The δ^{44}Ca-temperature calibration on fossil and cultured *Globigerinoides sacculifer*: New tool for reconstruction of past sea surface temperatures

T. F. Nägler

Isotopengeologie, Mineralogisch-petrographisches Institut, Universität Bern, CH-3012 Bern, Erlachstrasse 9a, Switzerland (naegler@mpi.unibe.ch)

A. Eisenhauer and A. Müller

GEOMAR, Forschungszentrum für marine Geowissenschaften, Wischhofstrasse 1-3, 24148 Kiel, Germany (aeisenhauer@geomar.de; amueller@geomar.de)

C. Hemleben

Institut für Geologie und Paläontologie, Sigwartstrasse 10, 72076 Tübingen, Germany (christoph.hemleben@uni-tuebingen.de)

J. Kramers

Isotopengeologie, Mineralogisch-petrographisches Institut, Universität Bern, CH-3012 Bern, Erlachstrasse 9a, Switzerland (kramers@mpi.unibe.ch)
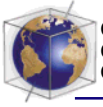
[1] **Abstract:** We report direct δ^{44}Ca-temperature calibration on cultured and fossil calcite foraminifera, showing that Ca isotopes are potentially a new proxy for past sea surface temperatures (SST). Samples have been analyzed using a ^{43}Ca-^{48}Ca double spike and thermal ionization mass spectrometry (TIMS). In order to avoid species-dependent isotope fractionation we focused our investigations on a single foraminifera species (*Globigerinoides sacculifer*), which is known to inhabit shallow euphotic waters in tropical and subtropical oceans. Ca isotope measurements were performed on cultured *G. sacculifer* that grew in seawater kept at temperatures of 19.5°, 26.5°, and 29.5°C. A δ^{44}Ca change of 0.24 ± 0.02 per 1°C is defined by the weighted linear regression through reproduced δ^{44}Ca data of the three temperatures (95% confidence level). Application of this new method to fossil *G. sacculifer* of an Equatorial East Atlantic sediment core (GeoB1112; 5°46.7′S, 10°45.0′W, 3125 m) indicates that the δ^{44}Ca difference between marine isotope stage 1 (MIS-1) and MIS-2 is 0.71 ± 0.24. According to the current δ^{44}Ca-temperature calibration this value corresponds to a temperature difference between MIS-1 and MIS-2 of ~3.0 ± 1.0°C.

1. Introduction

[2] Sea surface temperature (SST) at the ocean-atmosphere interface strongly influences gas exchange, global evaporation and precipitation patterns, sea and continental ice formation, and primary biological production [*Beck et al.*, 1992]. Therefore reliable SST time series are important for the reconstruction of past global climate change and the prediction of future greenhouse warming. It is now common practice to reconstruct variations in SST from $\delta^{18}O$ measurements [*Shackleton et al.*, 1983], Sr/Ca ratios [*Beck et al.*, 1992], and Mg/Ca ratios [cf. *Elderfield and Ganssen*, 2000; *Lear et al.*, 2000; *Nürnberg et al.*, 1996, 2000] on marine carbonates (e.g., corals and foraminifera). In general, to generate a temperature record from elemental or isotope data, four issues must be addressed. These are that of interspecific differences, preservation of primary elemental or isotope values, variation of past elemental or isotope ratios in seawater, and finally an element or isotope-temperature calibration [*Elderfield and Ganssen*, 2000]. The use of $\delta^{18}O$ as SST proxy is restricted by local variations of precipitation and evaporation patterns, as well as being controlled by the variable amount of water stored in continental ice sheets. Similar to that, Sr/Ca and U/Ca signals in corals are suspected to be species dependent, influenced by postdiagenetic alteration and changing ocean budgets. In contrast, *Lear et al.* [2000] and *Elderfield and Ganssen* [2000] demonstrated in recent publications that Mg/Ca ratios in calcitic foraminifera fulfill all requirements for a reliable past SST proxy.

