

Planktonic foraminiferal Mg/Ca as a proxy for past oceanic temperatures: a methodological overview and data compilation for the Last Glacial Maximum

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Abstract

As part of the Multi-proxy Approach for the Reconstruction of the Glacial Ocean (MARGO) incentive, published and unpublished temperature reconstructions for the Last Glacial Maximum (LGM) based on planktonic foraminiferal Mg/Ca ratios have been synthesised and made available in an online database. Development and applications of Mg/Ca thermometry are described in order to illustrate the current state of the method. Various attempts to calibrate foraminiferal Mg/Ca ratios with temperature, including culture, trap and core-top approaches have given very consistent results although differences in methodological techniques can produce offsets between laboratories which need to be assessed and accounted for where possible. Dissolution of foraminiferal calcite at the sea-floor generally causes a lowering of Mg/Ca ratios. This effect requires further study in order to account and potentially correct for it if dissolution has occurred. Mg/Ca thermometry has advantages over other paleotemperature proxies including its use to investigate changes in the oxygen isotopic composition of seawater and the ability to reconstruct changes in the thermal structure of the water column by use of multiple species from different depth and or seasonal habitats. Presently available data are somewhat limited to low latitudes where they give fairly consistent values for the temperature difference between Late Holocene and the LGM (2–3.5 °C). Data from higher latitudes are more sparse, and suggest there may be complicating factors when comparing between multi-proxy reconstructions.

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1. Introduction

Planktonic foraminiferal Mg/Ca thermometry is a relatively recent addition to the expanding set of proxies used for reconstructing past changes in sea surface temperature (SST). Mg²⁺ is one of several divalent cations which may substitute for Ca during the

formation of biogenic calcium carbonate. Its incorporation into foraminiferal calcite is influenced by the temperature of the surrounding seawater during growth such that foraminiferal Mg/Ca ratios increase with increasing temperature. The temperature sensitivity of foraminiferal Mg/Ca ratios was first reported by Chave (1954) and Blackmon and Todd (1959) using X-ray diffraction. Later studies by Kilbourne and Sen Gupta (1973) using atomic absorption analysis and by Duckworth (1977) using electron microprobe analysis reinforced this finding. Cronblad and Malmgren (1981) produced down-core records of foraminiferal Mg and Sr content variability and suggested the potential paleoclimatic significance of minor element composition

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variation. More recently Mg/Ca thermometry has been greatly refined and applied almost routinely to paleoceanographic questions concerning temperature variability through time (e.g. Nürnberg et al., 1996; Hastings et al., 1998; Lea et al., 1999, 2000, 2002; Mashiotta et al., 1999; Elderfield and Ganssen, 2000; Rosenthal et al., 2000; Koutavas et al., 2002; Stott et al., 2002; Pahnke et al., 2003; Rosenthal et al., 2003; Visser et al., 2003). Mg/Ca ratios of other calcifying organisms have also been shown to be sensitive to changes in temperature. These include benthic foraminifera (e.g. Izuka, 1988; Rathburn and De Deckker, 1997; Rosenthal et al., 1997; Lear et al., 2000; Toyofuku et al., 2000; Martin et al., 2002; Billups and Schrag, 2003), ostracods (e.g. Chivas et al., 1986; Dwyer et al., 1995; Wansard, 1996; De Deckker et al., 1999), coccoliths (Stoll et al., 2001) and corals (e.g. Mitsuguchi et al., 1996; Wei et al., 1999; Watanabe et al., 2001).

Mg/Ca thermometry has distinct advantages over other temperature proxies. The oceanic residence times for Ca and Mg are relatively long (10^6 and 10^7 years, respectively) therefore the Mg/Ca ratio of seawater may be considered to be constant over glacial/interglacial timescales. This assertion removes considerable uncertainty when reconstructing paleotemperatures using foraminiferal Mg/Ca ratios. In contrast, foraminiferal $\delta^{18}\text{O}$, which is also sensitive to changes in temperature, is strongly influenced by changes in the isotopic composition of seawater (δw). Since δw varies both as a function of global ice volume and local salinity differences, the direct interpretation of foraminiferal $\delta^{18}\text{O}$ is not straightforward. However, because these two proxies are attained from a single medium (i.e. foraminiferal calcite) they can be combined in order to reconstruct variations in δw over time (e.g. Mashiotta et al., 1999; Elderfield and Ganssen, 2000; Lea et al., 2002). A similar approach has been to combine foraminiferal $\delta^{18}\text{O}$ with other SST proxies such as alkenones and faunal counting (e.g. Rostek et al., 1993; Cayre et al., 1999; Arz et al., 2003). However, only Mg/Ca ratios coupled with $\delta^{18}\text{O}$ can guarantee a common source of the signal, averaging the same environmental conditions (season and spatial habitat). This is one of the greatest contributions of Mg/Ca paleothermometry since errors and uncertainties for δw reconstructions can be substantially minimized. Further, since temperature estimates based on Mg/Ca ratios are specific to the species employed they may be used to reconstruct temperatures from different depths in the water column depending on the species' habitat preferences. Measurement of foraminiferal Mg/Ca ratios is quite straightforward with modern techniques of elemental analysis and as a result, high resolution records may be attained in a relatively short time.

Foraminiferal Mg/Ca thermometry is still a relatively new proxy with respect to some of the more established

methods of paleotemperature estimation. The aim of this report is to bring together existing published and previously unpublished Mg/Ca measurements and temperature estimates from several species of planktonic foraminifera of both Late Holocene and Last Glacial Maximum (LGM) age. This synthesis of available Mg/Ca data contributes to the aims of the Multi-proxy Approach for the Reconstruction of the Glacial Ocean (MARGO) working group. In order to make a direct comparison of Mg/Ca data and inferred temperatures from different studies it is first necessary to review some of the various technical aspects of Mg/Ca thermometry. These include laboratory procedures, temperature calibrations, use of multiple species, dissolution effects, discussion of current data and comparison with other temperature proxies. This work does not aim to reinterpret or evaluate previous work by other authors. It is most importantly a synthesis of published data and summary of considerations applicable to Mg/Ca thermometry.

2. Calibration of planktonic foraminiferal Mg/Ca versus temperature

Studies on inorganic precipitation of calcite in seawater predict a positive temperature control on Mg incorporation (e.g. Kinsman and Holland, 1969; Katz, 1973; Mucci, 1987; Oomori et al., 1987). As discussed by Rosenthal et al. (1997) and Lea et al. (1999) thermodynamic considerations predict that the temperature dependence of Mg uptake into calcite should be exponential, with a sensitivity of around 3% per °C increase in temperature. This prediction is borne out by the work of Oomori et al. (1987) on inorganic calcite precipitates (Fig. 1a). The temperature dependence of Mg uptake into foraminiferal calcite is also generally accepted to be exponential, with a sensitivity of about 10% per °C (Fig. 1b). Measured Mg/Ca ratios of natural foraminiferal calcite are generally 1–2 orders of magnitude lower than those predicted for inorganic precipitates (Fig. 1). This suggests that biological influences play an important role in biogenic calcification. The offset in Mg/Ca between inorganic precipitates and foraminiferal calcite, together with differences between individual species of foraminifera (e.g. Lea et al., 1999) (Fig. 1c), stresses the importance for empirical determination of foraminiferal Mg/Ca thermometry calibrations.

