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An evaluation of controls on planktonic foraminiferal Sr/Ca: Comparison of water column and core-top data from a North Atlantic transect

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[1] Sr/Ca in planktonic foraminifera recovered from the water column over 0–800 m along a meridional transect in the North Atlantic Ocean from 30° to 60°N were compared with data from core-top samples on the same transect and with in situ temperatures determined from water column CTD profiles. Species belonging to the *globorotaliid* genus show significant variability in Sr/Ca from place to place, whereas non-*globorotaliid* species show no significant variability. This variability for the *globorotaliid* species in core-top samples has already been shown to covary with calcification temperature derived from $\delta^{18}O$, but it also covaries with bottom depth (symptomatic of a dissolution artifact). These alternatives are distinguishable from the water column data for which the *globorotaliid* species show a small temperature dependence of 0.025 mmol/mol/°C within the range 5–15°C. However, temperature dependence is not supported by glacial-interglacial differences in Sr/Ca for *globorotaliid* and non-*globorotaliid* species, and at least from this perspective, a $[CO_3^{2-}]$ influence seems more likely.

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1. Introduction

[2] The minor and trace elemental compositions of foraminiferal calcium carbonate have been used as proxies of past ocean chemistry. One current concern is whether or to what extent records of foraminiferal Sr/Ca provide information on past changes in seawater Sr/Ca [*Stoll and Schrag*, 1998; *Martin et al.*, 1999; *Stoll et al.*, 1999; *Elderfield et al.*, 2000, 2002]. A culture study of the planktonic

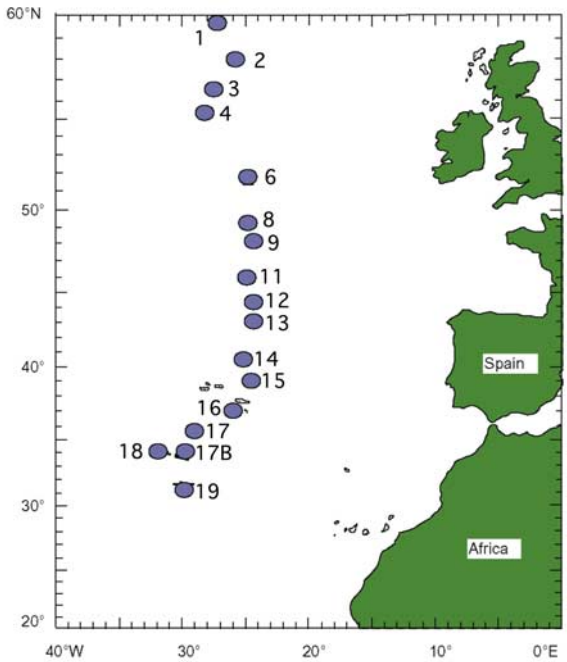

Figure 1. Map showing water column sample stations where planktonic foraminifera were collected for this study. Multinet sampling intervals were the same at each station: 0–50 m, 50–100 m, 100–150 m, 150–200 m, 200–300 m, 300–400 m, 400–550 m, 550–700 m, and 700–800 m. Numbers correspond to sampling stations.

species *Globigerina bulloides* and *Orbulina universa* revealed a ~1% increase in Sr/Ca per °C temperature increase [*Lea et al.*, 1999], unlike the situation for coralline aragonite where Sr/Ca decreases with increasing temperature [*Beck et al.*, 1992]. The weak temperature response for Sr/Ca in planktonic foraminiferal calcite contrasts with a ~10% increase in Mg/Ca per °C shown in core-top, culture, and sediment trap calibrations [e.g., *Nürnberg et al.*, 1996; *Rosenthal et al.*, 1997, 2000; *Hastings et al.*, 1998; *Lea et al.*, 1999; *Mashiotta et al.*, 1999; *Elderfield and Ganssen*, 2000; *Dekens et al.*, 2002; *Anand et al.*, 2003]. It is known that there are kinetic effects on Sr/Ca in abiogenic calcites [*Lorens*, 1981; *Tesoriero and Pankow*, 1996] as has been suggested for higher Sr/Ca ratios in coccolithophores [*Stoll and Schrag*, 2000; *Stoll et al.*, 2002; *Rickaby et al.*, 2002]. Recently, *Elderfield et al.* [2000] examined the relationship of various foraminiferal species to calcification temperature in a suite of North Atlantic sediment core-top samples, and also found positively correlated weak temperature dependence, especially for species belonging to the *globorotaliid* genus. However, Sr/Ca also covaried with bottom depth (similar to earlier work of *Brown and Elderfield* [1996]), suggestive of a depth-dependent dissolution effect on Sr/Ca, and it was impossible to resolve these influences using the core-top approach. In this study, we expand on the work of *Elderfield et al.* [2000] by examining planktonic foraminiferal Sr/Ca from the modern North Atlantic water column at the sites of the core-top study. This approach allows a temperature influence to be explored in an environment unaffected by dissolution. We also compare foraminiferal Sr/Ca data from glacial and interglacial records in order to distinguish a temperature influence from those other oceanographic parameters with which temperature covaries in the modern environment.

2. Materials and Methods

2.1. Sampling

[3] A series of sampling stations between about 31°N and 60°N (Figure 1) was occupied during the April 1988 Actuomicropaleontology Paleoceanography North Atlantic Project (APNAP II) cruise. Mean annual sea surface temperature (SST) ranges from 20°C in the south to 8°C in the north [*Levitus and Boyer*, 1994]. Thus the latitudinal range forms a meridional transect across a wide range of surface ocean thermal environments. At each of these sites, multinet deployments were used to collect water column planktonic foraminifera on a depth-discrete basis from the following intervals: 0–50 m, 50–100 m, 100–150 m, 150–200 m, 200–300 m, 300–400 m, 400–550 m, 550–700 m, and 700–800 m.

2.2. Analyses

[4] Samples were oxidized in a low-temperature asher in order to remove organic matter, and then separated into size fractions [*Ottens*, 1992]. For stable isotopic analysis, species-specific samples consisting of 2–4 individual shells (depending on species, availability, and size) were picked from the 250–500 μm fraction, although a preference for smaller samples within this interval means that the shells were likely between 250–350 μm. Stable isotopic analyses were performed on a Finnigan 251 gas source mass spectrometer equipped with an automated carbonate extraction line (Kiel device), at the Vrije Universiteit Amsterdam. The long-term reproducibility in $\delta^{18}O$ is better than ±0.09‰.

