, specifically from dissolution, and of difficulties in establishing the link with SST, although use of  $\delta^{18}$ O-derived calcification temperature circumvents the latter problem. All the previous calibration studies show similar exponential constants within error (0.09 ± 0.01). However, there are differences in pre-exponential constants, which are due to dissolution and other factors, e.g., different cleaning methods, inter laboratory differences etc.

[4] The third way to establish a calibration is through the use of foraminifera from the water column, with collection either by net (with the advantage of regional coverage) or by sediment trap (the advantage of seasonal and interannual records). Here, we report the results of a calibration based on 6 years of bimonthly trap samples from the Sargasso Sea. The work allowed us to define Mg incorporation into several species of planktonic foraminifera during changing seasonal cycles of hydrological conditions in the surface and near-surface waters at a site where information on seasonality and ecology of planktonic foraminifera was available [*Deuser et al.*, 1981; *Deuser*, 1987; *Deuser and Ross*, 1989; *Hemleben et al.*, 1985].

[5] Paired Mg/Ca and  $\delta^{18}$ O measurements were made on seasonally abundant planktonic foraminifera from the sediment traps and were used to evaluate: (1) seasonal and interannual variations in Mg/Ca and  $\delta^{18}$ O, (2) agreement between observed and predicted foraminiferal  $\delta^{18}$ O as a function of seasonal temperature and salinity variations in the water column so as to evaluate the habitat depths of foraminiferal species at the site, (3) the temperature dependence of Mg/Ca in twelve species of planktonic foraminifera, including interspecific differences, differences between calibrations based on calcification temperature and SST, the influence of size fraction, and comparisons with literature data.

### 2. Methodology

#### 2.1. Sediment Trap Deployment

A 6-year program of continuous sediment trap collec-[6] tion, "Seasonal Change in Isotopes and Flux of Foraminifera" (SCIFF), was carried out between 6 April 1978 and 17 May 1984 in the Sargasso Sea. The SCIFF site was located at 32°05.4'N, 64°15.4'W, 45 km south east of Bermuda. A long time series of temperature and salinity measurements (0 to 2600 m) was available from nearby station "S"  $(32^{\circ}10'N, 64^{\circ}30'W)$  (Figure 1). Thirty one of the trap deployments yielded a complete set of samples (Table 1), providing quantitative material for 83% of the elapsed time [*Deuser*, 1987]. Average deployment length was  $60 \pm 7 (1\sigma)$ days. No poisons or preservatives were used in the collection cup. In-situ oxidation of organic matter was below the level at which pH changes can cause calcite dissolution [Deuser, 1987]. Some evidence of slight dissolution in pteropod shells (aragonite) was observed in two spring samples [Deuser, 1987].

### 2.2. Foraminiferal Sampling and Analysis

[7] Twelve planktonic foraminiferal species present in the bimonthly sediment trap samples were analyzed (Table 2). *G. ruber* white and pink were distinguished, and also *G. sacculifer*, with and without a sac-like final chamber,

 
 Table 1. Dates and Duration of 31 Sediment Trap Deployments in the Sargasso Sea That Provided Samples Used in Study

Recovery	Start	End	Days 62	
1	78/04/06	78/06/07		
2	78/06/07	78/08/08	62	
3	78/08/09	78/10/10	62	
5	78/12/12	79/02/14	64	
6	79/03/24	79/05/31	68	
7	79/05/31	79/07/30	60	
9	79/10/12	79/12/03	52	
10	79/12/05	80/02/04	61	
11	80/02/06	80/04/07	61	
12	80/04/15	80/06/17	63	
13	80/06/20	80/08/11	52	
14	80/08/11	80/10/14	64	
15	80/10/17	80/12/09	53	
17	81/02/05	81/04/07	61	
18	81/04/08	81/05/26	48	
19	81/05/27	81/07/21	55	
20	81/07/21	81/09/15	56	
21	81/09/17	81/12/02	76	
22	81/12/02	82/02/02	62	
23	82/02/02	82/04/06	63	
24	82/04/13	82/06/08	56	
25	82/06/11	82/08/17	67	
27	82/10/18	82/12/07	50	
28	83/01/17	83/03/16	58	
29	83/03/16	83/05/25	70	
30	83/05/25	83/07/12	48	
31	83/0713	83/09/20	69	
32	83/09/20	83/11/15	56	
33	83/11/15	84/01/17	63	
34	84/01/17	84/0313	56	
35	84/03/28	84/05/17	50	

and O. universa with both thin and thick test. Foraminifera from the archive at Woods Hole Oceanographic Institution were picked from the >125 µm size fraction and three subfractions (250-350, 350-500, 500-1000 µm) separated. The size fractions used here are unusually large for Mg/ Ca work but this is a constraint of working with trap samples of limited foraminiferal numbers. Each paired analysis of foraminiferal  $\delta^{18}$ O and Mg/Ca was performed using a split of the same homogenized crushed samples to minimize error arising from sample heterogeneity. Foraminiferal samples were first gently crushed, using glass plates, to open chambers, homogenized and then divided. One part  $(\sim 2/3)$  was used for Mg/Ca and the second part  $(\sim 1/3)$  was used for  $\delta^{18}O$  measurements. The number of individuals used for each sample was variable, limited by availability, but typically was  $\sim$ 5-15 for Mg/Ca. Subsamples for Mg/Ca were cleaned to remove clays (water and methanol wash) and organic matter (hydrogen peroxide treatment) followed by a dilute acid polish prior to analysis. The cleaning method has evolved since *Elderfield and Ganssen* [2000] (a copy of the current method is available on request to he101@esc.cam.ac.uk). Additionally, for sediment trap samples, the organic matter removal step was extended (50% buffered H<sub>2</sub>O<sub>2</sub> for 45 min) as a precaution to eliminate the likelihood of higher organic matter contents than found in typical core material (also shown by *Pak et al.* [2000]).

[8] Elemental analyses were performed with a Varian Vista AX simultaneous inductively coupled plasma atomic-emission spectrometer [*de Villiers et al.*, 2002]. At the time of analysis, precision of measured Mg/Ca ratios

was <0.02 mmol/mol (1  $\sigma$  s.d.) for a standard solution of Mg/Ca = 5.13 mmol/mol. The second subsample was analyzed for  $\delta^{18}O(0.08\%; 1 \sigma$  s.d.) at the Godwin Institute, University of Cambridge.

