

Paleo-sea surface temperature calculations in the equatorial east Atlantic from Mg/Ca ratios in planktic foraminifera: A comparison to sea surface temperature estimates from $U_{37}^{K'}$, oxygen isotopes, and foraminiferal transfer function

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Abstract. We present two ~270 kyr paleo-sea surface temperature (SST) records from the Equatorial Divergence and the South Equatorial Current derived from Mg/Ca ratios in the planktic foraminifer *Globigerinoides sacculifer*. The present study suggests that the magnesium signature of *G. sacculifer* provides a seasonal SST estimate from the upper ~50 m of the water column generated during upwelling in austral low-latitude fall/winter. Common to both down-core records is a glacial-interglacial amplitude of ~3°-3.5°C for the last climatic changes and lower Holocene and glacial oxygen isotope stage 2 temperatures compared with interglacial stage 5.5 and glacial stage 6 temperatures, respectively. The comparison to published SST estimates from alkenones, oxygen isotopes, and foraminiferal transfer function from the same core material pinpoints discrepancies and conformities between methods.

1. Introduction

1.1. Paleo-Sea Surface Temperature Estimations

Although various $SST_{U_n^*}$ approaches were developed to reconstruct sea surface $SST_{U_n^*}$ temperatures (SST), the glacial record is especially debated. Ice core records from equatorial mountains [Thompson *et al.*, 1995] and glacial snow line depression [Broecker and Denton, 1989] suggest terrestrial temperatures to be as much as ~5°C cooler than during the Holocene. While Stute *et al.* [1995] inferred a 5°C temperature drop for the Last Glacial Maximum from noble gas measurements in groundwater, the revision of the groundwater data only lead to a 1.9°-2.5°C temperature decline [Ballentine and Hall, 1998]. A large temperature decline of ~4°-5°C is supported by coralline Sr/Ca records [Beck *et al.*, 1992; Guilderson *et al.*, 1994] and, recently, by temperature reconstructions from planktic tropical $\delta^{18}O$ records [Curry and Oppo, 1997]. These results contradict the reduced glacial temperature drop of only 2°C deduced from studies on marine faunal assemblages [Climate: Long-Range Investigation, Mapping, and Planning (CLIMAP), 1981] and stable oxygen isotopes in foraminifera [Broecker, 1986]. Unsaturated alkenone data provide evidence for a 2°-4°C temperature decline [Rostek *et al.*, 1993; Sikes and Keigwin, 1994; Rosell-Melé, 1998].

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1.2. Foraminiferal Mg/Ca Ratios as Paleotemperature Indicators

Because of the incompatibility of methods and their inconsistent results, the development of additional SST proxies seems useful since climate models largely rely on accurate estimations of the ocean paleotemperature. The interest in magnesium in biotic calcite for reconstructing paleo water temperatures is continuously growing, although the views on the processes controlling its uptake and distribution, its susceptibility to dissolution, and its applicability for paleo reconstructions remain controversial. Many studies could not reveal any relationship between magnesium and temperature [e.g., Krinsley, 1960; Savin and Douglas, 1973]. Delaney *et al.* [1985] concluded that additional environmental parameters may affect the calcium substitution by magnesium. In contrast, other investigators suggested a relationship between water temperature and magnesium from the investigation of core top biogenic calcite [e.g., Puechmille, 1985; Izuka, 1988]. The application for SST reconstructions is recently growing, partly stimulated by culture experiments with planktic foraminifera showing a temperature-related Mg/Ca shell ratio [Nürnberg *et al.*, 1996a, b].

Cronblad and Malmgren [1981] were the first to report down-core magnesium variations in planktic foraminiferal tests, correlating with late Quaternary climatic oscillations. Recently, Hastings *et al.* [1998] presented Mg/Ca-based SST records from the equatorial Atlantic and the Caribbean pointing out that the reliability of Mg/Ca records is not

perturbed by dissolution. *Mashiotta et al.* [1999] used a Mg/Ca-based SST record to reconstruct changes in global ice volume.

In fact, calcite dissolution may significantly alter the magnesium concentrations within foraminiferal tests and thus may prevent the applicability of magnesium as a tracer for water mass properties [Rosenthal and Boyle, 1993]. *Brown and Elderfield* [1996] recently estimated the effect of magnesium content on the solubility of low-magnesium biogenic calcite. They concluded that the depth of the saturation horizon for magnesian calcites is a function of their magnesium content. *Lohmann* [1995] showed in addition that *G. sacculifer* may start losing shell mass even ~2 km above the lysocline. Besides partial dissolution, other biases on the magnesium signal introduced by salinity and pH variations, amount of gametogenic calcite, and contaminant phases still need to be evaluated before foraminiferal Mg/Ca ratios may be accepted as a paleothermometer.

The objective of this study is to pursue further the investigation on the potential of magnesium for paleothermometry. In continuation to *Nürnberg et al.* [1996a, b], who showed a well-constrained Mg/SST calibration curve for primary calcite of cultivated *G. sacculifer*, this study compares magnesium-derived SST records over the last ~270 kyr to different paleo-SST proxies (foraminiferal transfer function, oxygen isotopes, and alkenone concentrations) on the same core material in order to resolve discrepancies and conformities between methods.

2. Study Area, Material, and Methods

2.1. Foraminiferal Species Selected for Analyses

G. sacculifer inhabits shallow euphotic waters in the tropical and subtropical oceans [Shackleton and Vincent, 1978; Hemleben and Spindler, 1983] because of the photosynthetic requirements of their dinoflagellate symbionts [Lee and Anderson, 1991]. Inferred from both abundances and isotopic temperatures, the depth habitat lies at ~25-75 m [Fairbanks et al., 1980; Erez and Honjo, 1981; Fairbanks et al., 1982; Hemleben et al., 1989] with prevailing habitat temperatures of 20°-30°C. For the equatorial Atlantic a depth habitat of ~0-50 m is proposed by *Emiliani* [1954] and *Hecht* [1971]. From plankton tow studies close to our area of investigation, *Ravelo et al.* [1990] conclude that highest abundances of *G. sacculifer* occur in ~0-40 m. Salinities from 24 to 47 are tolerated [Hemleben et al., 1989]. Reproduction is linked to the lunar cycle [Bijma and Hemleben, 1994]. In order to reproduce, *G. sacculifer* moves far below the euphotic zone. During gametogenesis a secondary layer of calcite, called gametogenic calcite, is secreted in 80-100 m [Bijma and Hemleben, 1994]. According to model results, nearly a third of the population even adds gametogenic calcite within the main thermocline at 300-800 m water depth [Duplessy et al., 1981]. Growth rate and frequency of gametogenesis are a function of feeding and illumination [Bé, 1980; Spindler et al., 1984]. *G. sacculifer* commonly feeds on copepods [Spindler et al., 1984] and prefers a low-nutrient oligotrophic environment [Bijma and Hemleben, 1994]. According to the ranking of *Berger* [1970], *G. sacculifer* is fairly susceptible to

dissolution, which should be critically considered when performing magnesium analyses.

