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# Tropical Atlantic SST history inferred from Ca isotope thermometry over the last 140ka

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## Abstract

Exploring the potentials of new methods in palaeothermometry is essential to improve our understanding of past climate change. Here, we present a refinement of the published $\delta^{44/40}$Ca-temperature calibration investigating modern specimens of planktonic foraminifera *Globigerinoides sacculifer* and apply this to sea surface temperature (SST) reconstructions over the last two glacial–interglacial cycles. Reproduced measurements of modern *G. sacculifer* collected from surface waters describe a linear relationship for the investigated temperature range (19.0–28.5 °C): $\delta^{44/40}$Ca[‰] = 0.22 (±0.05)∗SST [°C] −4.88. Thus a change of $\delta^{44/40}$Ca[‰] of 0.22 (±0.05) corresponds to a relative change of 1 °C. The refined $\delta^{44/40}$Ca$_{modern}$-calibration allows the determination of both relative temperature changes and absolute temperatures in the past. This $\delta^{44/40}$Ca$_{modern}$-calibration for *G. sacculifer* has been applied to the tropical East Atlantic sediment core GeoB1112 for which other SST proxy data are available. Comparison of the different data sets gives no indication for significant secondary overprinting of the $\delta^{44/40}$Ca signal. Long-term trends in reconstructed SST correlate strongly with temperature records derived from oxygen isotopes and Mg/Ca ratios supporting the methods validity. The observed change of SST of approximately 3 °C at the Holocene-last glacial maximum transition reveals additional evidence for the important role of the tropical Atlantic in triggering global climate change, based on a new independent palaeothermometer.

## 1. Introduction

Sea surface temperature (SST) is one of the most important variables in Earth's climate dynamics. In the last decade, considerable interest arises in the role of tropical oceans in global climate dynamics. Recent studies underscore the importance of the tropical Atlantic Ocean as an important forcing of global mean surface air temperatures (Lu, 2005). SST also determines the location of the Inner Tropical Convergence Zone (ITCZ) and influences the atmospheric moisture content, the strength of the African monsoon-controlled aridity and precipitation over Brazil

and Sahel (Chang et al., 1997; Biasutti et al., 2003; Schefuss et al., 2003). Furthermore, there is still controversy regarding the magnitude of tropical SST change on glacial–interglacial timescale (Crowley, 2000).

Several proxies for sea surface temperature, including $\delta^{18}$O and Mg/Ca of foraminiferal calcite, foraminiferal transfer function and alkenone unsaturation index $(U_{37}^{K'})$ have been developed serving as tools in palaeoceanography. Although an ideal proxy would be only influenced by one environmental parameter, recent studies clearly showed that existing SST proxies are effectively influenced by several other parameters apart from temperature (e.g., Shackleton and Opdyke, 1977; Mix et al., 1999; Herbert, 2001; Dekens et al., 2002). Thus, the results of a single SST proxy might be biased and have to be independently confirmed by at least one additional SST proxy. Beside the multiproxy approach to reconstruct past SST variations (cf. Mann, 2002), the successful development of new

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and in particular of isotope methods is still highly desirable.

Ca isotopic composition in primary foraminiferal calcite might serve as such an additional SST proxy. Skulan et al. (1997, 1999) were the first to investigate the biological influence on the Ca isotopic abundance in a variety of organisms. Comparing the $\delta^{44/40}$Ca of benthic and planktonic foraminifera they postulated that the temperature effect is small in comparison to effects they attributed to the trophic level. In contrast Zhu and MacDougall (1998) showed that among foraminifera, Ca isotopes exhibit species-dependent fractionation. Some species appeared to vary significantly with ocean water temperature or depth. The latter authors observed a $\delta^{44/40}$Ca difference of 0.6‰ for *G. sacculifer* between samples of the Holocene and the Last Glacial Maximum for the equatorial Pacific. Following recent publications on glacial–interglacial SST change in equatorial Pacific (Lea et al., 2000; Visser et al., 2003), this 0.6‰ difference would reflect a temperature change of around 3 °C. Nägler et al. (2000) published a direct $\delta^{44/40}$Ca-temperature calibration on cultured *G. sacculifer*. Here, a shift in $\delta^{44/40}$Ca of 0.24‰ would correspond to a temperature change of 1 °C. In a first attempt the authors applied this calibration to an equatorial East Atlantic sediment core (GeoB1112, 5°46.7′S, 10°45.0′W). The decrease of $\delta^{44/40}$Ca of $0.71 \pm 0.24$‰ at the Holocene-Last Glacial Maximum boundary is in line with Zhu and MacDougall observations and corresponds to a change in SST of $\approx 3.0 \pm 1.0$ °C. Although $\delta^{44/40}$Ca and Mg/Ca values generally correlate, $\delta^{44/40}$Ca seemed to predict higher SSTs. Recently, down-core shifts in Ca isotopic abundance have been successfully applied to the reconstruction of Caribbean SST and salinity fluctuations in response to the Pliocene closure of the Central American Gateway (approximately 4.0–4.6 Ma ago) adopting a multi-proxy approach (Gussone et al., 2004).

Gussone et al. (2003) developed a thermodynamic model describing the temperature-dependent Ca isotope fractionation behaviour. This model recombines the investigations of the $\delta^{44/40}$Ca-temperature relationship of inorganically precipitated aragonite and cultured planktonic foraminifera *Orbulina universa* with the findings of Nägler et al. (2000). One major conclusion is that the temperature-dependent fractionation of Ca isotopes in the studied carbonate species could be explained by kinetic fractionation. The shallow slope of inorganic precipitates and *O. universa* reflects the involvement of $Ca^{2+}$-aquacomplexes that are less susceptible to temperature-dependent kinetic isotope fractionation. In contrast the steep slope of *G. sacculifer* indicates that the $Ca^{2+}$-aquacomplexes are actively dehydrated and that biologically mediated processes at the seawater-cell interface are responsible for the temperature-controlled transport of pure $Ca^{2+}$-ions prior to calcification. The different slopes of *G. sacculifer* and *O. universa* were also observed by Deyhle et al. (2002). Lemarchand et al. (2004) noted that it is generally not appropriate to attribute the observed isotopic fractionation effects be-