## 2.3. Estimation of $\delta^{18}$ O of Seawater and Equilibrium Calcite, and Isotopic Calcification Temperature

[9] Temperature and salinity data from Bermuda biological station "S" (e.g., Figure 1) were used to calculate  $\delta^{18}O$ of seawater ( $\delta^{18}O_w$ ) and to predict  $\delta^{18}O$  of calcite ( $\delta^{18}O_c$ ) formed in equilibrium with seawater, seasonally and over 0-800 m, during the period for which the sediment trap was deployed. The reason for calculating equilibrium calcite  $\delta^{18}O$  was to compare with measured  $\delta^{18}O$  to estimate depth habitats. The isotopic temperatures based on the  $\delta^{18}O_w$  at different water depths and measured  $\delta^{18}O$  in foraminiferal calcite are used for the Mg calibration.

[10]  $\delta^{18}O_w$ , expressed as ‰ deviation from the standard mean ocean water (SMOW) scale, was calculated from the station "S" salinity data using the equation of *Duplessy et al.* [1991], itself obtained from  $\delta^{18}O_w$  and salinity for water samples collected in the upper 250 m of the Atlantic Ocean during the GEOSECS expedition:

$$\delta^{18}O_{\rm w} = -19.264 + 0.558 \times \text{salinity.} \tag{1}$$

Other relationships exist in the literature but values for  $\delta^{18}O_w$  obtained using equation (1) were the closest to measured  $\delta^{18}O_w$  available for 32°N 64°W [*Schmidt et al.*, 1999]. *Equilibrium*  $\delta^{18}O_c$  was calculated from  $\delta^{18}O_w$ , together with station "S" temperature data (T°C), using a rearrangement of the paleotemperature equation of *O'Neil et al.* [1969] and *Shackleton* [1974]:

$$\delta^{18}O_{c} = (\delta^{18}O_{w} - 0.27) + \left[4.38 - (4.38^{2} - 4) \times 0.1(16.9 - T)\right]^{0.5}/2 \times 0.1.$$
(2)

The factor 0.27 was used to convert from water on the SMOW scale to calcite on the Peedee Belemnite (PDB) scale.

**Table 2.** Species of Planktonic Foraminifera in Sargasso Sea Used in Study and Estimated of Calcification Depth From Comparison of Foraminiferal  $\delta^{18}$ O With Calcite in Equilibrium With Seawater

Species	Calcification Depth, m	
Globigerinoides ruber pink	0-25	
Globigerinoides ruber white	0-50	
Globigerinoides sacculifer	0-50	
Globigerinoides sacculifer with sac	0-50	
Globigerinella aequilateralis,	50-75	
Orbulina universa thin test	50-100	
Orbulina universa thick test	50-100	
Globigerinoides conglobatus	50-100	
Neogloboquadrina dutertrei	50 - 100	
Pulleniatina obliquiloculata	50-100	
Globorotalia inflata	100 - 400	
Globorotalia truncatulinoides	200 - 500	
Globorotalia crassiformis	500-800	
Globorotalia hirsuta	500-800	

[11] Isotopic calcification temperatures of the foraminifera were calculated, using the paleotemperature equation, from *measured*  $\delta^{18}O_c$  (from the planktonic foraminifera) and estimates of  $\delta^{18}O_w$  (as described above) based on their habitat depths defined as in sections 3.3 and 3.4:

$$T = 16.9 - 4.38 \left( \delta^{18} O_c - \left( \delta^{18} O_w - 0.27 \right) \right) + 0.1 \left( \delta^{18} O_c - \left( \delta^{18} O_w - 0.27 \right) \right)^2.$$
(3)

The abbreviation T is used for " $\delta^{18}$ O calcification temperature" in equations in this study. We have also used "monthly mean temperature" in Figure 1b that was obtained from Bermuda biological station "S" data set.

### 3. Results

[12] Results (Appendix 1<sup>1</sup>) obtained from the sediment trap samples represent averages over the trap deployment periods. The results show: (1) a small interannual variability in Mg/Ca and  $\delta^{18}$ O of planktonic foraminifera (Figure 2); (2) large intra-annual (seasonal) variations in Mg/Ca and  $\delta^{18}$ O of the surface dwelling planktonic foraminiferal species, e.g., *G. ruber* (white and pink), over a ~7 °C change in isotopic temperature (Figure 3); (3) variable depth habitats of planktonic foraminiferal species estimated from calcite isotopic equilibrium with seawater (Figure 4); (4) an exponential relationship between Mg/Ca and isotopic temperature showing a ~10% change in Mg/Ca per °C change in temperature for all except two species (Figures 5 and 6a); and (5) exceptionally high Mg/Ca in *O. universa* and *G. aequilateralis* (Figure 7b).

### 3.1. Interannual Variations

[13] Mg/Ca and  $\delta^{18}$ O data for the species *G. ruber* white, *G. ruber* pink, *G. aequilateralis*, and possibly *G. truncatulinoides*, showed a seasonally cyclic variation with little interannual variation over the 6 year period (Figure 2). For example, peak value for *G. ruber* white are Mg/Ca = 4.74 ± 0.26 mmol/mol,  $\delta^{18}$ O = -1.45 ± 0.1‰ and lows are Mg/Ca = 2.99 ± 0.14 mmol/mol,  $\delta^{18}$ O = -0.28 ± 0.02‰. There were not enough data for other species from the time series to fully evaluate interannual chemical variations but some evidence of seasonal cyclicity was also observed (Appendix I).

### 3.2. Seasonal Variations

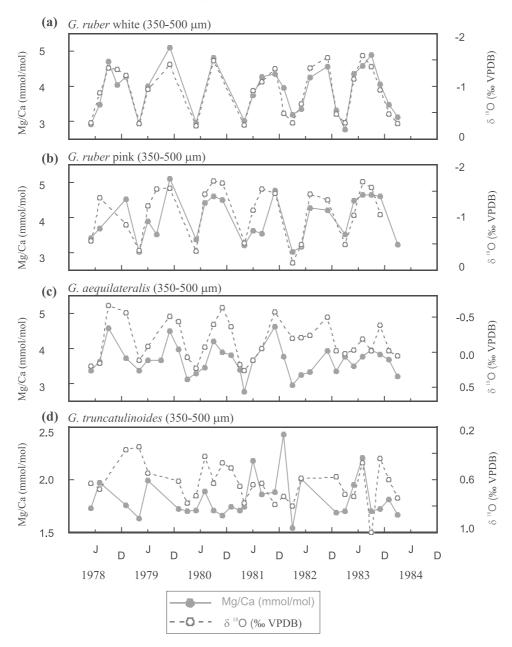
[14] Intra-annual (seasonal) changes in planktonic foraminiferal Mg/Ca and  $\delta^{18}$ O were identified for nine species (Figure 3; the standard deviation is plotted as a vertical bar representing interannual variation for a particular month). Data from the same months over the 6-year period were averaged and show large seasonal changes in all surfacedwelling planktonic species. Two size fractions of *G*. ruber, white and pink, (250-350 and 350-500 µm) showed clear variations in Mg/Ca and  $\delta^{18}$ O (Figures 3a and 3b). G. sacculifer without a sac-like final chamber showed a slightly higher Mg/Ca and a stronger trend in seasonal variation compared to without-sac individuals (Figure 3c). G. aequilateralis (also known as G. siphon*ifera*) showed similar Mg/Ca but heavier  $\delta^{18}$ O when compared to G. ruber in the same size fraction (350-500 µm). G. aequilateralis showed a higher Mg/Ca ratio in the 500–1000  $\mu$ m size fraction compared to 350–500  $\mu$ m, with no significant offsets in  $\delta^{18}$ O (Figure 3d). O. universa showed greater scatter in Mg/Ca compared to  $\delta^{18}$ O (Figure 3e) with higher Mg/Ca in the larger size fraction (500-1000 µm), for both thin and thick test, compared to the smaller size fraction (350–500  $\mu$ m, thin test). N. dutertrei and P. obliquiloculata showed a small annual variation (Figures 3f and 3g). Samples belonging to the deeper-dwelling Globorotaliid genus (G. truncatulinoides and G. hirsuta) showed a small variation in Mg/Ca and  $\delta^{18}$ O (Figures 3h and 3i).

