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North Atlantic *Globorotalia inflata* coretop Mg/Ca calibrations and temperature reconstructions over Termination I

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Abstract. Mg/Ca ratios from planktonic foraminifera are widely used as an independent proxy for ocean temperature. The choice of calibration is vital for reconstructing meaningful temperatures. We present preliminary results based on a new Mg/Ca-temperature calibration (Mg/Ca = $0.92e^{0.039T}$) for the thermocline-dwelling foraminifera *Globorotalia inflata*, derived using a suite of North Atlantic coretops. The downcore Mg/Ca record from core SU90-03 (40°N, 32°W) was used to compare how our new and existing calibrations performed for the Holocene and over the large scale change associated with Termination I.

1. Introduction

The measurement of Mg/Ca ratios in the tests of foraminifera is now a routine technique for estimating past ocean temperatures [1]. Advantages over other palaeothermometry techniques are the capacity to measure Mg/Ca on the same sample as $\delta^{18}O$, allowing the potential for palaeosalinity reconstructions, and the avoidance of non-modern-analogue issues that can be associated with the faunal assemblage based transfer function approach. Use of the Mg/Ca proxy has developed over the last decade and multi-species reconstructions based on species-specific temperature calibrations are now increasingly being employed [2-4]. This enables a profile of the water column properties at a particular site to be built up by comparing species from different depth habitats over time. This approach has huge potential for palaeoceanographic studies aiming to reconstruct past changes of different water masses.

More recently, research has begun to highlight complicating factors in the use of Mg/Ca and the key assumption that it records solely a temperature signal. Such factors include: sensitivity to salinity and seawater carbonate ion concentration [5-7]; partial dissolution, either where deep cores approach the carbonate compensation depth, with different species being affected to a greater or lesser degree [8, 9] or due to differences in the aggressiveness of the various cleaning routines applied to the samples [10]. The ecology of the species under study must also be taken into consideration when interpreting Mg/Ca records, since the limits of a species' environmental niche can vary – aspects such as seasonality and depth habitat may alter across a species' biogeographic range and through time. Whilst these factors need to be considered, discounted or corrected for, the reliability of the Mg/Ca temperature reconstruction is dependent ultimately on the calibration used to convert raw Mg/Ca ratios to temperatures. Due to the significant differences in Mg incorporation between species and locations [2, 3], detailed multi-species studies require accurate, species-specific and even region-specific calibrations.

Here we use a suite of coretop data from the North Atlantic to derive a new Mg/Ca-temperature calibration for the thermocline-dwelling species *Globorotalia inflata*. A downcore Mg/Ca record is then used as a case study to explore the existing temperature calibrations for this species and highlight the importance of calibration selection in the interpretation of Mg/Ca records.

2. Core sites and methods

This study was conducted using box core surface samples collected during the North East Atlantic Palaeoceanography and Climate Change (NEAPACC) program, along with coretop and downcore sediment samples from core SU90-03 (40° 30'N, 32° 03'W; 2475 m water depth), a piston core collected from the northern reaches of the subtropical gyre in the North Atlantic (Figure 1). Core SU90-03 is from a key area for monitoring the strength of the North Atlantic Current (NAC) during both glacial and interglacial periods, as previous work from this core indicated that this site remained south of the polar front even during the last glacial maximum (LGM) [11, 12]. The location of the core also allows a relatively rare opportunity to obtain a continuous Mg/Ca record from a single species across the major climatic transition of Termination I since *G. inflata* relative abundances show that this species is present throughout the last glacial-interglacial climate [12].

