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### Permalink

<https://escholarship.org/uc/item/8w1481s1>

### Journal

Earth and Planetary Science Letters, 265(1-2)

### ISSN

0012-821X

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### Publication Date

2008

### DOI

10.1016/j.epsl.2007.10.011

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Peer reviewed

# Systematic change of foraminiferal Mg/Ca ratios across a strong salinity gradient

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Received 19 June 2007; received in revised form 1 September 2007; accepted 2 October 2007

Available online 16 October 2007

Editor: H. Elderfield

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## Abstract

The Mg/Ca ratio of foraminiferal calcite is an important proxy for estimating past ocean temperatures. Used in conjunction with  $\delta^{18}\text{O}$  of foraminiferal calcite it allows deconvolution of temperature and ice-volume signals to infer past ocean temperatures and salinities (assuming the relationship between seawater  $\delta^{18}\text{O}$  and salinity is known). Such work assumes that temperature is the only, or at least the dominant, environmental controller of foraminiferal Mg/Ca. The semi-enclosed Mediterranean Sea, where salinity varies from 36 to 40 psu over a seasonal temperature range of between only 5 °C to 8 °C, provides a relevant setting to test this assumption outside the laboratory. In this study, planktonic foraminifera (*O. universa*, *G. siphonifera*, *G. bulloides* and *G. ruber* (white) and (pink)) were picked from 11 box core tops spanning the Mediterranean salinity gradient and analysed for their trace-element concentrations. Mg/Ca ratios are higher, for the associated calcification temperatures, than in other regions where calibrations have been conducted and correlate poorly with calcification temperature. Mg/Ca ratios are particularly high for samples from the Eastern Mediterranean where salinity is unusually high. Correlations of Mg/Ca with the calcification salinity are statistically significant with Mg/Ca changing by 15–59% per psu, suggesting that salinity may act as a control on Mg/Ca ratios in addition to the dominant temperature control. We show that contamination by non-carbonate material and diagenetic high-Mg carbonate overgrowths cannot account for the observed trend of increasing Mg/Ca with salinity. A relationship between Mg/Ca and salinity is also suggested by re-analysis of calibrations from open-ocean settings. These new Mediterranean results are from a region with unusually high salinity but suggest that the effects of salinity on the Mg/Ca palaeothermometer should be considered even in open-ocean settings, particularly where large salinity changes occurred in the past.

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**Keywords:** Mg/Ca; planktonic foraminifera; salinity; palaeotemperature; Mediterranean; recent

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## 1. Introduction

A concerted effort has taken place to provide quantitative information about past climate with which

to test the increasingly sophisticated models used to predict future climate change. Policy decisions regarding acceptable levels of anthropogenic influences, such as carbon dioxide emissions, are made using the results of these models (Houghton and Intergovernmental Panel on Climate Change, 2001) so it is important that they represent the sensitivity and responses of Earth's climate

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system as accurately as possible. A variety of proxies exist to reconstruct past environments but many gaps still remain in our understanding of the climate system. One of the most significant of these is that, although changes in past atmospheric carbon dioxide concentrations are well constrained from ice cores (Petit, 1999), the response of global temperatures to these changes is more difficult to reconstruct. In the oceans a range of water temperature proxies are available to palaeoceanographers including alkenones, foraminiferal assemblages, coralline Sr/Ca ratios and foraminiferal Mg/Ca ratios, but there remains significant disagreement (up to 5 °C) between Pleistocene temperatures reconstructed by these various proxies (Lea et al., 2000). It is therefore important to understand more fully the controls of palaeotemperature proxies to ensure that we can accurately reconstruct the past.

The Mg/Ca ratio in foraminiferal calcite is one of the more widely applied of these palaeotemperature proxies and is used to assess past sea surface temperatures (Barker et al., 2005). A powerful advantage in using the Mg/Ca palaeotemperature proxy is that it can be used to deconvolve the ocean temperature and ocean salinity components from the foraminiferal calcite  $\delta^{18}\text{O}$  record, assuming the relationship between salinity and  $\delta^{18}\text{O}$  seawater is known, and so allows quantitative estimates of past terrestrial ice volumes (Lear et al., 2000; Elderfield and Ganssen, 2000).