[3] Although Mg/Ca ratios can now be regarded as a robust and reliable SST proxy, having further independent isotope SST proxies available is still desirable. Ca isotopes ($\delta^{44}Ca$) may be such a further SST proxy. A paleo-SST proxy based exclusively on Ca as a major component of skeletons is unlikely to be susceptible to environmental and diagenetic alterations such as changes in elemental ratios in the ocean water or secondary partial dissolution. Ca has six stable isotopes (masses 40, 42, 43, 44, 46, and 48), with ^{40}Ca being by far the most abundant (∼96.98% [*Russell et al.*, 1978]). Besides mass-dependent natural fractionation, the production of ^{40}Ca from the radioactive decay of ^{40}K is responsible for variations in the precise isotopic composition of Ca. However, ocean water Ca can be considered constant through the Quaternary, as the Ca residence time (∼1 Ma [*Broecker and Peng*, 1982; *Zhu and MacDougall*, 1998]) is long compared to the mixing time of ocean water in the range of ∼10^3 years. This latter assumption was recently confirmed by the Ca isotope data of *Zhu and MacDougall* [1998] (four localities, 43- to 1300-m depths, within analytical uncertainty).

[4] *Russell et al.* [1978] presented the first data on Ca isotope fractionation in terrestrial material that combined modern high-precision mass spectrometry with the application of the Ca double-spike technique. The major finding of the study was that natural fractionation of Ca isotopes is relatively small, needing high precision to be resolved. No systematic biological fractionation was found in the analyzed data set. *Skulan et al.* [1997] focused their attention on the biological control of the Ca isotopic abundance. They analyzed Ca from various planktic foraminiferal species and concluded that Ca isotopic fractionation is relatively uniform in magnitude among vastly different types of organisms. The results of *Skulan et al.* [1997] indicated that Ca becomes isotopically lighter when it moves through food chains. *Zhu and MacDougall* [1998] suggested that Ca isotope data from foraminifera of a given species may significantly vary with ocean water temperature and/or depth. Both studies
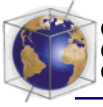
clearly point to the likelihood that the δ^{44}Ca ratios are controlled by biological processes and potentially by temperature fluctuations. This hypothesis was the impetus for the present study of temperature-controlled δ^{44}Ca variations on foraminifera (*G. sacculifer*) to possibly establish a temperature/δ^{44}Ca calibration curve for the purpose of paleo-SST reconstruction.

2. Sample Material

[5] In order to eliminate the species-dependent biological effect on isotope fractionation we focused on a single species, *G. sacculifer*, which is known to inhabit the euphotic zone in tropical and subtropical pelagic waters. For δ^{44}Ca measurements, cultured foraminifera were selected that grew in seawater kept at temperature in culture of 19.5°, 26.5°, and 29.5°C [*Hemleben et al.*, 1987, 1989), respectively (Table 1). The light and feeding conditions were adjusted to the open ocean environment nearby Barbados. The light intensity and quality corresponded to a water depth of 10–30 m, and the specimens were fed daily. Specimens were raised from a mean initial size of ∼220–240 μm

to the reproductive mean size ranging from 521 to 657 μm according to the different temperature and salinity regimes [*Hemleben et al.*, 1987].

[6] In order to extend our study we performed δ^{44}Ca measurements on foraminifers from sediment core GeoB1112 (5°46.7′S, 10°45.0′W, 3125 m) because for this core a very detailed Mg/Ca record of *G. sacculifer* was available [*Nürnberg et al.*, 2000]. For δ^{44}Ca-measurements foraminifera (*G. sacculifer*, 250–500 μm size fraction) were taken from selected core sections comprising glacial and interglacial climatic stages.