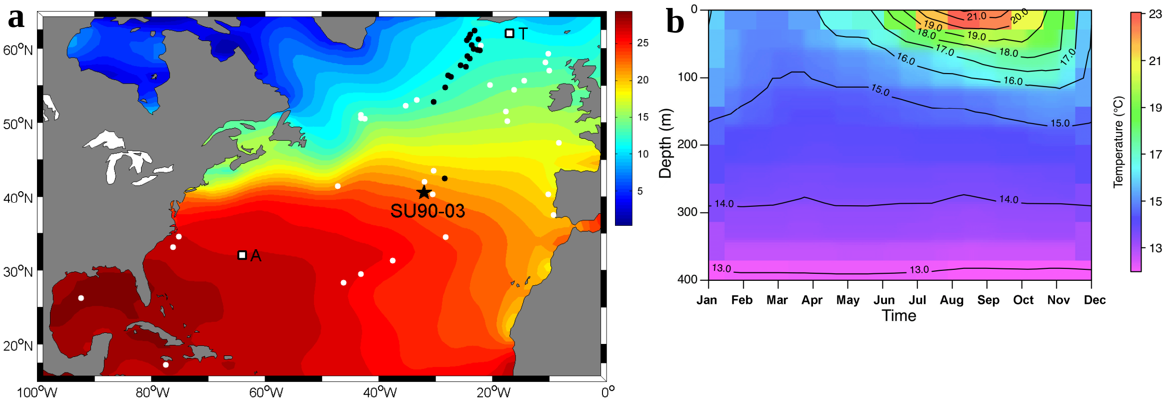

Figure 1: a. Core locations: NEAPACC cores in black, Cléroux *et al*. [3] coretops in white. Contours show August SST in the North Atlantic [13]. Core SU90-03 (used in this study and that of Cléroux *et al*. [3]) is marked, along with the sites used in the Anand *et al*. [2] (A) and Thornalley *et al*. [4] (T) studies; b. SU90-03 core site hydrography based on WOA98 [13].

At present, *G. inflata* is most abundant in temperate waters associated with the North Atlantic Current (NAC) but also ranges to subpolar and subtropical waters, with a temperature range of 8-18 ºC. It is a deep dwelling planktonic species associated with the base of the seasonal thermocline [14, 15], which at the mid-latitudes sites considered in this study is located at approximately 100m depth. The modern day hydrography at the site of core SU90-03 (Figure 1b) illustrates the development and deepening of the seasonal thermocline during summer months. Temperatures between the surface and 100 m range from 23 ºC to 15 ºC, with summer thermocline temperatures ranging from ~15-16 ºC. There are a number of Mg/Ca-temperature calibrations for *G. inflata* but the available data is limited, particularly at the cooler end of the species temperature range. In order to address this and create a calibration suitable for widespread usage across the mid-latitude North Atlantic, we analyzed *G. inflata* (300-355μm) in 18 NEAPACC coretops for both $\delta^{18}O$ and Mg/Ca.

3. Methods and Instrumentation

Mg/Ca analyses by ICP-AES were conducted using the intensity ratio calibration method of de Villiers *et al*. [16] and using the cleaning routine of Barker *et al*. [10]. Calibration standards were prepared from high purity $CaCO_3$ (NIST 915b), $SrCO_3$ (NIST 987) and Mg metal rod. Levels of contaminants for each were in agreement with the assay certificates. Analysis of the limestone reference standard ECRM 752-1, mean Mg/Ca = 3.97 mmol/mol, are consistent with results published by Greaves *et al.* [17] and interlaboratory reproducibility identified by Rosenthal *et al*. [18]. The ECRM 752-1 and two other solutions were used as internal consistency standards and were analyzed several times throughout each run to establish analytical reproducibility over time. The mean standard deviation of the Mg/Ca ratios (mmol/mol) for the internal standard is 0.027, with a mean relative standard deviation (RSD) of 0.49. When calculated with respect to temperature (ºC) the mean standard deviation is 0.049, with a mean RSD of 0.25. Further information on instrumentation are detailed in Farmer *et al*. [19]. Uncertainties associated with the calibration to temperature (see Section 4) are far greater than the intra-sample differences encountered for replicate foraminiferal Mg/Ca measurements.