Various approaches have been made to calibrate Mg/Ca versus temperature for several species of planktonic foraminifera. These include core-top, culture and sediment trap studies, each of which may have its advantages and disadvantages although as it turns out, very good agreement has been achieved between all three approaches (Table 1). Culture-based calibrations

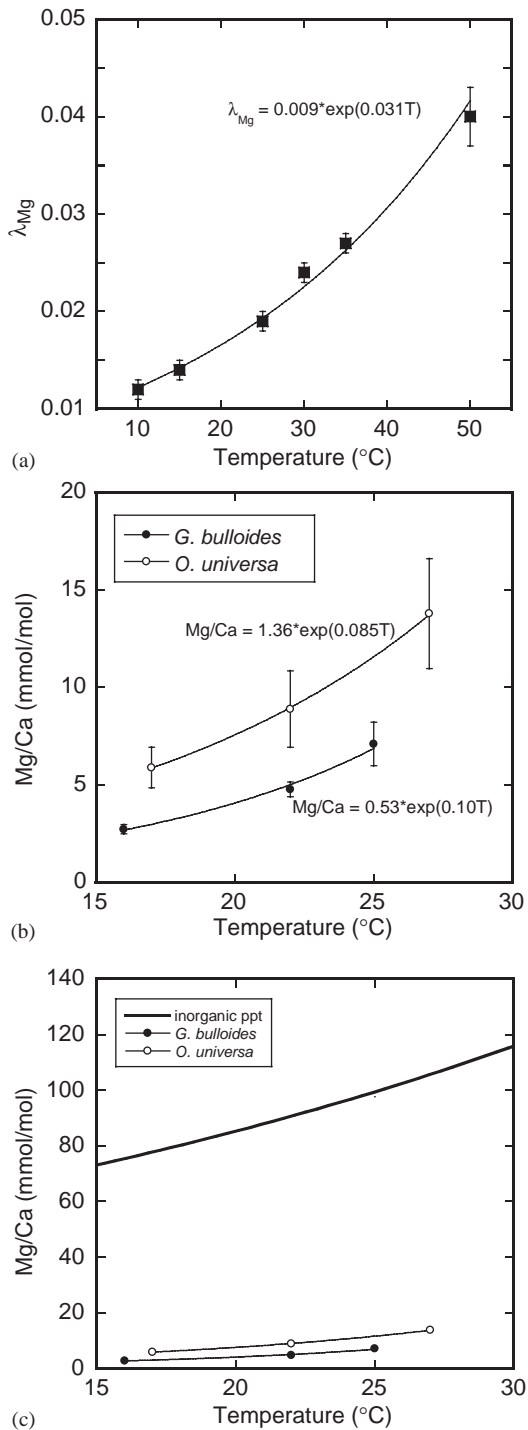


Fig. 1. (a) Results of an inorganic precipitation experiment by Oomori et al. (1987) showing an exponential relation between temperature and the distribution coefficient (λ_{Mg}) of Mg^{2+} ions between calcite and solution ($\lambda_{Mg} \approx (Mg/Ca)_{calcite} / (Mg/Ca)_{solution}$). The observed sensitivity is about 3% per °C. (b) Culturing experiments also suggest an exponential relation between foraminiferal Mg/Ca and calcification temperature with a sensitivity of about 9–10% per °C (modified after Lea et al., 1999). Offsets between species highlight the benefit of species specific calibrations. The importance of empirical calibrations is also highlighted by the difference between measured foraminiferal Mg/Ca ratios (Lea et al., 1999) and those predicted by inorganic precipitation experiments (Oomori et al., 1987) (c).

such as by Nürnberg et al. (1996) and Lea et al. (1999) have the distinct advantage that temperature (T) is constrained during the experiment i.e. it is an independent variable. This is not the case for core-top or plankton tow or trap studies where T must be estimated using either a climatological atlas or some derivation of the calcification temperature attained from foraminiferal $\delta^{18}O$ and δw (e.g. Elderfield and Ganssen, 2000; Anand et al., 2003). In these cases, T itself becomes a dependent variable and may introduce greater error into the calibration than the measurement of Mg/Ca (Anand et al., 2003). A potential disadvantage of culture calibrations is that laboratory conditions may not realistically reproduce the natural environment sufficiently to ensure natural chamber growth. Further, since foraminiferal reproduction cannot be achieved in the laboratory, juvenile specimens must be collected from their natural habitat before culturing. Controlled conditions and subsequent chemical analysis can therefore only be applied to later stages of test formation i.e. those chambers formed during culture. Routine determination of foraminiferal Mg/Ca ratios for paleotemperature reconstruction is performed on whole tests representing the entire period of test growth. Studies on foraminiferal test chemistry from various size fractions of foraminifera have shown that Mg/Ca ratios as well as other properties (e.g. Sr/Ca, $\delta^{13}C$ and $\delta^{18}O$) are controlled by test size (Oppo and Fairbanks, 1989; Ravelo and Fairbanks, 1995; Spero and Lea, 1996; Elderfield et al., 2002). Uncertainty in culture calibrations may therefore arise if differences in Mg/Ca during growth are caused by changing biological controls rather than solely by changes in temperature.

Calibrations determined using core-top material such as those by Elderfield and Ganssen (2000) are valuable since they are based on material that will eventually form the sedimentary record, having gone through a complete life cycle including gametogenesis and any secondary calcite formation. However, complications in calibrating the results may arise if the samples used have undergone post-depositional alteration. As discussed later, partial dissolution of foraminiferal calcite tends to cause a decrease in Mg/Ca. Since the solubility of carbonate tends to increase with depth at any location, core-top material from greater depths will be prone to alteration of Mg/Ca. Dekens et al. (2002) produced a core-top calibration using samples from the tropical Pacific and Atlantic. Their calibration included a correction term for dissolution effects on Mg/Ca in foraminifera which we discuss in Section 5.