Recently, culture experiments with living *G. sacculifer* revealed a significant magnesium increase in the foraminiferal tests for a 10°C increase in water temperature [Nürnberg et al., 1996a, b]. It could also be shown that gametogenic calcite has a significantly higher magnesium concentration than primary calcite, although secreted at the same temperature. A sac-like chamber, which may be built during the foraminifer's final stage of development [Bé et al., 1983; Hemleben et al., 1987], however, does not show enhanced magnesium concentrations compared to a normal final chamber [Nürnberg et al., 1996a].

2.2. Core Samples

Mg/Ca studies were performed on two sediment cores from the tropical Atlantic, for which major stratigraphical, sedimentological, and geochemical information was available. Sediment cores GeoB 1105-3/4 from the Equatorial Divergence and GeoB 1112-3/4 located ~400 km south in the low productive South Equatorial Current (SEC) were recovered from the Guinea Basin from 3225 (1°39.9'S, 12°25.7'W) and 3122 m water depth (5°46.2'S, 10°44.7'W), respectively (Figure 1). Stable isotope geochemistry, foraminiferal assemblage analyses and related SST reconstructions, fluxes of sedimentary biogenic components, grain size analyses, and organic carbon fluxes were previously published by *Meinecke* [1992], *Bickert and Wefer* [1996], *Schneider et al.* [1996], and *Wefer et al.* [1996]. A record of alkenone SST estimates is available only for core GeoB 1105-3/4 [Schneider et al., 1996] because the content of alkenones was insufficient for the proper calculation of U_{37}^K in core GeoB 1112.

For both cores, stratigraphic information is available from the PANGAEA Paleoclimate Data Center (Alfred-Wegener-Institute, Bremerhaven). The age models are based on graphic correlation of *Cibicides wuellerstorfi* $\delta^{18}O$ records to the $\delta^{18}O$ standard record of *Martinson et al.* [1987]. We choose the benthic record for stratigraphic correlation to minimize sea surface temperature effects that may occur between upwelling (Equatorial Divergence) and non upwelling regions (South Equatorial Current) and may include a time lag between planktic isotope signals. For detailed stratigraphic information, see *Bickert and Wefer* [1996] and *Schneider et al.* [1996]. The depth-age relationships for both cores demonstrate nearly 2 times higher overall sedimentation rates (4.16 cm/kyr) in core GeoB 1105 compared with core GeoB 1112 (2.54 cm/kyr) due to the enhanced biogenic sedimentation under the equatorial upwelling area at site GeoB 1105 [Bickert and Wefer, 1996].

In contrast to the western South Atlantic basins and the Cape Basin, the deep-sea areas that are mainly filled by Lower Circumpolar Deep Water (LCDW) undersaturated with respect to carbonate concentration, the deepest parts of the Guinea Basin are dominated by slightly supersaturated North Atlantic Deep Water (NADW) [Broecker and Peng, 1982]. This causes the lysocline of calcite to stay much deeper compared to the other South Atlantic basins [Biscaye et al., 1976; Thunneil, 1982]. Delta CO_3^{2-} values from the nearest Geochemical Ocean Sections Study (GEOSECS) site 109 [Bainbridge et al., 1981], indicating the difference between the *in situ* carbonate ion concentration and the pressure-corrected saturation carbonate

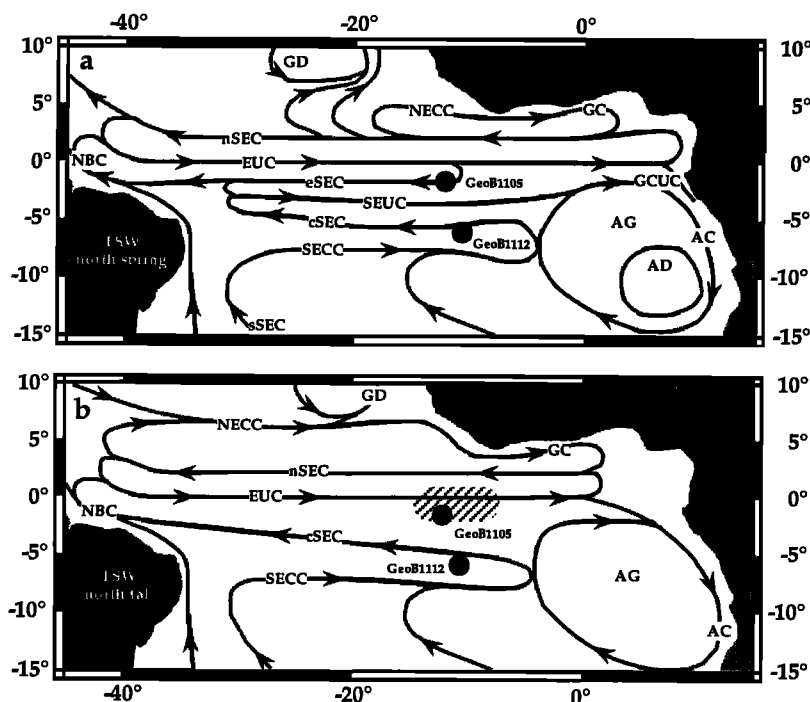


Figure 1. Area of investigation schematically SST₀ indicating the horizontal distribution pattern of currents for the tropical surface layer at ~0-100 m water depth for (a) northern spring and (b) northern fall according to *Stramma and Schott* [1999]. Core locations are indicated by large dots. NEC, North Equatorial Current; NECC, North Equatorial Countercurrent; GD, Guinea Dome; GC, Guinea Current; SEC, South Equatorial Current with the northern (NSEC), equatorial (ESEC), central (CSEC), and southern branches (SSEC); EUC, Equatorial Undercurrent; SEUC, South Equatorial Undercurrent; SECC, South Equatorial Countercurrent; NBC, North Brazil Current; GCUC, Gabbon-Congo Undercurrent; AG, Angola Gyre; AD, Angola Dome; AC, Angola Current. The hatched area indicates potential upwelling in the study area.

ion concentration (with respect to calcite), point toward water depths of ~4800 m for the calcite saturation horizon. Even during the entire late Pleistocene interval, the lysocline is not expected to have risen above ~3800 m water depth [*Bickert and Wefer*, 1996], suggesting that the cores are well above any reasonable calcite saturation horizon. The magnesian calcite horizon calculated for Mg/Ca = 10 mmol/mol (the upper limit of what is appropriate for planktic foraminiferal calcite) could have been as much as 150 m above the calcite saturation horizon.