A temperature dependence of Mg/Ca ratios in inorganic calcite was early demonstrated (Oomori et al., 1987; Katz, 1973) and later observed in both cultured foraminifera and modern foraminifera growing in the world's oceans (Lea et al., 2000; Elderfield and Ganssen, 2000; Lea et al., 1999; Delaney et al., 1985; Nürnberg et al., 1996). Mg/Ca ratios in modern planktonic foraminifera are assumed and have been demonstrated to be predominantly a function of the temperature and Mg/Ca ratio of the water in which they grew (Lea et al., 2000; Barker et al., 2005; Elderfield and Ganssen, 2000; Nürnberg et al., 1996; Anand et al., 2003; Dekens et al., 2002). For deep cores it is usual to apply a depth or weight dependent correction to take into account the preferential dissolution of more Mg-enriched calcite as the foraminifera are affected by calcite-undersaturated deep waters and porewaters during sedimentation (Dekens et al., 2002; Brown and Elderfield, 1996). The Mg/Ca ratio in seawater is spatially constant and unlikely to change on timescales of less than 1 million years due to the very long residence times of both Mg and Ca in the oceans (Broecker and Peng, 1982). However individual measurements show significant scatter around calibrations

of the Mg/Ca palaeothermometer (Elderfield and Ganssen, 2000; Anand et al., 2003). Furthermore there are notable differences between the various existing calibrations constructed in different ocean regions (e.g. for *Globigerinoides ruber* (white) as shown by the black curves on Fig. 1). This degree of scatter limits the precision of Mg/Ca as a palaeotemperature proxy and calls the accuracy of the technique into question. It is likely, therefore, that there are additional oceanographic variables that affect the incorporation of Mg into foraminiferal calcite.

Laboratory culture studies have shown that the pH, carbonate ion concentration and salinity of seawater act as controls on Mg/Ca ratios in foraminifera but suggest that their influence is small in comparison with temperature (Lea et al., 1999; Nürnberg et al., 1996; Russell et al., 2004; Elderfield et al., 2006). The effect of pH has been found to be small with foraminiferal Mg/Ca ratios decreasing by 6% per 0.1 pH increase (Lea et al., 1999). The carbonate ion concentration effect on Mg/Ca appears to be more complex. In benthic foraminifera, increased Mg/Ca ratios have been observed to correlate with increased carbonate ion concentrations (Elderfield et al., 2006; Boyle and Erez, 2003). In contrast, a laboratory study of planktonic foraminifera (Russell et al., 2004), showed decreasing Mg/Ca with increasing carbonate ion concentrations below 200  $\mu\text{mol/kg}$ , with no significant change at higher concentrations.

An influence of salinity on foraminiferal Mg/Ca ratios has been observed in several studies. In the laboratory, the only direct study of the effect of salinity on entire test Mg/Ca ratios (Lea et al., 1999) suggested a small increase with salinity of  $4\pm 3\%$  per psu in *Orbulina universa* grown at salinities of 27, 33 and 39 psu. Another study of the final chambers of *Globigerinoides sacculifer* grown at salinities of 26, 35 and 44 psu showed increases of Mg/Ca of over 100% at higher salinity, or approximately 11% per psu (Nürnberg et al., 1996). It is difficult, however, to accurately mimic the natural environment during laboratory culturing of foraminifera and, as yet, no systematic field studies of the role of salinity in controlling foraminiferal Mg/Ca ratios have been published.