[5] Species-specific samples consisting of ~5–10 individual shells were picked for elemental analysis from the archived 250–350 μm fraction. Prior to cleaning and under microscopic view, the

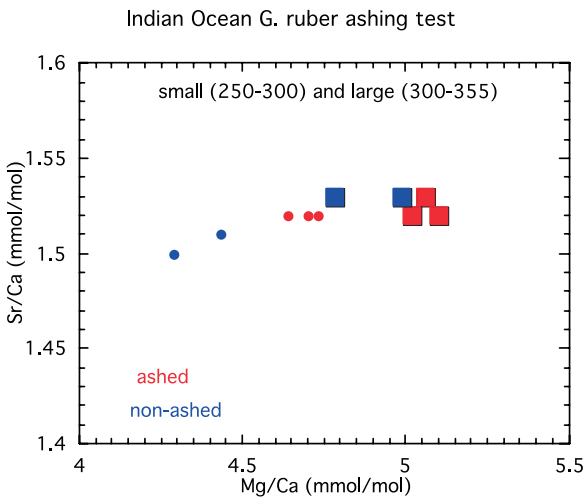

Figure 2. Explicit test of low temperature ashing influence on planktonic foraminiferal trace element composition. Modern Indian Ocean specimens of *G. ruber* were used to compare Mg/Ca and Sr/Ca compositions of ashed (red) and unashed (blue) foraminifera. Small circles correspond to 250–300 μm size fraction, while large squares correspond to 300–355 μm size fraction.

shells were gently crushed between glass plates to ensure that all foraminiferal chambers were opened without pulverizing the sample. The cleaning procedure involved washing with water and methanol to remove clays and other particles, hot alkaline oxidative washing to remove organic matter, and short (30 second) leaching with 0.001M nitric acid to remove adhering metal particles. The samples were then dissolved in 400 μL of 0.075M nitric acid.

[6] Elemental analyses were performed with a Varian Vista AX simultaneous inductively coupled plasma atomic-emission spectrometer (ICP-AES) at the University of Cambridge [*de Villiers et al.*, 2002]. At the time of analysis (July, November, 2000) precision of measured Sr/Ca ratios were <0.5% (1 σ r.s.d.).

[7] Analyses of Mg/Ca were made on these same samples, and show high values [*Mortyn et al.*, 2001] when compared with estimates based on calcification temperatures and published calibrations. One possibility is that the low-temperature ashing treatment of these samples retained refractory Mg-oxides (originally derived from organic matter) that may serve as a contaminant "overprint" to the Mg signal otherwise recorded in the calcite. Because we have never identified significant Sr levels associated with organic matter, and because the results of this study do not show the scatter seen in the Mg data (nor do Mg and Sr correlate), we believe that contamination did not affect the Sr results. An explicit test of the ashing influence on planktonic foraminiferal trace element ratios showed no effect on Sr/Ca (Figure 2).

3. Results and Discussion

3.1. Water Column Versus Core-Top Sr/Ca

[8] The Sr/Ca data (Table 1) show two distinctive features. First, there is a difference between the mean of species belonging to the *globorotaliid* genus and the mean of those species that do not (the non-*globorotaliid* species). Second, Sr/Ca ratios for water column specimens are higher than for specimens recovered from core tops, for both the non-*globorotaliid* species and the *globorotaliids.* This difference is much more pronounced for the *globorotaliids* (mean difference of approximately 0.15 mmol/mol) than for the former (mean difference of approximately 0.04 mmol/mol).

[9] Before considering mechanisms to account for the relatively elevated water column Sr/Ca values, we need to assess whether they reflect different estimated temperatures between the water column

Table 1. Sr/Ca Ratios of Different Planktonic Foraminiferal Species Across Latitudinal Transect

	Mean Sr/Ca (mmol/mol)	± s.d.	n[a]
Water Column			
Non-*globorotaliid* species			
G. bulloides	1.414	0.040	35
G. ruber	1.463	0.018	5
G. sacculifer	1.430	0.008	7
O. universa	1.392	0.004	3
N. pachyderma (d.)	1.448	0.028	6
Mean ± s.d.	1.423 ± 0.038		
globorotaliid species			
G. inflata	1.465	0.059	78
G. hirsuta	1.526	0.083	63
G. truncatulinoides	1.653	0.170	18
Mean ± s.d.	1.511 ± 0.104		
Core-Top			
Non-*globorotaliid* species			
G. bulloides	1.370	0.016	32
G. ruber	1.425	0.017	12
G. sacculifer	1.389	0.019	10
N. pachyderma	1.381	0.015	24
Mean ± s.d.	1.384 ± 0.025		
globorotaliid species			
G. inflata	1.359	0.040	23
G. hirsuta	1.352	0.097	27
G. truncatulinoides	1.385	0.051	16
Mean ± s.d.	1.363 ± 0.071		

[a] n, number of analyses.

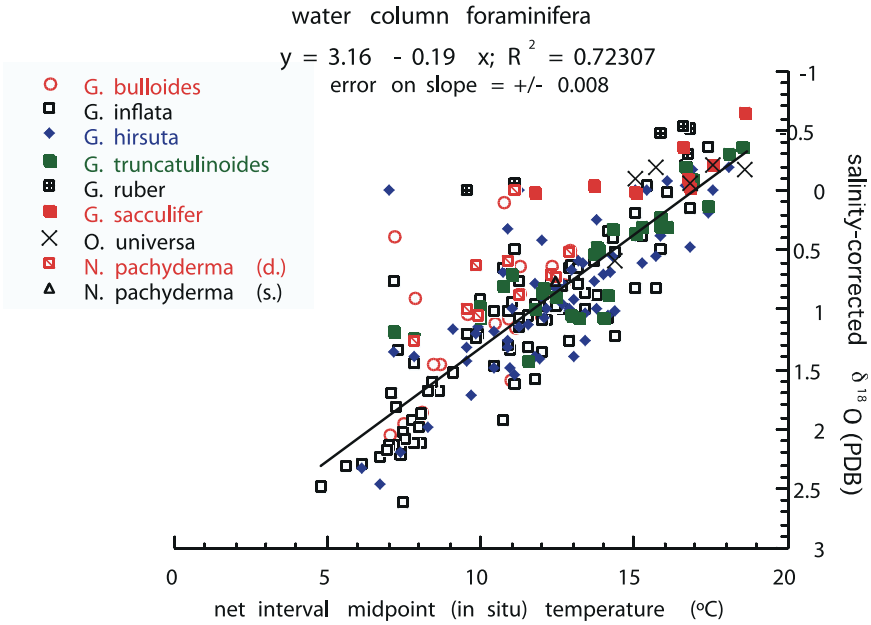

Figure 3. Plot of salinity-corrected (see text for details) foraminiferal $\delta^{18}O$ as a function of in situ temperature in the water column.

and core-top approaches. Examination of the *globorotaliid* data reveals 32 instances where a core-top calcification temperature is warmer than an in situ water column temperature from the same station. Of these, only 6 also show higher core-top Sr/Ca values relative to those from the water column. Furthermore, Sr/Ca values from all water column species are, on average, higher than the species from core tops (Table 1).

[10] We cannot be sure of the reason for the relatively high values for water column foraminifera. One possibility is that enhanced dissolution of the core-top specimens has effectively lowered their Sr/Ca values. Several previous studies have documented the dissolution effect on shell Sr/Ca due to shell heterogeneity and preferential solubility of Mg- and Sr-rich regions of individual tests [*Lohmann*, 1995; *McCorkle et al.*, 1995; *Brown and Elderfield*, 1996; *Rosenthal et al.*, 2000]. However, the similar temperature sensitivity for the *globorotaliid* species seen in water column and core-top samples (see below) would seem surprising had the core-top foraminifera lost Sr through dissolution.