### 4. Planktonic Foraminifera as Recorders of Near-Surface Hydrography

[15] In order to place the foraminiferal data within the context of the near surface hydrography, measured  $\delta^{18}O$  data of the various planktonic species were compared with predicted  $\delta^{18}O_c$  values for equilibrium of calcium carbonate with  $\delta^{18}O$  of seawater at depths from 0 to 800 m at station "S." Predicted  $\delta^{18}O_c$  data were averaged for two successive months in order to compare them with the measured bimonthly  $\delta^{18}O$  data obtained from foraminifera. They were used to estimate the depth habitat of the different species in the Sargasso Sea and in defining calcification temperatures. It should be stressed that the habitat depths so calculated are based on the assumption of oxygen isotope equilibrium between seawater and foraminiferal calcite as outlined in section 2.3.

[16] Overall, average depth habitats extending from surface waters down to 500-800 m were estimated (Table 2). G. ruber pink, G. ruber white and G. sacculifer calcified in near surface conditions (Figures 4a–4c). Measured  $\delta^{18}$ O for these species are in good agreement with predicted  $\delta^{18}O_c$  at 1-25 m, 25-50 m and 1-50 m depths, respectively. This is consistent with the depth habitat suggested for this area [*Deuser et al.*, 1981]. However, all of these species show lighter  $\delta^{18}$ O than predicted  $\delta^{18}$ O<sub>c</sub> of surface water from November to April. Deuser [1987] also showed an offset, up to a maximum of  $\sim 1.0\%$ , in predicted and measured  $\delta^{18}$ O in *G. ruber* white from these traps. There are several possible reasons for this offset. One is that, because G. ruber calcifies at warm temperatures, it may record temperatures higher than the 6-year averaged winter temperature. For example, it may calcify only in warm pool ring temperatures not represented by the station "S" averages. A second possibility is that there may be uncertainties in the representativity of sampling because wintertime fluxes of foraminiferal tests were much less than during the summer [Deuser, 1987; Deuser and Ross, 1989]. The winter flux of these species is very low, except for G. ruber white, and

<sup>&</sup>lt;sup>1</sup> Supporting materials are available via Web browser or via Anonymous FTP from ftp://ftp.agu.org, directory "apend" (Username = "anonymous", Password = "guest"); subdirectories in the ftp site are arranged by paper number. Information on searching and submitting electronic supplements is found at http://www.agu.org/pubs/esupp\_about.html.



**Figure 2.** Interannual variation in Mg/Ca (mmol/mol) and  $\delta^{18}$ O (‰ VPDB) in (a) *G. ruber* white, (b) *G. ruber* pink, (c) *G. aequilateralis*, and (d) *G. truncatulinoides*. Note the differences in scales for Mg/Ca and  $\delta^{18}$ O between some species. Abbreviations are: J, June and D, December.

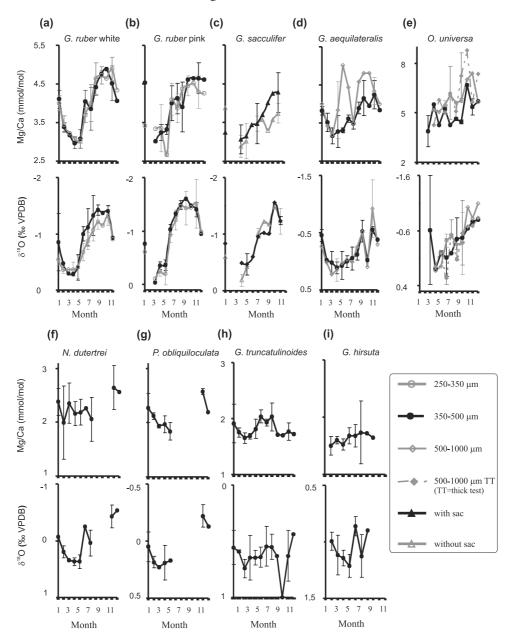
reaches fluxes close to zero. This leads to sampling limitations for such species during winter.

[17] *G. aequilateralis* and *O. universa* calcified in equilibrium with 50–100 m water depth (Figures 4d and 4e). *N. dutertrei* and *P. obliquiloculata* calcified in relatively deeper water and follow predicted  $\delta^{18}O_c$  values at 50–100 m water depth (Figure 4f). Less data were available for *G. hirsuta*, *G. inflata*, *G. crassaformis* and *G. conglobatus* from different seasons and hence it is difficult to evaluate their exact depth habitats (Table 2). Of course, observed  $\delta^{18}O$  for the deeper dwelling species may represent an average, reflecting calcification over a range from surface to deeper waters,

and do not imply that they were restricted to the estimated range.

# 5. Mg/Ca Thermometry From Foraminiferal Calcite

[18] A single paleotemperature equation [O'Neil et al., 1969; Shackleton, 1974] was used for calculating calcification temperature for all the species using  $\delta^{18}O_w$  values for the seasonally-defined species habitat depths (Table 2; Figure 4). There is some uncertainty in the habitat depths of the deeper dwelling species, reflected in their wide depth



**Figure 3.** Average intra-annual variation in Mg/Ca (mmol/mol) and  $\delta^{18}$ O (‰ VPDB) of several planktonic species. Each point represents the mean of bimonthly samples from the 6-year time series and the vertical bar is the standard deviation (interannual variation). Note the differences in scales for Mg/Ca and  $\delta^{18}$ O between some species: (a) *G. ruber* white, (b) *G. ruber* pink, (c) *G. sacculifer*, (d) *G. aequilateralis*, (e) *O. universa*. (f) *N. dutertrei*, (g) *P. obliquiloculata*, (h) *G. truncatulinoides*, (i) *G. hirsuta*.