[7] Core GeoB1112 covers the last 270,000 years (MIS-1 to -8), thus comprising three glacial/interglacial transitions (2/1, 6/5, 8/7) where the Mg/Ca ratios vary between 2.6 and 4.4 mmol/mol [*Nürnberg et al.*, 2000]. The paleo-SST record reconstructed from Mg/Ca ratios ($SST_{Mg/Ca}$) vary between 24° and 27°C, respectively, which is in the temperature range reported in the Levitus atlas for this region (∼23° to 26°C [*Levitus and Boyer*, 1994]). Paleo-SST reconstruction showed that the glacial/interglacial $SST_{Mg/Ca}$ variations

**Table 1.** The δ^{44}Ca Ratios of Cultured *Globigerinoides sacculifer* Growth

T, °C	δ^{44}Ca[a]	Uncertainties[b]	Analysis Type[c]
19.5	−3.19	0.13	$10^{11}\Omega$ resistor
19.5	−3.53	0.31	$10^{10}\Omega$ resistor
19.5	−3.24	0.12	weighted average
26.5	−1.59	0.24	$10^{11}\Omega$ resistor
26.5	−1.65	0.15	$10^{10}\Omega$ resistor
26.5	−1.64	0.13	weighted average
29.5	−0.86	0.14	$10^{11}\Omega$ resistor
29.5	−0.61	0.28	$10^{11}\Omega$ resistor
29.5	−0.23	0.50	$10^{10}\Omega$ resistor
29.5	−0.78	0.12	weighted average

[a]The δ^{44}Ca = (^{44}Ca/^{40}Ca$_{sample}$ /^{44}Ca/^{40}Ca$_{normal}$ − 1) × 1000. As "normal" we selected Ca from natural fluorite.
[b]Uncertainties are given as 2σ errors.
[c]The ^{44}Ca/^{40}Ca of our Ca standards reproduced within 0.03% (2σ standard deviation, $10^{10}\Omega$ resistor) and 0.011% ($10^{11}\Omega$ resistor), respectively.
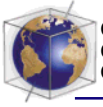
amount to ~3°C for the climatic transitions at 8/7, 6/5, and 2/1. This temperature variation is in general accord with other independent observations of glacial/interglacial SST variations of the order of ~2.5°C in this area [*Hastings et al.*, 1998].

3. Methods

[8] The foraminifera (about five individuals from fossil samples, a single one for cultured tests) were dissolved in 2.5 N HCl. Fossil samples were precleaned following the procedure described by *Nürnberg et al.* [2000] in order to eliminate any impurities. An aliquot corresponding to ~0.3 to 1 μg Ca was spiked with a ^{43}Ca-^{48}Ca double spike. Chemistry blanks are below ~1 ng.

[9] The $^{43}Ca/^{48}Ca$ ratio of the double spike ($^{43}Ca/^{48}Ca$ = 0.7866) was designed to resemble the natural $^{43}Ca/^{48}Ca$ ratio. As a result after spiking, the observed $^{43}Ca/^{48}Ca$ ratio in the measured Ca was never more than ~1% off the pure spike value, thus demagnifying uncertainties related to the within-run normalization. Calibration of the Ca isotopic composition of the double spike closely followed the critical-mixture approach of *Hofmann* [1971]. Natural fluorite was employed as the Ca standard and was supposed to be free of technical fractionation. Fluorite measured by *Russell et al.* [1978] is very similar to their value for unfractionated average Ca ($^{40}Ca/^{44}Ca$ = 47.165 ± 10 and 47.153, respectively). However, absolute Ca isotope ratios depend on the double-spike calibration procedure and measurement routines [cf. *Russell et al.*, 1978; *Zhu and MacDougall*, 1998]. We therefore give our data exclusively as relative deviations from a given standard material. In line with *Zhu and MacDougall* [1998] and *Skulan et al.* [1997] we present our values in the δ notation defined by $\delta^{44}Ca = (^{44}Ca/^{40}Ca_{sample}/^{44}Ca/^{40}Ca_{normal} - 1) \times 1000$.