tween crystals and fluids solely to kinetic processes. According to their study on the Ca isotopic abundance of inorganic precipitated calcite the authors conclude that the diffusive flow of carbonate ions ($CO_3^{2-}$, $HCO_3^-$) into the immediate neighbourhood of the crystal–solution interface is the rate-controlling mechanism and that Ca ions play a rather passive role for the system. The role of temperature is discussed to be the result of changes in the equilibrium constant with temperature. The work by Marriott et al. (2004) also favours equilibrium dynamics to describe Ca isotope fractionation, assuming a weaker bonding of Ca in the carbonate structure relative to that in aqueous structure. The similar fractionation behaviour of inorganic precipitates and *O. universa* they interpreted as direct precipitation of calcite from seawater by a simple process. The stronger temperature dependence of *G. sacculifer* is explained as the result of a superimposed additional biological fractionation effect assuming different biomineralisation processes for both species. The data set of Sime et al. (2005) who analysed 12 species of core-top planktonic foraminifera shows no evidence for temperature as major control over Ca isotope fractionation during calcite biomineralisation. Their results suggest that any temperature relationship is obscured by unquantified metabolic and physiological processes in nature. The obvious difference to the findings of Zhu and MacDougall (1998), Deyhle et al. (2002) and of Nägler et al. (2000) remains unresolved.

In the light of the above, the objective of this study is twofold: first, in continuation of the earlier work of Nägler et al. (2000) we attempt to test the older calibration and to derive a more precise $\delta^{44/40}$Ca-temperature relationship based on modern specimens of *G. sacculifer* captured at known SST conditions evaluating both relative and absolute temperatures. Second this new relationship is used on fossil *G. sacculifer* on the down-core record from tropical eastern Atlantic (GeoB1112) covering the last 140.000 years, i.e., the last two glacial-interglacial transitions. The results are then compared to available SST proxy data ($\delta^{18}$O, Mg/Ca) determined on the same core material, to further assess the suitability of Ca isotopes as a SST proxy in selected species.

## 2. Sample and core locations

Modern samples of *G. sacculifer* were collected in the South Atlantic Ocean and in subtropical and tropical North Atlantic on board of RV Meteor during leg M46-2 and leg M38-1. SST ranges from 19 to 22 °C and 25 to 27 °C, respectively. Further samples were obtained on board of RV Sonne (SO 164) in the Caribbean Sea with SST ranging from 27 to 29 °C (Fig. 1). The samples were collected from the surface water layer by constant pumping. The seawater was filtered using a plankton net (Hydrobios). Samples were rinsed with freshwater and ethanol. Individuals of *G. sacculifer* larger than 150 μm were separated, dried and stored for isotope analysis. We focused on individuals with neither final stage kummerform nor sac-like chamber.
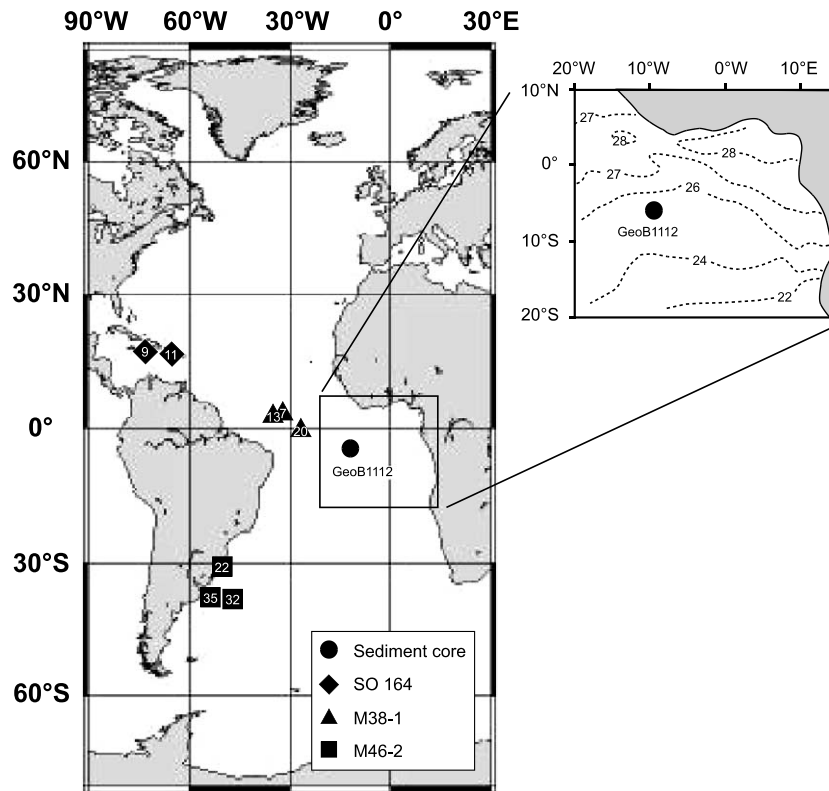
Fig. 1. Sample localities of modern specimens of *G. sacculifer* collected from surface waters on vessel cruises in the Caribbean Sea (SO164), the tropical Atlantic (M38-1), and the South Atlantic offshore Brazil (M46-2). Numbers indicate sample numbers (see Table 1). Sediment core GeoB1112 (5°46.2′S, 10°44.7′W, 3122 m) was recovered from the Guinea Basin and is located in the low productive South Equatorial Current (SEC). Inset, map of sea surface temperatures of the eastern tropical Atlantic.

Shells of fossil *G. sacculifer* were obtained from sediment core GeoB1112 (5°46.2′S, 10°44.7′W). It is located in the low productive south equatorial current (SEC) and was recovered from the Guinea Basin in 3122 m water depths (Fig. 1). Major information about the stratigraphy, sedimentology, geochemistry (e.g., $\delta^{18}O$) and the age model of this core can be found in the compendium of Wefer (1996) or is available from the PANGAEA Paleoclimate Data Center (Alfred-Wegener Institute, Bremerhaven). Mg/Ca-derived palaeo-SSTs were previously published by Nürnberg et al. (2000). Some samples were previously measured by Nägler et al. (2000) for $\delta^{44/40}Ca$.

## 3. Sample preparation and Ca isotope analyses

For Ca isotope analyses on core material about five to ten shells of *G. sacculifer* were selected from the 250 to 500 μm size fraction and pre-cleaned following the procedure described in Nürnberg et al. (2000). Around five tests larger than 150 μm were picked from samples of *G. sacculifer* collected by pumping. In both cases the calcite shells were dissolved in 2.5 N ultrapure HCl. An aliquot corresponding to 0.5–1.0 μg Ca was mixed with a $^{43}Ca$–$^{48}Ca$ double spike to correct for isotopic fractionation during the measurement. To eliminate any remaining organic impurities modern samples were treated with a $H_2O_2$–$HNO_3$ solution (Hippler et al., 2004). The sample-spike

mixture was dried and recovered in about 1 μl of 2.5 N HCl and then loaded on previously washed and outgassed single Re filament together with 1 μl of a $Ta_2O_5$-activator solution (Birck, 1986).

