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## Mg/Ca and Sr/Ca ratios in planktonic foraminifera: Proxies for upper water column temperature reconstruction

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[1] Reliable temperature estimates from both surface and subsurface ocean waters are needed to reconstruct past upper water column temperature gradients and past oceanic heat content. This work examines the relationships between trace element ratios in fossil shells and seawater temperature for surface-dwelling foraminifera species, *Globigerinoides ruber* (white) and *Globigerina bulloides*, and deep-dwelling species, *Globorotalia inflata*, *Globorotalia truncatulinoides* (dextral and sinistral) and *Pulleniatina obliquiloculata*. Mg/Ca and Sr/Ca ratios in shells picked in 29 modern core tops from the North Atlantic Ocean are calibrated using calculated isotopic temperatures. Mg/Ca ratios on *G. ruber* and *G. bulloides* agree with published data and relationships. For deep-dwelling species, Mg/Ca calibration follows the equation  $\text{Mg/Ca} = 0.78 (\pm 0.04) \times \exp(0.051 (\pm 0.003) \times T)$  with a significant correlation coefficient of  $R^2 = 0.74$ . Moreover, there is no significant difference between the different deep-dwellers analyzed. For the Sr/Ca ratio, the surface dwellers and *P. obliquiloculata* do not record any temperature dependence. For the *Globorotalia* species, the thermo dependence of Sr/Ca ratio can be described by a single linear relationship:  $\text{Sr/Ca} = (0.0182 (\pm 0.001) \times T) + 1.097 (\pm 0.018)$ ,  $R^2 = 0.85$ . Temperature estimates with a 1 sigma error of  $\pm 2.0^\circ\text{C}$  and  $\pm 1.3^\circ\text{C}$  can be derived from the Mg/Ca and Sr/Ca ratios, respectively, as long as the Sr geochemistry in the ocean has been constant through time.

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### 1. Introduction

[2] The determination of past ocean hydrography is a key element to reconstruct Quaternary climatic variations. Most studies focused on past surface water or deepwater conditions by analyzing either surface-dwelling planktonic or benthic organisms. Little paleoceanographic research has been carried out on temperature variations in the upper hundred meters of the water column, where energy storage and heat transport occur. Over this water depth range, deep-dwelling planktonic foraminifera have already been recognized as past thermocline condition recorders [Fairbanks *et al.*, 1980; Mulitza *et al.*, 1997; Cléroux *et al.*, 2007].

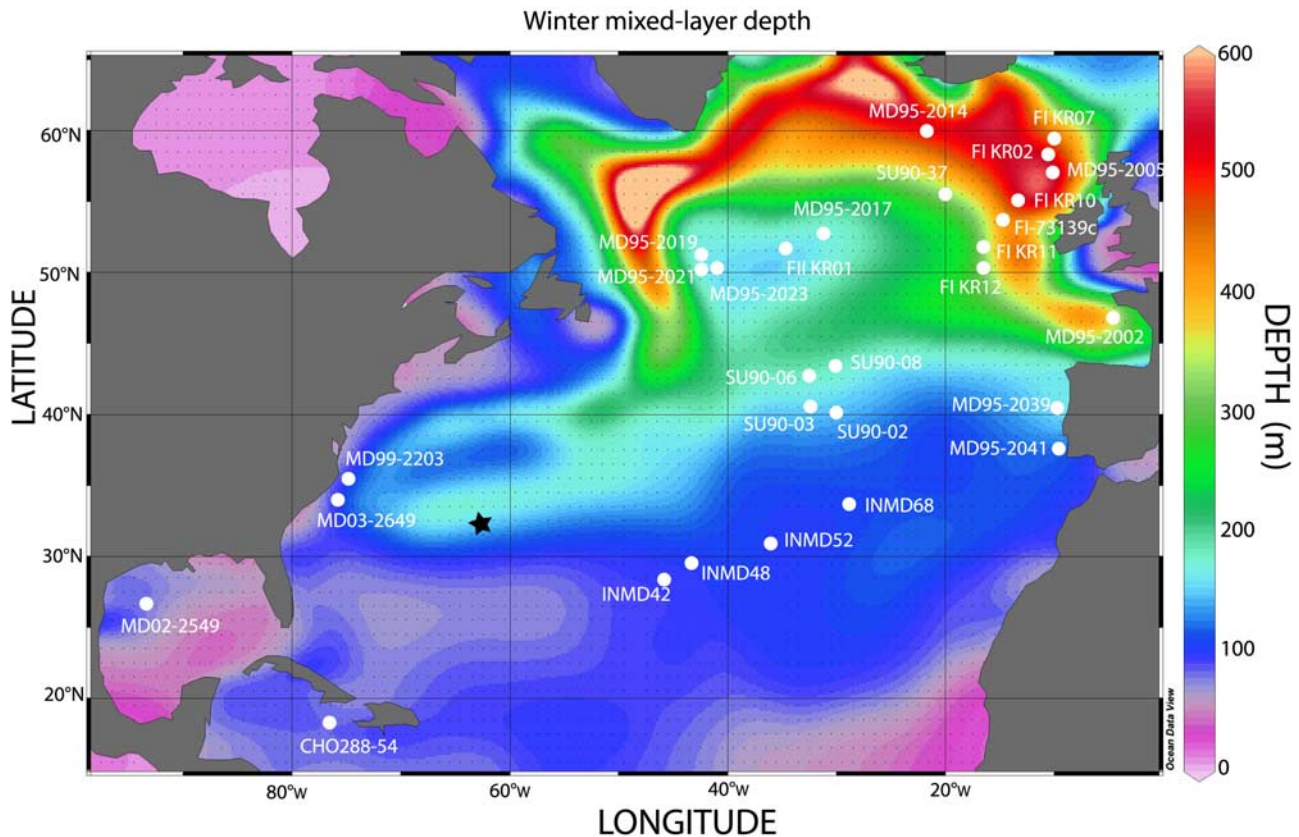
[3] The oxygen isotopic composition of foraminifera ( $\delta^{18}\text{O}_f$ ) depends on the oxygen isotopic composition of seawater ( $\delta^{18}\text{O}_{sw}$ ) and on temperature of calcification.  $\delta^{18}\text{O}_{sw}$  is, for modern samples, locally defined as a function of salinity both been affected by evaporation and precipitation, among others hydrological effects. On longer time-scales (e.g., glacial-interglacial),  $\delta^{18}\text{O}_{sw}$  also depends on

global changes in ice volume. An independent estimate of seawater temperature is necessary to derive past  $\delta^{18}\text{O}_{sw}$  from foraminifera  $\delta^{18}\text{O}_f$ . This is the method developed by Duplessy *et al.* [1991] to estimate past surface water salinities using sea surface temperatures estimated with transfer functions from foraminifera-specific distribution and  $\delta^{18}\text{O}_f$ . Temperatures derived from these transfer functions are based on the relative distribution of several species, each of them with its own ecology (seasonality, depth of habitat). Other approaches to estimate paleotemperature from coccolithophores [Chapman *et al.*, 1996] or diatoms [Koç Karpuz and Schrader, 1990] exist but in all these techniques, the links between of shell growth conditions in all these techniques and  $\delta^{18}\text{O}_f$  for an individual species are indirect. To alleviate this problem, past seawater temperature can be reconstructed using trace element content in calcite as a proxy. Trace element ratios and  $\delta^{18}\text{O}_f$  are measured on the same sample of foraminifera shells.

[4] Inorganic precipitation experiments indicate that Mg/Ca ratios of calcite increase with increasing temperature [Oomori *et al.*, 1987]. Several studies have shown that the Mg/Ca ratio in foraminiferal calcite also increases with temperature but faster, with apparent biological mediation [Nürnberg *et al.*, 1996; Elderfield and Ganssen, 2000; Lea *et al.*, 2000]. Additional studies have also found relationships between temperature and various elemental ratios such as Sr/Ca in bivalves [Freitas *et al.*, 2006], coccolithophores [Stoll *et al.*, 2002], abiotic calcite [Malone and Barker,

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**Figure 1.** Map showing winter mixed layer depth [Monterey and Levitus, 1997] over the area covered by (white circles) our samples. Black star represents the location of the sediment trap studied by Anand *et al.* [2003].

1999] and foraminifera [Elderfield *et al.*, 2000; Lea *et al.*, 1999].

[5] Trace element incorporation in foraminiferal calcite does not occur at thermodynamic equilibrium, and includes apparent species-specific effects [Elderfield and Ganssen, 2000; Rosenthal *et al.*, 2000]. The increase of Mg/Ca or Sr/Ca ratios with temperature must, therefore, be determined for each foraminiferal species.

[6] Both oxygen isotopes and trace element compositions were measured on the same foraminiferal sample so that temperature control on both proxies are the same. Trace element compositions of samples are then calibrated versus their isotopic temperatures (Tiso). The aim of this study is to establish such relationships for *Globigerinoides ruber*, *Globigerina bulloides*, *Globorotalia inflata*, *Globorotalia truncatulinoides* and *Pulleniatina obliquiloculata* on the basis of the analyses of a set of core tops from the North Atlantic Ocean.

## 2. Materials and Methods

### 2.1. Samples

[7] We analyzed 29 core tops that cover areas under various hydrographic regimes in the North Atlantic: from well-stratified low-latitude waters to areas with a deep mixed layer in the high latitudes (Figure 1). All the cores,

except for the 4 cores centered around 30°N, have an expanded Holocene section (70 cm to 4 m). This minimizes the influence of upward bioturbation (upward mixing) of older foraminiferal shells (from the early Holocene or deglaciation). Late Holocene ages are ensured by radiometric datations, foraminiferal counts or isotopic stratigraphy as define in MARGO [Kucera *et al.*, 2005] (Table 1).