## 2. Regional setting and samples

The Mediterranean Sea provides an ideal setting for examination of the influence of salinity on foraminiferal Mg/Ca and other trace element ratios. The Mediterranean Sea is a latitudinal basin which results in only a small range ( $\sim 4$  °C) in mean-annual sea-surface temperatures (although seasonal ranges are larger, reaching

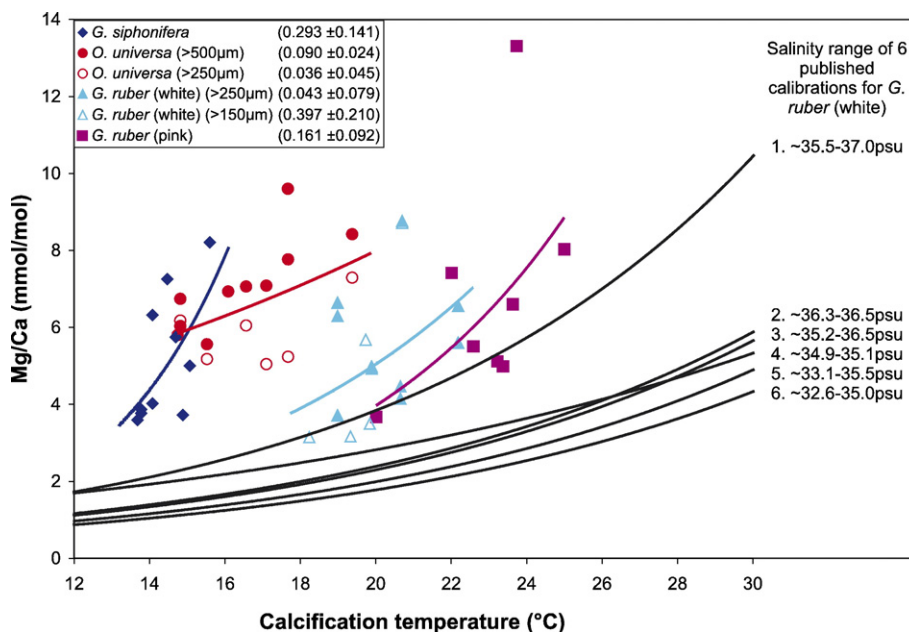


Fig. 1. Foraminiferal Mg/Ca ratios plotted against calcification temperature. Coloured lines are the lines of best fit for each species and the exponential factor is quoted in brackets in the legend along with the error at  $2\sigma$ . Errors are plotted at  $2\sigma$  and are within symbol size. Black curves labelled 1 to 6 are existing calcification temperature calibrations for *Globigerinoides ruber* (white) from different locations, with the exception of 6-Lea et al., 2000 which is a calibration to sea surface temperature.; 1-Elderfield and Ganssen, 2000 (Atlantic Ocean)  $Mg/Ca = 0.52 e^{0.1T}$ , 2-Anand et al., 2003 (Sargasso Sea)  $Mg/Ca = 0.395 e^{0.09T}$ , 3-Dekens et al., 2002 (Atlantic Ocean)  $Mg/Ca = 0.38 e^{0.09(T-0.61D)}$  where  $D$ =depth of core in km which in this figure is set to 0, 4-McConnell and Thunnell, 2005 (Gulf of California)  $Mg/Ca = 0.79 e^{0.064T}$ , 5-Dekens et al., 2002 (Pacific Ocean)  $Mg/Ca = 0.38 e^{0.09(T-0.61D-1.6)}$  where  $D$ =depth of core in km which in this figure is set to 0, 6-Lea et al., 2000 (Pacific Ocean)  $Mg/Ca = 0.3 e^{0.089SST}$ . Also labelled are the modern day salinity ranges at each location. Samples from core T83/2/1/67 are included.

a maximum of 8 °C in the autumn). In contrast there exists a large salinity gradient; from 36 psu in the west, where waters exchange with the open ocean through the Straits of Gibraltar, to unusually high values of nearly 40 psu in the east as a result of evaporation in the restricted basin (Fig. 2).