All Ca isotope measurements were carried out at the Institute of Geological Sciences at the University of Bern, Switzerland on a modified single cup AVCO mass spectrometer equipped with a Thermolinear ion source. It was operated in positive ion mode with a 7.6 kV acceleration voltage and a $10^{11}$ Ω resistor setting for the Keithley electrometer. Ca isotopes are measured successively in peak jumping mode in descending sequence (masses 48, 44, 43, and 40). During data acquisition $K^+$ and $Sr^{2+}$ were continuously monitored on mass 41 and 43.5 to trace possible isobaric interferences on masses 40, 43, and 44. No such interferences have been observed at measuring temperatures.

Measured ratios were corrected for analytical isotope fractionation online using a three-dimensional data reduction based on an exponential fractionation law (Siebert et al., 2001). The isotope variations of Ca are expressed in the δ-notation ($\delta^{44/40}Ca$ [‰] $= [(^{44}Ca/^{40}Ca)_{sample}/(^{44}Ca/^{40}Ca)_{standard} - 1] * 1000$). The measured $^{44}Ca/^{40}Ca$ ratios were compared to the $^{44}Ca/^{40}Ca$ ratio of a calcium fluorite standard ($CaF_2$, Hippler et al., 2003). The $^{44}Ca/^{40}Ca$ ratios of our internal $CaF_2$ standard reproduced within 0.11‰ (2σ standard deviation, $n = 30$). The 2σ-reproducibility of our sample $\delta^{44/40}Ca$[‰] is 0.15 determined

by repeated aliquot measurements. We present our Ca isotope data re-normalised relative to NIST SRM915a as recently proposed by Eisenhauer et al. (2004) and Coplen et al. (2002). The $\delta^{44/40}$Ca value of our internal CaF$_2$ standard is 1.47 ± 0.04 (‰ SRM915a). Furthermore, the calculated $\delta^{44/42}$Ca values are presented in the tables and are converted according to the equation published by Hippler et al. (2003). The cross-calibration of various Ca reference materials and seawater of Hippler et al. (2003) allows direct data comparison with previous published work.

## 4. Ca isotope thermometry

### 4.1. The $\delta^{44/40}$Ca-temperature calibration

The $\delta^{44/40}$Ca values of *G. sacculifer* collected from surface waters range from −0.74 to +1.51 (in ‰ SRM 915a) (Fig. 2A and Table 1). For the investigated temperature range (19.0–28.5 °C) we observe a linear trend, although the individuals were sampled from waters of different salinity, varying from 34.5 to 36.5‰. Data points represent the weighted means of at least two to three independent analyses.

The resulting $\delta^{44/40}$Ca-temperature regression (hereafter the $\delta^{44/40}$Ca$_{modern}$-temperature calibration) is expressed as

$$\delta^{44/40}\text{Ca}[‰\ \text{SRM915a}] = 0.22(\pm 0.05) * \text{SST}[°\text{C}] - 4.88.$$
(1)

Thus a change of $\delta^{44/40}$Ca of 0.22‰ corresponds to a relative temperature change of 1 °C.

### 4.2. Inter-calibration comparison

Within statistical uncertainties the temperature gradient of calibration Eq. (1) is identical to that of Nägler et al. (2000) which is based on cultured specimen of *G. sacculifer* (Fig. 2A). Adjusted to the SRM 915a standard, the latter

Table 1
The $\delta^{44/40}$Ca of modern specimen of *G. sacculifer*

| Locality | Sample | $T$ (°C) | $\delta^{44/40}$Ca | $2\sigma$ SE | $\delta^{44/42}$Ca |
|---|---|---|---|---|---|
| Western tropical | 11 | 28.2 | 1.51 | 0.11 | 0.76 |
| Atlantic Ocean, | | | 0.82 | 0.16 | 0.41 |
| Caribbean Sea | | | 1.09 | 0.11 | 0.55 |
| (SO164 Leg 1-3) | 9 | 28.1 | 1.15 | 0.15 | 0.58 |
| Central tropical | 13 | 27.2 | 1.16 | 0.16 | 0.58 |
| Atlantic Ocean | 20 | 27.0 | 1.29 | 0.20 | 0.65 |
| (M38-1) | 7 | 26.1 | 1.03 | 0.15 | 0.52 |
| | | | 0.74 | 0.19 | 0.37 |
| South Atlantic | 35 | 22.1 | −0.02 | 0.15 | −0.01 |
| Ocean, offshore | 22 | 21.1 | −0.41 | 0.16 | −0.21 |
| Brazil (M46-2) | | | −0.30 | 0.12 | −0.15 |
| | | | −0.10 | 0.21 | −0.05 |
| | 32 | 19.4 | −0.48 | 0.08 | −0.24 |
| | | | −0.74 | 0.20 | −0.37 |

$\delta^{44/40}$Ca and calculated $\delta^{44/42}$Ca values are given in (‰) relative to NIST SRM 915a.
$\delta^{44/42}$Ca values are calculated according to Hippler et al. (2003).
Uncertainties reflect the $2\sigma$ standard error of single analysis.

calibration (hereafter the $\delta^{44/40}$Ca$_{culture}$-temperature calibration) can be expressed as

$$\delta^{44/40}\text{Ca}[‰\ \text{SRM915a}] = 0.24(\pm 0.02) * \text{SST}[°\text{C}] - 6.53.$$
(2)

In general, calibrations based on cultures have the advantage that foraminifera calcify under pre-set conditions and known temperatures although the controlled laboratory environment may not fully reproduce natural growth. The study of Nägler et al. (2000) demonstrated that Ca isotope fractionation in *G. sacculifer* tend to be mainly controlled by temperature (samples were cultivated under constant salinity (36‰), see Hemleben et al., 1987), now confirmed by the consistency of two independent calibrations.