[8] Mg/Ca, Sr/Ca and  $\delta^{18}\text{O}$  measurements were performed on the deep-dwelling species *G. inflata*, *G. truncatulinoides* and *P. obliquiloculata* and on the surface-dwelling species *G. ruber* and *G. bulloides*. We separated results obtained on *G. truncatulinoides* right and left coiling since genetic evidence indicates that they are different species [de Vargas *et al.*, 2001]. Measurements on *G. ruber* and *G. bulloides* make it possible to compare our data to existing calibrations [Elderfield and Ganssen, 2000; Anand *et al.*, 2003].

[9] Foraminifera were picked in the same size fraction for paired oxygen isotopic and trace elemental measurements to minimize sample heterogeneity. *G. ruber* and *G. bulloides* were picked from the 250–315  $\mu\text{m}$  size fraction, about 10 and 20–30 specimens were used for  $\delta^{18}\text{O}$  and trace element ratio measurements, respectively. We selected deep-dwelling specimens in the 355–400  $\mu\text{m}$  size fraction,  $\delta^{18}\text{O}$  and trace element measurements were made on about 3 to 12 shells, respectively. Trace elemental measurements

**Table 1.** Core Top Locations and Stratigraphic Control<sup>a</sup>

| Core Top                 | Latitude (°N) | Longitude (°W) | Depth (m) | Age Control MARGO <sup>b</sup> | References <sup>b</sup>   |
|--------------------------|---------------|----------------|-----------|--------------------------------|---|
| CHO 288 54               | 17.25°        | 77.39°         | 1020      | 1                              | <i>Kucera et al.</i> [2005]   |
| MD 02–2549               | 26.25°        | 92.33°         | 2049      | 4                              | E. Michel (LSCE, unpublished data, 2002)  |
| INMD 42BX-8 <sup>c</sup> | 28.34°        | 46.21°         | 3774      | 3 and 4                        | <i>Kucera et al.</i> [2005] and J. Duprat (personal communication, 2007)              |
| INMD 48BX-1 <sup>c</sup> | 29.48°        | 43.13°         | 2836      | 3 and 4                        | <i>Kucera et al.</i> [2005] and J. Duprat (personal communication, 2007)              |
| INMD 52 P <sup>c</sup>   | 31.31°        | 37.52°         | 3631      |                                |   |
| MD03–2649                | 33.11°        | 76.15°         | 958       | 4                              | E. Michel (LSCE, unpublished data, 2002)  |
| INMD 68BX-6 <sup>c</sup> | 34.48°        | 28.21°         | 2520      | 3 and 4                        | <i>Kucera et al.</i> [2005] and J. Duprat (personal communication, 2007)              |
| MD99–2203                | 34.58°        | 75.12°         | 620       | 1                              | E. Michel (LSCE, unpublished data, 2002)  |
| MD95 2041                | 37.50°        | 09.30°         | 1123      | 3 and 4                        | J. Duprat (personal communication, 2007) and E. Michel (LSCE, unpublished data, 2002) |
| MD95 2039                | 40.34°        | 10.20°         | 3381      | 3                              | J. Duprat (personal communication, 2007)  |
| SU 9002 P                | 40.34°        | 30.56°         | 2220      | 3                              | J. Duprat (personal communication, 2007)  |
| SU 9003 P                | 40.5°         | 32°            | 2478      | 2 and 3                        | J. Duprat (personal communication, 2007) and E. Michel (LSCE, unpublished data, 2002) |
| SU 9006 P                | 42°           | 32°            | 3510      | 3                              | J. Duprat (personal communication, 2007)  |
| SU 9008 P                | 43.5°         | 30.35°         | 3080      | 3 and 4                        | J. Duprat (personal communication, 2007) and E. Michel (LSCE, unpublished data, 2002) |
| MD95 2002                | 47.27°        | 08.32°         | 2174      | 3 and 4                        | J. Duprat (personal communication, 2007) and E. Michel (LSCE, unpublished data, 2002) |
| F I KR 12                | 50.15°        | 17.37°         | 4787      | 3 and 4                        | <i>Kucera et al.</i> [2005] and J. Duprat (personal communication, 2007)              |
| MD95 2021                | 50.51°        | 42.44°         | 4283      | 3                              | J. Duprat (personal communication, 2007)  |
| MD95 2023                | 50.58°        | 43.13°         | 4198      | 3                              | J. Duprat (personal communication, 2007)  |
| MD95 2019                | 51.05°        | 43.13°         | 4262      | 3                              | J. Duprat (personal communication, 2007)  |
| F I KR 11                | 51.48°        | 17.68°         | 4654      | 3 and 4                        | <i>Kucera et al.</i> [2005] and J. Duprat (personal communication, 2007)              |
| F II KR 01               | 52.28°        | 35.25°         | 3886      | 3 and 4                        | <i>Kucera et al.</i> [2005] and J. Duprat (personal communication, 2007)              |
| MD95 2017                | 53.02°        | 33.31°         | 3100      | 3                              | J. Duprat (personal communication, 2007)  |
| F I 139 c                | 54.38°        | 16.21°         | 2209      | 1                              | <i>Kucera et al.</i> [2005]   |
| SU 9037 S                | 55.06°        | 20.44°         | 2676      | 3                              | J. Duprat (personal communication, 2007)  |
| F I KR 10                | 55.6°         | 14.48°         | 2216      | 3 and 4                        | <i>Kucera et al.</i> [2005] and J. Duprat (personal communication, 2007)              |
| MD95 2005                | 57.02°        | 10.03°         | 2130      | 3 and 4                        | J. Duprat (personal communication, 2007) and E. Michel (LSCE, unpublished data, 2002) |
| F I KR 02                | 58.08°        | 10.72°         | 2005      | 3                              | J. Duprat (personal communication, 2007)  |
| F I KR 07                | 59.25°        | 10.22°         | 482       | 3                              | J. Duprat (personal communication, 2007)  |
| MD95 2014                | 60.34°        | 22.04°         | 2397      | 3 and 4                        | J. Duprat (personal communication, 2007) and E. Michel (LSCE, unpublished data, 2002) |
| CH69-K09                 | 41.45°        | 47.21°         | 4100      | 1                              | <i>Kucera et al.</i> [2005]   |

<sup>a</sup>MARGO, Multiproxy Approach for the Reconstruction of the Glacial Ocean; LSCE, Laboratoire des Sciences du Climat et de l'Environnement.

<sup>b</sup>Chronostratigraphic quality levels go from 1 to 4 with different levels of uncertainty according to MARGO criteria: number 1 and 2 are for radiometric control within the interval 0–2 ka and 0–4 ka, respectively; number 3 is used for specific stratigraphic control (like percent *Globorotalia hirsuta* left coiling); and number 4 represents other stratigraphic constraints [*Kucera et al.*, 2005].

<sup>c</sup>Cores with no down core stratigraphy.

were made on both the 250–315  $\mu\text{m}$  and 355–400  $\mu\text{m}$  size fractions of *G. inflata*, but as in our previous isotopic analyses [*Cléroux et al.*, 2007], no size effect was observed on trace element ratios and, therefore, both data sets were mixed.

## 2.2. Trace Elemental Analyses

[10] Foraminifera shells for trace element analyses were gently crushed between two glass plates to open the chambers and then cleaned following the procedure of *Barker et al.* [2003]. The major steps of this method are (1) several water and ethanol washings to remove clay, (2) hydrogen peroxide treatment in a boiling water bath to eliminate organic matter and (3) a short (30 s) dilute acid leaching with 0.001 M nitric acid to eliminate any adsorbed contaminants from test fragments. Prior to measurement, samples are dissolved in 350  $\mu\text{l}$  of 0.075 M nitric acid, centrifuged to separate insoluble residues and analyzed with

a Varian Vista Pro AX simultaneous inductively coupled plasma atomic emission spectrometer (ICP-AES) at the Laboratoire des Sciences du Climat et de l'Environnement (LSCE). An intercalibration exercise has shown that our Mg/Ca and Sr/Ca ratios measurements agreed well with other laboratories (C. Caillon et al., unpublished data, 2007). For almost all samples, trace element measurements were replicated and up to 6 replicates were performed when enough material was available (Table S1)<sup>1</sup>.

## 2.3. Natural Contaminants of Foraminifera Trace Element Content

[11] Clay minerals are the major source for contamination in Mg/Ca analyses of foraminiferal calcite [*Barker et al.*,

<sup>1</sup>Auxiliary materials are available in the HTML. doi:10.1029/2007PA001505.

**Table 2.** Depth Where  $\delta^{18}\text{O}_{\text{seawater}}$  Values Were Taken for Each Species and Each Area<sup>a</sup>

| Species  | Location      | Level of the $\delta^{18}\text{O}_{\text{sw}}$ Data Set (m) |
|--|---------------|---|
| <i>G. ruber</i> and <i>G. bulloides</i>          | all           | 0   |
| <i>G. inflata</i> and <i>G. truncatulinoides</i> | north of 35°N | 100   |
| <i>G. inflata</i> and <i>G. truncatulinoides</i> | south of 35°N | 250   |
| <i>P. obliquiloculata</i>                        | all           | 100   |

<sup>a</sup>Data are from the *LeGrande and Schmidt* [2006] data set.

2003]. Following these authors, samples with Fe/Ca or Mn/Ca ratios higher than 0.1 mmol/mol were rejected.

[12] In cores MD95–2023, MD95–2021 and MD95–2019, we measured very high Mg/Ca ratios up to 17 mmol/mol, although microscopic observations of foraminiferal tests in these samples did not differ from other samples. The bulk sediment at the top of core MD95–2023 has been analyzed by X-ray diffraction. Among common components (quartz, calcite, albite and various types of clay minerals), significant amounts of dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ) were detected. Dolomite in this region has already been observed [Andrews et al., 2006] and is assumed to come from the extensive eastern Canada dolomite outcrop. Dolomite could be incorporated in tests either as microparticles during crystallization or by chemical exchange during early diagenesis process. A 1% weight contamination of dolomite in a pure calcite sample increases the overall Mg/Ca ratio by 5.6 mmol/mol, whereas for the same amount of montmorillonite, the increase is only 0.7 mmol/mol. The efficiency of the cleaning procedure to remove dolomite is unknown and no other trace element may be used to detect contamination by this mineral. MD95–2021, MD95–2023 and MD95–2019 are in the same hydrological and sedimentary context (Table 1). The occurrence of dolomite in the bulk sediment of these core tops might explain the high Mg/Ca ratios observed in these cores and so these Mg/Ca measurements were rejected.