2.3. Preparation and Analytical Approaches

Specimens of *G. sacculifer* were selected from the 250-500 μm size fraction. The large size ensures that specimens can be easily identified and that a relatively small number of specimens is sufficient for the geochemical investigation. Specimens visibly contaminated by ferromanganese oxides were discarded. Magnesium and calcium analyses were carried out by inductively coupled plasma optical emission spectrometry (ICP-OES).

Approximately 0.5-1.2 mg sample material usually consisting of ~30 specimens of *G. sacculifer* were gently crushed between glass plates in order to open the chambers and were subsequently placed into vials. In order to remove contaminant phases the material was rinsed three times with distilled deionized water with ultrasonical cleaning (2 min) steps after each rinse. One methanol (subboiled distilled)

cleaning step and, again, distilled deionized water rinses followed, alternated with ultrasonical cleaning. Subsequently, samples were treated with a hot (80°C) oxidizing NaOH/ H₂O₂ solution (30 ml 0.1 N NaOH (analytical grade); 10 μL 30% H₂O₂ (suprapur)) for 30 min. Every 10 min, ultrasonical cleaning steps (2 min) were applied. Afterward, three steps of distilled deionized water rinsing and ultrasonical treatment as above followed. The clean foraminiferal fragments were brought into new vials previously cleaned with 1 N HCl (subboiled distilled) and subsequently dissolved by 0.1 N HNO₃ (subboiled distilled) during ultrasonic treatment. The sample solution was then diluted with distilled deionized water up to 3 mL.

In order to assess the efficiency and necessity of our cleaning procedure we subjected sieved foraminifera (*Globigerina bulloides* and *Orbulina universa*, 250-500 μm) from core top samples off Portugal (39°04'N, 10°40'W; 1605 m water depth) to sequentially more rigorous cleaning. Various foraminiferal cleaning protocols described by *Boyle* [1981], *Boyle and Keigwin* [1985], *Brown* [1996] and *Hastings et al.* [1996] were adopted and/or modified. Cleaning step 1 comprises three rinses with distilled deionized water alternated with sonication (2 min). Cleaning step 2 subjects the foraminifera to three rinses with distilled deionized water, one rinse with methanol, and two subsequent rinses with distilled deionized water, each step alternated by sonication (2 min). This step significantly reduced the magnesium

contents of *G. bulloides* and *O. universa* in comparison to step 1. Further cleaning (step 3 as described above) with hot alkaline peroxide for 30 min with alternating sonication after each 10 min did not change the magnesium content within the measurement error nor did step 4, which applies a solution of NH_4Cl instead of hot alkaline peroxide. Step 5 is similar to step 3, but has no methanol rinse. Finally, the most extensive cleaning, step 6, comprises, besides sonication and rinsing with distilled dionized water and methanol, the treatment with NH_4Cl solution and hot alkaline peroxide. All cleaning steps after step 2 did not change the Mg/Ca ratios significantly. However, since we expect stronger contamination in the down-core samples compared to coretops, we systematically applied cleaning step 3.

Analyses were run on an ICP-OES (ISA Jobin Yvon-Spex Instruments S.A. GmbH) with polychromator applying yttrium as an internal standard. We selected element lines for analyses which appeared most intensive and undisturbed (Ca: 317.93 nm; Mg: 279.55 nm; and Y: 371.03 nm). Element detection was performed with photomultipliers, the hightension of which was adapted to each element concentration range. The relative standard deviation is $< 1\%$ for magnesium and calcite. The Mg/Ca reproducibility of 15 replicate samples of *G. sacculifer* is good ($r^2 = 0.98$, mean standard deviation is 0.04 mmol/mol, and maximum standard deviation is 0.11 mmol/mol). The error in terms of SST is maximum of $\pm 0.4^\circ\text{C}$.

The accuracy of our calcium and magnesium analyses can be evaluated with literature data. *Hastings et al.* [1998] published inductively coupled plasma mass spectrometry (ICP-MS) and atomic absorption spectrometry (AAS) derived Mg/Ca ratios of *G. sacculifer* selected from an equatorial Atlantic sediment core, the glacial-interglacial range of which lies between ~ 2.9 and 3.9 mmol/mol, thus being consistent with our ICP-OES-based data (~ 2.9 - 4.0 mmol/mol).

2.4. SST From Oxygen Isotopes

For core GEOB 1112 we calculated SST from the available $\delta^{18}\text{O}$ record of *G. sacculifer* by applying the *Erez and Luz* [1983] temperature equation:

$$T = 17.0 - 4.52 (\delta^{18}\text{O}_F - \delta^{18}\text{O}_w) + 0.03 (\delta^{18}\text{O}_F - \delta^{18}\text{O}_w)^2, \quad (1)$$

where $\delta^{18}\text{O}_F$ is the oxygen isotopic composition of the calcite (permille Peedee belemnite (PDB) and $\delta^{18}\text{O}_w$ is the oxygen isotopic composition of seawater (permille PDB); the conversion from $\delta^{18}\text{O}_w$ SMOW to $\delta^{18}\text{O}_w$ PDB is performed according to *Hut* [1987]. The $\delta^{18}\text{O}_w$ is assessed from the salinity versus $\delta^{18}\text{O}_w$ relationship established by *Wang et al.* [1995] for the low-latitude Atlantic. Assuming that *G. sacculifer* inhabits the upper ~ 100 m of the water column, we considered salinities of 35.5-36.1 at 100-0 m water depth [*Levitus and Boyer*, 1994] leading to a range of $\delta^{18}\text{O}_w$ values. Glacial-interglacial variations of seawater $\delta^{18}\text{O}_w$, which are driven by ice volume changes are taken from the mean $\delta^{18}\text{O}_w$ record of *Vogelsang* [1990]. *Vogelsang* [1990] proposes a mean ocean $\delta^{18}\text{O}_w$ increase by 1.1% during the Last Glacial Maximum, which is in accordance with pore water $\delta^{18}\text{O}$ measurements in sediment cores from the equatorial Atlantic [*Schrag et al.*, 1996]. Assuming a larger mean ocean $\delta^{18}\text{O}_w$ increase of 1.2 - 1.3% [*Fairbanks*, 1989] would result in warmer

glacial SST_{isotope} and would reduce the glacial-interglacial SST_{isotope} amplitude by maximum of 1°C .