The two temperature gradients of 0.22 (±0.05) and 0.24 (±0.02) are identical and estimated relative temperature changes would not deviate by more than 1.0 °C within the
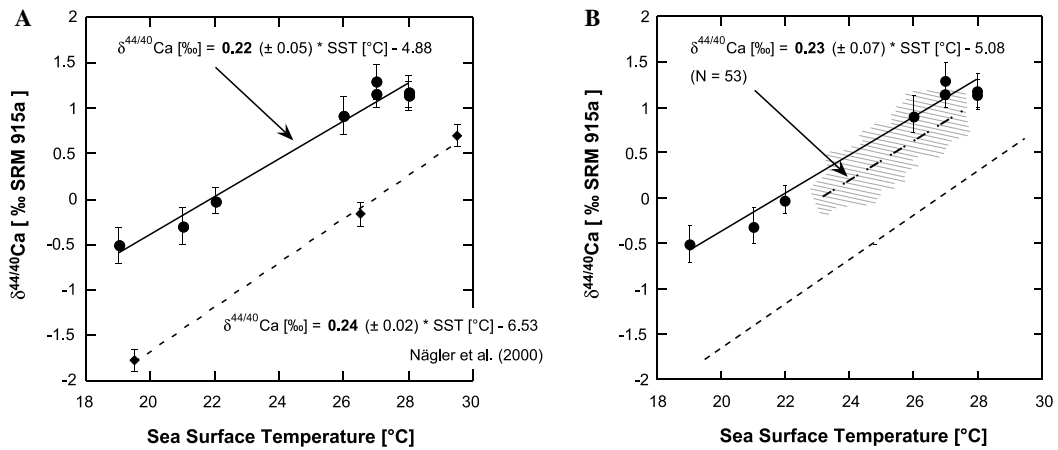


Fig. 2. (A) The $\delta^{44/40}$Ca ratios [‰ SRM 915a] of modern *G. sacculifer* collected from surface waters in comparison to Nägler et al. (2000) based on cultured samples (dashed line). Every data point represents the weighted means of either two or three independent measurements. The observed $\delta^{44/40}$Ca-temperature relationship results from the linear fit to the data (bold line). The error bars show the statistical uncertainties ($2\sigma$ SE). (B) Comparison of the $\delta^{44/40}$Ca$_{modern}$-temperature calibration and the $\delta^{44/40}$Ca-SST$_{Mg/Ca}$ cross-calibration. The shaded area marks the range of data defining the corresponding trend line ($N = 53$) (dotted-dashed line).

investigated temperature range (19–28.5 °C). Thus, the application of either the $\delta^{44/40}Ca_{modern}$- or $\delta^{44/40}Ca_{culture}$-temperature calibration as SST proxy over time would propose the same magnitude of cooling or warming. However, the study shows that there is an apparent offset between SST calculated from $\delta^{44/40}Ca_{modern}$ and $\delta^{44/40}Ca_{culture}$ concerning absolute temperature reconstruction. The observed temperature offset between both thermometers is 4.0–4.5 °C. As a result the $\delta^{44/40}Ca_{culture}$-calibration (Nägler et al., 2000) would predict much higher absolute sea surface temperatures than the refined $\delta^{44/40}Ca_{modern}$-calibration.

The $\delta^{44/40}Ca$ is in particular useful in combination with Mg/Ca. Comparison of the first $\delta^{44/40}Ca$-temperature calibration to Mg/Ca records indicated that both thermometers simultaneously reflect seawater temperature changes. However, the $\delta^{44/40}Ca$-thermometer tend to predict about 2.5 °C higher absolute SSTs compared to Mg/Ca derived temperatures (Nägler et al., 2000). Fig. 2B illustrates the matching of the $\delta^{44/40}Ca_{modern}$-temperature calibration and the $\delta^{44/40}Ca$-$SST_{Mg/Ca}$ cross-calibration, i.e., linking $\delta^{44/40}Ca$ values of fossil *G. sacculifer* to Mg/Ca based temperatures using the calibration of Nürnberg et al. (2000). Both calibrations show the same temperature gradients of 0.22 ($\pm 0.05$) and 0.23 ($\pm 0.07$) per 1 °C, respectively, and the range of data (including uncertainties) defining the respective relationship is overlapping. These observations imply that Mg/Ca and Ca isotopes give similar absolute temperatures if the $\delta^{44/40}Ca_{modern}$-temperature calibration is applied to Ca isotope data.

### 4.3. Preservation of the primary temperature signal

Several lines of evidence indicate that the Ca isotopic composition of foraminiferal calcite is well preserved in our samples, therefore the primary temperature signal is not overprinted by secondary alteration. In particular, concerning past SST reconstruction the preservation of the primary signal is of major concern. Among others e.g., dissolution and the addition of gametogenic calcite are two processes that have to be considered in this respect. First preliminary results of a partial dissolution experiment on shells of *G. sacculifer* provide evidence that there is no relationship between the degree of dissolution and the corresponding $\delta^{44/40}Ca$ values (Hönisch, 2002). In the case of Mg/Ca thermometry Dekens et al. (2002) were able to show in a multi-species comparison of core-top foraminiferal Mg/Ca ratios that *G. sacculifer* is among the species most resistant to dissolution. The result is in agreement with previous studies of selective dissolution susceptibility (Bé, 1977). Second, modern samples reflecting the $\delta^{44/40}Ca_{modern}$-temperature calibration are collected from surface waters that are generally supersaturated in respect to calcium carbonate, whereas cross check calibrations based on fossil material reflect the material buried. The core depth (3122 m) is well above both the present-day ($\approx 4800$ m) and the Pleistocene lysocline depth (deeper $\approx 3800$ m, Bickert and Wefer (1996)) With respect to

carbonate concentration also the deepest parts of the Guinea Basin are dominated by slightly supersaturated North Atlantic Deep Water (NADW) (Broecker and Peng, 1982) causing the lysocline of calcite to stay much deeper compared to other South Atlantic basins (Thunnel, 1982). Even if there is a growing consensus that dissolution might occur above the lysocline, the coherence of both temperature calibrations suggests a negligible dissolution impact. Furthermore, calculated SST in our down-core study resulted in representative Holocene and glacial SST (see Section 5.2). However, it is evident that further work on depth-transects of core-top samples is necessary to explore the uncertainty limits of the method with respect to post-depositional processes. Given the time consuming Ca isotope analytics (on average one sample per day during this study) a final conclusive data set was beyond reach.