#### 2.4. Isotopic Temperature Calculation

[13] Modern hydrographic data indicate that temperature changes in the upper 500 m of the ocean over the area covered by our study can be as large as 15°C. Depth habitat of deep-dwelling species is not precisely known, which makes it impossible to determine the calcification temperature of specimens using modern temperature profiles. Temperature of calcification was therefore calculated with the paleotemperature equation of Shackleton [1974]:

$$\text{Tiso} = 16.9 - 4.38 \times (\delta^{18}\text{O}_{\text{foraminifera}} + 0.27 - \delta^{18}\text{O}_{\text{seawater}}) + 0.1 \times (\delta^{18}\text{O}_{\text{foraminifera}} - \delta^{18}\text{O}_{\text{seawater}})^2$$

This equation does not differ from other paleotemperature equations [Epstein et al., 1953; Kim and O'Neil, 1997] by more than 0.8°C in the range 8–20°C.

[14]  $\delta^{18}\text{O}_{\text{seawater}}$  values were extracted from the data set of *LeGrande and Schmidt* [2006] at each core top location. We assumed that *G. ruber* and *G. bulloides* had calcified their tests in surface waters and used  $\delta^{18}\text{O}_{\text{seawater}}$  values at 0 m.

$\delta^{18}\text{O}_{\text{seawater}}$  is almost constant over the top 500 m in most parts of the Atlantic where the mixed layer is deep (Figure 1), but for deep-dwelling foraminifera, we took  $\delta^{18}\text{O}_{\text{seawater}}$  values at their approximate habitat depths. *Cléroux et al.* [2007] showed that *G. inflata* and *G. truncatulinoides* live preferentially at the base of the summer thermocline which is about 100 m deep north of 35° latitude, but calcify deeper in the main thermocline under warmer conditions. This deeper habitat can be broadly represented by the conditions at 250 m depth south of 35°N. This study also showed that *P. obliquiloculata* lives at the base of the summer thermocline, which is well represented by conditions around 100 m deep in the area where this species is distributed. Table 2 summarizes at which depth the  $\delta^{18}\text{O}_{\text{seawater}}$  was taken from the *LeGrande and Schmidt* [2006] data set for each species and each geographical area.

[15] Previous studies estimated small but contradictory  $\delta^{18}\text{O}_{\text{f}}$  vital effects for deep-dwelling foraminifera, in the range  $0 \pm 0.3\text{‰}$  [Deuser and Ross, 1989; Fairbanks et al., 1980; Ganssen, 1983; Niebler et al., 1999; Wilke et al., 2006]. *G. ruber* and *G. bulloides* are assumed to represent surface water conditions in their optimum environmental regimes without vital effects [Duplessy et al., 1991; Wang et al., 1995]. We therefore assumed constant and negligible vital effects when we calculated isotopic temperatures.

#### 2.5. Error Associated With Measurements and Tiso Calculation

[16] On the basis of the 1424 measurements, the mean instrumental precision on the Mg/Ca ratio for a standard solution of Mg/Ca = 5.238 mmol/mol is  $\pm 0.026$  mmol/mol ( $1\sigma$ ) or RSD = 0.50%. For the Sr/Ca ratio, instrumental precision is  $\pm 0.014$  ( $1\sigma$ ), RSD = 0.76% for a standard solution of Sr/Ca = 1.897 mmol/mol. The standard deviation of replicates is a more appropriate measure of the analytical error associated with the Mg and the Sr content within a natural sample. Individual replicates that exceed the mean sample value  $\pm 3\sigma$  are rejected. Then the average value and the standard deviation of the sample are recalculated. Taking all deep-dwelling core top planktonic foraminifera measurements, the average external reproducibility of sample split (one sigma standard deviation) is  $\pm 0.108$  mmol/mol (pooled RSD = 8.7%) on Mg/Ca ratios and  $\pm 0.036$  mmol/mol on Sr/Ca (pooled RSD = 1.6%).

[17] The error associated with Tiso, is driven both by uncertainties on  $\delta^{18}\text{O}_{\text{seawater}}$  and on  $\delta^{18}\text{O}_{\text{foraminifera}}$ . Maximal  $\delta^{18}\text{O}_{\text{seawater}}$  change over the first 500 m depth is 0.7‰, in stratified subtropical gyre water, leading to maximal error of  $\pm 1.5^\circ\text{C}$  on the isotopic temperature obtained by using the  $\delta^{18}\text{O}_{\text{seawater}}$  value at 250 m. This error is close to 0 at middle and high latitudes, where the mixed layer depth is deep. Instrumental error on individual  $\delta^{18}\text{O}_{\text{foraminifera}}$  measured by reproducibility of carbonate standards is  $\pm 0.07\text{‰}$ . The mean standard deviation of replicates is  $\pm 0.21\text{‰}$  for deep-dwelling and  $\pm 0.16\text{‰}$  for surface-dwelling planktonic foraminifera. Taking all these uncertainties into account, the maximal error on deep-dwelling foraminifera Tiso is  $\pm 1.7^\circ\text{C}$ . Taking into account a maximum vital effect of 0.3‰ for deep-dwelling foraminifera would introduce a systematic shift of 1.2°C on Tiso.

**Table 3.** Species-Specific Relationships Between Mg/Ca and Tiso<sup>a</sup>

| Species                              | Tiso Range (°C) | Mg/Ca =   | R <sup>2</sup> | Error on Estimated Temperature (°C) |
|--------------------------------------|-----------------|---|----------------|-------------------------------------|
| <i>G. ruber</i>                      | 16.8–28.4       | $0.76 \pm 0.14 e^{(0.070 \pm 0.007 * T_{iso})}$ | 0.93           | 1.3                                 |
| <i>G. bulloides</i>                  | 10.3–17.6       | $0.78 \pm 0.12 e^{(0.082 \pm 0.010 * T_{iso})}$ | 0.87           | 1                                   |
| <i>G. inflata</i>                    | 10.5–17.9       | $0.71 \pm 0.06 e^{(0.056 \pm 0.006 * T_{iso})}$ | 0.72           | 1.4                                 |
| <i>G. truncatulinoides</i> dextral   | 10.8–17         | $0.62 \pm 0.16 e^{(0.074 \pm 0.017 * T_{iso})}$ | 0.65           | 1.4                                 |
| <i>G. truncatulinoides</i> sinistral | 12–17.4         | $0.88 \pm 0.22 e^{(0.045 \pm 0.016 * T_{iso})}$ | 0.44           | 2                                   |
| <i>P. obliquiloculata</i>            | 20–25.2         | $1.02 \pm 0.20 e^{(0.039 \pm 0.008 * T_{iso})}$ | 0.84           | 0.8                                 |

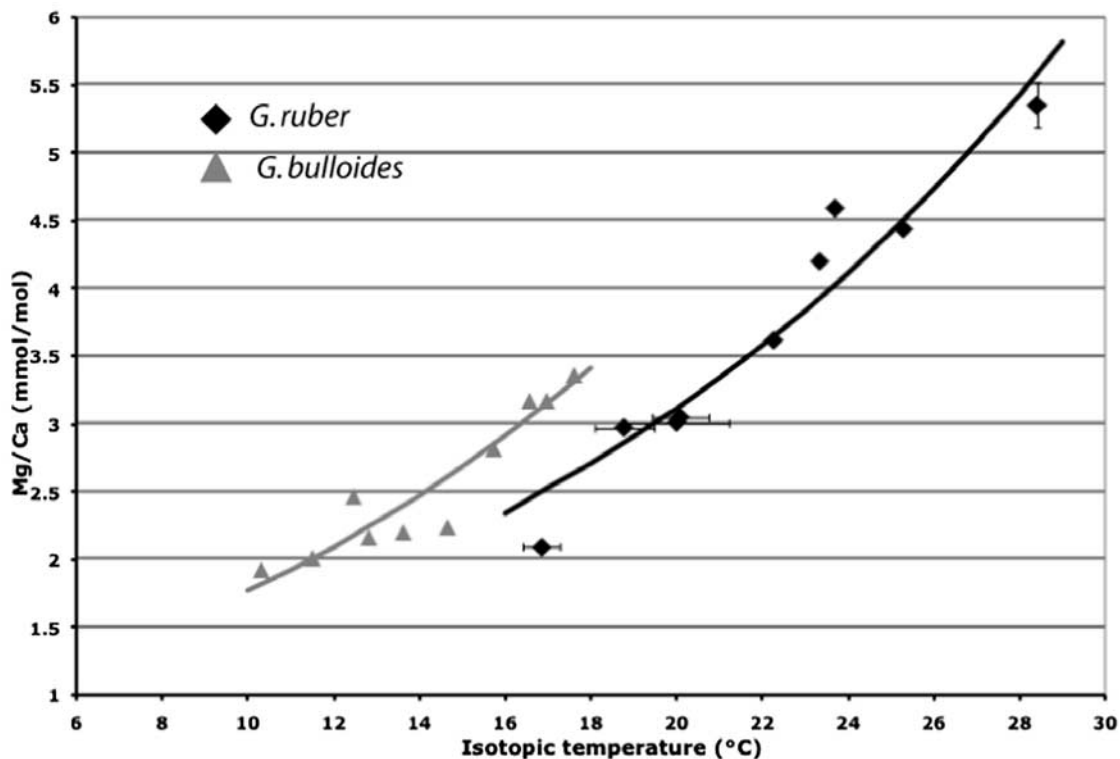
<sup>a</sup>The temperature range covered by the data and the correlation coefficient, calculated from the linear regression between  $\ln(\text{Mg/Ca})$  and Tiso, for each calibration are indicated. The last column gives the error associated with the temperature reconstruction. It is defined as the 1 sigma error on the difference between temperature calculated from the different equation and Tiso used for the regression. Tiso, isotopic temperature.