3.2. Temperature Measurements

[11] In order to compare foraminiferal $\delta^{18}O$ and Sr/Ca with in situ environmental data (salinity and temperature), we used conductivity-temperature-depth (CTD) data retrieved on the same cruise at the same sample station locations as for the multinet deployments. Because the vertical sampling resolution of the CTD casts is finer than that for the multinet foraminiferal sampling, we chose salinity and temperature values from the midpoint of each net interval range (i.e., 25 m for the 0–50 m interval, etc.). These are referred to as the in situ salinity and temperature. We considered whether it would be more appropriate to take mean temperatures over the net interval range rather than those from the interval midpoints. The two temperature data sets are highly correlated ($R^2 = 0.999$), so it is virtually irrelevant which one is chosen.

[12] Next, we tested whether the temperatures based on mid-interval in situ water column CTD data match foraminiferal $\delta^{18}O$ values. For example, do foraminifera captured at a deeper net interval, such as 300–400 m, precipitate their calcite shells (and hence record $\delta^{18}O$) at that same depth? Alternatively, do they record $\delta^{18}O$ from a shallower depth and sink to the depth of capture?

[13] Figure 3 shows salinity-corrected foraminiferal $\delta^{18}O$ versus in situ temperature for the foraminifera. The salinity correction involves subtraction from foraminiferal $\delta^{18}O$ of seawater $\delta^{18}O$ estimated from: $\delta^{18}O_{seawater} = -20.265 + 0.57536*\text{salinity}$, which is a local-scale linear relationship for the North Atlantic study area over the full depth range at which foraminifera were captured (G. Ganssen, unpublished data). For completion of this calculation,

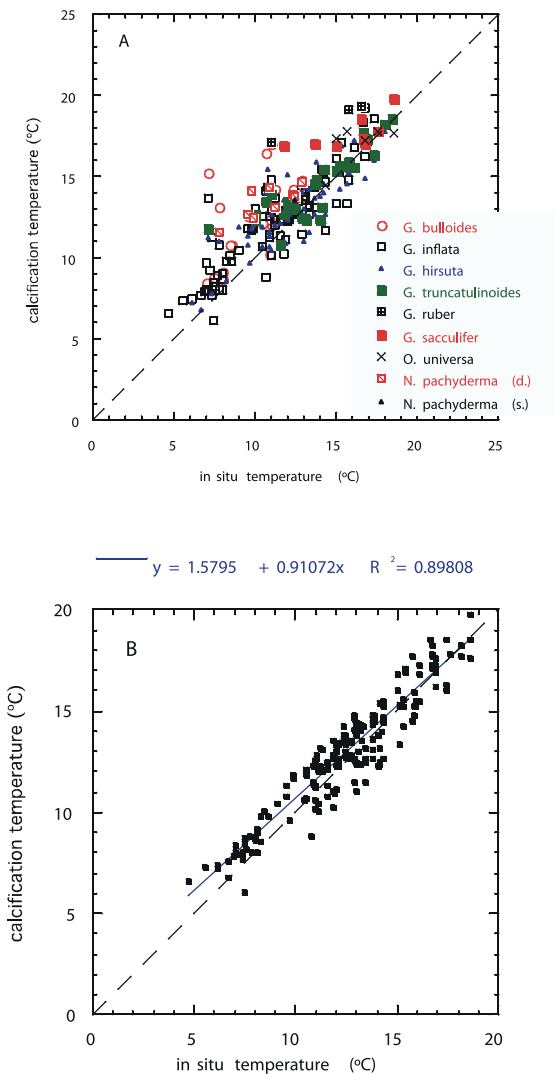

Figure 4. (a) Discrete comparison of calcification temperature (see text for details of calculation) versus in situ temperature for the various foraminiferal species. Dashed line marks the 1:1 relationship. (b) Plot of calcification temperature versus in situ temperature for combined foraminiferal species, although with outlier data points (calcification minus in situ difference >2°C (1 σ)) removed.

$\delta^{18}O$ was converted from standard mean ocean water (SMOW) units to Pee Dee Belemnite (PDB) units with the correction of *Hut* [1987]. There is some scatter about a best-fit line, some of which likely results from the effect of sinking foraminifera mentioned above. In addition, when examined on a species-specific basis, there are slight differences in slope that may highlight the need for species-specific $\delta^{18}O$-temperature calibrations [e.g., *Peeters et al.*, 2002; *Spero et al.*, 2003]. Despite these differences, the best-fit line through all of the data yields a slope close to 0.2‰/°C (with an error of ±0.008), the same as has been observed in most other $\delta^{18}O$-temperature calibrations, as summarized by *Bemis et al.* [1998].

[14] Another valid consideration in our approach is whether it is more appropriate to use calcification temperatures estimated from water column temperature and salinity data. Certainly this would be more consistent with approaches used in core-top and sediment trap studies, where depth-control of water column foraminifera must be estimated this way. Plankton towing, however, affords the opportunity for more discrete sampling of the foraminifera from precise depths. We estimated calcification temperatures using first the $\delta^{18}O_{seawater}$ derived from salinity as described above, followed by conversion to PDB units and temperature calculation using measured $\delta^{18}O_{calcite}$ and the paleotemperature equation of *Shackleton* [1974], the same that was used in the core-top calibrations of both Sr/Ca and Mg/Ca from the same study area (*Elderfield et al.* [2000] and *Elderfield and Ganssen* [2000], respectively). In comparing calcification temperature to in situ temperature we found that while the 2 data sets did fall along a 1:1 line (Figure 4a), there were some definite cases initially suggesting the "foram sinking effect" described above. Though as large as 8°C in extreme cases, the number of outliers was few for a sample set of 234 data points with an overall $R^2 = 0.72$. As the *Shackleton* [1974] work presents a cold water paleotemperature equation calibrated with benthic foraminifera, we also calculated the calcification temperature with a more recent culture calibration for planktonic foraminifera [*Bemis et al.*, 1998] and found a closer 1:1 correspondence with relatively fewer data points that are clearly warmer in calcification temperature relative to in situ temperature. This suggests that much of what may appear as a "foram sinking effect" in Figure 4a is simply due to the *Shackleton* [1974] paleotemperature equation not being the most appropriate. We stick with it, however, for more consistent water column versus core-top comparisons discussed below; future reassessment of this issue may be performed with new calculations using the equation of *Bemis et al.* [1998]. When we exclude the data points beyond one standard deviation (σ) for the calcification minus in situ temperature difference (2°C), the correlation between calcification and in situ temperatures becomes $R^2 = 0.90$ for a sample set of 184 data points (Figure 4b).