To reproduce *G. sacculifer* moves far below the euphotic zone. During gametogenesis it secretes a layer of secondary calcite, which may contain a subsurface temperature component. Bijma and Hemleben (1994) guess that gametogenic calcite is secreted in 80–100 m while Duplessy et al. (1991) postulate even deeper water depth within the main thermocline (300–800 m). Obviously, the $\delta^{44/40}Ca$ of individuals cultured under constant temperature cannot account for a subsurface temperature component. In contrast the $\delta^{44/40}Ca$ of modern and fossil samples of *G. sacculifer* comprises the natural variability related to their life cycles (including gametogenesis) and therefore might contain a muted surface signal. As shown above the $\delta^{44/40}Ca_{modern}$-temperature and $\delta^{44/40}Ca$-$SST_{Mg/Ca}$ cross-calibration of this study result within uncertainties in identical absolute SST estimates, with modern calculated core top SST values corresponding to Levitus and Boyer (1994). The observed temperature signal in foraminiferal calcite of *G. sacculifer* seems to be primary and a muted surface signal could be precluded. Concerning Mg/Ca-thermometry Dekens et al. (2002) quoted that *G. ruber* is the most accurate recorder of sea surface temperature, while *G. sacculifer* records temperatures below the surface at 20–30 m. As long as the calcification depth of *G. sacculifer* is controversial, the evidence whether $\delta^{44/40}Ca$ in *G. sacculifer* represents surface or subsurface temperatures can only be rendered by depth habitat tracking of both species. Comparing our $\delta^{44/40}Ca$-temperature calibrations on cultured, catched, and fossil samples we conclude that dissolution and the potential addition of gametogenic calcite have no significant impact on the reliability of Ca isotopes as SST proxy. Summarising our results we propose the use of the $\delta^{44/40}Ca_{modern}$-temperature relationship [1] for future palaeoceanographic applications.

## 5. Application of Ca isotopes as SST proxy

### 5.1. Down-core variations in $\delta^{44/40}Ca$ of fossil G. sacculifer

We measured $\delta^{44/40}Ca$ ratios on fossil calcite shells of *G. sacculifer* from sediment core GeoB1112 covering the

last about 140.000 years (marine isotope stages (MIS) 1–6) thus comprising two glacial–interglacial transitions (Fig. 3 and Table 2). Throughout the investigated time interval $\delta^{44/40}Ca$ values range between $-0.17$ and $+1.18$ (‰ SRM 915a). Given the observations that the Ca isotopic composition of seawater is homogenous throughout modern oceans (Zhu and MacDougall, 1998; Schmitt et al., 2001; Hippler et al., 2003) and no secular variations occur over the last 19 Ma (De La Rocha and DePaolo, 2000; Schmitt et al., 2003) these variations do not reflect changes in seawater Ca isotopic composition. The observed $\delta^{44/40}Ca$ down-core variations coincide with the Mg/Ca record for *G. sacculifer* (Nürnberg et al., 2000) and reflect glacial–interglacial cycles. Highest $\delta^{44/40}Ca$ values occur during interglacial periods while samples related to glacial times tend to have relatively low $\delta^{44/40}Ca$ values. We found pronounced $\delta^{44/40}Ca$ gradients at stage boundaries Holocene to Last Glacial Maximum (LGM) and MIS 5e to MIS 6, respectively. $\delta^{44/40}Ca$ values in the Holocene (MIS 1) range from 0.60 to 1.15‰. At stage boundary MIS 1/2 (Termination I) $\delta^{44/40}Ca$ drops to values of around $0.00 \pm 0.20$‰. LGM $\delta^{44/40}Ca$ values are low with small-scale variations between $-0.17$ and 0.17‰. During MIS 3 and MIS 4 the $\delta^{44/40}Ca$ ratio undulates between 0.00 and 1.02‰ describing an overall increasing trend towards the last interglacial. Measured $\delta^{44/40}Ca$ values in MIS 5 vary over a wide range with peak values of 1.18‰ at MIS 5e. Stage boundary MIS 5/6 (Termination II) exhibits a pronounced decrease to values of around 0.11‰.

Using the $\delta^{44/40}Ca_{modern}$-temperature calibration (see Eq. (1)) past temperatures could be calculated using the following equation:

$$SST[^{\circ}C] = 4.55 * \delta^{44/40}Ca[‰\ SRM915a] + 22.18$$
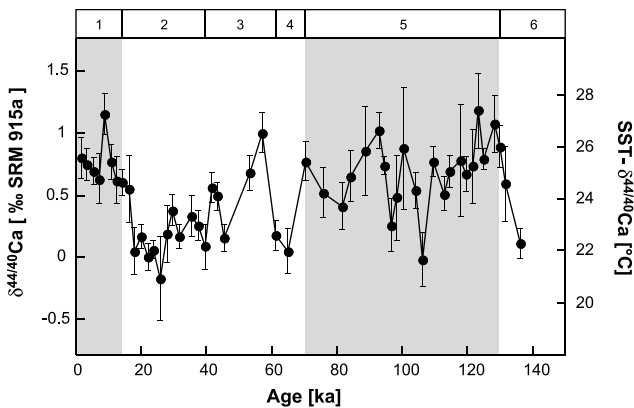$$= SST_{\delta_{44/40Ca}}[^{\circ}C]. \qquad (3)$$



Fig. 3. Down-core record of $\delta^{44/40}Ca$ values [‰ SRM 915a] of fossil *G. sacculifer* and reconstructed sea surface temperatures (SST). $SST_{\delta_{44/40Ca}}$ are calculated applying the $\delta^{44/40}Ca_{modern}$-temperature calibration ($\delta^{44/40}Ca[‰] = 0.22$ ($\pm 0.05$) per 1 °C) introduced in this study. Shaded bands represent the Holocene and the last interglacial period. Numbers on top of the diagram reflect marine oxygen isotope stages (MIS) after Martinson et al. (1987).

Table 2
Down-core variations in $\delta^{44/40}Ca$ of fossil *G. sacculifer* from core GeoB1112