The semi-enclosed nature of the Mediterranean Sea also results in the creation of significant gradients in other oceanographic variables, particularly in nutrient and carbonate ion concentrations. From west to east, phosphate concentrations show no clear trend but there is a strong decrease in nitrate concentrations from

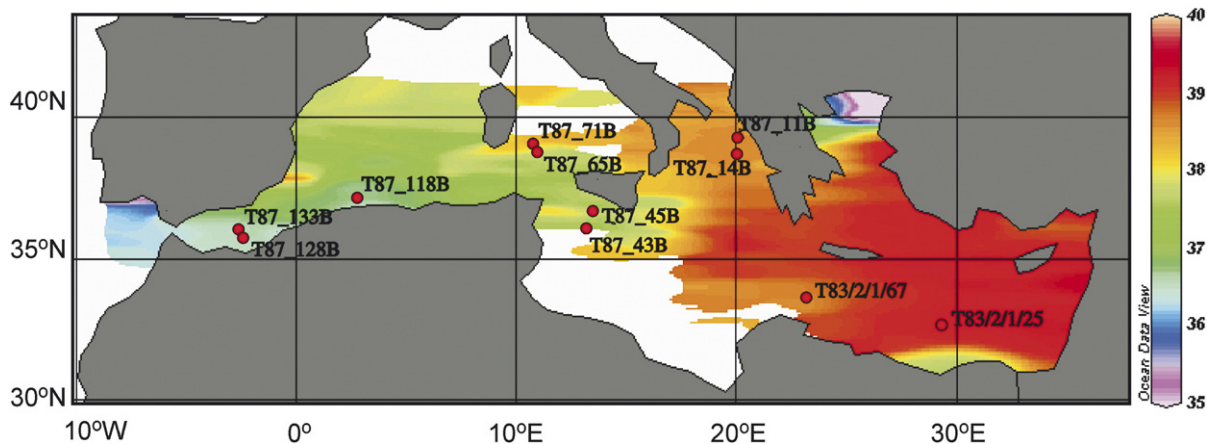


Fig. 2. Map of Mediterranean Sea salinity (Schlitzer, 2005) based on measurements from 6308 stations taken between 1980 and 1990 (MEDAR Group, 2002). Red circles mark the locations of the core tops used in this study.

4  $\mu\text{mol}$  to 0  $\mu\text{mol}$  (MEDAR Group, 2002). However, this range in nutrient concentrations, unlike salinity, is not unusual and is similar to extensive areas of the open oceans (Levitus and Boyer, 1994). Carbonate ion concentrations in the Mediterranean can be estimated (Boyle, 2005) from sparse alkalinity data (MEDAR Group, 2002) and known salinities and temperatures. These estimates suggest carbonate ion concentrations ranging from 170 to 300  $\mu\text{mol}/\text{kg}$  in the Mediterranean Sea. Although these values are somewhat high for the temperatures for which they are estimated, they are not significantly outside of the range of surface water carbonate ion concentration observed in the open ocean (110–280  $\mu\text{mol}/\text{kg}$ ) (Russell et al., 2004; Takahashi et al., 1980).

Planktonic foraminifera tests (*Orbulina universa*, *Globigerinella siphonifera*, *Globigerinoides ruber* (white) and (pink) and *Globigerina bulloides*) were picked from the sieved size fractions of 11 box core tops spanning the strong salinity gradient in the Mediterranean Sea (Fig. 2).

### 3. Analytical techniques

#### 3.1. Calculation of calcification temperatures and salinities

Calcification temperatures and salinities were analysed by averaging World Ocean Atlas 2005 data (Locarnini et al., 2006; Antonov et al., 2006) for appropriate depth habitats and season of peak abundance within the Mediterranean Sea (Supplementary Table 1). An extensive study of the depth habitat and seasonal abundances of Mediterranean Sea foraminifera has shown that depth habitats are variable across the basin (Pujol and Grazzini, 1995). *G. ruber* (pink) peak during the summer at 20 m throughout the Mediterranean. *G. ruber* (white) was found living in the summer at 20–50 m off the North African coast, in the Ionian Basin and in the Levantine Basin. It was also found living at 20–100 m in the Levantine Basin in the winter but the numbers at this season were extremely low so the contribution from this time can be disregarded. *O. universa* numbers peak in the summer at depths of 50–100 m off the North African coast but shallower at 50 m in the Ionian Basin. *G. siphonifera* is a deeper-dwelling foraminifera and is observed to live within 100–200 m throughout the Mediterranean during the winter. *G. bulloides* is the species with the most variable depth habitat. It was observed in spring in the Alboran Sea at 20–200 m, at 50–200 m in winter off the North African coast, at 20–50 m in winter in the Provençal

Basin, then at a greater depth of 200–400 m in winter in the Ionian Basin.