[10] Ca isotopic composition runs were done on a modified single cup AVCO® mass spectrometer equipped with a Keithley 624 LNFPA electrometer and a Schlumberger SI 7071 digital voltmeter. The sample ($CaCl_2$) was dissolved in 1-μL H_2O and loaded on previously washed and outgassed single Re filaments together with 1 μL of a Ta_2O_5 solution [*Birck*, 1986]. The ^{40}K interference on ^{40}Ca was ~1 ppm at the beginning of the measurements and 0.1 ppm after 100 cycles. Corrections for isobaric interferences were done online. There were no detectable amounts of Sr^{2+}. The $^{44}Ca/^{40}Ca$ ratios of our Ca standards reproduced within 0.03% (2σ standard deviation, $10^{10}\Omega$ resistor) and 0.011% ($10^{11}\Omega$ resistor), respectively. A numerical algorithm [*Compston and Oversby*, 1969] was used to calculate the relative fractionation of the Ca data. However, the linear fractionation law used in the algorithm was replaced by an exponential fractionation law.

4. Results

4.1. The δ⁴⁴Ca Measurements on Cultured Foraminifera

[11] The results of δ⁴⁴Ca measurements on cultured foraminifera are presented in Table 1 and are graphically displayed in Figure 1. The measured δ⁴⁴Ca values on cultured foraminifer vary between about −3.24 ± 0.12 and about −0.78 ± 0.12‰. From a linear fit to the data a preliminary δ⁴⁴Ca-temperature calibration curve (T (°C) = 4.1 × δ⁴⁴Ca + 32.91) can be established. Note that this linear calibration is based on three single measurements only and just represents a first attempt to establish a δ⁴⁴Ca-temperature calibration. In particular, we note that the δ⁴⁴Ca-temperature relationship is not necessarily linear but may also be controlled by more complex nonlinear functions like other
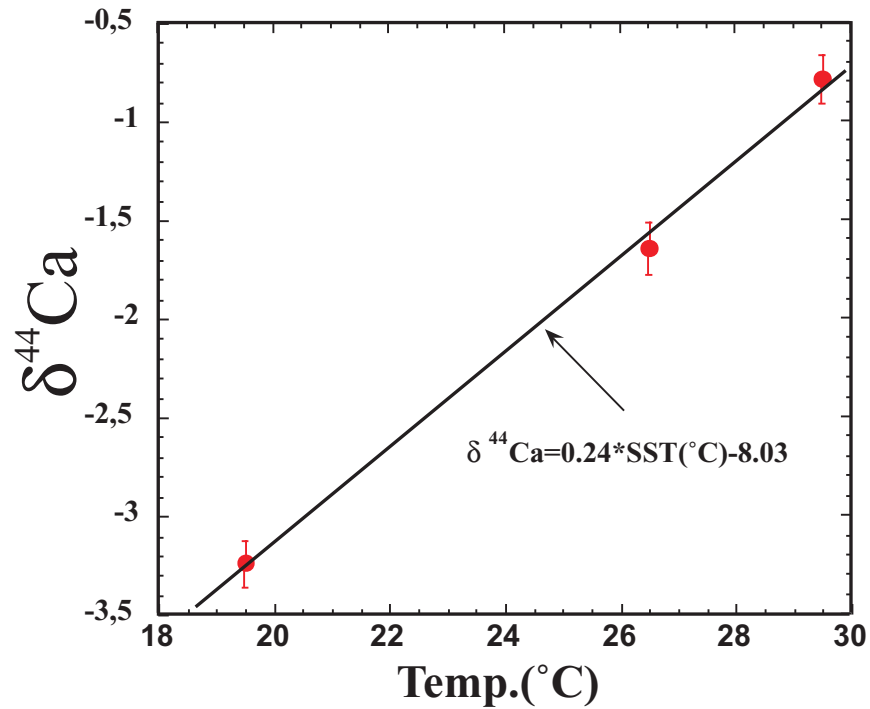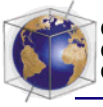
Figure 1. The δ^{44}Ca ratios *of G. sacculifer* cultured under controlled temperature conditions. Every data point represents the weighted means of two to three independent analyses. The bold line represents our current absolute temperature calibration. The error bars represent the statistical uncertainties.

geothermometers do. Therefore extrapolations of the calculated relationship to temperatures outside the investigated temperature range are unsupported.