Calibrations based on water column samples have the great advantage that the season of growth is known and therefore better constraints can be made on the specific temperatures used in calibrations. Trap material also has the advantage that it most closely represents the material entering the sedimentary record without

Table 1

Summary of published temperature calibrations for single and multiple species of planktonic foraminiferal Mg/Ca

Species	Source	Temperature	<i>B</i>	<i>A</i>	Reference
<i>N. pachyderma</i>	Coretops	0–200 m water depth	0.46	0.088	Nürnberg et al., 1995
<i>G. sacculifer</i>	Coretops	Annual SST	0.37	0.09	Dekens et al., 2002
<i>G. sacculifer</i>	Culture	Fixed	0.39 (±0.06)	0.089 (±0.008)	Nürnberg et al., 1996
<i>G. sacculifer</i>	Sediment trap	δ ¹⁸ O derived	0.35 (±0.01)	0.090	Anand et al., 2003
<i>G. bulloides</i>	Culture	Fixed	0.53 (±0.17)	0.102 (±0.008)	Lea et al., 1999
<i>G. bulloides</i>	Coretop/culture	Annual SST/fixd	0.47 (±0.03)	0.107 (±0.003)	Mashiotta et al., 1999
<i>G. ruber</i> (w)	Coretop	Annual SST	0.30 (±0.06)	0.089 (±0.007)	Lea et al., 2000
<i>G. ruber</i> (w)	Coretop	Annual SST	0.38	0.09	Dekens et al., 2002
<i>G. ruber</i> (w)	Sediment trap	δ ¹⁸ O derived	0.34 (±0.08)	0.102 (±0.01)	Anand et al., 2003
Mixed	Coretop	δ ¹⁸ O derived	0.52	0.100	Elderfield and Ganssen, 2000
Mixed	Sediment trap	δ ¹⁸ O derived	0.38 (±0.02)	0.090 (±0.003)	Anand et al., 2003
<i>Cibicides</i> ssp	Coretop	BWT	0.87 (±0.05)	0.109 (±0.007)	Lear et al., 2002

The data of Nürnberg et al. (1995, 1996) have been recalibrated using the general form $Mg/Ca = B \exp(A \times T)$. *G. ruber* (w) is the white variety picked from the 250–350 μm size fraction. The benthic calibration of Lear et al. (2002) is given for comparison. SST=sea surface temperature, BWT=bottom water temperature.

actually reaching the sediment surface. If a reliable temperature estimate can be made for water column samples, for example by δ¹⁸O derived temperature calculations (Anand et al., 2003), this may provide one of the most robust approaches to Mg/Ca thermometry calibration.

The points outlined above (specifically, problems in determining a reliable calcification temperature and partial dissolution) could potentially lead to differences between various calibrations. Further uncertainties may be caused by differences in analytical procedures and or sample preparation between different laboratories (see later). Nevertheless, as mentioned previously, results attained using very different approaches are remarkably consistent. Modern calibrations may be expressed by an exponential relation of the form:

$$Mg/Ca = B \exp(A \times T), \quad (1)$$

where *T* is the calcification temperature in °C. *A* and *B* are constants and dependent on species. The value of *A* is consistently found to be around 0.09–0.1 which reflects a temperature sensitivity in Mg/Ca of about 10% per °C increase in *T*. A summary of published calibrations for single and multiple species is given in Table 1. Calibrations for Mg/Ca in benthic foraminifera also suggest a similar temperature sensitivity to planktonic species (e.g. Rosenthal et al., 1997; Lear et al., 2002, Table 1).

The point has been made that empirically based calibrations are important since biological differences between species may cause significant offsets in Mg/Ca for a given temperature. However, for species where a narrow temperature range prohibits statistically meaningful calibration (see Anand et al., 2003) or for species now extinct, this requirement presents obvious difficulties. Fortunately, thanks to the growing number of calibration studies on multiple species of planktonic

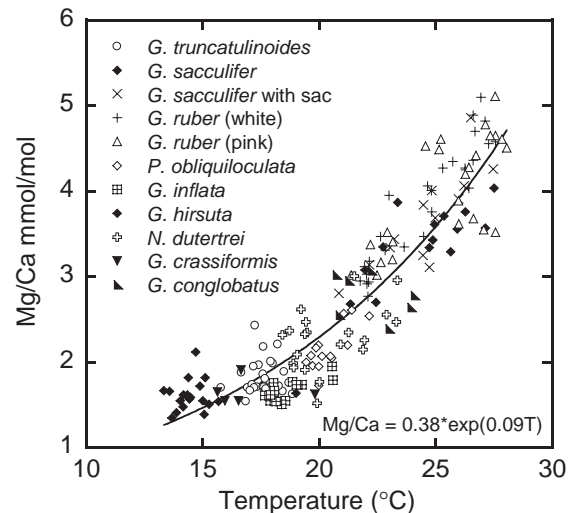


Fig. 2. Mg/Ca calibration results of Anand et al. (2003) for several species of planktonic foraminifera. Temperatures shown here are the isotopically derived calcification temperatures of Anand et al. (2003). A single temperature equation may be used to describe all data ($r = 0.93$). Modified after Anand et al. (2003).

foraminifera it appears that in fact a large number of species display a very similar relation between Mg/Ca and temperature. A recent study by Anand et al. (2003) suggests that 10 out of the 12 species they studied may be described by a single relation (Table 1, Fig. 2). The uncertainty associated with temperatures estimated using a generic equation will naturally be greater than by use of a species specific relationship for a given species. The deviation between the two estimates will depend on the species employed. For example, based on data from Anand et al. (2003), the average deviation of calculated temperature from isotopically derived “calcification” temperature using the species specific calibration for *Globigerinoides ruber* (w) (Anand et al., 2003) is

0.6 °C. This compares with 1.0 °C when using the generic calibration. The combined average deviation between calculated and isotopically derived temperatures for all species used in the generic calibration of Anand et al. (2003) increases from 0.9 to 1.5 °C for specific and generic calibrations, respectively. On the other hand, for *G. aequilateralis*, the average deviation increases from 1.0 to 3.8 °C. The increased uncertainty in this case is because this species has particularly high Mg/Ca values for a given temperature (Anand et al., 2003). Therefore although species specific calibrations are statistically preferable, where this is not possible, and with certain exceptions, some confidence may be ascribed to the use of a generic temperature calibration.

3. Intra- and inter-specific variability in Mg/Ca ratios

Planktonic foraminifera commonly migrate vertically throughout their life cycle, often forming calcite at deeper depths as they mature. This depth/temperature migration results in heterogeneity of Mg/Ca ratios within the tests of individual foraminifera (Duckworth, 1977; Nürnberg, 1995; Elderfield and Ganssen, 2000; Jha and Elderfield, 2000; Benway et al., 2003). Further intra-test variability occurs in many species due to the secretion of a secondary crust of calcite at the time of gametogenesis. Laboratory culture experiments have provided a unique source of information in this direction (e.g. Bé, 1980; Hemleben et al., 1985). For example, it has been observed that many planktonic species add a calcite crust (or “gametogenic crust”) in deeper, colder water immediately prior to reproduction. In the case of *G. sacculifer* gametogenic calcite can represent up to 30% of the test weight (Bé, 1980). This crust may have a Mg/Ca ratio distinct from other regions of the test, even when formed under similar temperature conditions, as a result of differing biophysiological controls on Mg uptake (e.g. Nürnberg et al., 1996). Thus individual fossil tests may comprise a range of compositions that reflect the changing conditions during an individual’s lifetime. Recent developments in Laser Ablation, LA-ICP-MS techniques provide a unique opportunity to accurately monitor intra-test variability in trace element concentrations and understand better the distinct signature of foraminiferal migration in calcite secretion (Eggins et al., 2003; Hathorne et al., 2003). Early results suggest a migration signal in the assimilation of Mg/Ca by individual chambers of *Neogloboquadrina dutertrei* while other species like *G. ruber* (w) appear to give rather constant Mg/Ca values (Eggins et al., 2003).