Some previous calibration studies of foraminiferal Mg/Ca ratios have used calcification temperatures calculated from foraminiferal  $\delta^{18}\text{O}$ , using the  $\delta^{18}\text{O}$  of seawater in the localities estimated from local salinity or measured previously (Elderfield and Ganssen, 2000; Anand et al., 2003).

Such an approach is complicated by the presence of vital effects (biologically mediated offsets from pure thermodynamic behaviour during oxygen isotope incorporation) which vary from species to species and with region. Vital effects for the species analysed here are often not well constrained with region, and can even change with temperature (for a summary see Table 2a in Rohling et al., 2004). This prevents accurate conversion of measured foraminiferal calcite  $\delta^{18}\text{O}$  to temperature. In the Mediterranean Sea, estimates for the vital offsets in foraminifera species are not generally available, with the exception of some modelled results (Rohling et al., 2004). The use of foraminiferal  $\delta^{18}\text{O}$  to assess calcification temperature is also confounded in the Mediterranean by sparse or absent seasonal seawater  $\delta^{18}\text{O}$  information and by large changes in sea surface  $\delta^{18}\text{O}$  (up to 1‰ seasonally (MEDAR Group, 2002)) due to its enclosed nature and high evaporation rates.

Given these difficulties in the use of foraminiferal  $\delta^{18}\text{O}$  to assess calcification temperature, we use World Ocean Atlas 2005 data (Locarnini et al., 2006) averaged over the observed depth habitats and peak seasonal abundances for the Mediterranean (Pujol and Grazzini, 1995) as a more consistent way of estimating calcification temperatures. This approach also allows us to make use of datasets of additional oceanographic variables such as salinity, which is not possible using foraminiferal  $\delta^{18}\text{O}$  alone.

#### 3.2. Sample preparation

Sediment was wet-sieved to yield a >500  $\mu\text{m}$  and a 150–500  $\mu\text{m}$  fraction, later separated by dry-sieving into a 300–500  $\mu\text{m}$  and a 150–300  $\mu\text{m}$ . Between 30 and 50 pristine-looking individual foraminifera of each species were picked, where possible, from each size fraction. Due to insufficient numbers of specimens of *G. ruber* (pink), *G. bulloides* and *G. siphonifera*, size fractions were combined to allow analysis. Few core tops contained sufficient numbers of *G. bulloides* for analysis so analyses do not span enough of the Mediterranean Sea oceanographic gradients to allow any meaningful discussion. Data is included in Supplementary Table 1 but is not included in subsequent



figures or discussion. This yielded a total of 56 samples for analysis. Before cleaning, each sample was gently crushed between two pieces of glass to ensure that the chambers of the foraminifera were open. Each sample was then cleaned following a full reductive-oxidative cleaning (Boyle, 1981) with frequent ultrasonification and rinses in 18 MΩ water. Initial rinses and ultrasonification in 18 MΩ water (three times), QD methanol (two times), and a final 18 MΩ rinse removes adhering clays. Heating for 30 min in a reducing solution of 1200 μl hydrous hydrazine in 10 ml ammonium hydroxide and 10 ml ammonium citrate removes surface metal oxides, and an oxidising solution of 250 μl hydrogen peroxide in 10 ml 0.1 M sodium hydroxide is used to remove any remaining organic material. Lastly, samples were leached gently with 0.001 M nitric acid then dissolved in 0.5 ml of 1% nitric acid.

In order to assess the heterogeneity of the foraminifera test chemistry, and the presence of any post-depositional overgrowths, sequential dissolution was carried out on additional samples of *G. ruber* (white) and *O. universa* from one central and two eastern Mediterranean sites. After the cleaning described above, samples were immersed for 1 min in 75 μl of 1% nitric acid with ultrasonification for 45 s. The acid was then pipetted off for analysis and additional aliquots of acid added and removed until the sample had completely dissolved. Each 75 μl sample was made up to 0.5 ml with 2% nitric acid for analysis.