Table 2. The δ^{44}Ca Ratios of *G. sacculifer* From Sediment Core GeoB1112[a]

Depth, cm	δ^{44}Ca	Uncertainties	Number of Analyses	MIS	Age, ka
3	−0.67	±0.16	3	1	2
23	−0.32	±0.16	1	1	9
33	−0.85	±0.19	1	1	12
43	−0.92	±0.27	1	2	16
58	−1.62	±0.14	1	2	22
68	−1.64	±0.34	2	2	26
78	−1.09	±0.13	2	2	30
98	−1.48	±0.60	1	3	38
188	−0.95	±0.20	1	4	76
233	−1.21	±0.21	1	5	97
243	−0.59	±0.49	1	5	100
293	−0.69	±0.45	1	5	118
298	−0.80	±0.14	3	5	120
348	−1.36	±0.12	2	6	136
603	−0.83	±0.16	1	7	239

[a]Analytical details as in Table 1. Uncertainties reflect the 2σ error within run precision for single analyses. For reproduced analyses a weighted mean error was calculated. MIS, marine isotope stages [*Martinson et al.*, 1987]; ka, 1000 years.
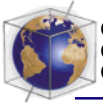
4.2. The δ⁴⁴Ca Measurements on Fossil Foraminifera of Core GeoB1112

[12] In core GeoB1112, δ⁴⁴Ca values of *G. sacculifer* were measured from selected core depths for the last 7 MIS (Table 2 and Figures 2 and 3). Measured δ⁴⁴Ca ratios vary between −1.64 ± 0.34 and −0.32 ± 0.16‰. Within statistical uncertainties, δ⁴⁴Ca ratios show a linear correlation to their corresponding Mg/Ca ratios (Figure 2). Foraminifera selected from core sections corresponding to interglacial periods (MIS-1, -5, -7) tend to have relatively high Mg/Ca ratios and more positive δ⁴⁴Ca ratios than those selected from core sections related to glacial periods (MIS-2, -4, -6, Figure 2). However, there is an offset of ∼2.5° to 3.5°C between δ⁴⁴Ca absolute temperature calibration and $SST_{Mg/Ca}$ reconstruction in this temperature range. In spite of this temperature offset it can be seen from Figure 3 that the δ⁴⁴Ca variations in core GeoB1112 closely follow the same glacial/interglacial variations than the Mg/Ca ratios.

[13] From the three Holocene (MIS-1) δ⁴⁴Ca ratios and the four MIS-2 δ⁴⁴Ca ratios, two mean δ⁴⁴Ca ratios of −0.61 ± 0.16 and −1.32 ± 0.18‰, respectively, can be calculated (see Table 2). The glacial/interglacial (MIS-1/MIS-2) difference of ∼0.71 ± 0.24‰ is in good agreement with an earlier estimate of 0.6 for MIS-1/MIS-2 difference determined from species assemblages in a west equatorial sediment core [*Zhu and MacDougall*, 1998]. Following our current
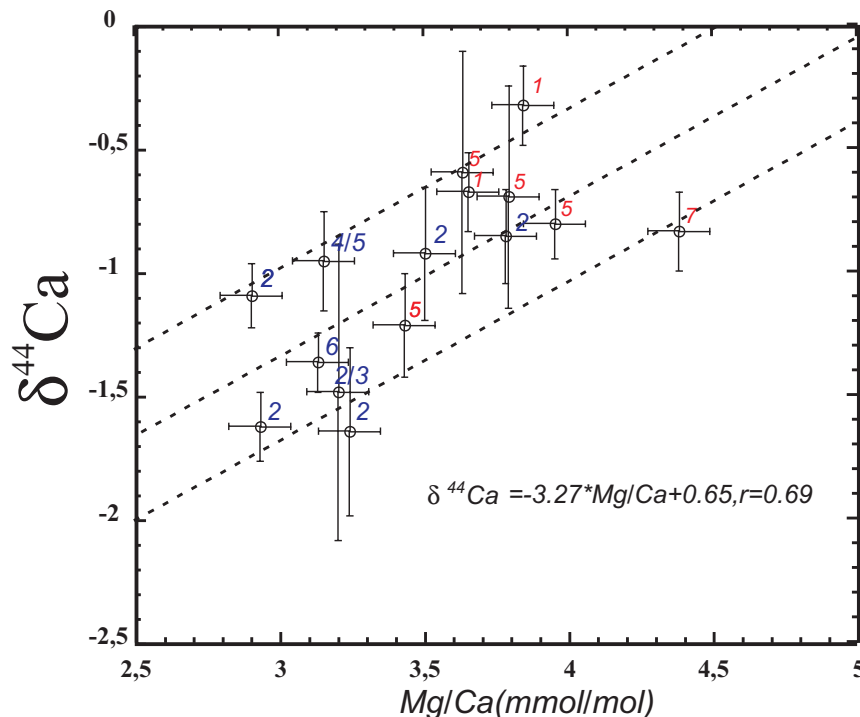