Parallel measurements of the $\delta^{18}O$ of foraminiferal calcite ($\delta^{18}O_f$) are used to estimate calcification temperature and calibrate the Mg/Ca palaeothermometer. Isotopic temperatures in this study were calculated for the coretops using the palaeotemperature equation of Shackleton [20]:

$$\mathrm{Tiso} = 16.9 - 4.38(\delta^{18}O_f - \delta^{18}O_{sw}) + 0.1(\delta^{18}O_f - \delta^{18}O_{sw})^2 \quad (1)$$

where $\delta^{18}O_f$ is the $\delta^{18}O$ from the foraminiferal calcite and $\delta^{18}O_{sw}$ is the $\delta^{18}O$ of the seawater. This is consistent with the methods used by Cléroux *et al*. [3] and Anand *et al*. [2], allowing for direct comparison of our results. Errors associated with isotopic temperatures (Tiso) are estimated to be of the order of ± 1.5 °C and take into account uncertainties primarily related to the estimation of $\delta^{18}O_{sw}$ [3, 15] and the selection of temperature equation used in the calculation of Tiso.

We then used these coretop data to compare with three published calibrations for *G. inflata* [2-4]. The coretop SU90-03 is included both in our new coretop dataset and in the Cléroux *et al.* [3] study. The similarity of the independently analyzed results (Figure 2) provides further confidence in the consistency and reliability of the new coretop dataset.

4. Coretop calibration

Existing calibrations specific to *G. inflata* differ significantly in their methodology. The Anand *et al*. [2] calibration is based on sediment trap samples from the Sargasso Sea (32º05.4'N, 64º15.4'W) and uses a slightly modified cleaning routine to overcome the higher levels of organic matter often found in sediment trap samples in comparison to typical sediment core material. *G. inflata* specimens from the 350-500 μm size fraction produced Mg/Ca ratios of 1.5-2.0 mmol/mol and a Tiso range of 17–21 ºC. The *G. inflata* calibration of Cléroux *et al*. [3] is based on 29 coretops from across the North Atlantic ranging from 60 ºN to 17 ºN, including the SU90-03 coretop, covering a range of Mg/Ca ratios of 1.1-2.0 mmol/mol and a Tiso range of 10.5-17.5 ºC. Specimens from the 250-315 μm and 355–400 μm size fractions were analysed but since there was no evidence of a significant size effect on trace metal ratios, the two datasets were combined. However, test size is known to affect $\delta^{18}O$ values and thereby Tiso, and Cléroux *et al*. [3] suggest that this could explain the differences between their own calibration and that of Anand *et al*. [2]. Different methodologies and the different types of sample material (sediment trap versus coretop sediments) are also likely play a part. The Thornalley *et al*. [4] calibration was generated to study the downcore record of the subpolar North Atlantic core RAPiD 12-1K and is derived from the coretop Mg/Ca and $\delta^{18}O$ of the same core, most likely making it a more subpolar- and location-specific calibration. No raw Mg/Ca data is presented in Thornalley *et al*. [4] but the reconstructed Holocene temperatures at the core site equate to Mg/Ca ratios of approximately 1.6-2.0 mmol/mol. The methodology in the present study is most directly comparable to the Cléroux *et al*. [3] study, although specimens from a different size fraction were analysed (300-355 μm), which could explain the offset in the $\delta^{18}O$ between the two SU90-03 coretop points as highlighted in Figure 2.

Results from our coretop analyses are plotted alongside the three published Mg/Ca-temperature calibration curves in Figure 2, with the coretops of Cléroux *et al*. [3] and the additional NEAPACC and SU90-03 coretops shown. We combined our new high latitude suite of coretops with the Cléroux *et al*. [3] coretops to generate a new calibration curve. In order to maintain consistency with our new dataset, where appropriate we calculated the mean for individual cores in the Cléroux *et al*. [3] dataset such that each location has equal weighting in the regression. The new calibration, based on the combined dataset, is:

$$\mathrm{Mg/Ca} = 0.916 \pm 0.07 e^{0.039 \pm 0.006T} \quad (r^2=0.52) \quad (2)$$