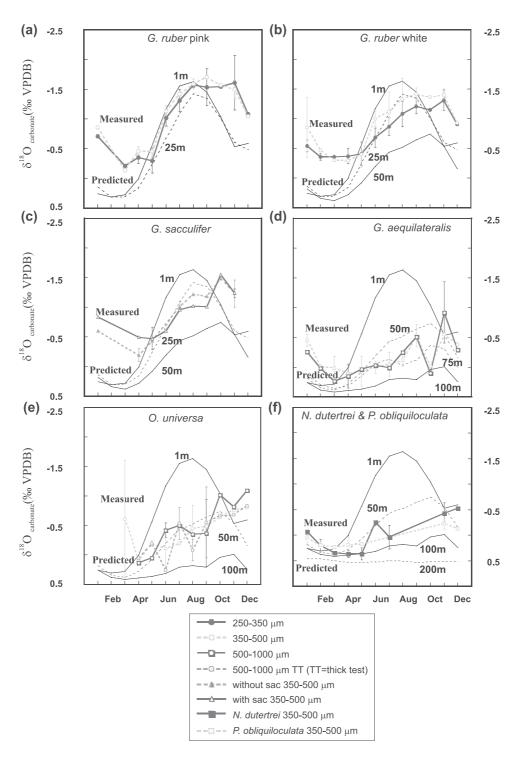
ranges in Table 2, but  $\delta^{18}O_{\rm w}$  varies little with depth over this range.

[19] Mg/Ca has been assumed to show an exponential dependence on temperature:

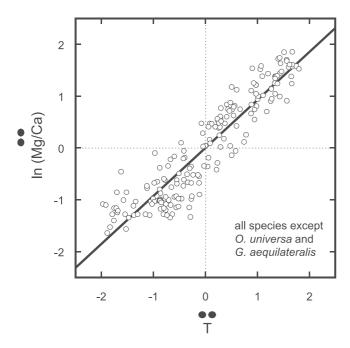
$$Mg/Ca = B \exp(AT), \tag{4}$$

where the pre-exponential and exponential constants are designated B and A and T is  $\delta^{18}$ O calcification temperature. There are two types of method that have been used for

multispecies regression analysis. The least squares regression method, is not the most appropriate for deriving calibration equations from Mg/Ca and isotopic temperature because both variables have significant errors and there is no independent variable. The reduced major axis (geometric mean) regression method, addresses this question and has been used for generating a single equation for the multi species data, after assuming that all species have same Mg/Ca temperature dependence but variable intercepts [*Rosenthal and Lohman*, 2002]. The advantage of



**Figure 4.** Determination of depth habitat of planktonic foraminiferal species in Sargasso Sea. Measured  $\delta^{18}O$  (‰ VPDB) of foraminiferal calcite (thick curve) is plotted versus calendar month, together with predicted  $\delta^{18}O$  (‰ VPDB) of calcite in equilibrium with seawater for various depths in the water column, using salinity and temperature profiles at time of the trap deployment. The predicted  $\delta^{18}O$  of calcite was calculated for an average of 6 years of temperature and salinity data on a calendar month scale and for various depths. (a) *G. ruber* pink, (b) *G. ruber* white, (c) *G. sacculifer*, (d) *G. aequilateralis*, (e) *O. universa*, (f) *N. dutertrei* and *P. obliquiloculata*.



**Figure 5.** Data for multiple species plotted as geometric means. Plotted on each axis are (value - mean of value)/ standard deviation of mean [see *Laws*, 1997].

geometric mean method is that it allows for normalizing (reducing) a multispecies data set to a single regression line and the slopes of the variables are reciprocal to each other so the selection of a notional independent variable is unimportant. Because of the different ranges in temperature of individual species of planktonic foraminifera, and the lack of a truly independent variable, the geometric mean method [*Laws*, 1997; *Rosenthal and Lohman*, 2002] has been used for linear regression analysis and applied to ln(Mg/Ca) versus T (an example of the approach is shown in Figure 5).

### 5.1. All Species

[20] Initially, we consider all species together comparing Mg/Ca with calcification temperature but only in one size fraction (350–500  $\mu m$ ). We have taken this approach because  $\delta^{18}O_c - \delta^{18}O_w$  records calcification temperature for all species but does not record SST for many of the species examined. A comparison with SST is shown later.

[21] When considered together, Mg/Ca for all the species, except two (*O. universa* and *G. aequilateralis*, which are considered later), show a significant correlation, r = 0.93, with temperature (Figure 6a). *G. ruber* white, *G. ruber* pink and *G. sacculifer* (with and without sac) represent the warmer temperature end of the calibration curve. Deeperdwelling species fall on the same curve toward the lower end of the correlation curve, representing colder temperatures. The temperature (T °C) calibration for all species considered together is described by:

$$Mg/Ca = 0.38 \exp(0.090T),$$
 (5)

with (Mg/Ca in mmol/mol). The pre-exponential and exponential constants have uncertainties of B  $\pm$  0.02 and A  $\pm$  0.003. The exponent is equivalent to a 9.0  $\pm$  0.3% change in Mg/Ca for a 1°C change in temperature. This temperature sensitivity is similar to most literature estimates, including a core-top multispecies calibration (Table 3). The preexponential constant is similar to calibration data from the literature for similar species. It is lower than for the published core-top multispecies calibration which includes *G. bulloides*, for which other literature data indicate a higher pre-exponential constant. The other possible reason for these differences could be due to the different Mg/Ca cleaning methods applied in the two studies.