Figure 2. The δ⁴⁴Ca and Mg/Caratios are positively correlated. Foraminiferal tests corresponding to interglacial periods (MIS-1, -5, -7) tend to have higher δ⁴⁴Ca and Mg/Ca ratios than tests corresponding to glacial periods (MIS-2, -4, -6).

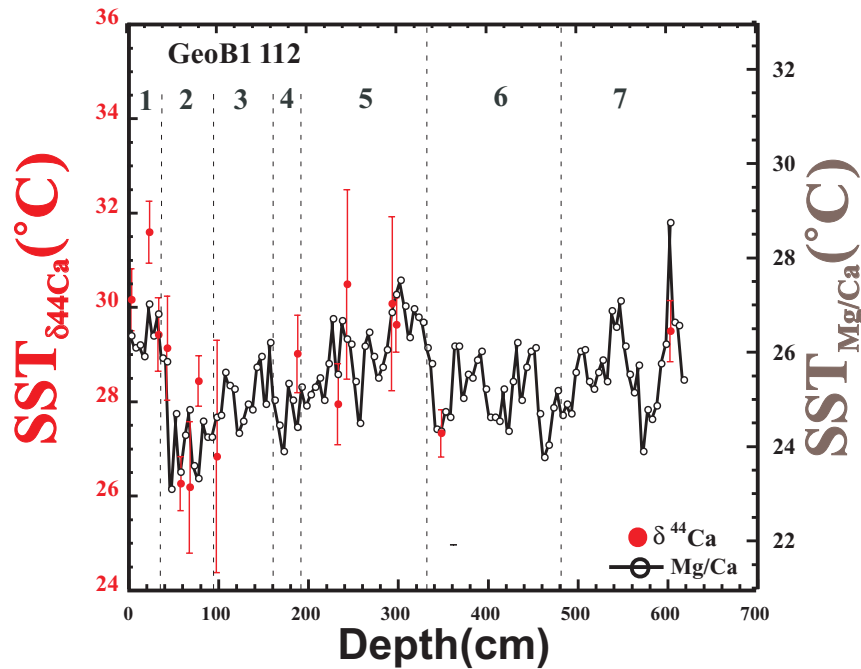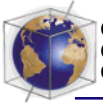**Figure 3.** Sea surface temperature (SST) reconstructed from δ⁴⁴Ca (SST$_{\delta44Ca}$ marked in red) and Mg/Ca ratios (SST$_{Mg/Ca}$) are shown as a function of core depth. SST$_{Mg/Ca}$ are calculated from the equation given by *Nürnberg et al.* [2000]. Dashed lines mark the transition between marine isotope stages. Both records show glacial/interglacial fluctuations predicting higher SSTs during interglacial and lower SST during glacial periods. Note that the SST$_{\delta44Ca}$ are significantly higher than their corresponding SST$_{Mg/Ca}$.