### 3.3. Mass spectrometry and microscopy techniques

Chemical analyses were performed on two instruments. Early analyses were carried out using a low-uptake (100 μl/min) spray-chamber nebuliser feeding into a PerkinElmer PESCIEX ELAN 6100 DRC Quadrupole Inductively-Coupled Plasma Mass Spectrometer (ICP–MS). Solution Ca concentrations were adjusted to ~100 ppm Ca to prevent coating of the cones of the mass spectrometer and to reduce internal errors. The analysis method uses a ‘peak-hopping’ method (Harding et al., 2006) adapted from Rosenthal et al. (1999), normalising trace element concentrations (Mg, Sr, U, Cd, Zn, Ba, Mn and Li) to Ca. A synthetic standard with approximate foraminiferal composition was run either side of each sample and acid blanks were run after every 5th sample. The external error, obtained from the standard deviation of the standards, was 2.4% ( $2\sigma$ ;  $n=24$ ) for Mg/Ca.

Forty-two of the original sample solutions were also analysed 18 months after this initial analysis for Al/Ca and

Fe/Ca to investigate the presence of clays using a Thermo Finnigan Element2 Mass Spectrometer. Mg/Ca ratios were reanalysed at the same time. This instrument was also used for analysis of the sequential dissolution samples. Sample solutions were diluted to 10 ppm Ca using 2% nitric acid. Samples with Ca concentrations less than 10 ppm were discarded. A synthetic standard (with composition close to typical foraminiferal values) and an acid blank were run after every 5th sample. The standard deviation of the standards ( $2\sigma$ ;  $n=10$ ) were approximately 0.04%, 1.43% and 1.18% for Mg/Ca, Al/Ca and Fe/Ca respectively.

In addition to chemical analysis, select samples were subjected to careful inspection by Scanning Electron Microscopy to search for post-depositional overgrowths. Foraminifera (*G. ruber* (white) and *O. universa*) from two sites in the eastern Mediterranean Sea, and one in the west for comparison, were crushed between two glass plates to open the chambers. They were then rinsed twice in 18 MΩ water, with ultrasonification, to remove fine coccoliths, clays and calcite particles clinging to the foraminifera, and examined using a Scanning Electron Microscope.

### 3.4. Screening of samples

As will be discussed in following sections, measured Mg/Ca ratios are significantly higher than those expected based on published temperature calibrations (Fig. 1). Here we consider whether these values can be explained by contamination by either clay minerals or a high-Mg-calcite overgrowth.

#### 3.4.1. Screening for contamination from iron-manganese coatings and detrital clays

Mn/Ca values, used to quantify the amount of likely contamination due to iron-manganese coatings in the sample after cleaning, are relatively low in all samples with an average Mn/Ca ratio of 9.86 μmol/mol (Table 1). Values for all samples are less than 25 μmol/mol, except those from core T87 133B which have Mn/Ca ratios of up to 80 μmol/mol (Supplementary Table 1), still low enough for these samples to be regarded as reliable using a commonly applied upper limit of 100 μmol/mol (Boyle, 1983). There is no correlation between Mg/Ca and Mn/Ca ratios.

Recently published work has used Fe/Ca and Al/Ca values to distinguish samples which may be contaminated with clays even after cleaning (Lea et al., 2005; Barker et al., 2003). Upper limits in Fe/Ca of 175 μmol/mol and in Al/Ca of 40 μmol/mol have been used in downcore studies of foraminiferal Mg/Ca records (Lea

Table 1  
Average trace element/Ca ratios for each species and size fraction  $\pm 1$  standard deviation