### 5.2. Varieties and Size Fractions of G. ruber

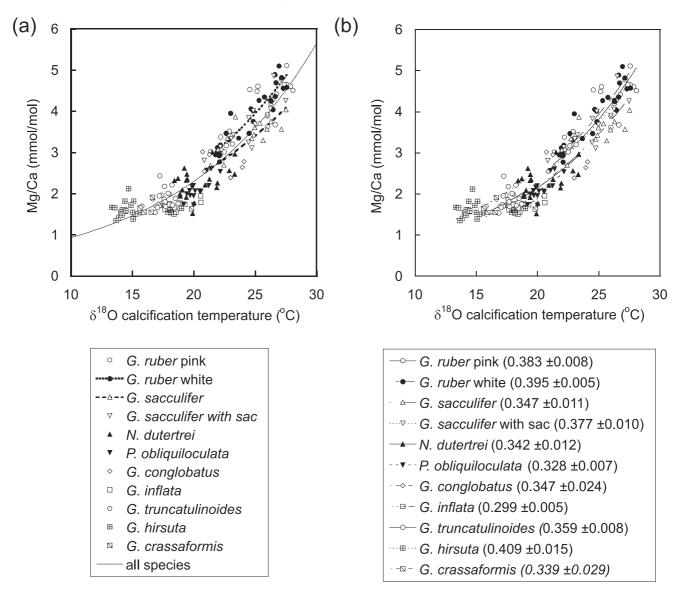
[22] *G. ruber* white and pink have similar Mg/Ca at the lower-temperature end of the calibration but at higher temperatures Mg/Ca of *G. ruber* white are higher (Figure 7a) resulting in small but significant differences in calibrations (Table 3). Correlations between Mg/Ca and calcification temperature for *G. ruber* pink are poorer than for the multispecies calibration and reveal no size fraction dependence. Correlations for *G. ruber* white are similar to that of the multispecies calibration and reveal a small size-related dependence. The difference between the two size fractions is, however, a reflection of small differences in  $\delta^{18}$ O between the two size fractions and not differences in Mg/Ca (Figure 3).

### 5.3. Interspecific Differences

[23] *O. universa* and *G. aequilateralis* have distinctly higher Mg/Ca ratios at a given temperature than the other species analyzed (Figure 7b). Data for *O. universa* show considerable scatter and although higher then for other species, are lower than seen in culture (which also show much scatter).

[24] Small interspecific differences in Mg/Ca versus temperature are apparent between some of the species which were used in the multispecies calibration. For example, Mg/Ca data for *G. ruber* white over the temperature range are higher than, and those for *G. sacculifer* are lower than, values predicted by the multispecies calibration (Figure 6a).

[25] It is not possible to construct statistically significant calibrations for all individual species simply because the ranges in calcification temperature are too narrow relative to the scatter in the data, and correlation coefficients (r) of 7 of the 15 individual species calibration equations are <0.74 (see Table 3). When the calibration curves for individual species are compared it can be seen that the constants B and A are correlated (Figure 8a). A mechanistic significance is unlikely: the most likely explanation is that it is a consequence that correlation equations with larger gradients (A) when extrapolated to A = 0 yield smaller intercept values (B) and vice versa. The species with low values for A are those for which the correlations are weaker (Figure 8b) and strengthens the view that all planktonic species show a similar temperature sensitivity when assessed using reliable calibrations. The value for the exponential constant in Figure 8b extrapolated to r = 1 is A = 0.09.



**Figure 6.** Mg/Ca versus  $\delta^{18}$ O calcification temperature. (a) All species except *O. universa* and *G. aequilateralis*. (b) Mg/Ca versus  $\delta^{18}$ O calcification temperature showing individual species calibrations assuming a constant exponential constant. Note that data are only for the size fraction 350–500 µm in both Figures 6a and 6b.

[26] Given that some species have not yielded statistically significant calibrations, an alternative approach is shown, which is the one adopted for a core-top multispecies data set [*Elderfield and Ganssen*, 2000] and assumes that the temperature dependence of the multispecies calibration (i.e.,  $A = 0.090 \pm 0.003$ ) applies to all species and thus describe interspecific differences via the pre-exponential constant (Figure 6b; Table 3) (values of B for *O. universa* and *G. aequilateralis* have been included for completeness). This is a satisfactory, although ad hoc, way to describe calibrations for individual species (see section 5.6). However, it should be emphasized that it does not constitute proof of a common temperature dependence for all species, although there is evidence (e.g., Figure 8b) that this may be the case. Single temperature dependence is also suggested

from benthic foraminiferal calibration studies [Rosenthal et al., 1997; Lear et al., 2002].

### 5.4. Spinose and Nonspinose Species

[27] A good example in support of a common temperature dependence is a comparison of species within the spinose group of planktonic foraminifer with those from the non-spinose group (Figure 9a). Grouping species in this way shows that the spinose group appear to have higher temperature sensitivity than the nonspinose group. It is interesting that the nonspinose foraminifera, mainly deeper dwelling species, have a temperature sensitivity closer to the thermodynamic value of  $\sim 0.03$  [Rosenthal et al., 1997; Lea et al., 1999]. Although it is tempting, and logical, to advocate different extents of nonequilibrium fractionation