It is clear that measured bulk test Mg/Ca ratios should be considered as an integration of the temperatures experienced during calcification. The Mg/Ca ratio of ‘whole-test’ samples therefore represents the integra-

tion of various depth habitats and (potentially) biological controls. As a result, the temperature derived from foraminiferal Mg/Ca ratios is the temperature of calcification at whatever depth range and season that particular species grew. This definition is distinct from the strict notion of sea surface temperature (SST) in that many species of planktonic foraminifera live at depths greater than 50 m or so (e.g. Erez and Honjo, 1981; Deuser and Ross, 1989; Anand et al., 2003). This issue does not seem to be critical for surface and mixed layer species such as *G. sacculifer* and *G. ruber* (w) as demonstrated by the close agreement between the calibrations for *G. ruber* (w) reported by Lea et al. (2000) using SST and Anand et al. (2003) using isotopically derived calcification temperatures (Table 1). However, the distinction becomes more important when dealing with deeper dwelling species.

Inter-species differences in Mg/Ca, due to differences in seasonal and or depth habitats, could be viewed as a limitation of the Mg/Ca method; for instance it is clear that the temperature derived from a thermocline dwelling species will not reflect sea surface temperature. However, application of Mg/Ca thermometry to multiple species of planktonic foraminifera within a single core provides a potentially powerful tool for reconstructing changes in water column structure. For instance, *G. ruber* (w) may be used to reconstruct surface and mixed layer temperatures while *N. dutertrei* generally represents thermocline conditions (Spero et al., 2003). By measuring Mg/Ca ratios in both species from a single core it is possible to reconstruct temporal changes in upper water column thermal gradient. A multi-species approach has been applied in several studies based on the stable isotope compositions of planktonic foraminifera ($\delta^{18}\text{O}$ and $\delta^{13}\text{C}$) (e.g. Mulitza et al., 1997; Spero et al., 2003; Simstich et al., 2003). These studies demonstrate that with a suitable selection of species, it is possible to reconstruct past oceanographic conditions for both the thermocline and mixed layer. But such an approach has not yet been broadly used for Mg/Ca studies. Elderfield and Ganssen (2000) analysed several different planktonic foraminifers in a site from the tropical Atlantic and observed that Mg/Ca temperature estimates provide consistently warmer or colder temperatures in accordance with the depth-habitat preferences of each of the species considered. They also showed that glacial–interglacial thermal variability evolved differently between the different habitats i.e. the upper water column thermal structure changed between glacial and interglacial times. Stott et al. (2002) studied two surface-dwelling species that they interpret to reflect different seasonal conditions for the region studied (western tropical Pacific). These early results open up new and promising perspectives for paleoceanographic reconstructions. The ability to reconstruct vertical and possibly seasonal temperature

gradients is an advantage over other geochemical proxies such as alkenone based SST reconstructions which strictly monitor the conditions of the euphotic layer in which the particular phytoplankton grow.

4. Methodology

Methods of preparing and analysing foraminiferal samples for Mg/Ca measurement vary between laboratories; there is no *standardised* method per se. Differences in methodology and analysis could lead to discrepancies between laboratories and as such it is important to know what differences exist and how these might affect the determination of Mg/Ca ratios. These questions have recently been addressed by an inter-laboratory comparison study by Rosenthal et al. (2004) in which several foraminiferal samples and standard solutions were run by a number of laboratories throughout Europe and the USA in order to assess the relative accuracy, precision and reproducibility of their methodologies. Results from this work suggest that analytical techniques used by a selection of laboratories produced generally good precision but poor inter-lab consistency. This was probably due to inaccuracies introduced during preparation of calibration standard solutions within particular laboratories and may be addressed in the future by use of a universal accuracy standard. The findings also point towards more significant disparities caused by differences in sample preparation (see below).

Modern analytical techniques for analysing bulk foraminiferal Mg/Ca ratios include Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (e.g. Rosenthal et al., 1999) and ICP-AES (Atomic Emission Spectrometry) (e.g. de Villiers et al., 2002). Both of these techniques provide high precision measurements of Mg/Ca ratios of the order $\pm 0.5\%$ (Rosenthal et al., 2004). An alternative approach to Mg/Ca analysis is by use of electron microprobe (e.g. Nürnberg, 1995) or Laser Ablation, LA-ICP-MS techniques (e.g. Eggins et al., 2003; Reichart et al., 2003). These sorts of technique allow investigation into heterogeneity in Mg/Ca throughout a single test which is of value to studies concerning the systematics of Mg incorporation during test formation or removal during dissolution. Another approach to investigating Mg/Ca heterogeneity is that of Haley and Klinkhammer (2002) using a sequential leaching technique (this method is discussed in more detail later).

Most modern techniques of sample preparation for measurement of foraminiferal Mg/Ca ratios follow the general procedures developed by Boyle (1981), Boyle and Keigwin (1985) and Lea and Boyle (1991) for the determination of foraminiferal Cd/Ca and Ba/Ca ratios. The general requirements for cleaning foraminiferal

calcite prior to Mg/Ca analysis are the removal of silicate phases (predominantly clays from within the test), organic matter and potentially a Mn-oxide coating. There has been discussion over the absolute necessity of the last of these steps (e.g. Brown and Elderfield, 1996; Haley and Klinkhammer, 2002; Martin and Lea, 2002; Barker et al., 2003). This has resulted in the evolution of essentially two variants of the Mg-cleaning protocol; one with a reductive step for removal of an oxide coating, the other without (the “Cd” and “Mg” versions as described by Rosenthal et al., 2004). The effect of reductive cleaning is to lower Mg/Ca. This is highlighted by a systematic difference (of about 8%) between laboratories using the “Cd” and “Mg” cleaning protocols (Rosenthal et al., 2004) (Fig. 3). Reductive cleaning involves bathing the sample in a hot buffered solution of hydrazine (Boyle and Keigwin, 1985) and causes some dissolution of foraminiferal carbonate. Since partial dissolution is known to cause a lowering of Mg/Ca ratios (see later), the reduction in Mg/Ca during reductive cleaning may be due either to removal of a contaminant phase or to the partial dissolution that occurs as a side-effect of reductive cleaning. Barker et al. (2003) point out that core-top samples having initially very low Mn/Ca ratios (presumably with only a very small amount of oxide coating) still show a significant ($\sim 10\%$) decrease in foraminiferal Mg/Ca after reductive treatment and suggest that this probably reflects loss through partial dissolution. It is also possible that the lowering of Mg/Ca during reductive cleaning may be due to the removal of some contaminating phase which is not necessarily the Mn-oxide coating but may itself be trapped by such a coating and only released by its