Species	Size fraction	Average Mg/Ca (mmol/mol)	Average Sr/Ca (mmol/mol)	Average U/Ca (nmol/mol)	Average D(Cd/Ca)	Average Zn/Ca (mol/mol)	Average Ba/Ca ( $\mu$ mol/mol)	Average Li/Ca ( $\mu$ mol/mol)	Average Mn/Ca ( $\mu$ mol/mol)
<i>Orbulina universa</i>	Total	6.4 $\pm$ 1.0	1.37 $\pm$ 0.03	7.1 $\pm$ 1.2	24 $\pm$ 21	18 $\pm$ 13	1.2 $\pm$ 0.6	1.41 $\pm$ 0.13	4.4 $\pm$ 4.9
	>500 $\mu$ m	6.8 $\pm$ 0.9	1.36 $\pm$ 0.02	7.5 $\pm$ 1.4	19 $\pm$ 17	14 $\pm$ 11	1.0 $\pm$ 0.3	1.39 $\pm$ 0.07	3.5 $\pm$ 2.6
	>300 $\mu$ m	5.8 $\pm$ 0.9	1.38 $\pm$ 0.03	6.5 $\pm$ 0.9	30 $\pm$ 25	25 $\pm$ 14	1.5 $\pm$ 0.8	1.43 $\pm$ 0.20	5.7 $\pm$ 7.4
<i>Globigerinella siphonifera</i>	>150 $\mu$ m	4.8 $\pm$ 1.3	1.29 $\pm$ 0.03	10.0 $\pm$ 3.2	84 $\pm$ 108	66 $\pm$ 35	2.7 $\pm$ 2.2	1.83 $\pm$ 0.22	15.0 $\pm$ 7.5
<i>Globigerinoides ruber</i> (pink)	>150 $\mu$ m	5.9 $\pm$ 1.5	1.41 $\pm$ 0.04	16.1 $\pm$ 4.3	51 $\pm$ 55	41 $\pm$ 28	1.8 $\pm$ 0.5	1.88 $\pm$ 0.12	18.0 $\pm$ 28.2
<i>Globigerinoides ruber</i> (white)	Total	4.8 $\pm$ 1.3	1.43 $\pm$ 0.03	8.7 $\pm$ 2.9	21 $\pm$ 20	17 $\pm$ 8	1.4 $\pm$ 0.4	1.78 $\pm$ 0.05	5.5 $\pm$ 9.8
	>250 $\mu$ m	5.3 $\pm$ 1.1	1.43 $\pm$ 0.01	9.0 $\pm$ 3.5	14 $\pm$ 5	15 $\pm$ 9	1.3 $\pm$ 0.3	1.77 $\pm$ 0.05	2.0 $\pm$ 1.6
	>150 $\mu$ m	3.9 $\pm$ 1.2	1.43 $\pm$ 0.05	8.2 $\pm$ 1.6	35 $\pm$ 31	21 $\pm$ 7	1.7 $\pm$ 0.5	1.80 $\pm$ 0.06	12.6 $\pm$ 15.7
<i>Globigerina bulloides</i>	>150 $\mu$ m	4.4 $\pm$ 1.3	1.35 $\pm$ 0.05	14.1 $\pm$ 6.7	33 $\pm$ 16	34 $\pm$ 14	4.7 $\pm$ 1.5	2.20 $\pm$ 0.37	15.6 $\pm$ 15.0

Individual results can be found in Supplementary Table 1.

et al., 2005; Bice et al., 2005). Thirty-two of the 42 samples have Fe/Ca values lower than this upper limit but Al/Ca values are higher. *G. ruber* (white) from site T87 14B showed very high Fe/Ca (Supplementary Table 1) and so is removed from further discussion with the exception of Fig. 1. The high Al/Ca and Fe/Ca ratios might be explained by continued leaching of clays in the 18 months after dissolution of the foraminifera. A similar effect has been reported where samples analysed 2 years after dissolution contained 10 times higher Al/Ca and Fe/Ca ratios than samples, from the same interval in the core, analysed immediately (Lea et al., 2005). Regardless of the source of the high values, it is reassuring that neither Fe/Ca nor Al/Ca correlate with Mg/Ca (Fig. 3), unlike the relationship seen in a previous study (Lea et al., 2005). This absence of any relationship between Al/Ca and Mg/Ca indicates that the high Al/Ca ratios cannot be used to screen Mg/Ca values in this setting. As an example, the two samples with the lowest observed Al/Ca values have Mg/Ca ratios of 6.0 and 8.4 mmol/mol (Supplementary Table 1), significantly higher than expected based on published temperature relationships.