3. Results and Discussion

3.1. Mg/Ca Signal in Planktic Foraminifera From the Equatorial Divergence and the South Equatorial Current

The down-core Mg/Ca records of both Guinea Basin cores GeoB 1105 and 1112 cover the last $\sim 270,000$ years (oxygen isotope stages 1-8), thus comprising three glacial-interglacial changes. In both cores, Mg/Ca ratios range between 2.6 and 4.4 mmol/mol at most (Tables A1 and Table A2¹). The long-term variability in Mg/Ca ratios by far exceeds the standard error of the measurements and thus has to be considered as real. Although the short-term scatter of the Mg/Ca ratios is also significant from the analytical point of view, its paleothermal relevance is questioned. It is likely that these small-scale variations are due to the intraspecific inhomogeneity of the magnesium incorporation. *Nürnberg* [1995] already stated that the large range of magnesium concentrations within a single foraminiferal test, which may exceed a factor of 3 along chamber walls, may lead to quantitative differences between different tests of one sample. Replicate ICP-OES analyses varying on average by ~ 0.05 mmol/mol contribute to the scatter of the magnesium data down-core. In order to exclude the short-term scatter of the data from further discussion we applied a simple seven-point smoothing procedure (least squares smoothing filter) [*Paillard et al.*, 1996] on the original Mg/Ca records (Figures 2 and 3).

The comparison of Mg/Ca ratios in both cores reveal that the Mg/Ca ratios in the Equatorial Divergence (GeoB 1105) are lower compared to the South Equatorial Current (core GeoB 1112). This observation coincides with the observation of generally heavier stable oxygen isotope values in core GeoB 1105 [*Meinecke*, 1992] (Figures 2 and 3). The down-core variations of both Mg/Ca ratios and oxygen isotopes match fairly well, thereby clearly reflecting glacial-interglacial changes. Highest Mg/Ca ratios occur during interglacials, and lowest values occur during glacials with pronounced concentration gradients at stage boundaries 8/7, 6/5, and 2/1.

Spectral analysis [*Paillard et al.*, 1996] reveals that the Mg/Ca variability in core GeoB 1112 is dominated by Milankovitch frequencies with periods close to 100, 41, and 23 kyr. The length of time series of $\sim 270,000$ years, in fact, is too short to definitely resolve for variability in the eccentricity band (100-kyr cycle). The cross-spectral analysis [*Blackman and Tukey*, 1958] of the Mg/Ca and the $\delta^{18}\text{O}$ records derived from *G. sacculifer* from the same samples indicates that the two time series correlate ($R = -0.54$) with Mg/Ca leading the $\delta^{18}\text{O}$ signal. The comparison of phase angles of Mg/Ca and $\delta^{18}\text{O}$ reveals that changes in Mg/Ca lead changes in $\delta^{18}\text{O}$ by 12.0 ± 2.1 kyr at the 100 kyr orbital period, by 5.5 ± 1.0 kyr at the 41 kyr orbital period, and by 2.6 ± 0.7 kyr

¹Supporting Tables A1 and A2 are available electronically at World Data Center-A for Paleoclimatology, NOAA/NGDC, 325 Broadway, Boulder, Colorado (e-mail: paleo@mail.ngdc.noaa.gov; URL: <http://www.ngdc.noaa.gov/paleo>).

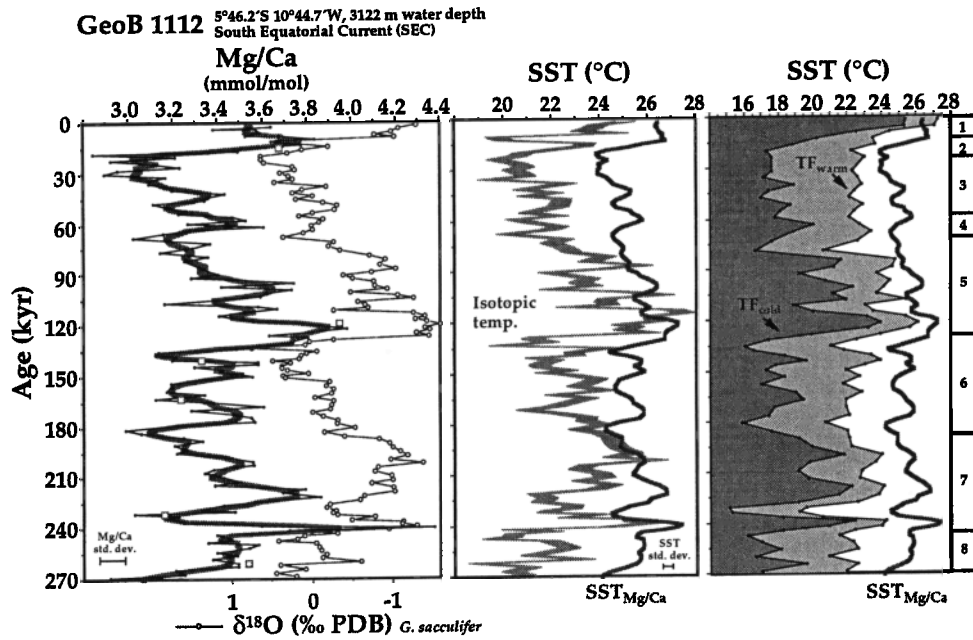


Figure 2. (left) Down-core Mg/Ca record of core GeoB 1112-3/4 for the last ~270,000 years in comparison to the stable oxygen isotope curve (*G. sacculifer*) [Wefer et al., 1996]. Replicate Mg/Ca analyses are indicated by squares. The smoothed record is included as a thick line. (middle) SST temperature curve from oxygen isotopes in comparison to the smoothed SST_{Mg/Ca} record. The broad band of SST_{isotope} gives reference to different salinities applied for calculating δ¹⁸O_w. (right) Calculated SST_{Mg/Ca} of core GeoB 1112 versus age in comparison to SST derived from foraminiferal transfer functions [Wefer et al., 1996].