| Depth (cm) | Age (kyr)[a] | $\delta^{44/40}Ca$ (‰)[b] | Uncertainty[c] | $\delta^{44/42}Ca$ (‰)[d] | Number of analyses[e] |
|---|---|---|---|---|---|
| 3 | 1.71 | 0.80 | 0.16 | 0.40 | 3[f] |
| 8 | 3.52 | 0.75 | 0.13 | 0.38 | 1 |
| 13 | 5.34 | 0.69 | 0.11 | 0.35 | 1 |
| 18 | 7.14 | 0.63 | 0.20 | 0.32 | 1 |
| 23 | 8.95 | 1.15 | 0.16 | 0.58 | 1[f] |
| 28 | 10.77 | 0.77 | 0.14 | 0.39 | 1 |
| 33 | 12.57 | 0.62 | 0.19 | 0.31 | 1[f] |
| 38 | 14.38 | 0.60 | 0.10 | 0.30 | 1 |
| 43 | 16.19 | 0.55 | 0.27 | 0.28 | 1[f] |
| 48 | 18.00 | 0.05 | 0.19 | 0.03 | 2 |
| 53 | 19.96 | 0.17 | 0.10 | 0.09 | 1 |
| 58 | 21.92 | 0.00 | 0.11 | 0.00 | 3 |
| 63 | 23.88 | 0.06 | 0.07 | 0.03 | 1 |
| 68 | 25.83 | −0.17 | 0.34 | −0.09 | 2[f] |
| 73 | 27.79 | 0.19 | 0.23 | 0.10 | 1 |
| 78 | 29.75 | 0.38 | 0.13 | 0.19 | 2[f] |
| 83 | 31.71 | 0.17 | 0.10 | 0.09 | 2 |
| 93 | 35.63 | 0.33 | 0.16 | 0.17 | 1 |
| 98 | 37.58 | 0.26 | 0.12 | 0.13 | 2 |
| 103 | 39.54 | 0.09 | 0.18 | 0.05 | 1 |
| 108 | 41.50 | 0.56 | 0.12 | 0.28 | 1 |
| 113 | 43.46 | 0.49 | 0.11 | 0.25 | 1 |
| 118 | 45.42 | 0.16 | 0.11 | 0.08 | 2 |
| 128 | 49.33 | 1.19 | 0.18 | 0.60 | 1 |
| 138 | 53.25 | 0.68 | 0.14 | 0.34 | 1 |
| 148 | 57.17 | 1.00 | 0.16 | 0.50 | 1 |
| 158 | 61.08 | 0.18 | 0.12 | 0.09 | 1 |
| 168 | 65.00 | 0.05 | 0.18 | 0.03 | 1 |
| 178 | 70.50 | 0.77 | 0.16 | 0.39 | 2 |
| 188 | 76.00 | 0.52 | 0.20 | 0.26 | 1[f] |
| 198 | 81.50 | 0.41 | 0.19 | 0.21 | 2 |
| 203 | 84.25 | 0.65 | 0.20 | 0.33 | 1 |
| 213 | 88.91 | 0.86 | 0.36 | 0.43 | 1 |
| 223 | 92.73 | 1.02 | 0.14 | 0.51 | 1 |
| 228 | 94.64 | 0.74 | 0.07 | 0.37 | 1 |
| 233 | 96.55 | 0.26 | 0.21 | 0.13 | 1[f] |
| 238 | 98.45 | 0.48 | 0.34 | 0.24 | 1 |
| 243 | 100.36 | 0.88 | 0.49 | 0.44 | 1[f] |
| 248 | 102.27 | 1.26 | 0.13 | 0.63 | 1 |
| 253 | 104.18 | 0.54 | 0.14 | 0.27 | 1 |
| 258 | 106.09 | −0.02 | 0.22 | −0.01 | 1 |
| 268 | 109.69 | 0.77 | 0.12 | 0.39 | 1 |
| 278 | 113.06 | 0.51 | 0.14 | 0.26 | 1 |
| 283 | 114.75 | 0.69 | 0.13 | 0.35 | 1 |
| 293 | 118.13 | 0.78 | 0.45 | 0.39 | 1[f] |
| 298 | 119.81 | 0.67 | 0.14 | 0.34 | 3[f] |
| 303 | 121.50 | 0.73 | 0.30 | 0.37 | 1 |
| 308 | 123.19 | 1.18 | 0.30 | 0.59 | 1 |
| 313 | 124.88 | 0.79 | 0.09 | 0.40 | 1 |
| 323 | 128.25 | 1.07 | 0.23 | 0.54 | 1 |
| 328 | 129.94 | 0.89 | 0.17 | 0.45 | 1 |
| 333 | 131.63 | 0.59 | 0.30 | 0.30 | 1 |
| 348 | 136.45 | 0.11 | 0.12 | 0.06 | 2[f] |

[a] Age model taken from Meinecke (1992).
[b] $\delta^{44/40}Ca$ values in (‰) relative to NIST SRM 915a. For reproduced analyses a weighted average is given.
[c] Uncertainties reflect the $2\sigma$ standard error for single and the weighted mean error for reproduced analyses, respectively.
[d] $\delta^{44/42}Ca$ values in (‰) relative to NIST SRM 915a are calculated according to Hippler et al. (2003).
[e] Number of analyses.
[f] Data from Nägler et al. (2000).

The corresponding $\delta^{44/40}Ca_{modern}$-derived temperature record of sediment core GeoB1112 is displayed in Fig. 3. During the Holocene calculated $SST_{\delta_{44/40Ca}}$ values range between 24.0 and 26.5 °C. Minimum $SST_{\delta_{44/40Ca}}$ between 21.0 and 23.0 °C persists during the Last Glacial Maximum and MIS 6, while peak $SST_{\delta_{44/40Ca}}$ of 27 °C is reached during the Last Interglacial MIS 5e. The overall glacial-interglacial amplitude for the investigated time interval is 3.5 ± 1.0 °C, whereas the temperature change at the Termination II is more distinct than at the Holocene-LGM transition.

### 5.2. $SST_{\delta_{44/40Ca}}$ core-top estimates and comparison to recent conditions

Applying the $\delta^{44/40}Ca_{modern}$-temperature calibration [see Eq. (1)], estimates of absolute SST of core top sample in core GeoB1112 correspond to the upper limit of what is expected from Levitus and Boyer (1994). The calculated $SST_{\delta_{44/40Ca}}$ signal is in agreement with the temperature situation averaged for the entire year within the uppermost 50 m of the water column, the assumed habitat of pregametogenic *G. sacculifer*. According to Levitus and Boyer (1994) the core location of GeoB1112 is characterised by rather constant temperatures throughout the year. The adjacent equatorial upwelling lasting from May to August has no significant impact on seasonal temperature variations in the core-collected region. Considering further the low temporal resolution of the core, our data do not allow a more detailed seasonal assignment. The previous work of Nürnberg et al. (2000) additionally included an upwelling-influenced sediment core (GeoB1105, 1°39.9′S, 12°25.7′W, 3225 m). From the comparison of these two Mg/Ca derived SST-records the authors concluded that for the area of

investigation the observed $SST_{Mg/Ca}$ signal of *G. sacculifer* reflects the austral low-latitude fall/winter upwelling situation within the uppermost 50 m of the water column.