This calibration extends the lower limit of the *G. inflata* temperature range to 8 ºC, although the best fit calibration curve does not differ markedly from the relationship defined in the Cléroux *et al*. [3] calibration. In comparison, the curve describing the Anand *et al*. [2] calibration in Figure 2, shows a shift to lower Mg/Ca or higher Tiso – for the reasons previously discussed, suggesting higher Mg/Ca derived temperatures. The Thornalley *et al*. [4] calibration curve departs markedly from the low exponential of the other three calibrations (due to the higher exponent in their calibration: 0.1 rather than 0.058, 0.056 and 0.039 for Anand *et al*. [2], Cléroux *et al*. [3] and this study, respectively). The Thornalley *et al*. [4] calibration involves much higher Mg/Ca ratios for any given Tiso, such that to generate a temperature of 15 ºC, a Mg/Ca ratio in excess of 3.0 mmol/mol would be necessary, rather than the 1.8 mmol/mol required by both the Cléroux *et al*. [3] calibration and the new calibration presented here, or the 1.25 mmol/mol of the Anand *et al*. [2] calibration. This calibration is thus likely to return markedly cooler temperatures than the other calibrations for the range of Mg/Ca ratios seen in our coretops.

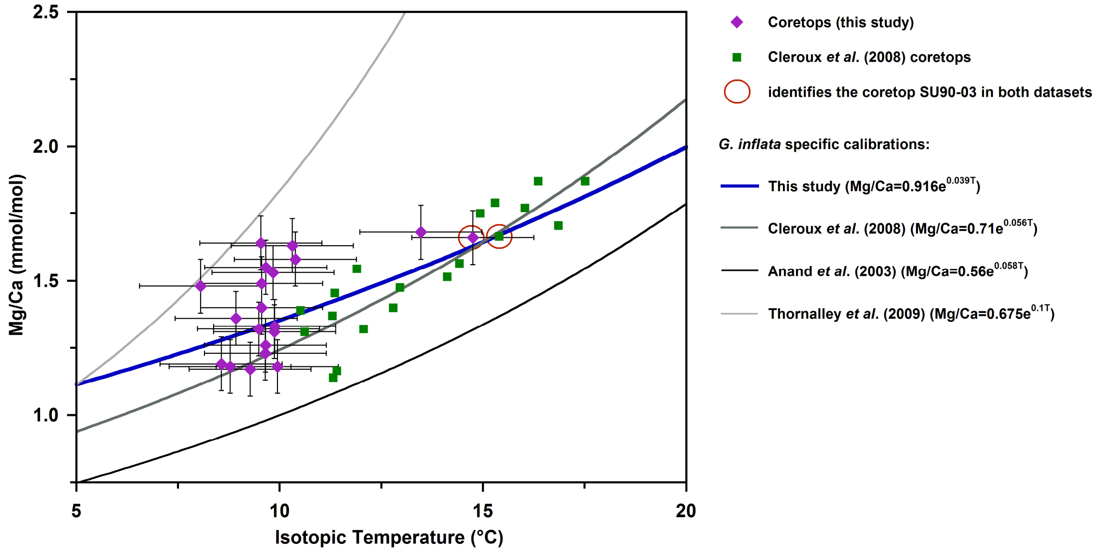

Figure 2: *G. inflata* Mg/Ca–temperature calibrations. Purple points mark the new coretop data from this study, green points mark the coretops used in the Cléroux *et al*. [3] study. The uppermost pale grey line shows the calibration curve of Thornalley *et al*. [4]; the lower black line shows the Anand *et al*. [2] calibration. The dark grey line is the Cléroux *et al*. [3] calibration curve, overlapping with the new calibration curve in thick blue. Red circles identify coretop data for SU90-03 from both datasets.