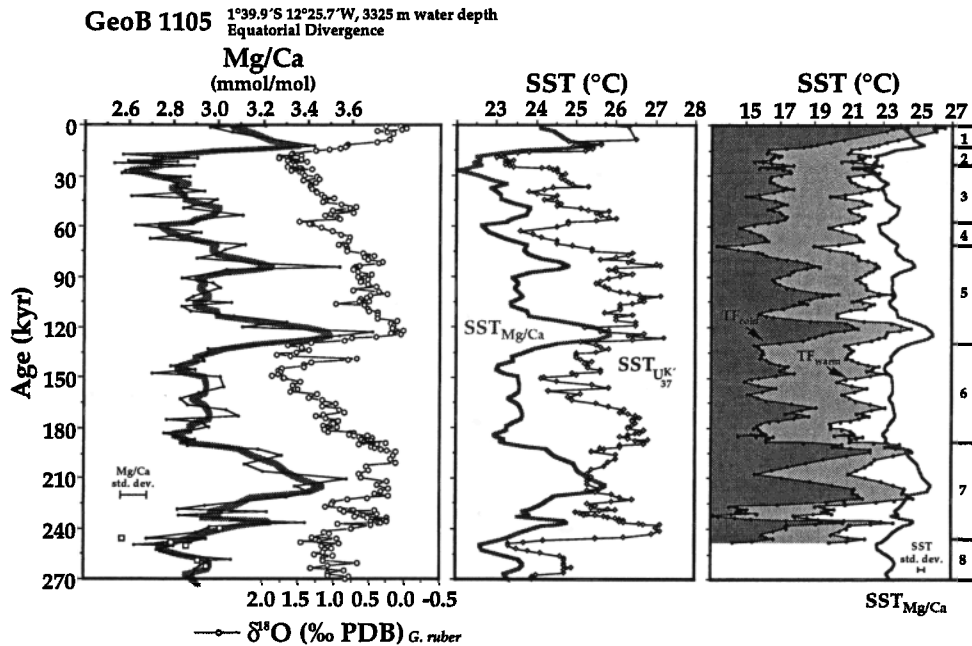


Figure 3. (left) Down-core Mg/Ca record of core GeoB 1105-3/4 for the last ~270,000 years in comparison to the stable oxygen isotope curve (*G. ruber*) [Wefer et al., 1996]. Replicate Mg/Ca analyses are indicated by squares. The smoothed record is included as a thick line. (middle) SST temperature curve from alkenones in comparison to the smoothed SST_{Mg/Ca} record. (right) Calculated SST_{Mg/Ca} of core GeoB 1105 versus age in comparison to SST derived from foraminiferal transfer functions [Wefer et al., 1996].

at the 23 kyr orbital period. The coherency of the two time series is 0.87 at 1/100 kyr, 0.82 at 1/41 kyr, and 0.78 at 1/23 kyr. All these coherencies exceed the 95% confidence interval for coherency (≈ 0.62). The correlation coefficient of the two time series improves to $R = -0.71$, when assuming a time lag of 5500 years (at the 41 kyr orbital period) between both the equally sampled and smoothed Mg/Ca and $\delta^{18}\text{O}$ records.

In core GeoB 1112 the stage 8/7 boundary (Termination III) exhibits a pronounced Mg/Ca increase from ~ 3.2 to ~ 3.9 mmol/mol. At stage 6/5 boundary (Termination II), Mg/Ca ratios increase from 3.1 to up to 3.9 mmol/mol, and at stage 1/2 boundary (Termination I) they increase from 3.0 to 3.8 mmol/mol. The overall glacial-interglacial amplitude of the smoothed Mg/Ca records is ~ 0.7 - 0.8 mmol/mol.

For core GeoB 1105 we observe a Mg/Ca ratio increase from ~ 2.7 to 3.2 mmol/mol at stage boundary 8/7, from 2.8 to 3.5 mmol/mol at stage boundary 6/5, and from 2.6 to 3.4 mmol/mol at stage boundary 2/1, thus showing a glacial-interglacial amplitude of 0.5-0.8 mmol/mol, which is comparable to the values in core GeoB 1112.

3.2. SST Information From Foraminiferal Mg/Ca Ratios in Comparison to Recent Conditions

It is of considerable importance, for the paleo-SST reconstruction from down-core Mg/Ca records (hereafter

indicated as $\text{SST}_{\text{Mg/Ca}}$), which Mg/SST relationship is applied. Up to now, only a few species-specific Mg/SST calibration curves from cultivating experiments exist. For primary calcite of *G. sacculifer*, Nürnberg *et al.* [1996a, b] suggested a strict relationship between the foraminiferal Mg/Ca ratios and temperature. They chose an exponential model to fit their data, although studies on the partition coefficient of magnesium in magnesian calcite overgrowths are still ambivalent, showing both linear and exponential relationships between magnesium and temperature [Chilingar, 1962; Kinsman and Holland, 1969; Katz, 1973; Füchtbauer and Hardie, 1976; Mucci, 1987; Oomori *et al.*, 1987]. Since the foraminiferal Mg/Ca ratios are orders of magnitude lower compared to inorganically precipitated calcite, it was suggested that the foraminifera are capable of physiologically controlling the magnesium concentration in their shells [Nürnberg *et al.*, 1996a]. Such physiological control is apparently the dominant driving force, although temperature seems to affect these processes the way that a direct magnesium-temperature relationship is pretended.

The slight deviation of the relationship applied here from the one originally proposed by Nürnberg *et al.* [1996b] stems from the correction made to adjust the microprobe measurements of Nürnberg *et al.* [1996b] to the ICP-OES data of this study:

Table 1. Core Top SST Estimates and Glacial-Interglacial SST Amplitudes From Various Proxies

Method	SST		Period			
	GeoB1105, °C	GeoB1112, °C				
<i>Levitus</i> [1994]	26.2-20.4	26.5-23.2	May-June			
<i>Levitus</i> [1994]	24.8-19.9	25.1-22.8	May-Aug.			
<i>Levitus</i> [1994]	26.2-22.9	25.7-23.3	Sept.-April			
<i>Levitus</i> [1994]	26.2-22.3	25.5-23.3	annual			
Mg/Ca _{smoothed}	24.1	26.1				
U ^K ₃₇	25.7	n.d.				
TF _{cold}	23.5	25.4				
TF _{warm}	26.1	27.3				
$\delta^{18}\text{O}_{\text{min}}$	n.d.	24.7				
$\delta^{18}\text{O}_{\text{max}}$	n.d.	25.5				
Method	SST Amplitude, GeoB1105, °C			SST Amplitude, GeoB1112, °C		
	MIS 2 / MIS 1	MIS 6 / MIS 5	MIS 8 / MIS 7	MIS 2 / MIS 1	MIS 6 / MIS 5	MIS 8 / MIS 7
Mg/Ca _{smoothed}	3.4	2.9	2.9	2.9	2.9	1.9
U ^K ₃₇	3.5	3.1	3.8	n.d.	n.d.	n.d.
TF _{cold}	7.2	6.1	6.5	8.0	7.9	6.3
TF _{warm}	5.2	3.9	3.7	4.9	5.1	2.7
$\delta^{18}\text{O}_{\text{min}}$				5.1	7.7	6.5
$\delta^{18}\text{O}_{\text{max}}$				5.1	7.7	6.5