Table 2. Anomalous Data Points Removed From Consideration, on the Basis of $\delta^{18}O$ Disequilibrium

Station	Depth, m	Species	Degree of Disequilibrium (‰ PDB)
3	350	*Globorotalia hirsuta*	~2
8	125	*Neogloboquadrina pachyderma (d.)*	~1.5
9	75	*Globorotalia hirsuta*	~1.5
16	75	*Globorotalia hirsuta*	~2
17	25	*Globorotalia hirsuta*	>1
18	750	*Globigerinoides ruber*	~2

[15] Another way to approach the "foram sinking" problem is to construct profiles of the predicted $\delta^{18}O_{calcite}$ values, and compare them to the measured foraminiferal $\delta^{18}O_{calcite}$ values for all sample stations, depths, and species. We performed this analysis and observed that foraminiferal values are generally isotopically depleted compared to predicted values, as observed in other recent water column foraminiferal studies [*Peeters*, 2000; *Mortyn and Charles*, 2003]. From this approach it might be tempting to systematically exclude certain species from certain depths, for example at stations where shallow-dwellers are found at deep depths or deep-dwellers are found at shallow depths. It might also be tempting to group equilibrium or disequilibrium observations according to latitude, as the surface oceanography changes across the transect of our study area. Since we were generally satisfied with the $\delta^{18}O$ results (Figure 3), the calcification temperature versus in situ temperature comparisons (Figure 4), and the consequent similarity between either approach and Sr/Ca data (further discussion below), we chose to exclude only 6 data points by virtue of obvious disequilibrium. These "flyers" are summarized in Table 2 and were excluded from all comparisons in terms of $\delta^{18}O$ or Sr/Ca. The basis for this is that with such large disequilibrium, >2‰ PDB in some cases, these anomalous foraminifera obviously did not calcify near the depths at the stations where they were actually captured. These "flyers" were not only identified on the basis of $\delta^{18}O$ disequilibrium, but also by species being far out of their traditional depth habitat, *Globigerinoides ruber* as deep as 750 m (Station 18) for example. Figure 5 shows one of the disequilibrium profiles, from Station 16, and how selection of an anomalous outlier (*Globoratalia hirsuta* from 75 m) becomes clear on the basis of $\delta^{18}O$ value.

[16] In the end and with the exclusion of the anomalous data points, we chose to retain the in situ temperature method, explicitly taking advantage of the plankton tow approach without resorting to the limitations of the calcification temperature calculation, especially if it is not warranted by the data. Figure 6 shows Sr/Ca data as a function of calcification temperature; as it is similar to the Sr/Ca data with respect to in situ temperature (Figure 7), our decision to stay with the latter is further justified.

3.3. Sr/Ca–Temperature Relationships

[17] In comparing Sr/Ca with temperature, we follow *Elderfield et al.* [2000] in distinguishing *globorotaliid* and non-*globorotaliid* species (Figure 7). The non-*globorotaliids* show no resolvable temperature sensitivity, as with these species in core tops (Figure 8). In contrast, there is significant

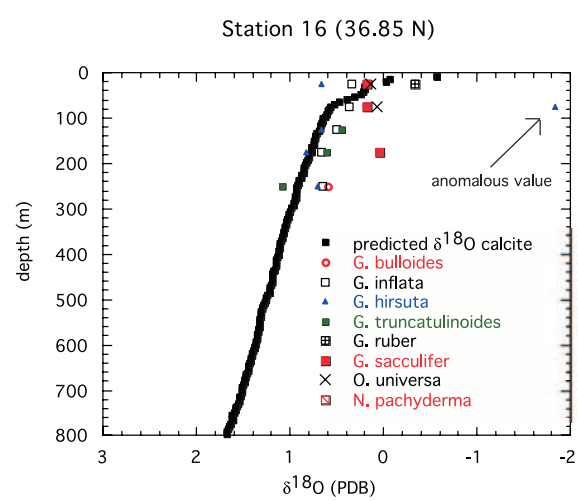

Figure 5. Disequilibrium profile from Station 16. The $\delta^{18}O$ of equilibrium calcite, referred to as "predicted" values, was calculated according to the paleotemperature equation of *Shackleton* [1974]. Salinity from the water column was converted to $\delta^{18}O_{seawater}$ (SMOW) and then to $\delta^{18}O$ (PDB) as described in the text. As with salinity, temperature was derived from the water column CTD data and the predicted $\delta^{18}O_{calcite}$ is shown with depth. For comparison purposes, the various foraminiferal species' $\delta^{18}O$ values, at the depths they were captured, are also shown.

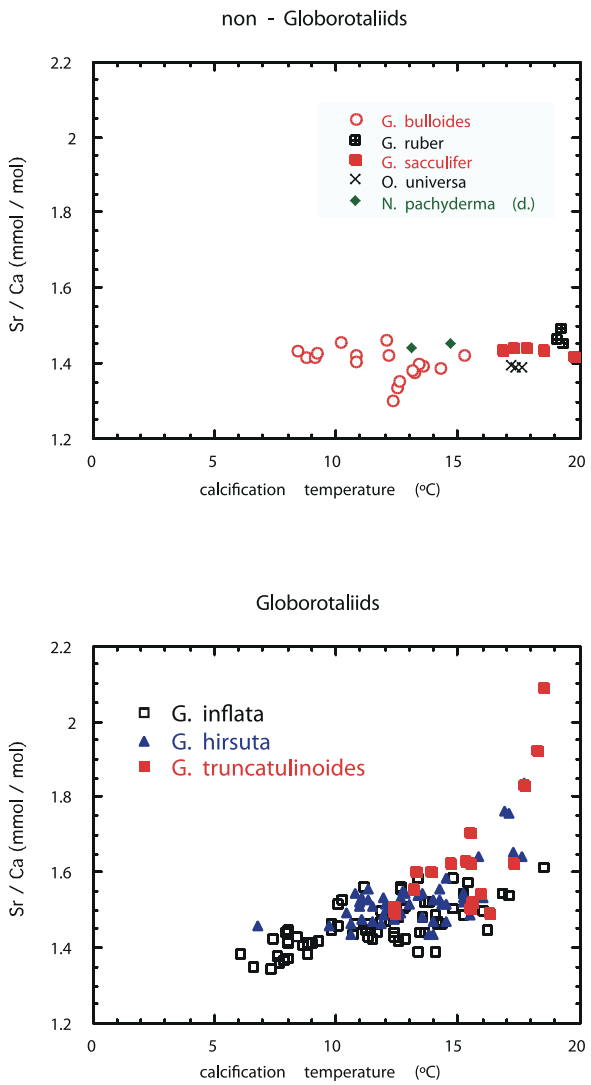

Figure 6. Plots of foraminiferal Sr/Ca as a function of calcification temperature. The top panel shows individual species not belonging to the *globorotaliid* genus, while the bottom panel shows the various *globorotaliid* species.

temperature sensitivity in each of the *globorotaliid* species, *G. inflata, G. hirsuta*, and *G. truncatulinoides*, although with an apparently large break in slope at a temperature near 15°C.