δ⁴⁴Ca-temperature calibration the interglacial-glacial δ⁴⁴Ca variations in core GeoB1112 reflect SST$_{\delta44Ca}$ variations that amount to ~3.0 ± 1.0°C. This temperature difference is in accordance with the results from Mg/Ca calibration, which predicts a temperature change at the transition from MIS-2 to MIS-1 of ~3° to 3.5°C [*Nürnberg et al.*, 2000].

5. Discussion

[14] Before the observed SST$_{\delta44Ca}$ variations can be considered to be reliable recorders of past SST it has to be verified how interspecific differences, preservation of primary Ca isotope values, and variation of past δ⁴⁴Ca ratios in seawater control the δ⁴⁴Ca signals in foraminifera.

[15] Concerning the δ⁴⁴Ca-temperature calibration the amount of preexperiment calcite in the foraminifera before the culture experiment is unknown and may have influenced the temperature calibration. Furthermore, in the present state of our investigations, there is no information about Ca isotope variations of past seawater. While it is true that the Ca isotopic composition of seawater on less than million year timescales will not be affected by ice volume, salinity variations, and other environmental factors, there is no information on what effect these variables have on biological fractionation of Ca isotopes or on preservation of the isotopic signal over time. Likewise, further tests concerning the effects of dissolution and/or diagenesis on the Ca isotopic composition of carbonate have to be performed.
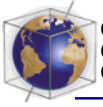
[16] In addition, to our knowledge, there is no physicochemical or biological model available describing Ca isotope fractionation in foraminifera; thus our hypothesis that Ca isotope fractionation is temperature controlled is based on statistical arguments only. However, it is clearly demonstrated that Ca isotope fractionation in cultured foraminifera is positively correlated with SST. Similar to that glacial/interglacial SST fluctuations recorded in fossil foraminifera are reflected in corresponding δ^{44}Ca variations. In addition, predicted differential glacial/interglacial $SST_{\delta44Ca}$ variations are in general accord with the results from the $SST_{Mg/Ca}$.

[17] Although there is general agreement between δ^{44}Ca and Mg/Ca concerning glacial/interglacial variations, δ^{44}Ca tend to predict ~2.5°C higher SST than the Mg/Ca ratios. This may be a consequence of kinetic fractionation during the cultural experiments that might have caused a δ^{44}Ca offset between absolute temperature and Mg/Ca calibration. Under laboratory conditions, foraminifera grew from a size naturally around 220 to ~657 μm [*Hemleben et al.*, 1987]. Thus increased calcification rates may have favored preferential incorporation of the lighter Ca isotopes, superimposing the temperature-controlled fractionation process.

[18] While the magnitude of Ca isotope fractionation by the foraminifera in this experiment and sediment core cannot be calculated because the isotopic composition of Ca in seawater relative to the standard used here is yet unknown, the data do show that the δ^{44}Ca ratio increases with increasing temperature. Because *Skulan et al.* [1997] and *Zhu and MacDougall* [1998] showed that foraminifera produce calcium carbonate with lower δ^{44}Ca ratios than seawater calcium, it might be possible that the magnitude of fractionation decreases with increasing temperature during a calibration experiment.

6. Conclusions

[19] Ca isotope measurements on cultured *G. sacculifer* that grew in seawater kept at temperatures of 19.5°, 26.5°, and 29.5°C indicate a δ^{44}Ca change of 0.24 ± 0.02 per 1°C based on the weighted linear regression (95% confidence level). Application of this new method to *G. sacculifer* from Equatorial East Atlantic sediment core GeoB1112 shows that the SST difference between the Holocene and the Last Glacial Maximum (LGM) amounts to 3.0 ± 1.0°C. Although SST reconstruction from Mg/Ca and δ^{44}Ca are in general accord, δ^{44}Ca tend to predict higher SSTs.

Acknowledgments

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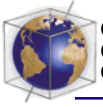
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