The new coretops show a relatively large scatter at lower temperatures which reduces the r^2 of the calibration to 0.52, from the 0.72 of the original Cléroux *et al*. [3] calibration. Further work is needed to resolve this scatter, in the form of additional Mg/Ca and $\delta^{18}O$ replicates and further assessment of the quality of the coretop material. Since these temperatures are at the very extreme of *G. inflata* temperature tolerance, it may well be that this scatter represents populations under stress, such that ecological factors including discontinuous productivity and changing seasonality and depth habitat become increasingly significant. For the new calibration, the uncertainties associated with the temperature estimates were calculated by looking at the difference between the Mg/Ca derived temperature and Tiso values. The mean of all the differences is 2 ºC and the standard deviation on the differences is 1.5 ºC. Errors quoted by Cléroux *et al*. [3] and Thornalley *et al*. [4] are 1.4 ºC and 1.3 ºC respectively.

5. Application of Mg/Ca-temperature calibrations

The results obtained when applying the alternative *G. inflata* Mg/Ca-temperature calibrations to the downcore Mg/Ca record from core SU90-03 are shown in Figure 3. The shaded bar represents the modern day temperature at the core site at 100 m water depth, i.e. near the supposed *G. inflata* calcification depth at the base of the summer thermocline. Error bars associated with each calibration are drawn on the right to give an indication of the statistical significance of the differences between the reconstructed temperatures. The various calibrations produce values ranging from 5 ºC to 11 ºC for the maximum magnitude of temperature shift between full glacial and interglacial conditions. These results demonstrate how the choice of calibration plays a key role in determining not only individual temperature values, but also the amplitude of the relative change in temperature over time. Such a divergence in results is not helpful and needs to be better constrained if meaningful palaeoceanographic interpretations are to be drawn.

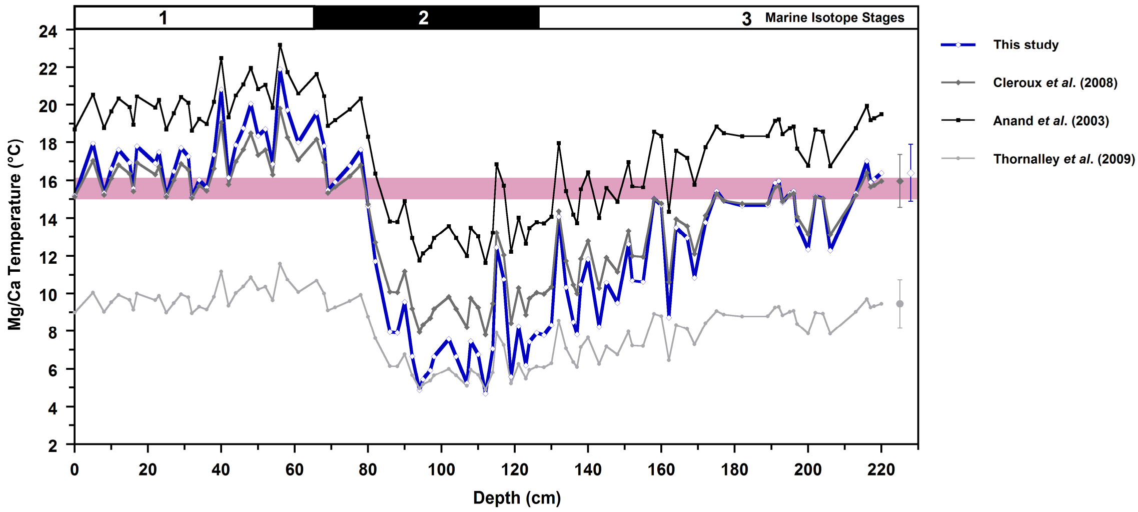

Figure 3. Mg/Ca temperature reconstructions from Anand *et al*. [2] (topmost black line), Thornalley *et al*. [4] (lower pale grey line) and Cléroux *et al*. [3] (mid grey line). The reconstruction based on the new calibration is shown in blue. Shaded bar indicates modern summer thermocline temperatures at the core site (100 m depth).