(top) SST estimates are for cores GeoB 1105 and GeoB 1112 in comparison to modern *Levitus and Boyer* (1994) water temperatures. The *Levitus and Boyer* (1994) temperatures of the upper 50 m of the water column are given for the beginning equatorial upwelling (May to June), the upwelling period (May to August), the remaining year (September to April), and the entire year. (bottom) Glacial-interglacial SST amplitudes of various SST proxies are compared for Termination I, (MIS 2/1), II, (MIS 6/5), and III, (MIS 8/7), differentiated for both cores. Here n.d. is no data.

$$T = (\log \text{Mg/Ca} - \log 0.491)/0.033 \quad R^2 = 0.92. \quad (2)$$

The uppermost Holocene samples in cores GeoB 1112 and GeoB 1105 reveal a $\sim 2^\circ\text{C}$ offset in $\text{SST}_{\text{Mg/Ca}}$ with lower temperatures at core GeoB 1105 (Table 1), which generally persists over the entire time period investigated. Today, only during equatorial upwelling from May to August/beginning September, SST in the Equatorial Divergence are considerably cooler than in the South Equatorial Current at 0-50 m water depth [Levitus and Boyer, 1994] (Figure 4).

Unfortunately, information about abundance maxima of the oligotrophic *G. sacculifer* during that time is sparse. B. Donner (personal communication, 1998) gathered a long-term abundance record for planktic foraminifera from the equatorial East Atlantic revealing an abundance peak of *G. sacculifer* during the beginning upwelling from austral low-latitude late fall/early winter. During summer, instead, no *G. sacculifer* were observed in the eastern South Atlantic

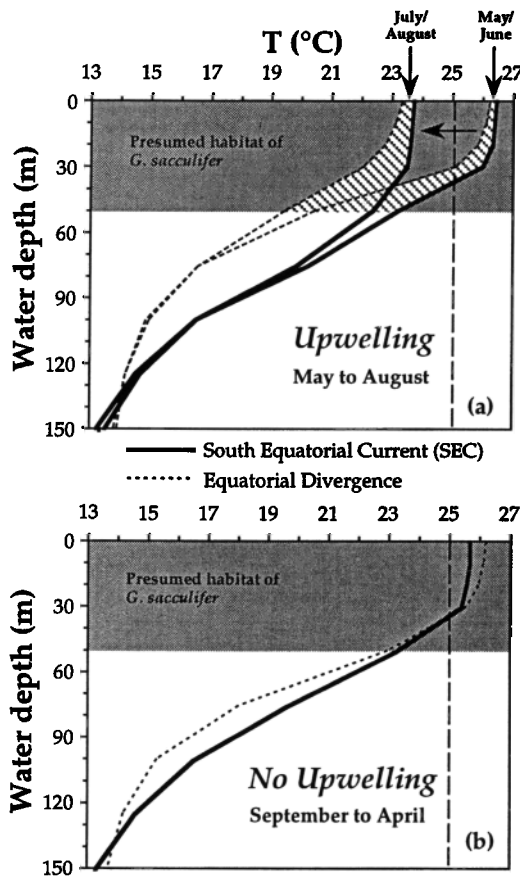


Figure 4. Water temperature data for the Equatorial Divergence (thin dashed lines) and the South Equatorial Current (thick solid lines) averaged for (a) the upwelling season (May to August) and (b) the remaining year [Levitus and Boyer, 1994]. For the upwelling season we differentiated between the beginning (May to June) and the remaining upwelling (July to August). The shaded area marks the presumed habitat of pre-gametogenic *G. sacculifer* (upper 50 m of the water column). Time and depth at which the Equatorial Divergence is significantly cooler than the South Equatorial Current and at which the Mg/Ca signal is presumably being generated are marked by the hatched area. The arrow points to considerable surface water cooling during ongoing upwelling in austral low-latitude fall/winter.

[Oberhänsli et al., 1992]. Ufkes et al. [1998] report high abundances during austral low-latitude spring (October to November), when a deep mixed layer has established in the eastern South Atlantic.

Taken together, the $\sim 2^\circ\text{C}$ difference between the two core sites and the presumed abundance maximum during austral low-latitude fall/winter suggest that at site GeoB 1105 the $\text{SST}_{\text{Mg/Ca}}$ signal reflects the thermal situation within the upper ~ 50 m of the water column during upwelling (May to August), while site GeoB 1112 is not affected by upwelled waters. The latest holocene $\text{SST}_{\text{Mg/Ca}}$ of $\sim 26^\circ \pm 0.4^\circ\text{C}$ and $24^\circ \pm 0.4^\circ\text{C}$ at core sites GeoB 1112 and GeoB 1105, respectively, fairly well reflect the upwelling situation [Levitus and Boyer, 1994]. The error in $\text{SST}_{\text{Mg/Ca}}$ calculations to lower values, which may raise from the presence of varying portions of gametogenic calcite enriched in magnesium [Nürnberg et al., 1996b], may provide enough amount of scope to even explain the rapid SST drop, which takes place during the ongoing upwelling in July and lasts until August [Levitus and Boyer, 1994] (Figure 4).

From September on when upwelling ceases, SST slowly increases again in both areas by $\sim 1\text{-}3^\circ\text{C}$, and surface mixed layer temperatures in the Equatorial Divergence never fall below the ones observed within the South Equatorial Current (Figure 4). We therefore conclude for the area of investigation that the $\text{SST}_{\text{Mg/Ca}}$ signal reflects the austral low-latitude fall/winter upwelling situation within the uppermost ~ 50 m of the water column (the assumed habitat of pre-gametogenic *G. sacculifer*).