		Mg/Ca =	B exp(AT)	Reference
Species	Source	В	А	
Ten planktonic species, <sup>b</sup> 350-500 µm	sediment trap (North Atlantic)	0.38 (±0.02)	0.090 (±0.003)	this study $(r = 0.93)$
G. ruber white, $250-350 \mu m$	sediment trap	0.34 (±0.08)	$0.102 (\pm 0.010)$	this study $(r = 0.91)$
G. ruber white, $350-500 \mu m$	sediment trap	0.48 (±0.07)	0.085 (±0.006)	this study $(r = 0.94)$
G. ruber pink, 250–350 µm	sediment trap	0.88 (±0.20)	0.058 (±0.009)	this study $(r = 0.81)$
G. ruber pink, 350–500 µm	sediment trap	0.73 (±0.17)	0.067 (±0.009)	this study $(r = 0.85)$
G. sacculifer with sac, $350-500 \ \mu m$	sediment trap	0.67 (±0.31)	0.069 (±0.013)	this study $(r = 0.85)$
G. sacculifer without sac, 350-500 µm	sediment trap	1.06 (±0.21)	0.048 (±0.012)	this study $(r = 0.75)$
P. obliquiloculata, 350–500 µm	sediment trap	0.18 (±0.1)	0.12 (±0.03)	this study $(r = 0.79)$
<i>G. inflata</i> , 350–500 μm	sediment trap	0.56 (±0.16)	0.058 (±0.015)	this study $(r = 0.74)$
G. aequilateralis, 350–500 µm	sediment trap	0.86 (±0.24)	0.068 (±0.013)	this study $(r = 0.67)$
Eight planktonic species <sup>c</sup>	core tops (North Atlantic)	0.65 (±0.04)	0.085 (±0.005)	Elderfield and Ganssen [2000]
G. ruber white, $250-350 \mu m$	core tops (equatorial Pacific)	0.3 (±0.06)	0.089 (±0.007)	Lea et al. [2000] versus SST
G. ruber white, $250-350 \mu m$	core tops	0.38	0.09	Dekens et al. [2002] versus SST
G. sacculifer and N. pachyderma sinistral	culture + core tops	0.47 (±0.03)	0.082 (±0.006)	Nuernberg et al. [1996]
G. sacculifer	culture	0.39 (±0.06)	$0.089(\pm 0.008)$	Nuernberg et al. [1996]
G. sacculifer without sac, 250-350 µm	core tops	0.37	0.09	Dekens et al. [2002] versus SST
O. universa	culture	1.38 (±0.05)	0.085 (±0.002)	Lea et al. [1999]
N. dutertrei, 250–350 μm	core tops	0.60	0.08	Dekens et al. [2002] versus SST
G. bulloides	core tops (North Atlantic)	0.81 (±0.04)	0.081 (±0.005)	Elderfield and Ganssen [2000]
G. bulloides	culture	0.51 (±0.1)	0.104 (±0.01)	Lea et al. [1999]
G. bulloides	culture + core tops	0.47 (±0.03)	0.108 (±0.003)	Mashiotta et al. [1999]
G. ruber white, 250–350 μm	sediment trap	0.449 (±0.006)	0.090	this study (A assumed)
G. ruber white, 350–500 µm	sediment trap	0.395 (±0.009)	0.090	this study (A assumed)
G. ruber pink, 250–350 µm	sediment trap	0.381 (±0.01)	0.090	this study (A assumed)
G. ruber pink, 350–500 µm	sediment trap	0.383 (±0.008)	0.090	this study (A assumed)
G. sacculifer with sac, 350–500 µm	sediment trap	0.377 (±0.01)	0.090	this study (A assumed)
G. sacculifer without sac, 350-500 µm	sediment trap	0.347 (±0.011)	0.090	this study (A assumed)
G. conglobatus, 350-500 µm	sediment trap	0.347 (±0.024)	0.090	this study (A assumed)
N. dutertrei, 350–500 μm	sediment trap	0.342 (±0.012)	0.090	this study (A assumed)
P. obliquiloculata, 350-500 µm	sediment trap	0.328 (±0.007)	0.090	this study (A assumed)
<i>G. inflata</i> , 350–500 μm	sediment trap	0.299 (±0.005)	0.090	this study (A assumed)
G. truncatulinoides, 350–500 µm	sediment trap	0.359 (±0.008)	0.090	this study (A assumed)
G.crassaformis, 350-500 µm	sediment trap	0.339 (±0.029)	0.090	this study (A assumed)
<i>G. hirsuta</i> , 350–500 μm	sediment trap	0.409 (±0.015)	0.090	this study (A assumed)
<i>O. universa</i> , 350–500 μm	sediment trap	0.595 (±0.042)	0.090	this study (A assumed)
G. aequilateralis, 350–500 µm	sediment trap	0.532 (±0.008)	0.090	this study (A assumed)

Table 3. Calibration Equations Based on Geometric Mean Method From This Study Compared With Literature Data<sup>a</sup>

<sup>a</sup>Recalculated using geometric mean method except for *Dekens et al.* [2002]. Equations based on ad hoc method after assuming A = 0.09 also provided. <sup>b</sup>G. ruber white, G. ruber pink, G. sacculifer, G. conglobatus, G. aequilateralis, O. universa, N. dutertrei, P. obliquiloculata, G. inflata, G. truncatulinoides, G. hirsuta, G. crassaformis.

<sup>c</sup>G. bulloides, G. ruber, G. sacculifer, G. siphonifera, N. pachyderma, G. hirsuta, G. inflata, G. truncatulinoides.

between the two groups, calibrations of individual spinose species for which Mg/Ca and temperature are well correlated, as in this study and in culture work (Table 3), have much higher temperature sensitivities ( $\sim$ 0.1). Therefore, in likelihood, this observation is an artifact of sparse data sets and scatter in the data, as shown when the geometric means are plotted (Figure 9b), and emphasizes the need for further work.

#### 5.5. Calcification Temperature and SST

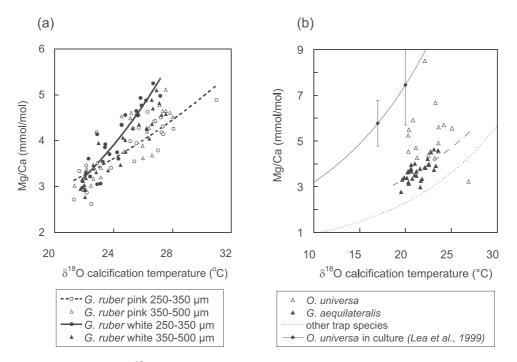
[28] It is obvious from the estimates of calcification depth (Table 2) that calibrations for some of the species considered here would never be employed to estimate sea surface temperature. However, the species *G. ruber* and *G. sacculifer* calcify at or close to the sea surface and represent mixed layer temperature. While it is logical to link Mg/Ca to calcification temperature in their calibrations, nevertheless paleoceanographic data are used to define records of SST, and these species are the most promising for this purpose [*Dekens et al.*, 2002]. Therefore it is useful to compare data with temperature derived from both approaches (Figure 10). The calibration versus monthly

mean temperature at calcification depth for these species (see Table 2) is much weaker than with calcification temperature. This arises principally from ignoring depth habitat. As seen in Figure 1, the strong summer thermocline results in a temperature gradient of about 8°C over the upper 100 m which is equivalent in magnitude to all of the seasonal SST variation. The average calcification temperatures estimated from unweighted mean Mg/Ca data for each species are  $\sim 2^{\circ}$ C warmer than average monthly mean temperatures. This is probably because the species, favoring warmer temperatures, calcify in somewhat warmer than monthly average sea surface temperatures (see section 5).

### 5.6. Accuracy of Temperature Calibrations

[29] A comparison of calcification temperatures estimated from Mg/Ca thermometry with the calcification temperatures used in the construction of the calibrations gives a good indication of the uncertainty inherent in the calibration equations. Mg/Ca temperatures were obtained using the two approaches discussed in section 5.3 (Table 3). Both methods gave similar accuracy when applied to species for which the

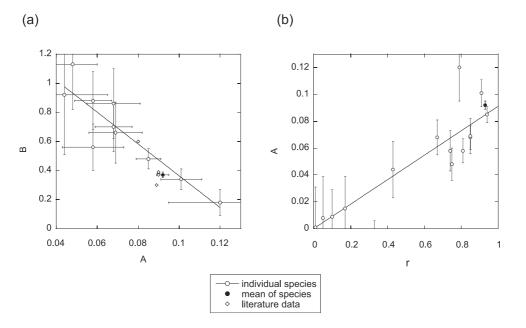




**Figure 7.** Mg/Ca versus  $\delta^{18}$ O calcification temperature. (a) *G. ruber* white and pink in two size fractions. (b) O. *universa* and *G. aequilateralis*, compared with culture data and equation for multiple species.

individual species-specific calibrations equations had correlation coefficients >0.74 (see Table 3). The species-specific equations obtained by the geometric mean method for 7 species (where r < 0.74) gave much poorer estimates of temperature sensitivity than the ad hoc method. This is because the ad hoc method assumes that the same value for the exponential constant (Table 3) applies to these remaining species.