## 2.6. Regression Calculation

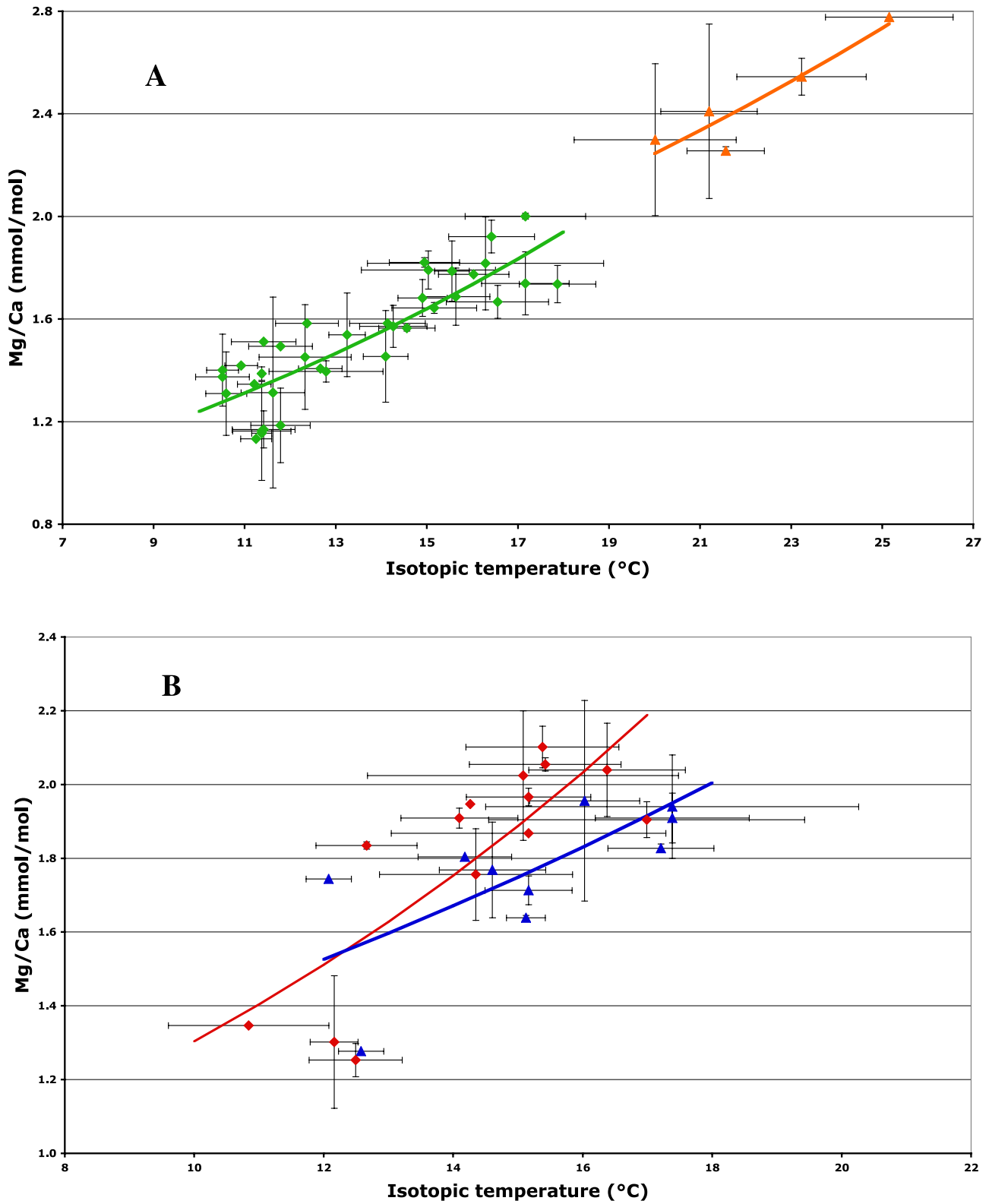
[18] Thermodynamics indicate that the Mg/Ca ratio depends exponentially on the calcification temperature (T). Thus, we used a regression equation of the form:  $\text{Mg/Ca} = B \exp(A \times T)$  to calculate our foraminifera Mg/Ca ratio dependency on calcification temperature. The exponential constant A reflects the temperature sensitivity, and several studies on surface-dwelling planktonic foraminifera species have concluded that this constant is close to 0.090 [Dekens et al., 2002; Lea et al., 2000; Nürnberg et al., 2000]. Therefore one way to build species-dependent calibrations is to keep the term A fixed to 0.09 and adapt the B factor [Elderfield and Ganssen, 2000; Anand et al., 2003]. We did not adopt this approach because there is some

evidence that deep-dwelling foraminifera may have an A constant significantly different from 0.090. Anand et al. [2003] showed that there could be a difference between spinose and nonspinose foraminifera Mg/Ca and T relationship. Thus, neither the A nor the B constants of our calibration equations were fixed initially, and they were calculated using a least square regression method.

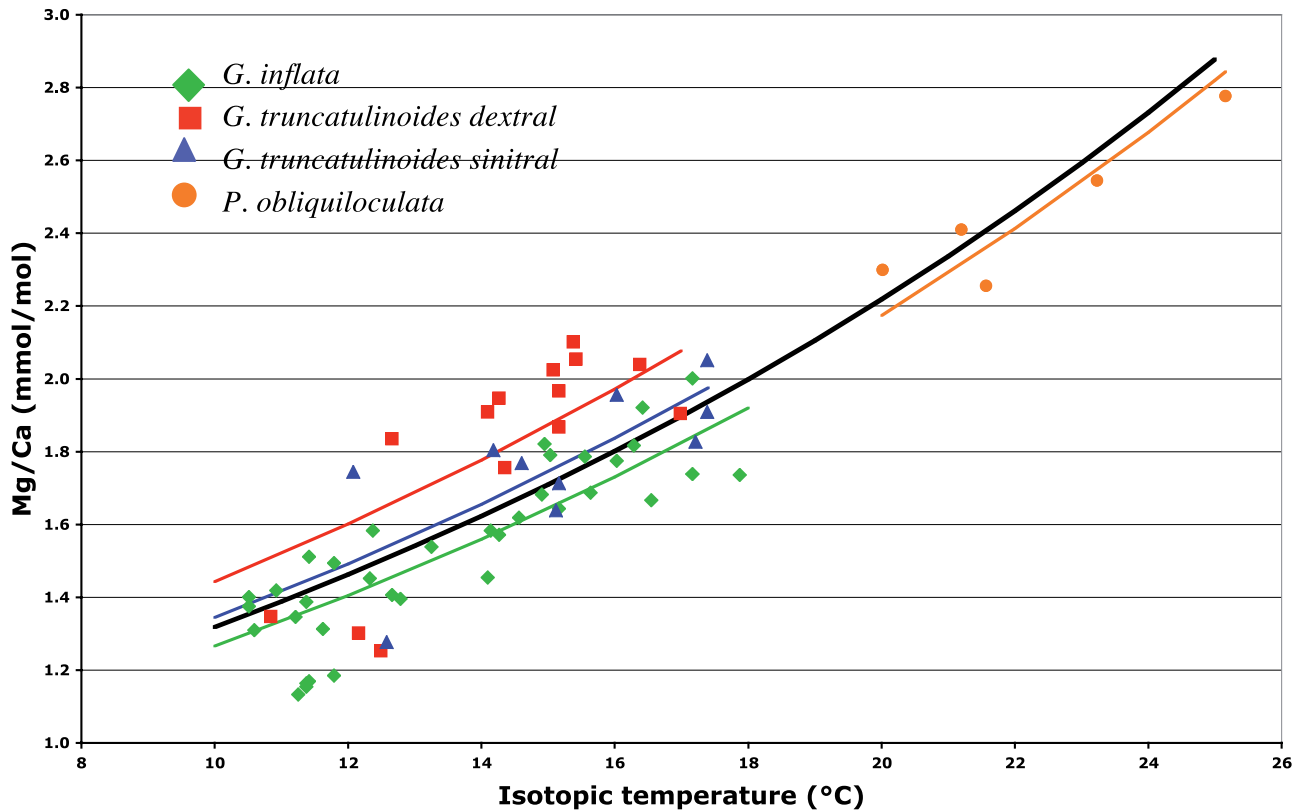
[19] Unlike Mg, no thermodynamic relationship between Sr/Ca ratio and temperature is available since SrCO<sub>3</sub> does not form a solid solution with calcite [Astilleros et al., 2002]. As generally done in studies carried out on Sr paleothermometry [Elderfield et al., 2000], we calculated linear Sr/Ca calibrations using the least squares regression method,  $\text{Sr/Ca} = B + A \times T$ .



**Figure 2.** Mg/Ca ratio versus isotopic temperature (Tiso) for *G. ruber* and *G. bulloides*. One sigma error bar is shown on Tiso and Mg/Ca ratio calculated from replicates.



**Figure 3.** Mg/Ca ratio versus T<sub>iso</sub> for (a) (green) *G. inflata* and (orange) *P. obliquiloculata* and (b) (red) *G. truncatulinoides* dextral and (blue) *G. truncatulinoides* sinistral. Error bars show the 1 sigma error on T<sub>iso</sub> and Mg/Ca ratio calculated from replicates.



**Figure 4.** Mg/Ca ratios versus Tiso for all deep-dwelling planktonic foraminiferal species. The black curve is the exponential regression for all data. Colored curves are the species-specific regressions with the exponential constant (A) fixed at 0.052.

[20] Regressions between trace elemental abundances and Tiso were calculated on mean replicates of both analyses for each sample.