Whether salinity changes perturb the magnesium signal is still a matter of debate. From live culturing of *Orbulina universa*, Lea et al. [1999] infer an increase of $4 \pm 3\%$ in Mg/Ca per salinity unit at 22°C . For *G. sacculifer*, Nürnberg et al. [1996a] pointed out that pronounced salinity changes (greater than ~ 10) apparently dominate over the temperature effect with respect to the magnesium uptake, possibly caused by an enhanced metabolic activity at high salinity levels. Small-scale salinity differences below 3, instead, are not resolved by the Mg/Ca ratios [Nürnberg et al., 1996a]. Since, at the study sites, annual salinity variations of $\sim 35.1\text{-}36.1$ [Levitus and Boyer, 1994] within the upper 100 m water column (which is the assumed depth habitat of *G. sacculifer*) give rise to Mg/Ca ratio variations of ~ 0.25 mmol/mol at most, which is close to the analytical error, we do not expect salinity to have any pronounced effect on the foraminiferal Mg/Ca ratio.

3.3. Paleo-SST Information From Foraminiferal Mg/Ca Ratios

The paleo- $\text{SST}_{\text{Mg/Ca}}$ records of both cores resemble each other, although the $\text{SST}_{\text{Mg/Ca}}$ estimates of core GeoB 1105 are generally lower in comparison to core GeoB 1112. It is apparent that both $\text{SST}_{\text{Mg/Ca}}$ records are $\sim 1\text{-}2^\circ\text{C}$ higher than the corresponding paleosummer SST_{TF} records of Wefer et al. [1996] derived from planktic foraminiferal transfer functions (Figures 2 and 3). The overall range of the down-core $\text{SST}_{\text{Mg/Ca}}$ is smaller (3.6° and 4.0°C in cores GeoB 1112 and GeoB 1105, respectively) than the maximum range observed from transfer functions, which even exceeds 8.0°C . In fact, the glacial-interglacial $\text{SST}_{\text{Mg/Ca}}$ amplitudes at stage 8/7, 6/5, and 2/1 boundaries are $\sim 3^\circ\text{C}$ for each of the boundaries (Table 1),

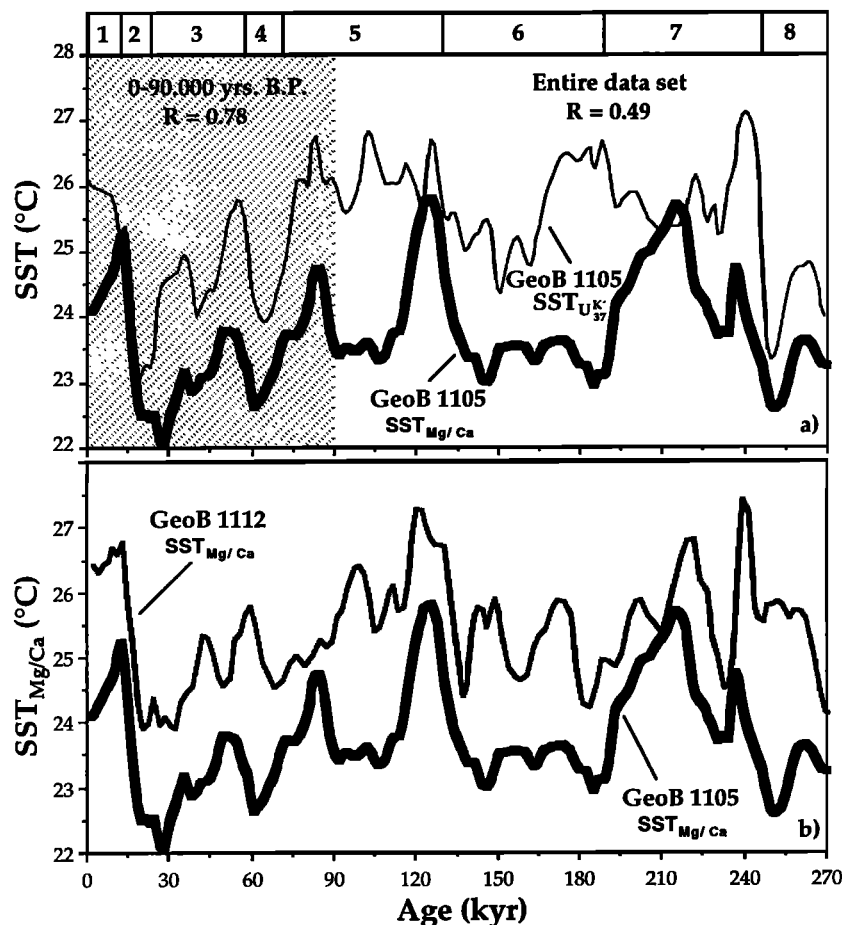


Figure 5. (a) Comparison of $SST_{Mg/Ca}$ and $SST_{U^K_{37}}$ from core GeoB 1105 and (b) comparison of $SST_{Mg/Ca}$ for both cores investigated. The hatched area marks the time period for which a good correlation between $SST_{Mg/Ca}$ and $SST_{U^K_{37}}$ exists ($R = 0.78$). Marine oxygen isotope stages are indicated.

whereas the SST_{TF} amplitudes are larger and often exceed 5°C . The magnitude of the glacial-interglacial $SST_{Mg/Ca}$ gradient corresponds to that of *Hastings et al.* [1998], who described a temperature drop of $\sim 2.5^{\circ}\text{C}$ during glacial stage 2 in the equatorial Atlantic based on $SST_{Mg/Ca}$. Studies of *Van Campo et al.* [1990], who pointed out that African sea level temperatures were $3^{\circ}\text{--}4^{\circ}\text{C}$ lower during the Last Glacial Maximum, further support the magnesium-derived SST reconstructions.

Both the smaller amplitude and the generally higher temperature estimates may result from the fact that the $SST_{Mg/Ca}$ signal reflects seasonal temperature conditions from the uppermost water column, whereas the SST_{TF} integrates summer temperatures from the surface waters down to the subthermocline when considering the entire planktic foraminiferal faunal spectrum [Meinecke, 1992]. Also, foraminiferal abundances in this specific area might be related to vertical water column hydrography and nutrient distribution rather than to sea surface temperature alone [Ravelo and Fairbanks, 1992; Sikes and Keigwin, 1994].

Holocene SST estimates derived from oxygen isotope data of *G. sacculifer* (SST_{isotope}) from core GEOB 1112 range from $\sim 23^{\circ}\text{--}25.5^{\circ}\text{C}$ (Figure 2) and thus are considerably lower than

$SST_{Mg/Ca}$ and warm SST_{TF} . In pre-Holocene sections, SST_{isotope} reconstructions significantly deviate in amplitude from the warm SST_{TF} data, although the SST_{isotope} amplitude better fits to warm SST_{TF} than to $SST_{Mg/Ca}$. The temporal amplitude of the $SST_{Mg/Ca}$ is considerably smaller than for SST_{isotope} (Table 1). It needs to be pointed out that in contrast to SST_{isotope} the accuracy of SST_{isotope} suffers considerably from assumptions regarding the ice effect, the recent, and the paleo- $\delta^{18}\text{O}_w$ values. Since the magnesium signal in *G. sacculifer* definitely leads the oxygen isotope signal and a considerable portion of the $\delta^{18}\text{O}$ signal reflects global ice volume changes, we conclude that changes in SST precede changes in global ice volume at this site.