[18] The *globorotaliids* and non-*globorotaliids* do not appear to have different Mg/Ca behavior in the core-top calibration study of *Elderfield and Ganssen* [2000] from the same study area. We therefore look to other explanations instead to explain the difference between these groups. It could be that differences in shell construction are key. *Globorotaliids* are typically thicker in their calcite structures than the non-*globorotaliids*. Alternatively, perhaps depth-habitat is crucial, such that shallower dwellers occupy a habitat where so many variables (besides temperature) change, masking what is more simply deciphered as temperature-sensitivity in deeper waters. One approach currently being undertaken to understand the *globorotaliid* difference is to assess it in other locations (NE Pacific, SE Atlantic), to help determine whether it is of global significance.

[19] The new water column data allows us to distinguish between the effects of temperature and of depth-related dissolution in the core-top data of *Elderfield et al.* [2000]. When the temperature-sensitivity seen in the water column *globorotaliid* samples is compared with the relationship between core-top foraminiferal Sr/Ca and δ^{18}O-derived

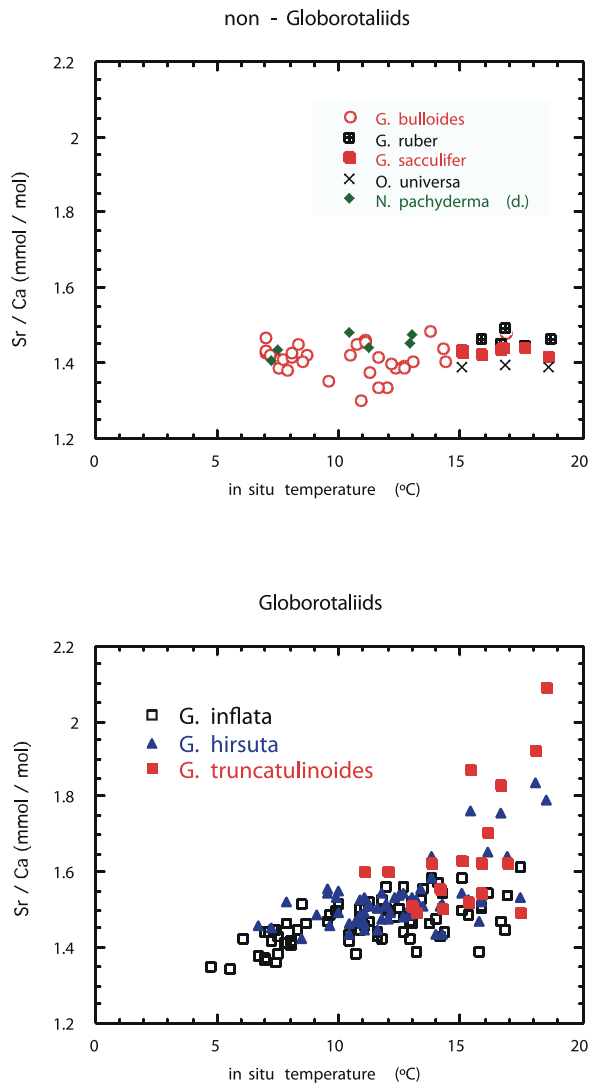

Figure 7. Plots of foraminiferal Sr/Ca as a function of in situ water column temperature. Panel arrangement as in Figure 6.

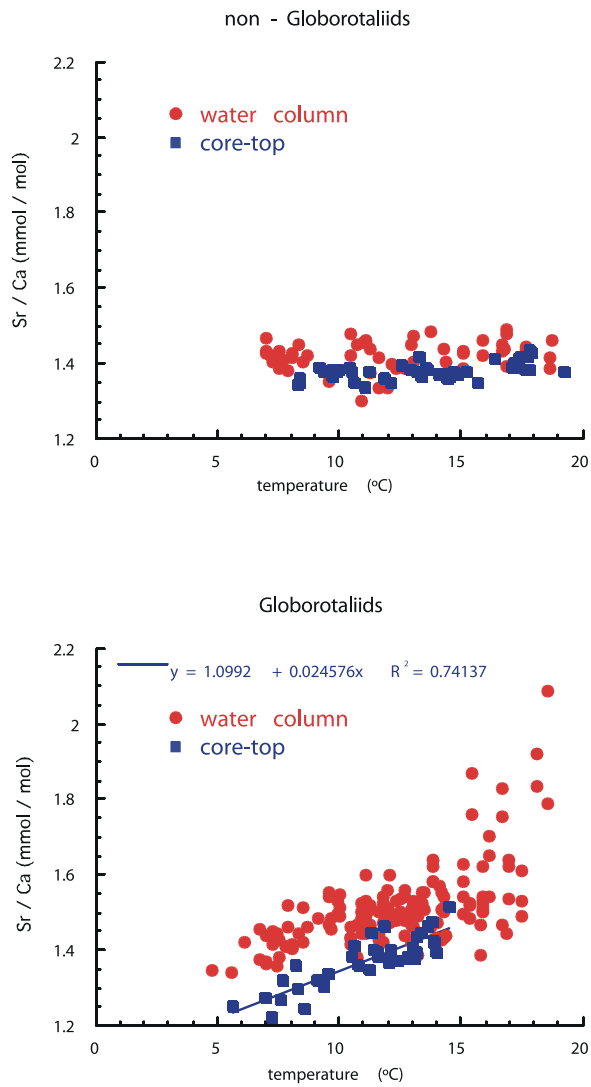

Figure 8. Explicit comparisons of both water column and core-top foraminiferal Sr/Ca as a function of temperature (in situ for the water column, and calcification temperature in the case of the core-tops [*Elderfield et al.*, 2000]). Panel arrangement as in Figures 6 and 7.

calcification temperature for this genus (Figure 8), we see the same temperature sensitivity within the temperature range 5–15°C of 0.025 mmol/mol/°C, despite higher overall Sr/Ca values by up to 0.15 mmol/mol. One possibility is that seasonal changes in temperature or foraminiferal abundance can explain some of this difference. This seems unlikely, however, given the similar slopes for both the water column and core-top foraminifera with respect to temperature. The only way to adequately assess the seasonality issue, however, would be with other water column plankton tow studies during seasons other than spring, when those from the present study were collected.

[20] With the *globorotaliid* water column data of Figure 8, there is an obvious break in slope, or "kink," in the Sr/Ca-temperature relationship at 15°C. One possibility for this is that the temperature sensitivity is not linear as has been assumed by *Lea et al.* [1999]. Alternatively there may be a threshold above which the temperature sensitivity may change, for example as species reach their normal environmental limits. To explore whether the "kink" is merely a visual artifact of the water column data, we also tried fitting an exponential curve and came up with a correlation coefficient of $R^2 = 0.41$, substantially lower than that seen for the linear fit. Given this, and the correspondence between the water column and core-top data, we lean toward an interpretation of linear temperature sensitivity (at least before the $[CO_3^{2-}]$ analysis below) with an apparent upper limit, or threshold value, of 15°C.