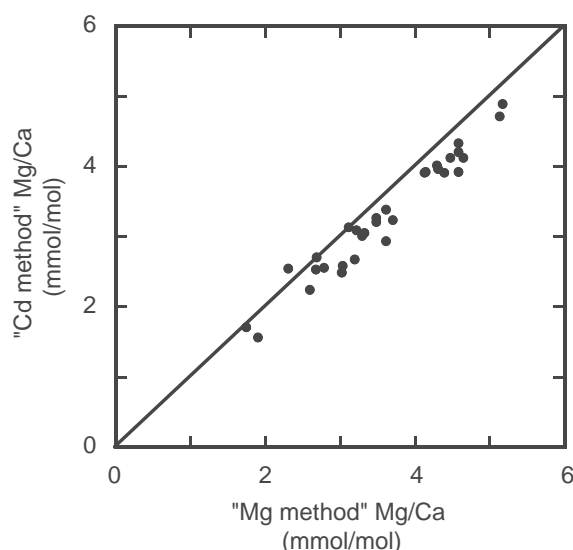


Fig. 3. Comparison of two cleaning procedures (“Cd” versus “Mg”) used on splits of the same foraminiferal samples. Results using the “Cd method” are almost consistently lower than by use of the “Mg method”—see text for details. Data are from Rosenthal et al. (2004).

removal. This issue is yet to be resolved but it is clear that if contaminant Mg is present, it should be removed.

Intra-lab reproducibility of measured foraminiferal Mg/Ca ratios using a consistent cleaning protocol can be better than $\pm 2\%$ (or about 0.2°C) (Barker et al., 2003). Use of a consistent method of sample preparation between laboratories would presumably lead to greater inter-lab reproducibility and may therefore be desirable. If reductive cleaning is deemed unnecessary for Mg/Ca work, it seems logical to omit this step. But as pointed out by Rosenthal et al. (2004) those laboratories wishing to simultaneously measure other trace metal ratios such as Cd/Ca will presumably continue with the “Cd” method. Although the difference in measured Mg/Ca ratios attained by use of the two versions is systematic, it is also pointed out by Barker et al. (2003) that the offset (equivalent to perhaps 1°C) is approximately equal to the uncertainty quoted for Mg/Ca temperature calibrations of 1.3°C (Lea et al., 1999) and 1.2°C (Anand et al., 2003). It may also be suggested that samples should be cleaned by the same method as that employed for constructing the temperature calibration chosen for their interpretation. Once again, since calibrations made using the “Cd” and “Mg” methods are almost identical within error, it appears that differences may not be too problematic. Some further work is required to establish firmly whether differences produced by the two cleaning protocols result in different interpretations of temperature changes through time. It should also be mentioned that samples from certain locations and or time intervals may demand a more or less rigorous cleaning procedure than others. For instance, sediments from strongly reducing environments may be more prone to contamination from Mg associated with ferromanganese phases and therefore reductive cleaning may be necessary. Similarly, sediments containing significant amounts of coarse-grained terrigenous material will require extra care to remove such material from foraminiferal samples.

5. Effects of partial dissolution

Several studies have shown that foraminiferal Mg/Ca ratios systematically decrease through post-depositional dissolution under the influence of undersaturated bottom-waters or pore-waters (Fig. 4) (Lorens et al., 1977; Rosenthal and Boyle, 1993; Russell et al., 1994; Brown and Elderfield, 1996; Rosenthal et al., 2000). The cause of this reduction is thought to be the preferential dissolution of high Mg/Ca regions of the test i.e. those formed in warmer waters (Brown and Elderfield, 1996; Rosenthal et al., 2000). The effect of partial dissolution is therefore a biasing of mean test Mg/Ca values towards colder temperatures.

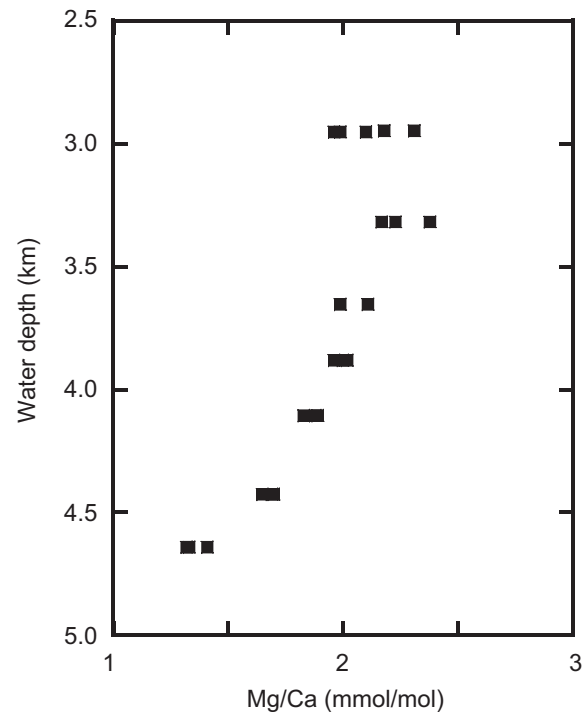


Fig. 4. Coretop Mg/Ca data for *G. tumida* from the Atlantic Ocean show a strong relationship with water depth, demonstrating the effect of partial dissolution on Mg/Ca (after Russell et al., 1994).

If the interpretation of foraminiferal Mg/Ca ratios is influenced by post-depositional alteration, it is necessary to estimate the uncertainty due to such alteration and if possible, correct for it. There have been various methods suggested for accounting for Mg/Ca variations due to dissolution. Lea et al. (2000) show that Mg/Ca ratios in *G. ruber* (w) from core-top samples across the Ontong Java Plateau (OJP) decrease by about 12% per kilometre increase in water depth. They use this finding to suggest a potential uncertainty in their glacial paleotemperature reconstructions of about $+0.5^\circ\text{C}$ taking into account published records of carbonate preservation from that region (Farrell and Prell, 1989; Le and Shackleton, 1992). This uncertainty may be compared with their calculated glacial-interglacial temperature changes of up to 5°C over the last 450 ka. Dekens et al. (2002) approach the problem by incorporating a dissolution term (in this case water depth or bottom-water carbonate ion concentration, $[\text{CO}_3^{2-}]_{\text{bw}}$, into the calibration of Mg/Ca with temperature. Using $[\text{CO}_3^{2-}]_{\text{bw}}$ rather than water depth allows use of a single equation for both the Atlantic and Pacific Ocean basins since the saturation state of bottom waters at a particular depth differs markedly between these ocean basins. An interesting observation made by Dekens et al. (2002) is that different species show varying responses to dissolution with respect to their Mg/Ca ratios. These responses are not necessarily related to the overall

susceptibility of a particular species to dissolution. For example, on the OJP *N. dutertrei* showed a decrease in Mg/Ca of 20% per km increase in water depth (Dekens et al., 2002). This may be compared to a response in *G. sacculifer* of 5% per km. Berger (1970) ranked these two species 16 and 5, respectively, out of 22 in his dissolution index (1 being the most susceptible to dissolution) i.e. Mg/Ca in *N. dutertrei* appears to be more sensitive to dissolution than in *G. sacculifer*. Observations of this sort may become important when comparing multi-species records from sites where temporal changes in preservation are suspected.