SST estimates obtained from alkenone concentrations ($SST_{U^K_{37}}$) established for core GeoB 1105 [Schneider et al., 1996] exceed the $SST_{Mg/Ca}$ by $\sim 1^{\circ}\text{--}2^{\circ}\text{C}$, while for most of the time span covered, the temporal pattern of both temperature reconstructions match well (Figure 5). The overall correlation between both the smoothed $SST_{Mg/Ca}$ time series and the smoothed $SST_{U^K_{37}}$ time series is $R = 0.49$. The correlation for samples younger than 90,000 years, for which a good visual correlation exists, improves to $R = 0.78$. The overall glacial-interglacial amplitudes at Terminations I and II range from 2.9°

to 3.5°C in both the SST_{Mg/Ca} and SST_{U₃₇^K} records, while at Termination III the amplitude of the SST_{Mg/Ca} is only ~2.9°C compared with the 3.8°C amplitude of the SST_{Mg/Ca} record (Table 1). Major discrepancies can be observed in oxygen isotope stage 7 and basal stage 6. While the SST_{U₃₇^K} record clearly indicates warming of surface waters, the SST_{Mg/Ca} stays low. Also, in substage 5.3 the SST_{U₃₇^K} record indicates a significant warming, which is not reflected by the magnesium signal.

For core GeoB 1112 the SST_{Mg/Ca} estimates fall into the range of the SST_{U₃₇^K} published for core GeoB 1105, being slightly higher (maximum of 0.5°C) during peak interglacials (Figure 5). The glacial-interglacial SST_{Mg/Ca} amplitude of ~3°C is comparable to the SST_{U₃₇^K} amplitude of core GeoB 1105. Similar to core GeoB 1105, discrepancies can be observed during late stage 7 and basal stage 6, where the SST_{U₃₇^K} record definitely shows sea surface warming, while the SST_{Mg/Ca} stay cool. Also, substage 5.1, which exhibits warm SST_{U₃₇^K}, is not reflected in SST_{Mg/Ca}.

Both the absolute temperature offset and the discrepancies between the down-core records of SST_{U₃₇^K} and SST_{Mg/Ca} in the Equatorial Divergence are most presumably explained by the time of signal generation and the different depth habitats of the U₃₇^K signal producing coccolithophorids on the one hand and foraminifera on the other hand. Conte *et al.* [1993], Sikes and Keigwin [1994], Herbert *et al.* [1998], and Müller *et al.* [1998] consistently concluded that the sedimentary U₃₇^K ratio essentially reflects annual mean mixed layer temperatures (~0-10 m water depth). In fact, the U₃₇^K temperature calculated for the uppermost sample in core GeoB 1105 of 25.7°C matches the annual mean temperature of the uppermost ~10 m of the water column of 25.6°C [Levitus and Boyer, 1994]. Seasonal variations of 24°-27.5°C observed in this area are apparently averaged out. The SST_{Mg/Ca} of ~24°C at the same site, instead, reflects the austral low-latitude fall/winter signal beneath the mixed layer down to ~50 m water depth [Levitus and Boyer, 1994].

The prevailing temperature offset of ~1°-2°C through time between Equatorial Divergence and South Equatorial Current (Figure 5) points to continuous upwelling within the Equatorial Divergence, comparable to the recent situation. The increasing temperature offset observed in stage 7, stage 6, and substage 5.3 may be interpreted as the thermal decoupling of a warm thin surface layer from cooler water masses beneath and thus a stronger or longer period of stratification. In contrast, a decreasing temperature offset mainly observed during the cold events of glacial and interglacial stages would propose less strong seasonal differences in the upper ~50 m of the water column.

The correspondance of the SST_{Mg/Ca} and SST_{U₃₇^K} records and their disparity to temperature records derived from transfer

functions are further expressed by the fact that both chemically derived temperature reconstructions reveal (1) higher interglacial stage 5e temperatures in comparison with the Holocene and (2) colder glacial stage 2 conditions in comparison with glacial stage 6. Similar conditions are reported from SST_{U₃₇^K} reconstructions of the northern North Atlantic [Villanueva *et al.*, 1998] and the Indian Ocean [Rostek *et al.*, 1993]. The temperature records derived from transfer functions, instead, reveal warmer Holocene and stage 2 temperatures compared to stages 5e and 6 conditions.

4. Conclusions

Since the disparity between terrestrial and marine SST estimates is most obvious in tropical regions, this study attempts to contribute new aspects by applying Mg/Ca ratios in the planktic foraminifer *G. sacculifer* as a tool for estimating SST in the past to two sediment cores from the eastern equatorial Atlantic covering the last ~270 kyr. The down-core Mg/Ca variations were calibrated using the species-specific, exponential Mg/SST relationship established for primary calcite of *G. sacculifer* [Nürnberg *et al.*, 1996a]. SST estimations reveal an accuracy of approximately ±0.4°C.

Holocene SST estimates amount to ~26°C for the South Equatorial Current and ~24°C for the Equatorial Divergence suggesting that the chemical signature must have generated during upwelling in austral low-latitude fall/winter in ~0-50 m water depth. Within the South Equatorial Current, pre-Holocene SST vary between ~24°C and 27.5°C at most, whereas the cooler Equatorial Divergence exhibits SST of only 22°-25.5°C for the last 270,000 years. Common to both records is a glacial-interglacial amplitude of ~3-3.5°C for the last climatic changes, thus being consistent to paleotemperature estimates derived from unsaturated alkenones. Furthermore, both records imply lower Holocene and glacial oxygen isotope stage 2 temperatures compared to interglacial stage 5.5 and glacial stage 6 temperatures, respectively.

The comparison of SST_{Mg/Ca} to other SST proxies underlines the applicability of foraminiferal Mg/Ca ratios for paleothermal reconstructions and thus may reinforce the discussion on SST reconstructions. Our study emphasizes the need for caution when applying single paleotemperature techniques to reconstruct climate dynamics and stresses the importance of a multiproxy approach.

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