### 3. Results

#### 3.1. Mg/Ca and Temperature Calibrations

[21] The Mg/Ca ratio shows well defined changes with Tiso for all species studied (Table 3, Table S1). The regressions for *G. bulloides* and *G. ruber* have high correlation coefficients of 0.87 and 0.93, respectively (Figure 2). However, they are built on few measurements and are used here only for comparison with previous works (see discussion). Calibrations for *G. inflata*, *G. truncatulinoides* dextral and *G. truncatulinoides* sinistral have lower correlation coefficients of 0.72, 0.65 and 0.44, respectively (Figure 3, Table 3). In the Atlantic Ocean, the occurrence of *P. obliquiloculata* is limited to the warm part of the North Atlantic Drift. The correlation coefficient for this species is high (0.84) but only based on five core top measurements (Figure 3).

[22] We plotted all deep-dwelling foraminifera Mg/Ca measurements on the same figure (Figure 4). By mixing these data, the regression between Mg/Ca and Tiso gives the following equation:

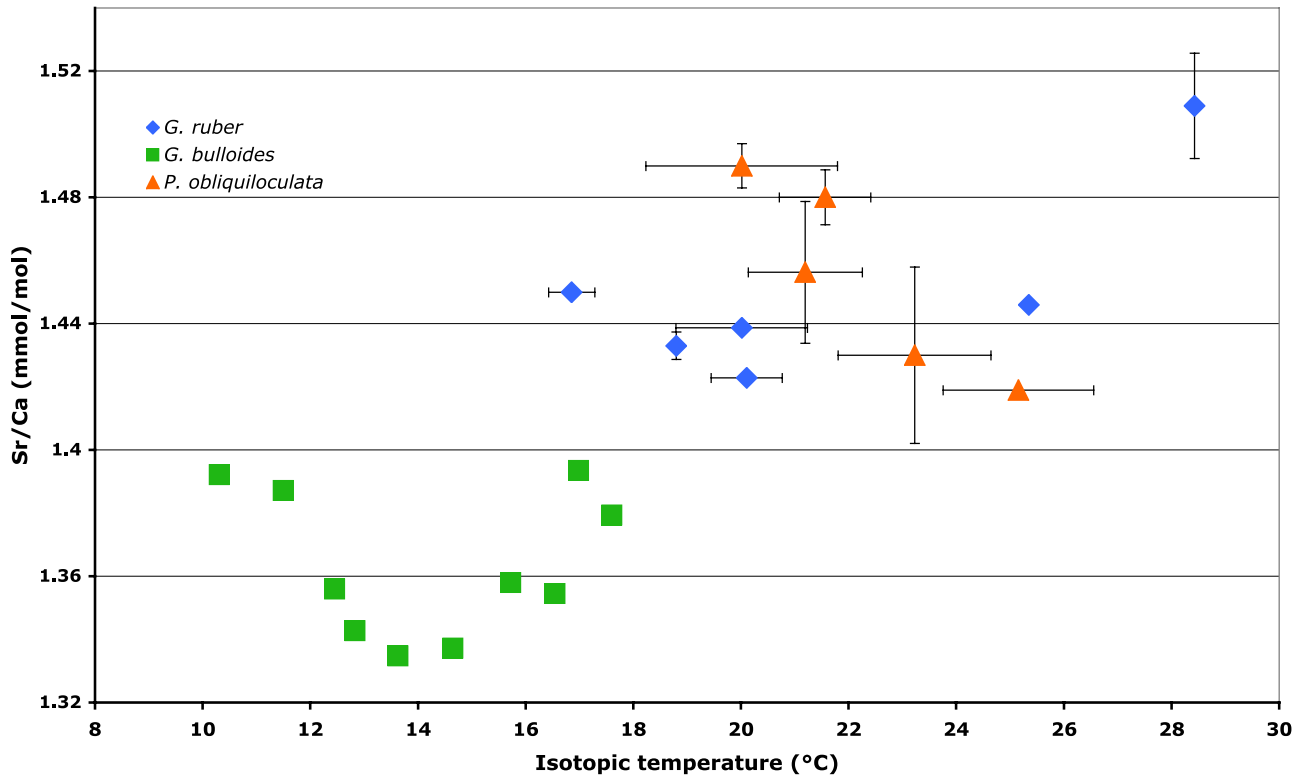
$$\begin{aligned} \text{Mg/Ca} &= 0.78(\pm 0.04) \times \exp(0.052(\pm 0.003) \times T) \\ R^2 &= 0.75. \end{aligned} \quad (1)$$

[23] Separate regressions, done with the same exponential coefficient, but taking different B constants for each species, are not significantly different, taking into account the data scatter. A comparison of the different equations is given in Table S2.

[24] The standard error of temperature estimates, calculated as the mean residual between temperatures used for the construction of the calibration and temperatures calculated from equation (1), is 2.0°C.

#### 3.2. Sr/Ca and Temperature Calibrations

[25] The Sr/Ca ratio does not present a clear dependence on temperature for *G. ruber*, *G. bulloides* and *P. obliquiloculata* (Figure 5). *G. inflata* and *G. truncatulinoides*, on the other hand, present a well defined linear dependence between calcification temperature and Sr/Ca ratio with a mean slope of 2% per °C (Table 4, Figure 6), as was already observed for the *globorotaliid* genus in a previous core top study [Elderfield et al., 2000]. Mortyn et al. [2005] in plankton tow samples have found a similar slope for *Globorotaliids* between approximately 5 and 15°C, but they record Sr rich values around 18°C. We do not have enough warm samples in our data set to compare our results in this temperature range. For *G. inflata* and *G. truncatulinoides*, correlation coefficients obtained for the Sr/Ca versus temperature relationships are higher than those obtained for the Mg/Ca versus temperature relationships. Standard error of temperature estimates for *G. inflata*, *G. truncatulinoides*



**Figure 5.** Sr/Ca ratios versus Tiso for (blue) *G. ruber*, (green) *G. bulloides* and (orange) *P. obliquiloculata*. Error bars show the 1 sigma error on Tiso and Mg/Ca ratio calculated from replicates. The relationship is not clear for the three species.

dextral and sinistral are 0.9°C, 0.8°C and 1.0°C, respectively.

[26] Putting together Sr/Ca measurements on *G. inflata* and *G. truncatulinoides* (regardless of coiling directions), we can compute a single equation for all of these species (Figure 7):

$$\begin{aligned} Sr/Ca &= 0.0217(\pm 0.001) \times Tiso + 1.052(\pm 0.021)R^2 \\ &= 0.74. \end{aligned} \quad (2)$$

[27] Separate regressions, done with the same slope, but taking different B constants for each species, are not significantly different, taking into account the data scatter. A comparison of the different equations is given in Table S3. Therefore we define only one linear regression equation for these species. The standard error of temperature estimates, calculated as the mean residual between temperature

used for the construction of the calibration and calculated temperature from equation (2), is 1.3°C.

## 4. Discussion

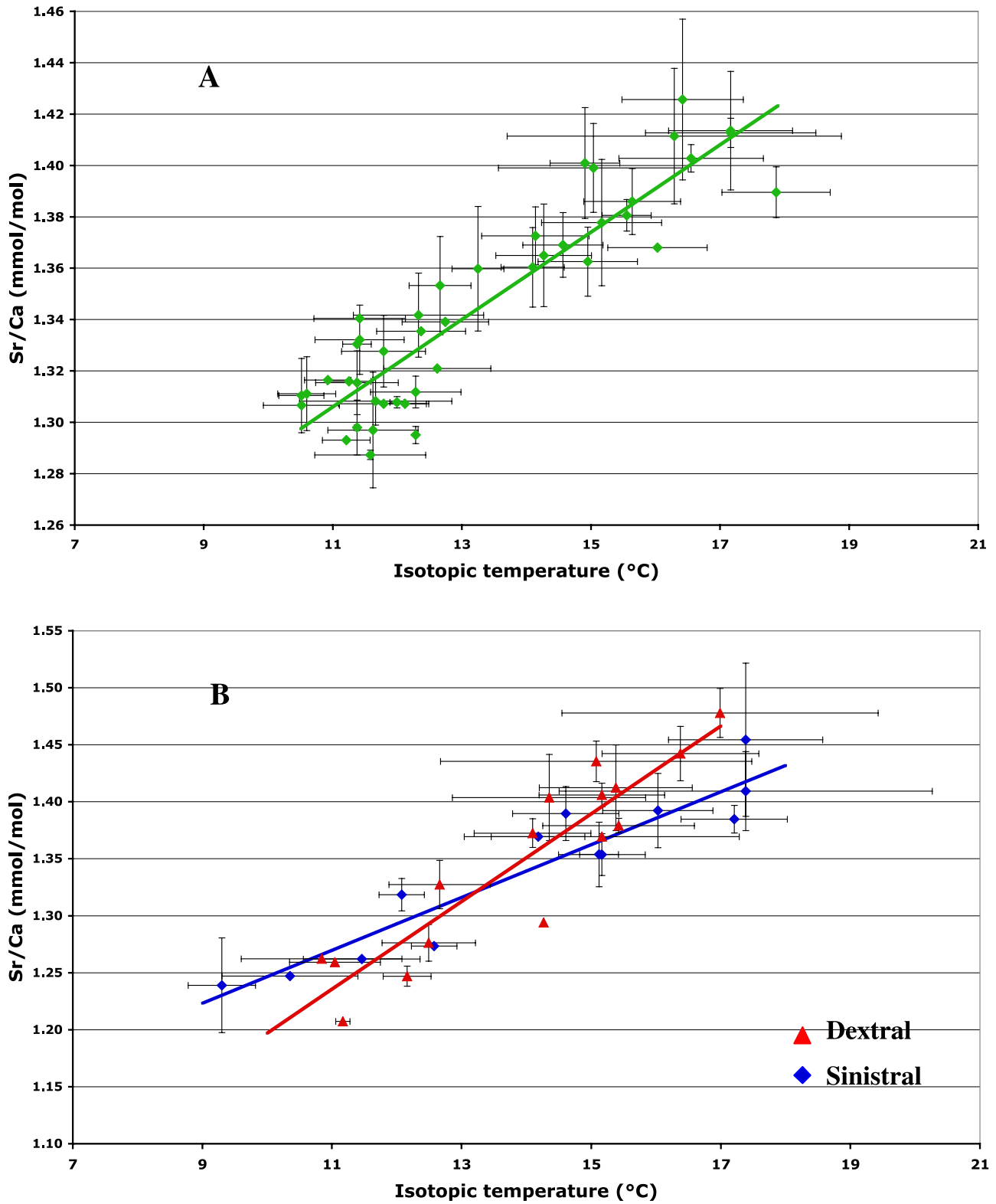
### 4.1. Comparison With Previous Mg/Ca: Temperature Calibrations for *G. ruber* and *G. bulloides*