[30] Data obtained using the ad hoc method yield a slope of the linear regression of the data as a whole



**Figure 8.** (a) Comparison of pre-exponential (B) and exponential (A) constants for species; constants related by  $B = 1.46 \pm 0.14 + (-10.94 \pm 1.86)^*$  A (r = 0.9). (b) Comparison of A and correlation coefficient (r) of calibration equation (note A = 0.90 at r = 1). Values for A, B, and r were obtained using geometric mean method.

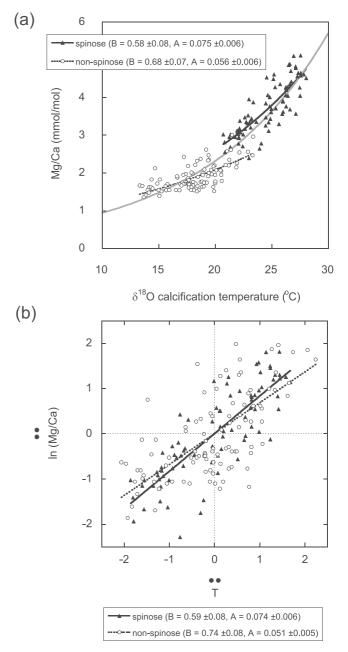
(Figure 11a) which is not significantly different from unity but with a small positive intercept (data for *O. universa* and *G. aequilateralis* have been included although, as discussed earlier, the calibration data, especially for *O. universa*, show considerable scatter). The scatter in Figure 11a is equivalent to a standard deviation in Mg/Ca temperature estimate of  $\pm 1.13$ °C (Figure 11b). *Dekens et al.* [2002] suggest a standard error of between  $\pm 1.2$  and  $\pm 1.4$ °C from core-top studies in different oceans.

[31] The scatter is not attributable to analytical error in measurement of Mg/Ca which makes a trivial ( $\sim \pm 0.05^{\circ}$ C) contribution. The foraminiferal cleaning procedure results in variability dependent on inferred temperature but typically of  $\sim \pm 0.2^{\circ}$ C which is less than half of the natural variability in a population of 20 individuals [Barker, 2002]. Fewer individuals were used for analysis than is our normal practice as well as a wider size range than normal (there is a size effect [Elderfield et al., 2002], for example of up to about 0.2°C between G. ruber white in 300-350 and 425-500 µm fractions). Taken together, up to, perhaps, about ±0.5°C can be attributable to Mg/Ca temperature estimation. The remainder is most likely associated with  $\delta^{18}O$ calcification temperature, resulting from calculation of  $\delta^{18}O_w$  and thus assignment of habitat depth and temperature. It should also be remembered that  $\delta^{18}$ O equilibrium between foraminiferal calcite and seawater has been assumed.

### 5.7. Estimation of Thermocline Structure From Mg/Ca

[32] The average Mg/Ca temperature and habitat depth derived from oxygen isotopes (Figure 4; Table 2) for each species have been plotted along with measured average annual, December–January and July–August temperatures from Bermuda biological station "S" (Figure 12). The Mg/Ca temperature was obtained using the ad hoc method after assuming a constant exponent value A = 0.09.

[33] Both estimates of depth habitat (from Mg/Ca temperature and  $\delta^{18}O$  of foraminifera) are in good agreement (Figure 12). G. ruber pink calcifies near surface conditions and represents summer temperature based on Mg/Ca. G. ruber white and G. sacculifer with sac records a temperature range of average annual to the warmest month (July-August) and lives in the mixed layer (Figure 12). G. sacculifer with sac chamber calcifies at slightly deeper water depth compared to G. ruber white based on Mg/Ca temperature. This is consistent with previous work based on Mg/Ca on the two species [Rosenthal et al., 2000; Dekens et al., 2002; Rosenthal and Lohman, 2002]. P. obliquiloculata, N. dutertrei, G. aequilateralis, O. universa and G. conglobatus calcify over a range of temperatures extending from upper to lower thermocline position in the water column (Figure 12). Globorotaliid species in this study show a deeper depth of calcification compared to other species although the depth estimates from Mg/Ca temperature give a narrow depth range compared to the  $\delta^{18}$ O approach except for *G. crassaformis* (Figure 12). Thus estimation of Mg/Ca temperature, along with  $\delta^{18}$ O, for multiple species of planktonic foraminifera from individual samples has



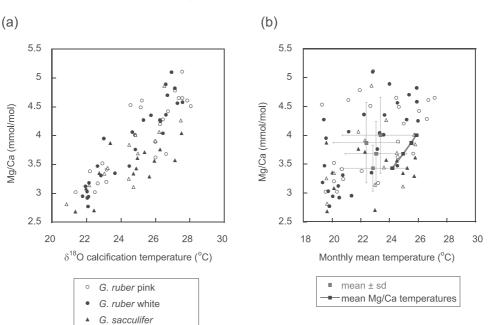
**Figure 9.** Comparison of spinose and nonspinose species. (a) Mg/Ca versus  $\delta^{18}$ O calcification temperature, and (b) geometric mean plot.

potential for reconstructing the structure of the thermocline in the past.

### 5.8. Comparison of Temperature Estimates

[34] The calibration data from this study have been added to a compilation of literature data (Table 3). Three important issues should be considered in comparing these data:

[35] 1. Different laboratories employ different preanalysis cleaning procedures for Mg/Ca (some laboratories, including ours, have modified/refined procedures and therefore may have used different procedures for different publications). There has, as yet, been no interlaboratory comparison.



**Figure 10.** Mg/Ca versus temperature for *G. ruber* and *G. sacculifer*. (a)  $\delta^{18}$ O calcification temperature. (b) Monthly mean temperature. Monthly mean temperature is the average temperature based on habitat depth range of each species, obtained from measured hydrological data at biological station "S." Black squares without error bar is the Mg/Ca temperature and gray squares with error bars are mean monthly temperatures for these species.

G. sacculifer with sac

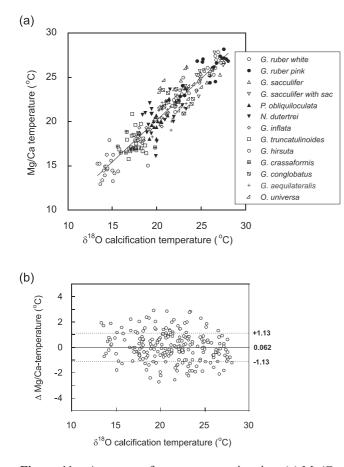
[36] 2. The method of estimating temperature may be different between calibrations. Only the temperature fixed in culture experiments may be considered to be an independent variable. In other calibrations (core tops and sediment traps) temperature is estimated from various measured parameters, sometimes using different equations, and is a dependent variable. This has a small effect on statistical procedures. As discussed above, the uncertainty in temperature estimate is probably greater than the uncertainty in Mg/Ca. In some cases calibration is made versus SST, although it is known that the species may not calcify at the sea surface, for the useful expedient of its paleoceanographic application to estimate past SST.