### 5.3. Past sea surface temperature reconstruction in the tropical Atlantic

We compared the $\delta^{44/40}Ca$ record with the available $\delta^{18}O$ and Mg/Ca records of core GeoB1112 in Figs. 4A and B. The results broadly coincide and confirm postulated trends of tropical palaeo-reconstruction.

The $SST_{\delta_{18O}}$ record was calculated (see Appendix A) from the available $\delta^{18}O$-record of Meinecke (1992) by applying the $\delta^{18}O$-temperature relationship of Mulitza et al. (2003). The $SST_{\delta_{18O}}$ record reflects the main glacial-interglacial cycles. However, $SST_{\delta_{18O}}$ is considerably lower than the corresponding $SST_{\delta_{44/40Ca}}$. The observed offset is 2.0 ± 1.0 °C (Fig. 4A). According to the detailed discussion of Mulitza et al. (2003) $SST_{\delta_{18O}}$ based on calibrations of *G. sacculifer* should record a muted surface signal. The depth ranking of four examined species based on $\delta^{18}O$ analyses by Spero et al. (2003) suggests that *G. sacculifer* inhabits a slightly deeper/cooler environment. These findings are in accordance with relationships derived from pH-controlled culturing experiments of Bemis et al. (1998). The uncertainty on calculated absolute palaeotemperatures resulting from the use of either the $\delta^{18}O$-temperature relationship of Mulitza et al. (2003), Bemis et al. (1998) or Spero et al. (2003) would amount to less than 1.5 °C. The latter authors note that the palaeothermometers proposed by Shackleton (1974) or Erez and Luz (1983) give reliable estimates for relative temperature change but seem to overestimate absolute temperatures. Apart from the
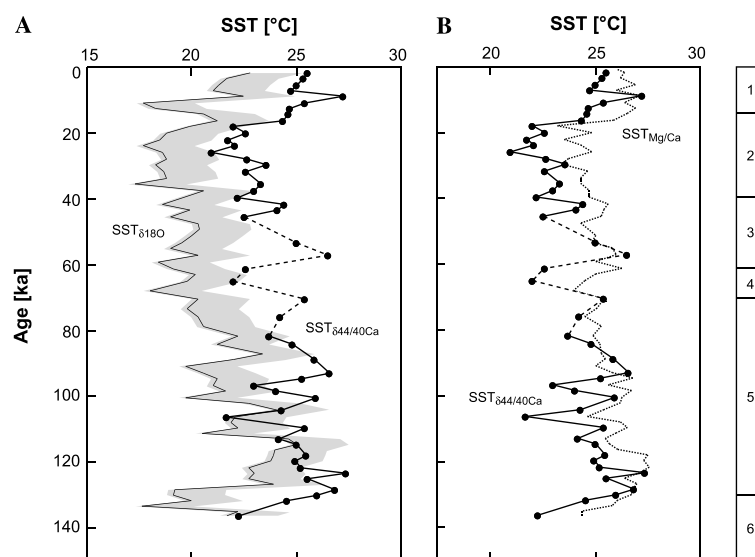


Fig. 4. Calculated $SST_{\delta_{44/40Ca}}$ record (dots) of core GeoB1112 over the last 140.000 years in comparison to SST calculated from (A) $\delta^{18}O$ (Meinecke, 1992) and (B) Mg/Ca (Nürnberg et al., 2000). There is a general agreement of the SST pattern derived from $\delta^{18}O$ and $\delta^{44/40}Ca$, although $\delta^{44/40}Ca$ predicts about 2.0 ± 1.0 °C higher temperatures. In contrast, there is an excellent correlation between Mg/Ca and $\delta^{44/40}Ca$ without a significant offset. The shaded area accompanying the $\delta^{18}O$ record illustrates the range of predicted absolute temperatures when using the alternative $\delta^{18}O$-temperature relationship of Bemis et al. (1998) or Spero et al. (2003).

observed offset in absolute temperatures the general pattern of calculated $SST_{\delta_{18O}}$ and $SST_{\delta_{44/40Ca}}$ is in good agreement. Even the smaller-scale temporal amplitudes of both records reveal similar amounts of tropical temperature change. Apparently, the greater deviation during MIS 3 and MIS 4 might be a direct consequence of the lower sample resolution of the $SST_{\delta_{44/40Ca}}$ record.

The temporal pattern of the palaeo-SST records calculated from Mg/Ca (Nürnberg et al., 2000) and $\delta^{44/40}$Ca is in overall agreement, although the $SST_{Mg/Ca}$ appear generally higher in comparison to $SST_{\delta_{44/40Ca}}$ (Fig. 4B). Furthermore, several species-specific Mg/Ca-temperature relationships were published recently e.g., by Dekens et al. (2002) and Anand et al. (2003). Application of the latter calibrations results in similar absolute temperatures within errors. The apparent offset to $SST_{\delta_{44/40Ca}}$ (1–2 °C) becomes negligible considering the uncertainties of the respective temperature record ($SST_{\delta_{44/40Ca}}$ and $SST_{Mg/Ca}$). In particular, the consistency of the temporal phasing of both records ($\delta^{44/40}$Ca and Mg/Ca) is evident in the point-to-point comparison of both records at the transitions Holocene-Last Glacial Maximum (LGM) and MIS 5 to MIS 6. This feature is apparently not reached to the same extent during MIS 3 and MIS 4 because the sample resolution of both records is not equivalent. Throughout both SST records amplitudes of short temporal variations are more distinct for $SST_{\delta_{44/40Ca}}$ especially during interglacials. Common to both down-core records is the glacial-interglacial amplitude of approximately 3 °C for the last climatic changes with less pronounced Holocene-LGM temperatures compared to the interglacial stage 5 to glacial stage 6 Table 3.

One of the most important challenges in palaeoceanography involves the magnitude of SST changes during the last ice age. The CLIMAP study (1981) initially suggested a drop in SST in the tropics of about 1.5 °C at the Holocene-LGM transition. This assumption has long been used as boundary conditions for simulations of the climate of the LGM (e.g., COHMAP Project, 1988). In contrast, there is now a growing consensus about glacial temperatures in the tropics from both the Atlantic and the Pacific Ocean. Temperature reconstruction based on various proxies using different marine archives ($\delta^{18}$O, Mg/Ca, Sr/Ca, $U_{37}^{K'}$), and

**Table 3**
Core top SST estimates for various proxies in comparison to Levitus and Boyer (1994)

| Reference | Method | SST (°C) | Remarks |
|---|---|---|---|
| Levitus and Boyer (1994) | | 23.3–25.5[a] | Annual |
| This study | $SST_{\delta_{44/40Ca}}$ | 25.6 | Core top |
| | $SST_{\delta_{18O}}$[b] | 22.8 | Core top |
| Nürnberg et al. (2000) | $SST_{Mg/Ca}$ | 26.1 | Core top |

[a] The Levitus and Boyer (1994) water temperatures represent an average value of the upper 50 m of the water column for the entire year.
[b] $\delta^{18}$O record of Meinecke (1992) and calculated SST based on the $\delta^{18}$O-temperature relationship published by Mulitza et al. (2003).