One of the greatest obstacles in correcting for dissolution effects on foraminiferal Mg/Ca ratios is quantifying the extent of dissolution undergone by a particular sample. For core-top samples, correction may be made since bottom water conditions are known but for reliable correction of paleo-Mg/Ca ratios it would be desirable to be able to quantify dissolution by some independent dissolution indicator, ideally one coupled with the foraminiferal sample in question. One such approach is by the use of foraminiferal test weights. Based on the work of Lohmann (1995) Broecker and Clark (2001a) demonstrated that weight loss in the tests of planktonic foraminifera, caused by partial dissolution, in core-top samples could be calibrated with $[\text{CO}_3^-]_{\text{bw}}$. They subsequently used these calibrations to reconstruct paleo- $[\text{CO}_3^-]_{\text{bw}}$ in the glacial oceans (e.g. Broecker and Clark, 2001b; Broecker et al., 2001). Rosenthal and Lohmann (2002) demonstrated that the pre-exponential constant, B , in the Mg/Ca temperature calibration equation (Eq. (1)) varied as a function of test weight during dissolution for the tropical species *G. ruber* (w) and *G. sacculifer*. Using this relationship Mg/Ca data may be corrected for dissolution by incorporating test weight variability into temperature reconstructions. Tachikawa et al. (2003) applied this approach to a core from the Arabian Sea, which is characterised by highly variable productivity. After applying a dissolution correction based on foraminiferal test weights, Mg/Ca-based temperatures were in good agreement with alkenone-based temperatures. This result suggests that the correction of Rosenthal and Lohmann (2002) is valuable for dissolution caused by metabolic respiration within sediments. A possible limitation of this method is the observation that initial test weights of several species of planktonic foraminifera vary both regionally and temporally (Barker and Elderfield, 2002). Shell weights are thought to be sensitive to changes in the $[\text{CO}_3^-]$ of seawater in which they grow and hence may vary in parallel with changes in atmospheric CO_2 through time (Spero et al., 1997; Bijma et al., 1999; Barker and Elderfield, 2002). Obviously the initial test weight must be known in order to calculate weight loss due to dissolution.

Another potential method for quantifying foraminiferal dissolution is by the measurement of so-called ‘crystallinity’ (Barthelemy-Bonneau, 1978; Bonneau et al., 1980). Crystallinity is quantitatively the peak width (at half maximum height) of the 104 calcite diffraction peak measured by X-ray diffraction (XRD). It is essentially a measure of how ‘perfect’ the calcite lattice is; a perfect calcite crystal would comprise a single crystallised domain of effectively infinite dimension and would have a very narrow 104 diffraction peak. As a foraminiferal test dissolves at the sea-floor, “poorly crystallized” regions of calcite within the test tend to dissolve preferentially, thereby causing the measured 104 calcite peak of the sample to narrow. Hence foraminiferal crystallinity is sensitive to increasing water depth (Barthelemy-Bonneau, 1978; Bassinot et al., 2004) and as such may potentially be used to correct for dissolution in foraminiferal Mg/Ca ratios if initial environmental influences have negligible effects (Bassinot et al., 2001).

During dissolution, decreasing Mg/Ca is thought to represent the preferential removal of calcite formed at warmer temperatures (Brown and Elderfield, 1996; Rosenthal et al., 2000). The region of calcite within a foraminiferal test with the highest Mg/Ca ratio probably reflects the warmest temperature experienced by that individual and therefore may give the best impression of near surface temperatures. Benway et al. (2003) describe a method addressing the issues of dissolution and heterogeneity using the flow-through leaching technique described by Haley and Klinkhammer (2002) which allows continuous measurement of Mg/Ca during dissolution. The results show how Mg/Ca ratios of sequential leaches decrease during dissolution, presumably because higher Mg/Ca calcite is dissolved first. The high Mg/Ca ratios of the earliest stages of dissolution are interpreted to reflect calcification temperatures of near surface waters. Providing some of the high Mg/Ca calcite remains, this method may provide the opportunity to assess calcification temperatures even after partial dissolution at the seafloor.

6. Mg/Ca temperature reconstructions for the LGM

Mg/Ca paleothermometry is still a relatively new proxy and as such there are a limited number of published records relative to other, more established paleotemperature proxies. Within the framework of the MARGO project, we have developed a compilation of Mg/Ca data representing surface ocean temperature conditions during the LGM (implementing the EPILOG-defined LGM chronozone: 19–23 kyr BP Mix et al., 2001) and Late Holocene (MARGO-defined LH chronozone: 0–4 cal. kyr BP) periods. We have included Mg/Ca data from the mixed layer-dwelling foraminiferal

Table 2

Summary of current Mg/Ca reconstructions covering the LGM listed according to the annotation of Fig. 5. (<http://www.pangaea.de/Projects/MARGO/>)

Map #	Source reference	Core	Calibr. used	Species	LGM Mg/Ca temp	LH-LGM Mg/Ca temp dif.
1	Banakar (unpublished data)	SK129/CR2	6	<i>G. sacculifer</i>	27.6	0.8
2	Barker and Elderfield, 2002	NEAP 8K	8	<i>G. bulloides</i>	9.7	1.2
3	Barker (this manuscript)	16867-2	2	<i>G. ruber</i>	17.7	(*)
		13289-2	2	<i>G. ruber</i>	16.9	1.6
		13289-2	2	<i>G. bulloides</i>	14.6	2.9
		15637-1	2	<i>G. ruber</i>	14.6	4.3
		15637-1	2	<i>G. bulloides</i>	13.9	(*)
		KF09	2	<i>G. ruber</i>	15.4	(*)
		KF13	2	<i>G. ruber</i>	15.0	(*)
		15612-2	2	<i>G. ruber</i>	13.3	2.9
4	Cacho et al. (in prep.)	MD95-2043	2	<i>G. bulloides</i>	14.3	3.7
5	Elderfield and Gassen, 2000	BOFS 31K	2	<i>G. ruber</i>	15.4	0.7
		BOFS 31K	2	<i>G. bulloides</i>	17.1	1.9
6	Hastings et al., 1998	EN066-17GGC	6	<i>G. sacculifer</i>	22.7	1.4
		TT9108-1GC	6	<i>G. sacculifer</i>	23.2	1.8
		CP6001-4PC	6	<i>G. sacculifer</i>	23.1	2
7	Kiefer et al., 2003	ODP883	2	<i>N. pachyderma</i> (s)	5.6	−0.6
8	Koutavas et al., 2002	V21-30	6	<i>G. sacculifer</i>	21.3	1.0
9	Lea et al., 2000	ODP806B	4	<i>G. ruber</i>	26.2	2.4
		TR163-22	4	<i>G. ruber</i>	22.3	3.1
		TR163-20B	4	<i>G. ruber</i>	21.1	2.4
		TR163-19	4	<i>G. ruber</i>	23.3	2.9
		TR163-18	4	<i>G. ruber</i>	23.3	2.4
10	Lea et al., 2003	PL07-39PC	1	<i>G. ruber</i>	23.9	2.9
11	Mashiotta et al., 1999	RC11-120	5	<i>G. bulloides</i>	7.9	3.8
		E11-2	5	<i>N. pachyderma</i> (s)	2.8	(*)
12	Nürnberg et al., 2000	GeoB 1112	6	<i>G. sacculifer</i>	24.1	1.7
		GeoB 1105	6	<i>G. sacculifer</i>	22.5	2.1
13	Pahnke et al., 2003	MD97-2120	5	<i>G. bulloides</i>	8.3	4.3
14	Palmer and Pearson, 2003	ERDC-92	1	<i>G. sacculifer</i>	26.7	1.7
15	Rosenthal et al., 2003	MD97-2141	7	<i>G. ruber</i>	26.7	2.3
16	Skinner and Elderfield (subm.)	MD99-2334K	2	<i>G. bulloides</i>	15.7	1.0
17	Stott et al., 2002	MD98-2181	6	<i>G. ruber</i>	27.0	2.5
18	Visser et al., 2003	MD982162	3	<i>G. ruber</i>	25.7	3.4