[28] The Mg/Ca ratio is sensitive to dissolution of foraminifera shells in sediment [Dekens *et al.*, 2002; de Villiers, 2003; Regenberg *et al.*, 2006] and to the cleaning procedure used [Barker *et al.*, 2003]. In addition, there are indications that the calibrations may be specific to individual oceanic basins [McConnell and Thunell, 2005]. We therefore limit the comparison of our data to the calibrations established on North Atlantic samples treated with the same chemical procedure used in this work (Figure 8). Anand *et al.* [2003] published a calibration for *G. ruber* using a 6-year record of bimonthly sediment trap samples from the Sargasso Sea. All our values for this species, except one, are

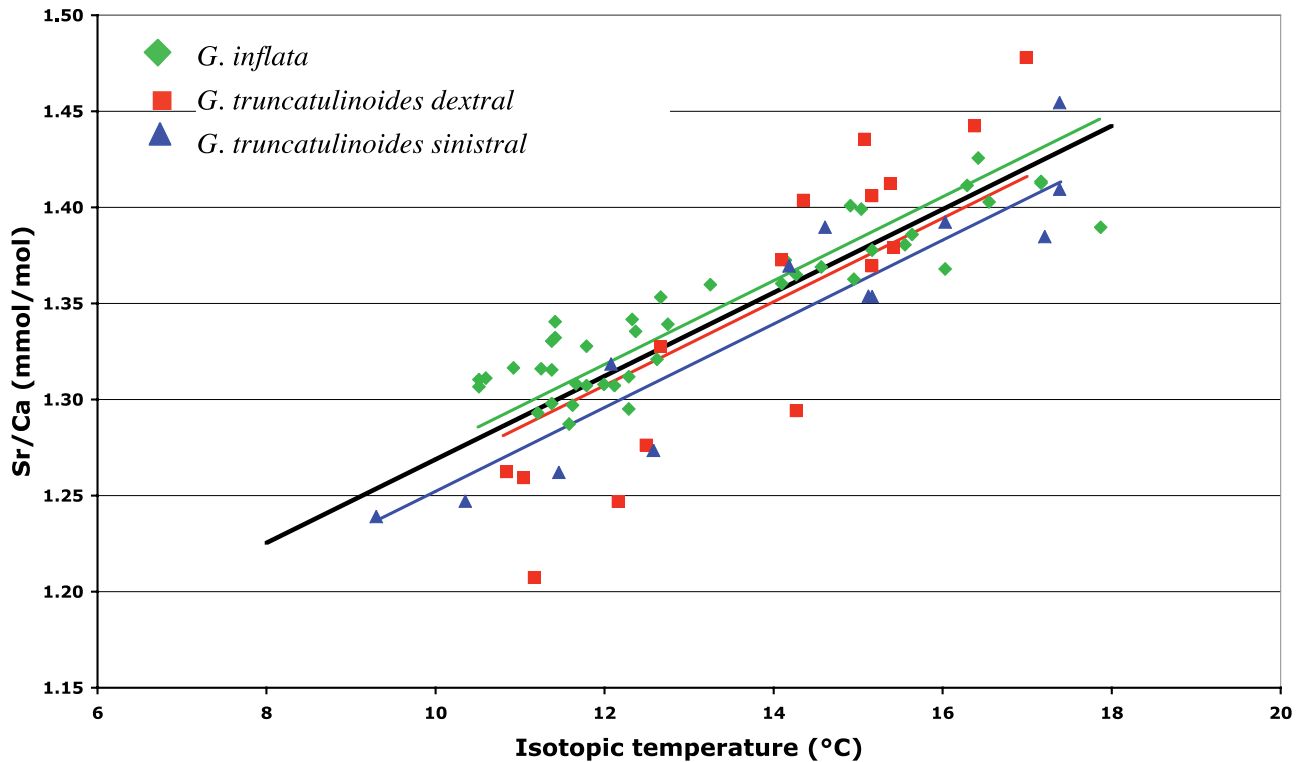
**Table 4.** Species-Specific Relationships Between Sr/Ca and Tiso<sup>a</sup>

| Species                              | Tiso Range (°C) | Sr/Ca =                                       | R <sup>2</sup> | Error on Estimated Temperature (°C) |
|--------------------------------------|-----------------|---|----------------|-------------------------------------|
| <i>G. inflata</i>                    | 10.5–17.9       | Sr/Ca = 0.0170 ± 0.0012 * Tiso + 1.119 ± 0.01 | 0.83           | 0.9                                 |
| <i>G. truncatulinoides</i> dextral   | 10.8–17         | Sr/Ca = 0.0385 ± 0.004 * Tiso + 0.812 ± 0.060 | 0.85           | 0.8                                 |
| <i>G. truncatulinoides</i> sinistral | 9.3–17.4        | Sr/Ca = 0.0232 ± 0.003 * Tiso + 1.014 ± 0.039 | 0.88           | 1.0                                 |

<sup>a</sup>The temperature range covered by the data and the correlation coefficient for each calibration are indicated.



**Figure 6.** Sr/Ca ratios versus T<sub>iso</sub> for (a) *G. inflata* and (b) *G. truncatulinoides* (dextral and sinistral). Error bars show the 1 sigma error on T<sub>iso</sub> and Mg/Ca ratio calculated from replicates.



**Figure 7.** Sr/Ca ratios versus Tiso for *G. inflata* and *G. truncatulinoides* (dextral and sinistral). The black curve is the exponential regression taking all the data together. Colored curves are the species-specific regressions with the slope (constant A) fixed at 0.0217.

within the 2 sigma error of Anand *et al.*'s calibration. Our measurements on *G. bulloides* are more scattered than the North Atlantic core top measurements of Elderfield and Ganssen [2000]. However, both data sets reflect a similar relationship between the Mg/Ca ratio of *G. bulloides* and temperature. Thus, our data sets confirm the calibration equations proposed by Anand *et al.* [2003] and Elderfield and Ganssen [2000] for these two surface-dwelling species.

#### 4.2. Comparison With Previous Mg/Ca and Sr/Ca Temperature Calibrations for Deep-Dwelling Foraminifera Species

[29] In the North Atlantic, the only relationships available between trace element measurements and calcification temperature for *G. inflata*, *G. truncatulinoides* and *P. obliquiloculata*, are those published by Anand *et al.* [2003] (Figure 9) and Elderfield *et al.* [2000]. The second ones were also established on core tops but were built with different analytical method (electron microprobe) and on smaller specimens which prevent accurate comparison. The data sets of Anand *et al.* [2003] for *G. inflata* and *G. truncatulinoides* cover a smaller temperature range (about 16 to 19°C) than our measurements but for the three species both data sets agree reasonably well. The measurements from Anand *et al.* [2003], however, exhibit a small shift toward higher isotopic temperatures or lower Mg/Ca ratios. Shell size is known to affect  $\delta^{18}\text{O}$  and thus isotopic temperature. The small difference between the two data sets may therefore be reasonably attributed to this factor, since Anand *et al.* [2003] analyzed foraminifera picked from a larger size fraction

(350–500  $\mu\text{m}$ ). C. Cleroux (unpublished data, 2005) highlights large differences in  $\delta^{18}\text{O}$  and trace element ratio between large (350–500  $\mu\text{m}$ ) and small (200–300  $\mu\text{m}$ ) *P. obliquiloculata* and *G. truncatulinoides*. Both species show a difference of around  $-0.5\text{‰}$  between the two size fractions. For *P. obliquiloculata*, this difference is about 0.6 mmol/mol on Mg/Ca ratio and 0.04 mmol/mol on Sr/Ca ratio whereas trace element ratios of *G. truncatulinoides* show no systematic differences.

[30] Anand *et al.* [2003] also measured Sr/Ca ratios for *G. inflata* and *G. truncatulinoides* in the Sargasso Sea sediment trap samples. These results compare well with our core top data within the common temperature range (Figure 10).