[37] 3. Mg/Ca is subject to dissolution effects, probably because of heterogeneous shell chemistry which results in preferential loss of calcite with higher than average Mg, and affects different species to different extents. This is a subject of active debate but it is safe to say that the effect should be considered in core-top calibrations, even above the calcite lysocline. It is also possible that dissolution affects estimates of calcification temperature via  $\delta^{18}O$ .

[38] Despite these constraints, some consensus appears to be developing as to appropriate calibration equations. The good fit of data from a number of different species to a single calibration is encouraging both because it implies that the temperature effect of Mg uptake is being properly described, and because the equation might be used for extinct planktonic species. In particular, a number of studies appear to be converging on the same calibrations, within error, for *G. ruber* white and *G. sacculifer*. This is important because of their suitability for charting SST or near-SST.

[39] The effect of dissolution, and some complexities of detail, is illustrated from a comparison of the G. ruber data in Table 3. Core-top data (250-350 µm) from the Equatorial Pacific [Lea et al., 2000] gave Mg/Ca = 0.30 exp(0.089T), which was subsequently corrected for dissolution [Dekens et al., 2002] by increasing pre-exponential constants to yield a "zero water depth" equation: Mg/Ca =  $0.38 \exp(0.090T)$ . This is similar to the sediment trap equation: Mg/Ca =  $0.34 \pm 0.08 \exp(0.102T) (250-350 \,\mu\text{m})$ . It is safe to conclude that an upward correction (which is equivalent to 1.5°C) is warranted, because of the known depth effect on dissolution [Rosenthal and Boyle, 1993; Brown and Elderfield, 1996; Rosenthal et al., 2000] despite the correction being of the order of the uncertainty in the constant B. Rosenthal and Lohman [2002] has also suggested for correction on pre-exponential constant for dissolution effect in Mg/Ca calibration study.

[40] As far as can be judged, calibrations for the other species considered here are consistent with a similar temperature dependence but further studies are needed, although these will be difficult because of the narrow temperature ranges for some species. Calibrations for *O. universa*, *G. aequilateralis* and *G. bulloides* appear to have higher pre-exponential constants than other species studied. These three species coincidentally fall toward the apex of the triangular plot based on amino acid compositions of foraminifera, constructed by *King and Hare* [1972]. Perhaps that there is a link between the amino acids in a protein



**Figure 11.** Accuracy of temperature estimation. (a) Mg/Ca temperature versus  $\delta^{18}$ O calcification temperature. The equation of the line is Mg/Ca temperature = 1.003(±0.004)  $\delta^{18}$ O calcification temperature (r = 0.93). Mg/Ca temperature is calculated using ad hoc method after assuming A = 0.090. (b) Mg/Ca temperature minus  $\delta^{18}$ O calcification temperature versus  $\delta^{18}$ O calcification temperature, the mean and standard deviations are shown.

template for foraminiferal calcification and Mg/Ca. The use of a single oxygen isotope paleotemperature equation for the calculation of calcification temperature should be borne in mind when applying the calibrations.

### 6. Summary and Conclusions

[41] There is a small interannual variability in Mg/Ca and  $\delta^{18}$ O in planktonic foraminiferal calcite from a sediment trap time series in the Sargasso Sea. However, a strong intra-annual variability occurs in the foraminiferal Mg/Ca and  $\delta^{18}$ O of all the surface dwelling planktonic species with a lesser effect in deeper dwelling species. The  $\delta^{18}$ O measurements and sea surface salinity and temperature data were used to evaluate the depth habitat of the common planktonic foraminiferal species in the Sargasso Sea. Knowledge of foraminiferal depth habitat is important in order to estimate the  $\delta^{18}$ O<sub>w</sub> and calcification temperature for the foraminiferal species.

[42] An empirical calibration between Mg/Ca (mmol/mol) and calcification temperature (T °C) was obtained when all

the species except two within  $350-500 \ \mu m$  size fraction are considered together: Mg/Ca = 0.38 exp (0.090T), equivalent to a 9.0 ± 0.3% change in Mg/Ca for a 1°C change in temperature. *G. aequilateralis* and *O. universa*, (and also *G. bulloides*) have significantly higher Mg/Ca values at a given temperature than the other species analyzed. Only small differences exist in calibrations between the other species. The sediment trap calibrations for *G. ruber* and *G. sacculifer* are in agreement with literature data where dissolution effects can be excluded.

[43] The Mg/Ca temperature estimates can be used for reconstructing temperatures of near surface (using *G. ruber* pink), mixed layer (using *G. ruber* white and *G. sacculifer*) and thermocline temperatures (using *N. dutertrei*, *P. obliquiloculata*, *G. aequilateralis* etc.) at this site. The single calibration equation will be useful especially for extinct species in the paleoceanographic record but the use of species-specific equations will provide more accurate temperature estimates.

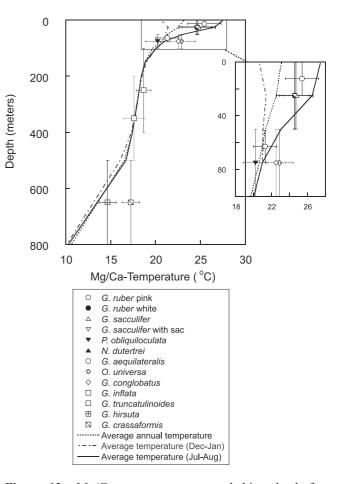


Figure 12. Mg/Ca temperature versus habitat depth for species (Table 2). Mean annual temperature, mean temperatures for December and January (coldest), and mean temperatures for July and August (warmest) are also shown. Mg/Ca temperatures are calculated using ad hoc method after assuming A = 0.090. Error bars are standard deviations of Mg/Ca temperature and depth range for individual species.

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is a contentious issue, and the approach was recommended by *Laws* [1997], we have retained it here and shall consider his criticism elsewhere). We also thank Dorothy Pak and David Lea at UCSB for their advice on use of higher peroxide strength during Mg cleaning. Research funded by a Cambridge Commonwealth Trust Studentship (to P.A.) and grants to H.E. from the Natural Environment Research Council (GR3/1310 and GR3/JIF/05a) and The European Commission (EVR1-CT-40018: CESOP).

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