**Table 4**
Magnitude of tropical SST cooling at the transition Holocene-Last Glacial Maximum

| Reference | SST (°C) | Method |
|---|---|---|
| *Global Oceans* | | |
| CLIMAP study (1981) | 1.0–2.0 | Faunal assemblages |
| *Atlantic Ocean* | | |
| This study | 2.5–3.5 | $SST_{\delta_{44/40Ca}}$ |
| Van Campo et al. (1990) | 3.0–4.0 | Global circulation model |
| Guilderson et al. (1994) | ≈5.0 | $SST_{Sr/Ca}$ (corals) |
| Hastings et al. (1998) | 2.6 ± 1.3 | $SST_{Mg/Ca}$ |
| Wolff et al. (1998) | 2.0–3.0 | $SST_{\delta_{18O}}$ |
| Rühlemann et al. (1999) | 3.5 | $SST_{UK'37}$ |
| | 3.0–4.0 | $SST_{\delta_{18O}}$ |
| Nürnberg et al. (2000) | ≈2.5 | $SST_{Mg/Ca}$ |
| Lea et al. (2003) | 2.6 ± 0.5 | $SST_{Mg/Ca}$ |
| *Pacific Ocean* | | |
| Lea et al. (2000) | ≈3.0 | $SST_{Mg/Ca}$ |
| Kienast et al. (2001) | ≈3.0 | $SST_{UK'37}$ |
| Visser et al. (2003) | 3.5–4.0 | $SST_{Mg/Ca}$ |
| Rosenthal et al. (2003) | 2.3 ± 0.5 | $SST_{Mg/Ca}$ |

modelling studies point to an intermediate cooling of surface water masses of around 3.0 °C (for references see Table 4). Our result based on the herein introduced independent Ca isotope palaeothermometer toe perfectly in this context.

## 6. Summary and conclusion

Systematic Ca isotope analyses on tests of modern *G. sacculifer* covering a temperature range between 19 and 29 °C provide an additional and robust tool for the reconstruction of past sea surface temperatures. A change in $\delta^{44/40}$Ca [‰] of 0.22 (±0.05) corresponds to a temperature change of 1 °C. Secondary processes like dissolution or gametogenesis have no significant impact on the temperature-dependent Ca isotope fractionation as shown by the comparison of three independent calibrations. Estimates of relative temperature changes are compatible with previous results of Nägler et al. (2000). Furthermore, the accuracy of absolute temperatures is supported by the conformity of calculated $SST_{\delta_{44/40Ca}}$ from core top sample and modern annual SST according to Levitus and Boyer (1994). This improvement over the initial calibration (Nägler et al., 2000) points to a $\delta^{44/40}$Ca bias in cultured *G. sacculifer* of the latter.

We propose the use of the $\delta^{44/40}Ca_{modern}$-temperature calibration ($\delta^{44/40}$Ca[‰] = 0.22(±0.05) ∗ SST [°C] − 4.88) for future applications in palaeoceanography. Adopting this calibration to down-core fossil *G. sacculifer* our results indicate that the equatorial Atlantic was about 3–4 °C colder than present-day conditions during the last two glacial periods. The use of a multi-proxy approach and the comparison with what is known from literature confirm our findings about past tropical SST history.

The strong temperature dependence of Ca isotope fractionation observed in biogenic calcite tests of *G. sacculifer*

can provide new insights in biomineralization processes. Within the data set presented here there is no obvious influence of the complex biology, like yet unquantified metabolic and physiological processes in nature that would unsettle the confidence in the potential of Ca isotopes as SST proxy when using selective planktonic foraminifera species.

## Acknowledgments

## Appendix A. SST Estimates derived from oxygen isotopes

Within the scope of our multi-proxy comparison we determined past SSTs from the available $\delta^{18}O$ record of *G. sacculifer* (Meinecke, 1992) by applying the species-specific temperature–$\delta^{18}O$ relationship established by Mulitza et al. (2003):

$$T[^\circ C] = -4.35(\delta^{18}O_{cal} - \delta^{18}O_{sw}) + 14.91. \qquad (4)$$

Here $\delta^{18}O_{cal}$ stands for the oxygen isotopic composition of the calcite (in ‰ Peedee Belemnite (PDB)) and $\delta^{18}O_{sw}$ is the oxygen isotopic composition of seawater (in ‰ Standard Mean Ocean Water (SMOW)). The conversion of $\delta^{18}O_{sw}$ from the SMOW to the PDB scale is performed according to Hut (1987) proposing a correction factor of $-0.27‰$. Estimating SST from the $\delta^{18}O$ of foraminiferal calcite, local salinity effects on the $\delta^{18}O_{sw}$ have to be considered. To do this we chose estimates of $\delta^{18}O_{sw}$ from the Global Seawater Oxygen-18 Database (Schmidt et al., 1999) available at (http://www.giss.nasa.gov/data/o18data/) (Schmidt, 1999; Bigg and Rohling, 2000). According to Levitus and Boyer (1994) salinities of approximately 35.5‰ prevail at 0–100 m water depth in low-latitude Atlantic. For the core location of GeoB1112 we obtained representative $\delta^{18}O_{sw}$ values for the tropical east Atlantic of $0.79 \pm 0.10‰$. This value is in good agreement with what would be calculated using $\delta^{18}O$ versus salinity relationships proposed in the literature (Duplessy et al., 1991; Wang et al., 1995). Investigating glacial-interglacial cycles secular variations of seawater $\delta^{18}O$ driven by ice volume changes have to be taken into account. We considered the so-called "ice effect" by subtracting the mean $\delta^{18}O_{sw}$ record

of Vogelsang, 1990 (modified after Labeyrie et al., 1987). The mean $\delta^{18}O_{sw}$ increase of 1.1‰ during the LGM is in accordance with direct measurements of oxygen isotopes of relict glacial pore water (Schrag et al., 1996), high-resolution $\delta^{18}O$ records of benthic foraminifera (Labeyrie et al., 1987) and combined studies of Shackleton (2000).

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