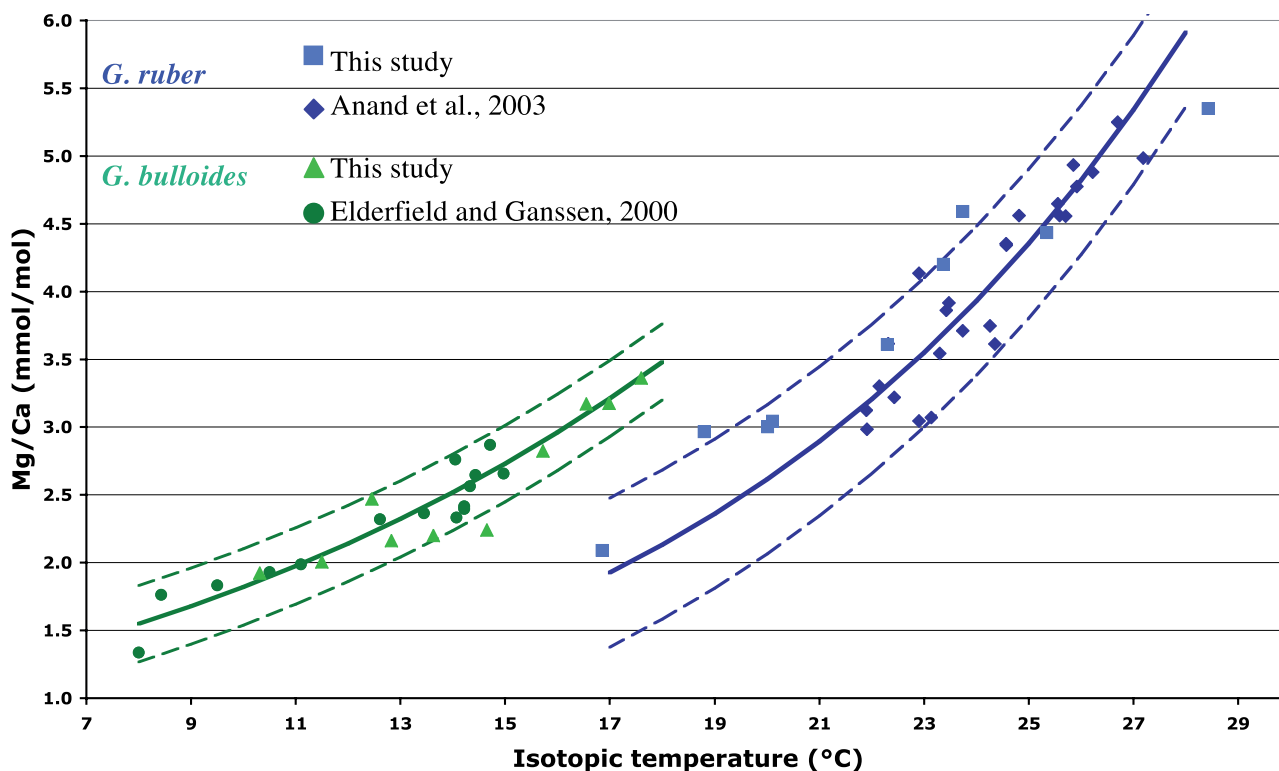
#### 4.3. Factors Influencing Sr/Ca Ratio in Foraminifera

[31] As we have seen, Sr/Ca ratios appear to show a relationship to temperature only for the *Globorotalia* species, at least among the foraminifera that we analyzed.

[32] Several other factors such as carbonate ion concentration, growth rates of foraminiferal calcite, deep water dissolution, or changes in seawater Sr content may also influence the foraminiferal Sr/Ca ratio [Brown and Elderfield, 1996; Elderfield *et al.*, 2000; Erez, 2003; Mortyn *et al.*, 2005].

##### 4.3.1. $\text{CO}_3^{2-}$ Concentration in Seawater

[33] Russell *et al.* [2004] studied the incorporation of trace elements in the shells of the foraminifera species *Orbulina universa* and *G. bulloides* in laboratory culture experiments with different  $\text{CO}_3^{2-}$  concentrations. They found that the Sr/Ca ratio depends only slightly to  $[\text{CO}_3^{2-}]$



**Figure 8.** Comparison of Mg/Ca and Tiso data of *G. ruber* and *G. bulloides* from this study with previous North Atlantic works on the same species. (thick line) Calibration equations and (dashed lines) 2 sigma standard deviation extended on the temperature range of our values of Anand *et al.* [2003] and Elderfield and Ganssen [2000] are also plotted.

(the ratio increases less than 10% over the whole 100 to 500  $\mu\text{mol/kg}$  range for *O. universa*, and appears constant for *G. bulloides*). They did not test other species for this effect. Globorotaliids are subsurface species and they would therefore grow in a depleted  $[\text{CO}_3^{2-}]$  environment compared to surface species. However, for North Atlantic samples like ours, separation of the effect of temperature and  $[\text{CO}_3^{2-}]$  is difficult, as both parameters covary in the upper waters [Broecker and Peng, 1982; Goyet *et al.*, 2000; Mortyn *et al.*, 2005].

#### 4.3.2. Growth Calcification Rates

[34] Calcification rates may play a key role in the incorporation of Sr into calcite [Lorens, 1981; Erez, 2003]. Experimental studies on nonbiogenic calcite show that Sr partitioning increases with increasing calcite growth rate in the range 0.016 nm/s to 1 nm/s [Gabitov and Watson, 2006]. Outside this range, Sr/Ca partitioning appears a function of temperature only. 0.016 nm/s or 1.4  $\mu\text{m/day}$  would be the approximate rate of foraminiferal chamber thickening for surface-dwelling species [Bé *et al.*, 1981; Caron *et al.*, 1987]. Deep-dwelling foraminifera have a longer life cycle than surface-dwelling species [Schiebel and Hemleben, 2005] and possibly a slower calcification rate. Difference in calcification rate between species, in one or other side of this threshold, might therefore explain the different Sr partitioning observed in the different species. Different calcification mechanisms and growth rates might also explain why Sr/Ca ratio seems a more reliable paleother-

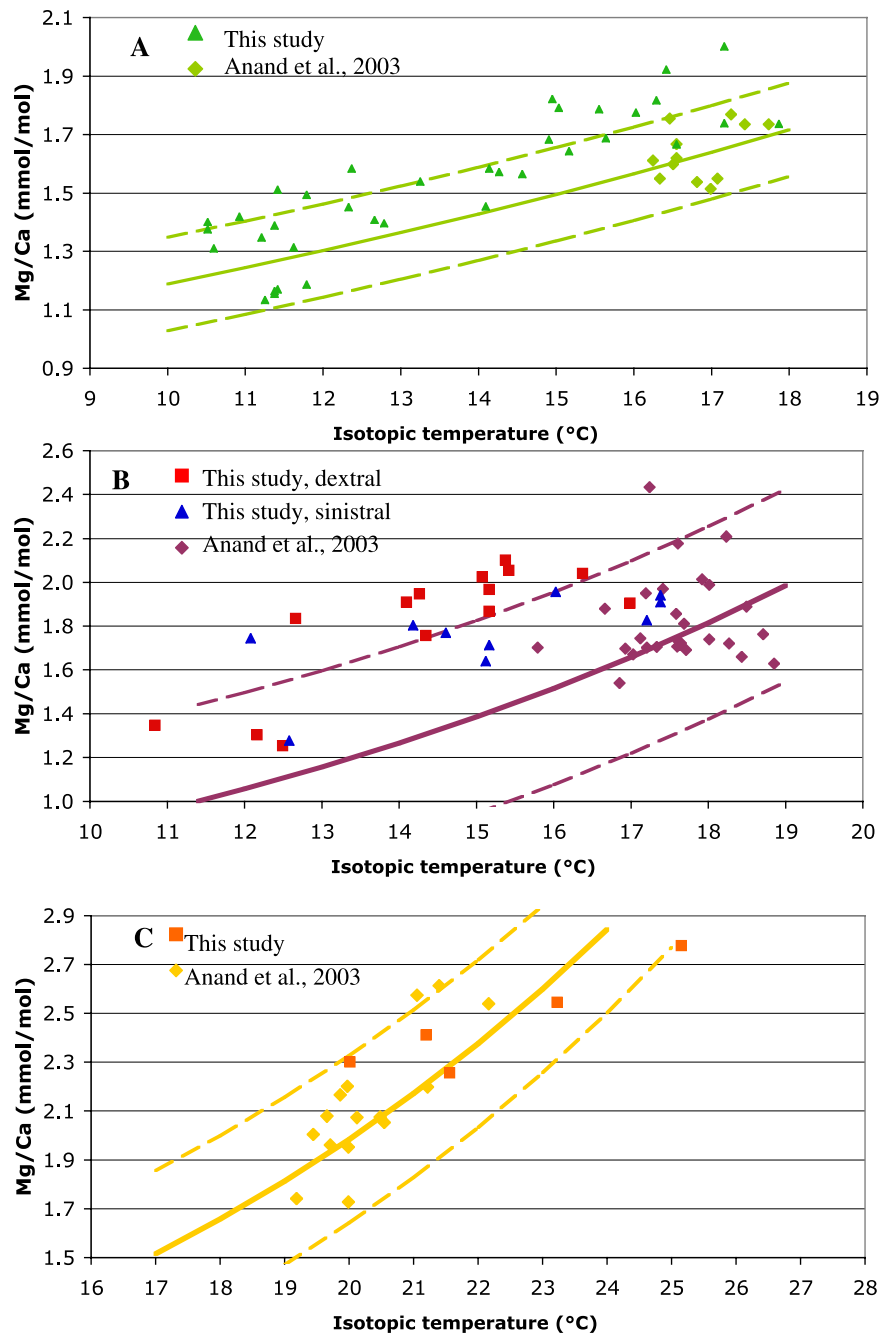
момeter in corals [de Villiers *et al.*, 1994] than in most studied foraminifera species. More studies will however be necessary to check this hypothesis and the applicability of the Gabitov and Watson [2006] relationship with precise measurements of foraminifera shell thickening in relation to Sr partitioning and temperature.