The Mg/Ca based temperature reconstructions vary significantly between the calibrations, although, as expected, the new calibration and the original Cléroux *et al*. [3] calibration are largely within error of each other. The only interval where these two deviate notably is during the coldest periods, during the last glacial maximum (LGM), with the new calibration producing values as much as 3 ºC lower than the Cléroux *et al*. [3] calibration. The robustness of both these calibrations for modern day temperature ranges is indicated by their ability to correctly reconstruct modern day thermocline temperatures at the core site (shaded bar). The Anand *et al*. [2] calibration produces the highest temperatures, with Holocene estimates notably higher then modern day thermocline temperatures and actually closer to modern day surface temperatures. In places the derived temperatures exceed the species' maximum temperature range reflected in the coretop Tiso measurements (Figure 2). The Thornalley *et al*. [4] calibration produces the coldest reconstruction, with relatively muted variability and with a maximum temperature almost 11 ºC cooler than that of Anand *et al*. [2]. Interestingly, the new calibration draws closer to the Thornalley *et al*. [4] calibration at the cold extreme. This suggests that the new calibration is capable of reconstructing both the subtropical conditions of the present day and the much cooler conditions of the last glacial period for this region. However, the lowest temperatures of 5 ºC are below the lower limit of the species temperature range in the coretops (taking into account the calibration errors). More work is needed to constrain the extent of the temperature changes and assess whether other factors are asserting a significant influence on the glacial-interglacial shift in Mg/Ca ratios.

In spite of the differences in the temperature records, it is clear that thermocline temperature changes at the site of core SU90-03 accompanied the build-up of the ice sheets during the last glacial period and the subsequent disintegration of the ice sheets following the LGM. Early marine isotope stage (MIS) 3 exhibits maximum temperatures that are not too dissimilar to modern conditions. Thermocline temperatures appear to steadily decline towards the LGM, punctuated by a number of brief warmings, reaching a minima of ~ 5 ºC, according to the new calibration. The warming into the Holocene is rapid and step-like and suggests a period of early Holocene warmth at depth before temperatures at the thermocline cooled and the modern day conditions of ~16 ºC were established. This record provides a rare opportunity to study a single species' response to large scale climatic change in the northern subtropical gyre. Further work and additional proxies are required to develop a better understanding of glacial to interglacial changes in this region and to examine the relationship between thermocline and near surface temperature histories during large scale events and under different climatic regimes.

6. Conclusions

We define a new Mg/Ca-temperature calibration ($Mg/Ca = 0.92e^{0.039T}$) for the thermocline-dwelling foraminifer *G. inflata* based on a series of North Atlantic coretops. This calibration builds upon and is largely consistent with the work of Cléroux *et al*. [3] although it appears to better estimate the cooler temperatures associated with the lower limit of *G. inflata's* temperature range. The suitability of the new coretop calibration is supported by its ability to reconstruct the present day temperatures at the site of core SU90-03. Two other calibrations were compared in order to highlight how the choice of calibration can have a significant impact on the interpretation of the Mg/Ca record. A comparison of the reconstructed temperatures using downcore data from North Atlantic core SU90-03 demonstrates that the choice of calibration affects not only the absolute temperatures but the amplitude of events, particularly over large scale climatic transitions such as Termination I. This potentially has major implications for errors associated with reconstruction of the $\delta^{18}O$ of the seawater/palaeosalinity and surface temperature gradients based on Mg/Ca records from multiple foraminiferal species.

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References

[1] Elderfield H and Ganssen G 2000 Past temperature and δ18O of surface ocean waters inferred from foraminiferal Mg/Ca ratios Nature 405 442-5.