Calib: (1) Dekens et al., 2002. (2) Elderfield and Ganssen, 2000. (3) Hastings et al., 2001. (4) Lea et al., 2000. (5) Mashiotta et al., 1999. (6) Nürnberg et al., 1996. (7) Rosenthal and Lohman, 2002. (8) Barker and Elderfield, 2002.

(*) No data available for the Late Holocene Chronozone.

species *G. ruber* (w), *G. sacculifer*, *G. bulloides*, and *N. pachyderma* (s). The data summarize results from 33 sites (Table 2), and are available on the MARGO website (<http://www.pangaea.de/Projects/MARGO/>). Most of these sites are concentrated in the equatorial-tropical band (Fig. 5), but more studies are now focussing on higher latitudes which, until very recently, were a barren territory for Mg/Ca studies. Further LGM Mg/Ca reconstructions are presented in Meland et al. (2004) for the North Atlantic and Nordic Sea, also included in the MARGO website.

SST reconstructions in the tropics have been a controversial issue due to the ambiguity of reconstructions based on different proxies from both terrestrial and marine sources (Broecker and Denton, 1989). The CLIMAP reconstruction (CLIMAP, 1976) suggested little change in tropical SSTs between LGM and modern. This finding is in conflict with terrestrial and

coral derived SST reconstructions which suggest low latitude LGM temperatures were up to 5–6 °C colder than the present day (e.g. Clapperton, 1993; Guilderson et al., 1994; Stute et al., 1995). Mg/Ca paleothermometry has provided insight to this paleoclimate problem; several Mg/Ca-based temperature reconstructions have yielded tropical LGM temperatures that are 2.0–3.5 °C colder than modern. This range is more in line with modelling results which suggest an LGM cooling of about 2.5 °C in equatorial regions (Crowley, 2000).

Mg/Ca records from the Western Pacific warm pool suggest a LH-LGM difference of 2.3 °C and 2.5 °C for the Sulu Sea and the nearby Mindanao Sea respectively, based on *G. ruber* (w) and *G. sacculifer* (Stott et al., 2002; Rosenthal et al., 2003). These values are comparable to the 2.4 °C LH-LGM temperature change estimate for the Ontong Java Plateau (Lea et al., 2000), and the 1.7 °C LH-LGM temperature difference