3.4. Carbonate Ion and Other Potential Influences

[21] Over the study transect, temperature is highly correlated with other oceanographic variables. For example, temperature is positively correlated with salinity and negatively with phosphate (Figure 9). In the modern Atlantic Ocean surface temperature and carbonate ion concentration, $[CO_3^{2-}]$, also correlate positively [*Barker and Elderfield*, 2002] (Figure 10), and there are several lines of evidence that suggest that $[CO_3^{2-}]$ influences foraminiferal Sr/Ca composition. A $[CO_3^{2-}]$ control on planktonic foraminiferal Sr/Ca was suggested by *Stoll et al.* [1999] and for benthic foraminiferal Sr/Ca by *Elderfield et al.* [1996]. The kinetic effect on Sr/Ca in abiogenic calcites [*Lorens*, 1981; *Tesoriero and Pankow*, 1996] suggests that higher Sr/Ca will be associated with higher growth rates. Studies on coccolithophores [*Stoll and Schrag*, 2000; *Stoll et al.*, 2002; *Rickaby et al.*, 2002] have further suggested a positive correlation between Sr/Ca and calcification rate. It has also been suggested that higher $[CO_3^{2-}]$ might lead to faster foraminiferal shell growth [*Lea et al.*, 1999] and there is clear evidence that higher $[CO_3^{2-}]$ leads to thicker shells [*Barker and Elderfield*, 2002]. Because of the strong positive correlation between temperature and $[CO_3^{2-}]$ it is impossible to distinguish between the two factors from modern regional empirical calibrations.

[22] However, we can use glacial-interglacial records to attempt to distinguish between the two alternatives. If temperature controls Sr/Ca we would expect, all other things being equal, glacial

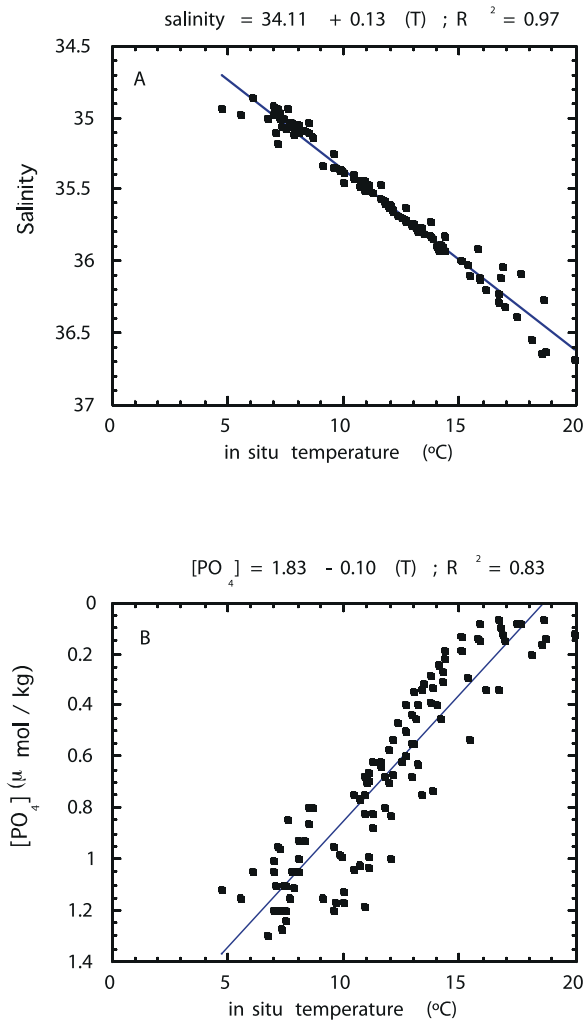

Figure 9. (a) Comparison of salinity versus in situ water column temperature for the study transect. (b) Comparison of $[PO_4]$ versus in situ water column temperature for the study transect.

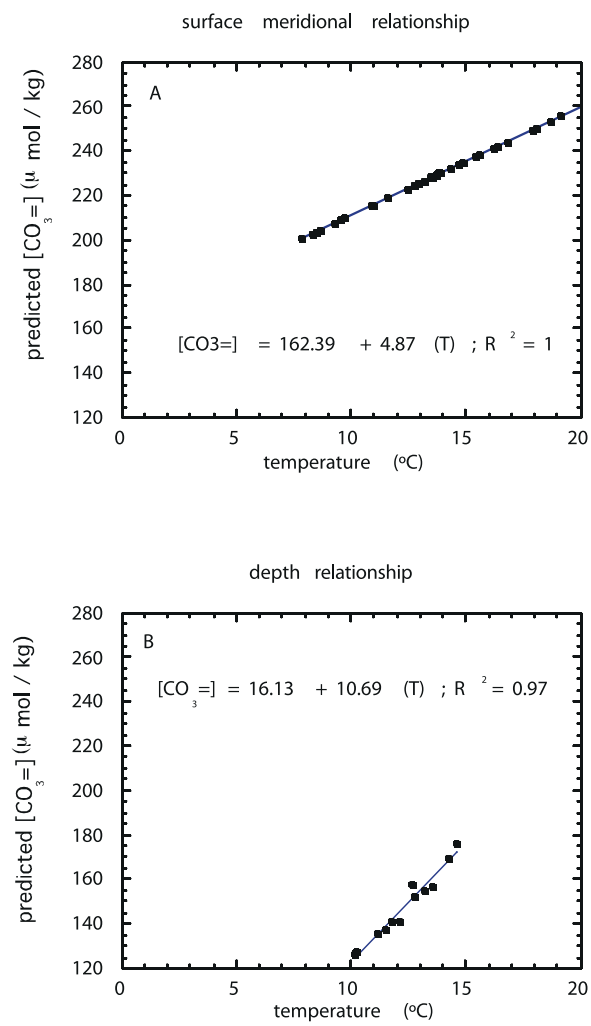

Figure 10. Two different modern comparisons of temperature versus predicted $[CO_3^{2-}]$ using recent World Ocean Circulation Experiment (WOCE) data. Despite differences in both space and time compared to the April 1988 foraminiferal sampling from this study, modern WOCE data were carefully selected to mimic our 1988 sample set as well as possible, considering hydrography, surface circulation, and fit of certain stations to represent our transect as a whole. Figure 10a presents this T versus $[CO_3^{2-}]$ relationship at a depth of 30 m over a latitudinal range of approximately 35°–60°N during the month of May 2003. Figure 10b presents the same relationship using transect A16N, station 49 data (41°N, 20°W; July 2003), between approximate depths of 80–700 m. $[CO_3^{2}]$ was predicted using CO2 SYS software version 1.05. Either with shallow depth across a range of latitudes (Figure 10a) or with variable depth at a given station (Figure 10b), the coupling between modern temperature and $[CO_3^{2-}]$ is strongly linear, suggesting that interpretations of variable Sr/Ca as a function of T may be oversimplistic.

values for the same species to be lower than core-top values, whereas a $[CO_3^{2-}]$ effect should lead to relatively high glacial values.