#### 4.3.3. Dissolution With Water Depth

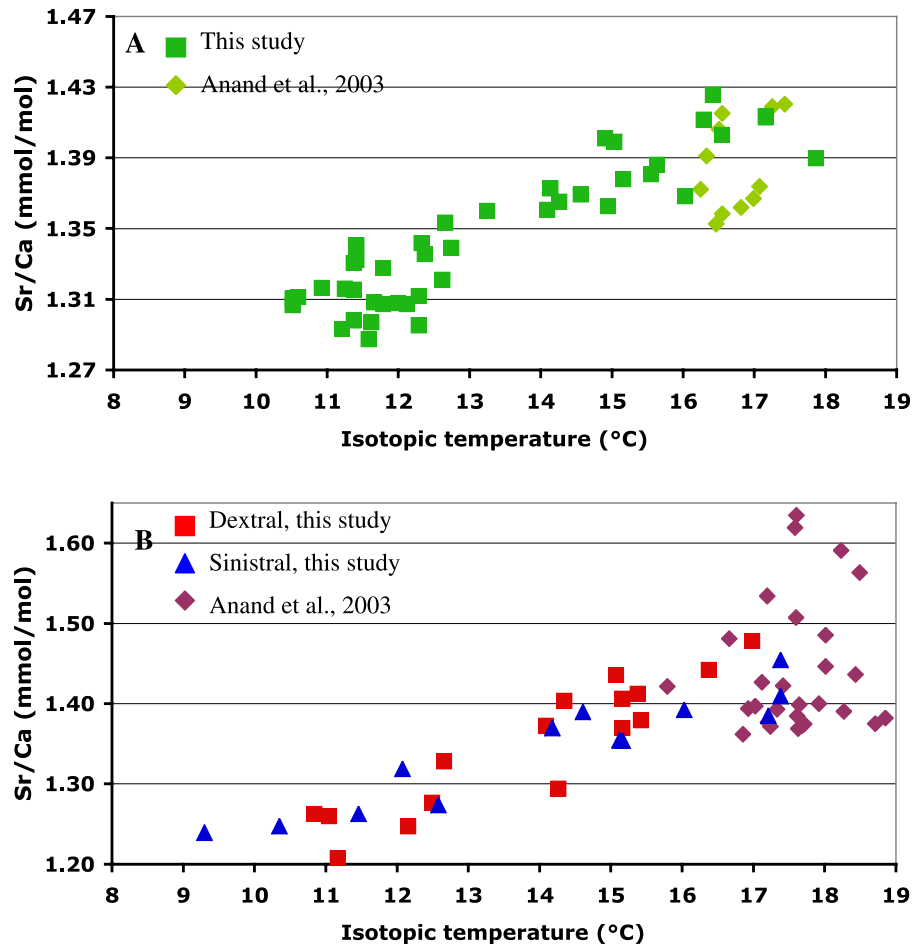
[35] Foraminifera rich in Sr are more sensitive to dissolution [Elderfield *et al.*, 2000]. Mortyn *et al.* [2005] have shown, comparing water column and core top samples, a lowering of this Sr/Ca ratio, by dissolution, of about 0.15 mmol/mol during the water column transit. Yet our data, plotted versus water depth for each sediment core (Figure 11), do not show any trend, except for a possible increase in the case of *P. obliquiloculata*. In addition, the core top Sr/Ca results agree very well with the sediment trap results from Sargasso Sea. Therefore, our Sr/Ca results do not appear to be affected by dissolution.

#### 4.3.4. Variability of Oceanic Sr Content

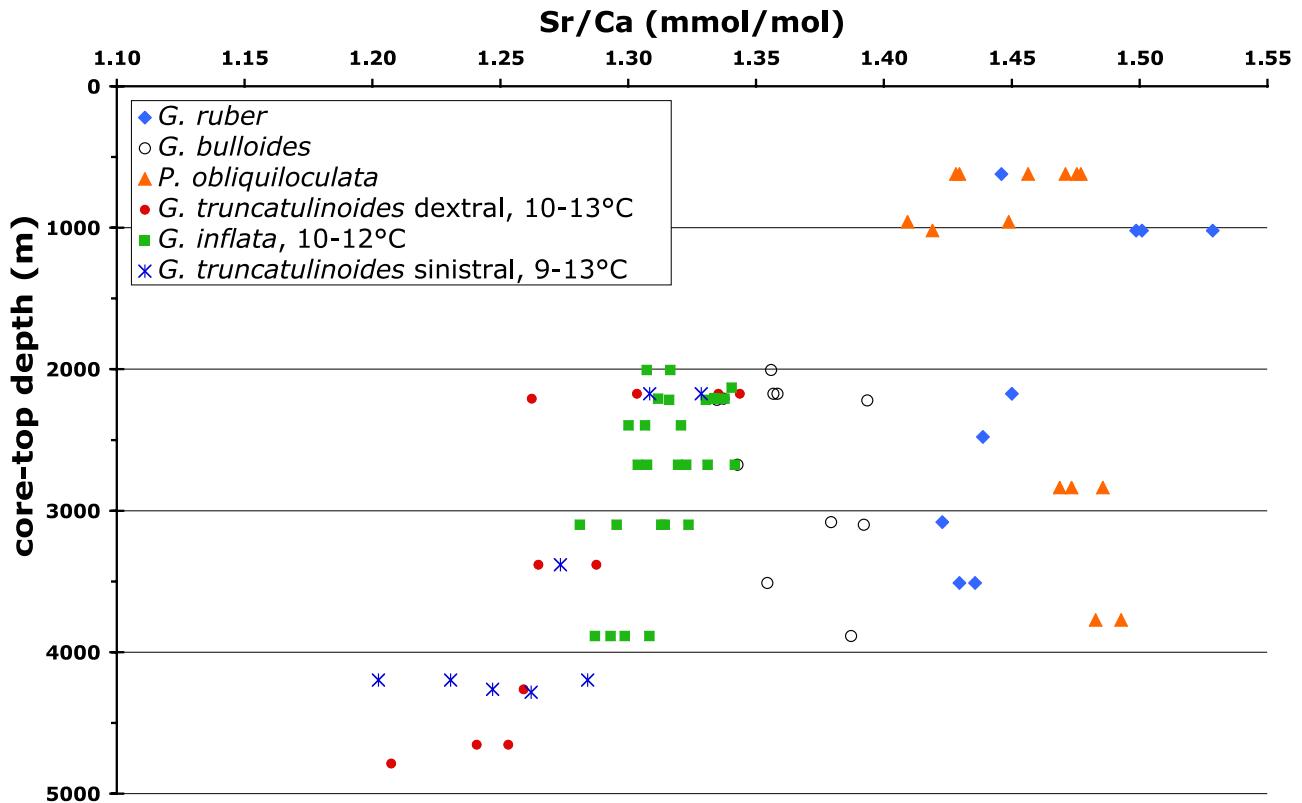
[36] Variability of oceanic Sr concentration should also affect Sr concentration in foraminifera, albeit equally for all species. Two factors have potential impact on the seawater Sr/Ca ratio: celestite production by acantharia in surface waters, and dissolution of carbonate shelves during sea level changes [Elderfield *et al.*, 2000]. The first factor produces a maximum deficit of 2% for the surface seawater Sr/Ca ratio in the North Atlantic [De Deckker, 2004; de Villiers, 1999]. Such an effect would introduce a maximum bias of about



**Figure 9.** Comparison between the calibration study of *Anand et al.* [2003] and Mg/Ca data obtained within the present work on (a) *G. inflata*, (b) *G. truncatulinoides* dextral and sinistral and (c) *P. obliquiloculata*. (thick lines) Calibration equations and (dashed line) 2 sigma standard deviation extended on the temperature range of our values of *Anand et al.* [2003] are plotted.



**Figure 10.** Plot showing mean Sr/Ca ratio and Tiso obtained from (a) *G. inflata* and (b) *G. truncatulinoides* from core tops (this study) and measurements from the sediment trap samples [Anand et al., 2003] for these species.



**Figure 11.** Sr/Ca ratio versus core top water depth for (dark blue) *G. ruber*, (black) *G. bulloides*, (orange) *P. obliquiloculata*, (green) *G. inflata*, (red) *G. truncatulinoides* dextral and (light blue) *G. truncatulinoides* sinistral. To distinguish between temperature and dissolution effect, only data with Tiso lower than 13°C are plotted for *G. inflata* and *G. truncatulinoides*. All replicates are plotted.

–1.3°C using our calibration if acantharia productivity drops to zero.

[37] Exposure and weathering of aragonite from continental shelves during sea level changes and changes in river flux over glacial cycles are the main factors influencing Sr concentration of seawater [Stoll and Schrag, 1998]. By modeling the Sr and Ca budget of the ocean during Quaternary cycles, Stoll *et al.* [1999] predicted variation in seawater Sr/Ca ratio of less than 2.3% for the Last Glacial Maximum, which is slightly lower than the 3% to 5% variation in seawater Sr/Ca over full glacial cycles suggested by the study of Martin *et al.* [1999]. This effect may explain the high Sr/Ca ratio measured in foraminifera during glacial periods [Elderfield *et al.*, 2000] but would not affect the seawater Sr/Ca ratio during period of constant sea level, such as the Holocene.

## 5. Conclusion

[38] Mg/Ca and Sr/Ca ratios measured in five planktonic foraminifera species are compared to their isotopic temperatures of calcification. Mg/Ca ratios are significantly correlated to isotopic temperatures for *G. ruber*, *G. bulloides*, *G. inflata*, *G. truncatulinoides* (dextral and sinistral) and *P. obliquiloculata*. Sr/Ca ratios are related to isotopic temperatures only in *G. inflata* and *G. truncatulinoides* (dextral

and sinistral), showing an even stronger relationship to temperature than Mg/Ca ratio.

[39] Our Mg/Ca data for *G. ruber* and *G. bulloides* fit well with the calibrations of Anand *et al.* [2003] and Elderfield and Ganssen [2000], respectively. Mg/Ca and Sr/Ca calibrations derived by combining all deep-dwelling foraminifera species measurements give temperature estimates as precise as those obtained using the species-specific relations. These calibrations allow temperature reconstruction with an uncertainty of  $\pm 2^\circ\text{C}$  and  $\pm 1.3^\circ\text{C}$  for Mg/Ca and Sr/Ca ratios, respectively.

[40] Different calcification rates may explain why Sr/Ca is related to temperature only in *G. inflata* and *G. truncatulinoides*. For these species Sr/Ca ratios might give more accurate temperature estimates than those based on Mg/Ca ratios, but should be limited to temperature reconstructions over the Holocene, pending better constraints on the impact of external factors such as glacial/interglacial changes in  $[\text{CO}_3^{2-}]$  and the Sr/Ca ratio of seawater.

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