[2] Anand P, Elderfield H and Conte M H 2003 Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series *Paleoceanography* **18** 28-1. doi: 10.1029/2002PA000846

[3] Cléroux C, Cortijo E, Anand P, Labeyrie L, Bassinot F, Caillon N and Duplessy J C 2008 Mg/Ca and Sr/Ca ratios in planktonic foraminifera: Proxies for upper water column temperature reconstruction *Paleoceanography* **23** doi: 10.1029/2007pa001505

[4] Thornalley D J R, Elderfield H and McCave I N 2009 Holocene oscillations in temperature and salinity of the surface subpolar North Atlantic *Nature* **457** 711-4. doi: 10.1038/nature07717

[5] Nürnberg D, Bijma J and Hemleben C 1996 Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures *Geochimica et Cosmochimica Acta* **60** 803-14.

[6] Lea D W, Mashiotta T A and Spero H J 1999 Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing *Geochimica et Cosmochimica Acta* **63** 2369-79.

[7] Ferguson J E, Henderson G M, Kucera M and Rickaby R E M 2008 Systematic change of foraminiferal Mg/Ca ratios across a strong salinity gradient *Earth and Planetary Science Letters* **265** 153-66. doi: 10.1016/j.epsl.2007.10.011

[8] Dekens P S, Lea D W, Pak D K and Spero H J 2002 Core top calibration of Mg/Ca in tropical foraminifera: Refining paleotemperature estimation *Geochemistry Geophysics Geosystems* **3** doi: 10.1029/2001GC000200

[9] Mekik F, Francois R and Soon M 2007 A novel approach to dissolution correction of Mg/Ca-based paleothermometry in the tropical Pacific *Paleoceanography* **22** doi: 10.1029/2007PA001504

[10] Barker S, Greaves M and Elderfield H 2003 A study of cleaning procedures used for foraminiferal Mg/Ca paleothermometry *Geochemistry Geophysics Geosystems* **4** doi: 10.1029/2003GC000559

[11] Chapman M R and Shackleton N J 1998 Millennial-scale fluctuations in North Atlantic heat flux during the last 150,000 years *Earth and Planetary Science Letters* **159** 57-70.

[12] Chapman M R, Shackleton N J and Duplessy J C 2000 Sea surface temperature variability during the last glacial- interglacial cycle: assessing the magnitude and pattern of climate change in the North Atlantic *Palaeogeography Palaeoclimatology Palaeoecology* **157** 1-25.

[13] NODC WOA98. http://www.esrl.noaa.gov/psd/

[14] Cléroux C, Cortijo E, Duplessy J C and Zahn R 2007 Deep-dwelling foraminifera as thermocline temperature recorders *Geochemistry Geophysics Geosystems* **8** doi: 10.1029/2006gc001474

[15] Ganssen G M and Kroon D 2000 The isotopic signature of planktonic foraminifera from NE Atlantic surface sediments: implications for the reconstruction of past oceanic conditions. *J. Geol. Soc. Lond.* **157** 693–9.

[16] de Villiers S, Greaves M and Elderfield H 2002 An intensity ratio calibration method for the accurate determination of Mg/Ca and Sr/Ca of marine carbonates by ICP-AES *Geochemistry Geophysics Geosystems* **3** doi: 10.1029/2001GC000169

[17] Greaves M, Barker S, Daunt C and Elderfield H 2005 Accuracy, standardization, and interlaboratory calibration standards for foraminiferal Mg/Ca thermometry, *Geochemistry, Geophysics, Geosystems* **6** doi: 10.1029/2004GC000790.

[18] Rosenthal Y et al., 2004 Interlaboratory comparison studyof Mg/Ca and Sr/Ca measurements in planktonic foraminifera for paleoceanographic research *Geochemistry, Geophysics, Geosystems* **5** doi: 10.1029/2003GC000650.

[19] Farmer E J, Chapman M R and Andrews J E 2008 Centennial-scale Holocene North Atlantic surface temperatures from Mg/Ca ratios in Globigerina bulloides *Geochemistry Geophysics Geosystems* **9** doi: 10.1029/2008gc002199

[20] Shackleton N J 1974 Attainment of isotopic equilibrium between ocean water and the benthonic foraminifera genus *Uvigerina*: isotopic changes in the ocean during the last glacial *Cent. Natl. Rech. Sci. Colloq. Int.* **219** 203-10.