[23] *Martin et al.* [1999] clearly show *G. bulloides* Sr/Ca to be elevated relative to interglacial values over several climatic cycles. The glacial-interglacial differences in Sr/Ca are very large compared to what might be inferred from temperature sensitivity [*Lea et al.*, 1999] and in the wrong direction. *Elderfield et al.* [2000] show data for several species from the Last Glacial relative to the Holocene. All species also show large variations in Sr/Ca, perhaps larger than would be inferred for a temperature influence on Sr/Ca (Figure 8) and, more importantly, often in the wrong direction. The range in Sr/Ca for the one *globorotaliid* species studied, *G. inflata*, is similar to

those of the other species, *G. ruber*, *G. bulloides*, and *Neogloboquadrina pachyderma*, whereas the pattern for the *globorotaliid* species in the calibrations differs from that of the non-*globorotaliid* species (Figure 8). The Sr/Ca records do not match what might be expected from changes in atmospheric CO_2 (and hence surface water $[CO_3^{2-}]$) in that, except for *N. pachyderma*, Sr/Ca maxima tend to occur during the deglaciation. However, they also do not match what would be expected for changes in temperature. The general feature of the records shown by *Elderfield et al.* [2000] is that Sr/Ca is low at the core-top (modern) and increases with age. Although the records are complex and, without doubt, further investigation is required, this pattern is more consistent with a $[CO_3^{2-}]$ effect than with a temperature effect.

[24] Further insight on this issue comes from the magnitude of glacial-interglacial Sr/Ca change observed in the downcore records of *Elderfield et al.* [2000]. The observed glacial-interglacial variability of Sr/Ca for the 4 planktonic species analyzed is between 0.05–0.10 mmol/mol. By comparison to our modern observations, we see about 0.20 mmol/mol Sr/Ca change for the *globorotaliids* over a temperature range of 5–15°C and below the "kink" described above. Taking the modern slope of 10.7 $[CO_3^{2-}]$ increase for every 1°C increase (Figure 10b), we would expect a contrast of about 107 μmol/kg $[CO_3^{2-}]$ over the 10°C span. As the glacial-interglacial Sr/Ca contrast is about half that of the modern study transect, approximately half the $[CO_3^{2-}]$ contrast can be expected as well, arriving at about 25–50 μmol/kg $[CO_3^{2-}]$ glacial-interglacial variability. Estimates of glacial-interglacial $[CO_3^{2-}]$ contrasts for North Atlantic surface waters estimated from foraminiferal shell weights are about 60 μmol/kg [*Barker and Elderfield*, 2002], in line with changes in atmospheric CO_2, assuming air-sea equilibration.

3.5. Seawater Sr/Ca

[25] Differences in the Sr/Ca composition of seawater are important to rule out if the observation of *globorotaliid* Sr/Ca temperature-sensitivity is to hold up. A study of surface seawater Sr/Ca in the same North Atlantic region [*de Villiers*, 1999] revealed only 0.04 mmol/mol variability over the 30°N–60°N range. By contrast, *globorotaliid* variability in the same region is more than six times larger, about 0.25 mmol/mol, ranging from 1.35–1.6 mmol/mol from 5–15°C (Figure 8). In addition, a North Atlantic depth profile of seawater Sr/Ca from near the northern extreme of our study area (60°N, 20°W) reveals increasing values with depth down to 2500 m (from 8.55 to 8.60 mmol/mol [*de Villiers*, 1999]). This pattern is much like that of a seawater nutrient profile, and thus displays an opposite tendency with temperature (increasing Sr/Ca with decreasing temperature) than our observations. A recent study has been performed in the eastern Indian Ocean with a possible Acantharia-secretion explanation of this effect, at least from more tropical locations [*De Deckker*, 2004]; currently we have no basis for exploring or suggesting a similar mechanism at work in our study area, however. From these combined observations we conclude that seawater Sr/Ca differences, either with latitude or with depth, cannot explain the Sr/Ca variability observed in the water column foraminiferal samples.

4. Conclusions

[26] We have shown that variability in Sr/Ca seen within the *globorotaliid* genus for both water-column and core-top foraminiferal data from a meridional transect in the North Atlantic Ocean is consistent with the same temperature sensitivity of about a 2–3% increase in Sr/Ca per °C. This similar temperature sensitivity is restricted to the range of approximately 5–15°C, and seems to hold despite apparent dissolution-related lowering of about 0.15 mmol/mol Sr/Ca in transit from the water column to the sediment/water interface. Despite this similarity in pattern, temperature sensitivity is not suggested by comparing records of foraminiferal Sr/Ca across glacial-interglacial transitions, and $[CO_3^{2-}]$ influences are implicated instead. Therefore it is somewhat enigmatic that the rather simple picture seen from water-column and core-top studies is not reflected through time.

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References

Anand, P., H. Elderfield, and M. H. Conte (2003), Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series, *Paleoceanography*, *18*(2), 1050, doi:10.1029/2002PA000846.

Barker, S., and H. Elderfield (2002), Foraminiferal calcification response to glacial-interglacial changes in atmospheric CO_2, *Science*, *297*, 833–836.

Beck, J. W., R. L. Edwards, E. Ito, F. W. Taylor, J. Recy, F. Rougerie, P. Joannot, and C. Henin (1992), Sea-surface temperature from coral skeletal strontium/calcium ratios, *Science*, *257*, 644–647.

Bemis, B. E., H. J. Spero, J. Bijma, and D. W. Lea (1998), Reevaluation of the oxygen isotopic composition of planktonic foraminifera: Experimental results and revised paleotemperature equations, *Paleoceanography*, *13*, 150–160.

Brown, S. J., and H. Elderfield (1996), Variations in Mg/Ca and Sr/Ca ratios of planktonic foraminifera caused by post-depositional dissolution: Evidence of shallow Mg-dependent dissolution, *Paleoceanography*, *11*, 543–551.

De Deckker, P. (2004), On the celestite-secreting Acantharia and their effect on seawater strontium to calcium ratios, *Hydrobiologia*, *517*, 1–13.

Dekens, P. S., D. W. Lea, D. K. Pak, and H. J. Spero (2002), Core top calibration of Mg/Ca in tropical foraminifera: Refining paleotemperature estimation, *Geochem. Geophys. Geosyst.*, *3*(4), 1022, doi:10.1029/2001GC000200.

de Villiers, S. (1999), Seawater strontium and Sr/Ca variability in the Atlantic and Pacific Oceans, *Earth Planet. Sci. Lett.*, *171*, 623–634.

de Villiers, S., M. Greaves, and H. Elderfield (2002), An intensity ratio calibration method for the accurate determination of Mg/Ca and Sr/Ca of marine carbonates by ICP-AES, *Geochem. Geophys. Geosyst.*, *3*(1), 1001, doi:10.1029/2001GC000169.

Elderfield, H., and G. Ganssen (2000), Reconstruction of temperature and $\delta^{18}O$ of surface ocean waters using Mg/Ca of planktonic foraminiferal calcite, *Nature*, *405*, 442–445.