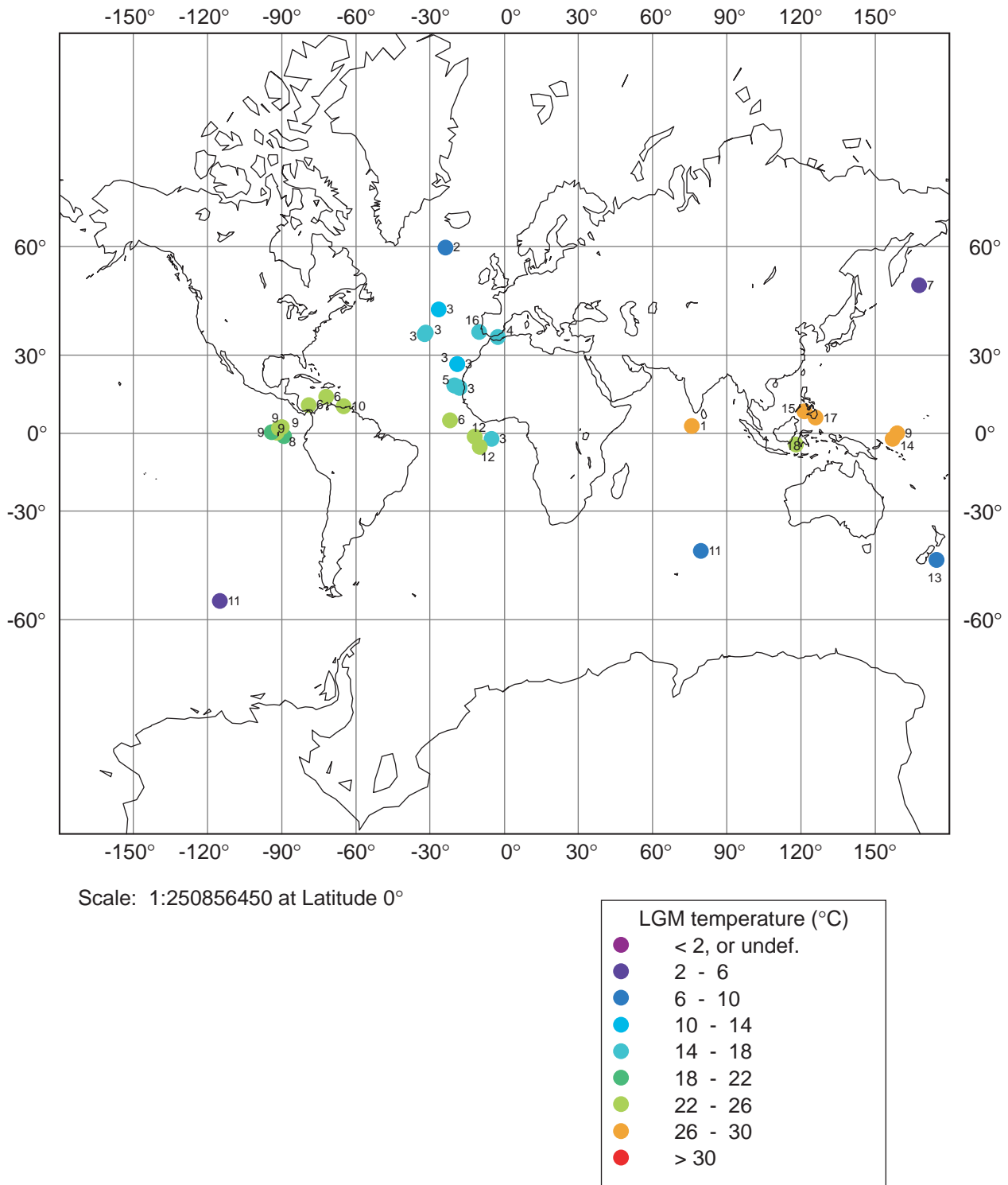


Fig. 5. LGM Mg/Ca estimated temperatures from planktonic foraminifers, data available in the MARGO data set (<http://www.pangaea.de/Projects/MARGO/>). (1) Banakar (unpublished data); (2) Barker and Elderfield, 2002; (3) Barker (this manuscript); (4) Cacho et al. (in prep.); (5) Elderfield and Ganssen, 2000; (6) Hastings et al., 1998; (7) Kiefer et al., in press; (8) Koutavas et al., 2002; (9) Lea et al., 2000; (10) Lea et al., 2003; (11) Mashiotta et al., 1999; (12) Nürnberg et al., 2000; (13) Pahnke et al., 2003; (14) Palmer and Pearson, 2003; (15) Rosenthal et al., 2003; (16) Skinner (unpublished data); (17) Stott et al., 2002; (18) Visser et al., 2003.

obtained further south, also in the western tropical Pacific (Palmer and Pearson, 2003). A recent Mg/Ca temperature reconstruction from the Indo-Pacific warm

pool shows a slightly larger LH-LGM temperature change of 3.4 °C (Visser et al., 2003). These results agree with alkenone-based SST estimates from the same

region (Pelejero et al., 1999; Kienast et al., 2001). In the eastern tropical Pacific just north of the equator, Lea et al. (2000) estimated a LH-LGM temperature change of $\sim 2.8^\circ\text{C}$ based on four Mg/Ca records from *G. ruber* (w). However, a Mg/Ca reconstruction based on *G. sacculifer* from the equatorial cold tongue region yielded a LH-LGM temperature change of only $\sim 1^\circ\text{C}$ (Koutavas et al., 2002). These results may collectively suggest an intensified LGM cross-equatorial gradient (Koutavas and Lynch-Stieglitz, 2003).

In the tropical Atlantic Ocean results are less numerous but they are consistent with those from the Pacific Ocean. Results from *G. sacculifer* indicate that the LH-LGM SST difference was about 2°C in the Caribbean Sea and in the eastern equatorial Atlantic Ocean (Hastings et al., 1998; Nürnberg et al., 2000) and nearly 3°C for the Cariaco basin based on *G. ruber* (w) (Lea et al., 2003). *G. ruber* (w) results from the eastern tropical Atlantic also show a LH-LGM difference of 2°C (Elderfield and Ganssen, 2000; this manuscript) but the amplitude is larger (4°C) further north in the eastern tropical Atlantic (this manuscript).

When we move to higher latitudes *G. ruber* (w) and *G. sacculifer* become less dominant within the foraminiferal assemblage, particularly for glacial times. Therefore, the species chosen for mid- to high-latitude studies is commonly *G. bulloides*. *N. pachyderma* (s) has also been used in those studies from colder regions. High latitude Mg/Ca reconstructions are too sparse to provide conclusive results regarding LGM-LH temperature changes. However, a synthesis of the available data suggests that the situation may be rather complex, particularly for those sites from the Northern Hemisphere. Results for *G. bulloides* in the North Atlantic show little to no temperature difference for LH-LGM at 60°N (Barker and Elderfield, 2002). At this latitude, results from different SST proxies are conflicting. Alkenone-based SSTs suggest that the LGM was warmer than the LH, whereas foraminiferal assemblages suggest that the LGM was $\sim 5^\circ\text{C}$ cooler than the LH (see the MARGO database). Nordic sea Mg/Ca reconstructions (Meland et al., this issue) also show conflicting results, particularly for the central part of the Nordic Sea where LGM temperature reconstructions are unrealistically warm. But Mg/Ca reconstructions for the eastern and southern part of the Nordic Sea show consistent results with those estimated from $\delta^{18}\text{O}$ reconstructions, suggesting 0.5°C colder temperatures for the LGM. Moving southward, the LGM-LH contrast is $\sim 4^\circ\text{C}$ at 45°N (this manuscript), 1°C at 39°N near the western Iberian margin (Skinner and Elderfield, submitted), and 4°C at 36°N in the western Mediterranean Sea (Cacho et al., in prep). Alkenone-based SST reconstructions from comparable locations suggest larger LH-LGM temperature differences of 6, 4, and 7.5°C , respectively (Cacho et al., 2001; Calvo et al.,

2001; Paillet and Bard, 2002). The discrepancies between these two SST proxies in the Mediterranean may reflect changes in the seasonal production of *G. bulloides*. Identification of seasonal variability in foraminiferal species abundances is important since it may affect both Mg/Ca and stable isotope reconstructions.

In the Southern Hemisphere a Mg/Ca record for *G. bulloides* indicates a LH-LGM cooling of 3.8°C for the sub-Antarctic Indian Ocean (Mashiotta et al., 1999). This is in general agreement with warm season temperature estimates based on radiolarian analyses. A recent study in the Southwest Pacific, also based on *G. bulloides*, suggests a LH-LGM SST temperature difference of 4.3°C (Pahnke et al., 2003) which is comparable to alkenone results (3.5°C) from a near by core (Sikes et al., 2002).

7. Summary and conclusions

We have reviewed the present status of planktonic foraminiferal Mg/Ca thermometry and presented a compilation of published and unpublished Mg/Ca temperatures for the LGM. We have highlighted the potential advantages of this method over other paleotemperature proxies and outlined some issues regarding analytical methods, and dissolution. These issues should be addressed before more overreaching interpretation of the available data may be made. For example, results attained from deeper core sites may need to be corrected for dissolution once this has been quantified. Results originating from different laboratories should be compared with caution over the possible effects of differing techniques. Nevertheless, Mg/Ca thermometry has distinct strengths as a paleotemperature proxy; firstly Mg/Ca measurements may be combined with stable isotopes in order to reconstruct variations in $\delta^{18}\text{O}_{\text{seawater}}$. Secondly the use of multiple species, representing environmental conditions at different depths and/or seasons can provide more hydrographic information than is possible from SST reconstructions alone.

The Mg/Ca data currently available for the LGM are still very sparse. However, this proxy has already provided a significant contribution to the question of tropical cooling during the LGM. Most Mg/Ca reconstructions are concentrated in tropical regions and results consistently suggest LGM temperatures $2.0\text{--}3.5^\circ\text{C}$ cooler than the Late Holocene for these regions. Results from northern latitudes are very scarce and some of them show inconsistencies with other proxies, particularly in those areas in which the temperature change associated with the last deglaciation is believed to be particularly large ($>4^\circ\text{C}$). Further data are required before any firm conclusions can be made regarding the origin of these disparities.

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