Elderfield, H., C. J. Bertram, and J. Erez (1996), A biomineralisation model for the incorporation of trace elements into foraminiferal calcium carbonate, *Earth Planet. Sci. Lett.*, *142*, 409–423.

Elderfield, H., M. Cooper, and G. Ganssen (2000), Sr/Ca in multiple species of planktonic foraminifera: Implications for reconstructions of seawater Sr/Ca, *Geochem. Geophys. Geosyst.*, *1*(11), doi:10.1029/1999GC000031.

Elderfield, H., M. Vautravers, and M. Cooper (2002), The relationship between shell size and Mg/Ca, Sr/Ca, (18O, and $\delta^{13}C$ of species of planktonic foraminifera, *Geochem. Geophys. Geosyst.*, *3*(8), 1052, doi:10.1029/2001GC000194.

Hastings, D. W., A. D. Russell, and S. R. Emerson (1998), Foraminiferal magnesium in Globigerinoides sacculifer as a paleotemperature proxy, *Paleoceanography*, *13*, 161–169.

Hut, G. (1987), Consultants' Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations, Report to the Director General of the International Atomic Energy Agency, 42 pp., Vienna.

Lea, D. W., T. A. Mashiotta, and H. J. Spero (1999), Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing, *Geochim. Cosmochim. Acta*, *63*, 2369–2379.

Levitus, S., and T. R. Boyer (1994), *World Ocean Atlas 1994*, vol. 4, *Temperature*, Natl. Oceanic and Atmos. Admin., Silver Spring, Md.

Lohmann, G. P. (1995), A model for variation in the chemistry of planktonic foraminifera due to secondary calcification and secondary dissolution, *Paleoceanography*, *10*, 445–457.

Lorens, R. B. (1981), Sr, Cd, Mn and Co distribution coefficients in calcite as a function of calcite precipitation rate, *Geochim. Cosmochim. Acta*, *45*, 553–561.

Martin, P. A., D. W. Lea, T. A. Mashiotta, T. Papenfuss, and M. Sarnthein (1999), Variation of foraminiferal Sr/Ca over Quaternary glacial-interglacial cycles: Evidence for changes in mean ocean Sr/Ca?, *Geochem. Geophys. Geosyst.*, *1*(1), doi:10.1029/1999GC000006.

Mashiotta, T. A., D. W. Lea, and H. J. Spero (1999), Glacial-interglacial changes in Subantarctic sea surface temperature and $\delta^{18}O$-water using foraminiferal Mg, *Earth Planet. Sci. Lett.*, *170*, 417–432.

McCorkle, D. C., P. A. Martin, D. W. Lea, and G. P. Klinkhammer (1995), Evidence of a dissolution effect on benthic foraminiferal shell chemistry: $\delta^{13}C$, Cd/Ca, Ba/Ca, and Sr/Ca results from the Ontong Java Plateau, *Paleoceanography*, *10*, 699–714.

Mortyn, P. G., and C. D. Charles (2003), Planktonic foraminiferal depth habitat and $\delta^{18}O$ calibrations: Plankton tow results from the Atlantic sector of the Southern Ocean, *Paleoceanography*,*18*(2), 1037, doi:10.1029/2001PA000637.

Mortyn, P. G., G. M. Ganssen, H. Elderfield, and M. Greaves (2001), Planktonic foraminiferal Mg/Ca ratios from the water column and their implications for paleothermometry, paper presented at European Geophysical Society XXVI General Assembly, Nice, France.

Nürnberg, D., J. Bijma, and C. Hemleben (1996), Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures, *Geochim. Cosmochim. Acta*, *60*, 803–814.

Ottens, J. J. (1992), Planktic foraminifera as indicators of ocean environments in the Northeast Atlantic, Ph.D. dissertation, Vrije Univ. Amsterdam, Amsterdam.

Peeters, F. (2000), The distribution and stable isotope composition of living planktic foraminifera in relation to seasonal changes in the Arabian Sea, Ph.D. dissertation, Vrije Univ. Amsterdam, Amsterdam.

Peeters, F. J. C., G.-J. A. Brummer, and G. Ganssen (2002), The effect of upwelling on the distribution and stable isotope composition of *Globigerina bulloides* and *Globigerinoides ruber* (planktic foraminifera) in modern surface waters of the NW Arabian Sea, *Global Planet. Change*, *34*, 269–291.

Rickaby, R. E. M., D. P. Schrag, I. Zondervan, and U. Riebesell (2002), Growth rate dependence of Sr incorporation during calcification of *Emiliania huxleyi*, *Global Biogeochem. Cycles*, *16*(1), 1006, doi:10.1029/2001GB001408.

Rosenthal, Y., E. A. Boyle, and N. Slowey (1997), Environmental controls on the incorporation of Mg, Sr, F and Cd into benthic foraminifera shells from Little Bahama Bank: Prospects for thermocline paleoceanography, *Geochim. Cosmochim. Acta*, *61*, 3633–3643.

Rosenthal, Y., G. P. Lohmann, K. C. Lohmann, and R. M. Sherrell (2000), Incorporation and preservation of Mg in *Globigerinoides sacculifer*: Implications for reconstructing

the temperature and $^{18}O/^{16}O$ of seawater, *Paleoceanography*, *15*, 135–145.

Shackleton, N. J. (1974), Attainment of isotopic equilibrium between ocean water and the benthonic foraminifera genus Uvigerina: Isotopic changes in the ocean during the last glacial, *Cent. Natl. Rech. Sci. Colloq. Int.*, *219*, 203–209.

Spero, H. J., K. M. Mielke, E. M. Kalve, D. W. Lea, and D. K. Pak (2003), Multispecies approach to reconstructing eastern equatorial Pacific thermocline hydrography during the past 360 kyr, *Paleoceanography*, *18*(1), 1022, doi:10.1029/2002PA000814.

Stoll, H. M., and D. P. Schrag (1998), Effects of Quaternary sea level cycles on strontium in seawater, *Geochim. Cosmochim. Acta*, *62*, 1107–1118.

Stoll, H. M., and D. P. Schrag (2000), Coccolith Sr/Ca as a new indicator of coccolithophorid calcification and growth rate, *Geochem. Geophys. Geosyst.*, *1*(5), doi:10.1029/1999GC000015.

Stoll, H. M., D. P. Schrag, and S. C. Clemens (1999), Are seawater Sr/Ca variations preserved in Quaternary foraminifera?, *Geochim. Cosmochim. Acta*, *63*, 3535–3547.

Stoll, H. M., C. M. Klaas, I. Probert, J. R. Encinar, and J. I. G. Alonso (2002), Calcification rate and temperature effects on Sr partitioning in coccoliths of multiple species of coccolithophorids in culture, *Global Planet. Change*, *34*, 153–171.

Tesoriero, A. J., and J. F. Pankow (1996), Solid solution partitioning of Sr^{2+}, Ba^{2-}, and Cd^{2+} to calcite, *Geochim. Cosmochim. Acta*, *60*, 1053–1063.