Any possible impact from detrital contamination can also be assessed using a simple mass-balance calculation. In Mediterranean Sea clays, reported Mg/Al ratios vary between 0.24 mol/mol (Jiménez-Espejo et al., 2006) and 0.34 mol/mol (Rutten, 2001). Using these values, the amount of Mg associated with the Al introduced by the silicate material in the samples only accounts for 10% of the excess Mg/Ca above the values expected based on published temperature calibrations. This mass balance therefore also suggests that the high Mg/Ca ratios cannot be explained by detrital contamination.

### 3.4.2. Screening for high Mg overgrowths

When examined using a Scanning Electron Microscope it is possible to see a thin (a few  $\mu$ m) layer of encrusting inorganic high-Mg calcite ( $\sim 10$  wt.% Mg) on the inside surface of some foraminifera chambers (Sexton et al., 2006). This layer is particularly visible on samples from one site (T83/2/1/67) in the Eastern Mediterranean Sea (Fig. 4). Significantly, it was not possible to distinguish a high-Mg calcite phase encrusting the exterior of any foraminifera tests. The high-Mg calcite visible using Scanning Electron Microscopy is more soluble than low-Mg foraminiferal calcite and so should be removed preferentially during the vigorous cleaning procedures. The sequential dissolution results allow a test of this assertion. Three of the four samples showed no decrease in Mg/Ca during sequential dissolutions, confirming that none of the observed high-Mg calcite remains after the normal cleaning (Fig. 5). Sequential dissolution of *G. ruber* (white) from T83/2/1/67 showed some high-Mg calcite remained after cleaning as indicated by successive dissolution steps showing preferential dissolution of a higher Mg/Ca phase before a constant Mg/Ca ratio is attained, representing the primary foraminiferal Mg/Ca ratio. This primary foraminiferal Mg/Ca ratio is  $\approx 5.25$  mmol/mol and therefore still significantly higher than expected for this temperature based on published calibration curves. We note, however, that samples of several species from this one site showed particularly high Mg/Ca ratios so, to ensure that results were not biased by overgrowths that escaped the cleaning process, we exclude all data from this site T83/2/1/67 from further discussion with the exception of Fig. 1. We stress that the partial dissolution experiments on all other sites indicate that the high observed Mg/Ca in the cleaned Eastern

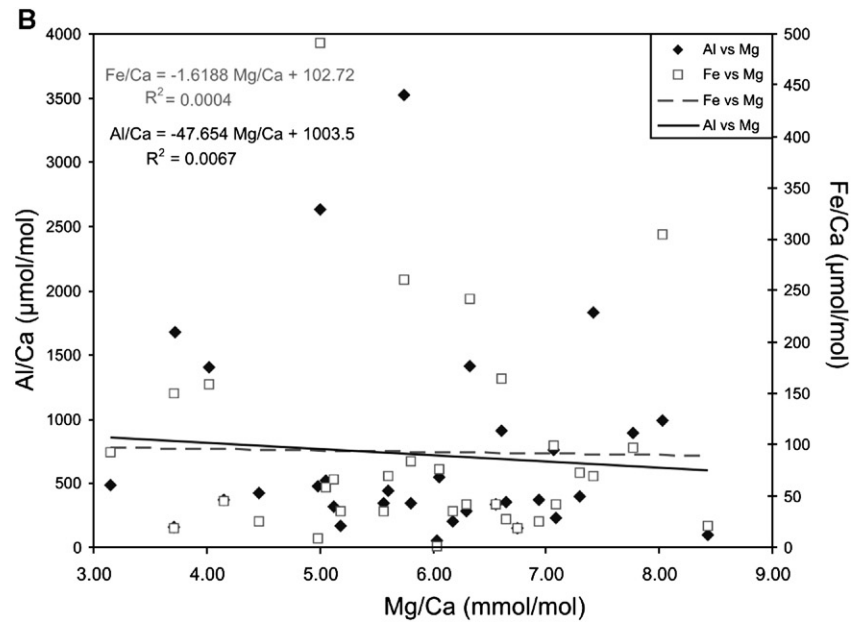
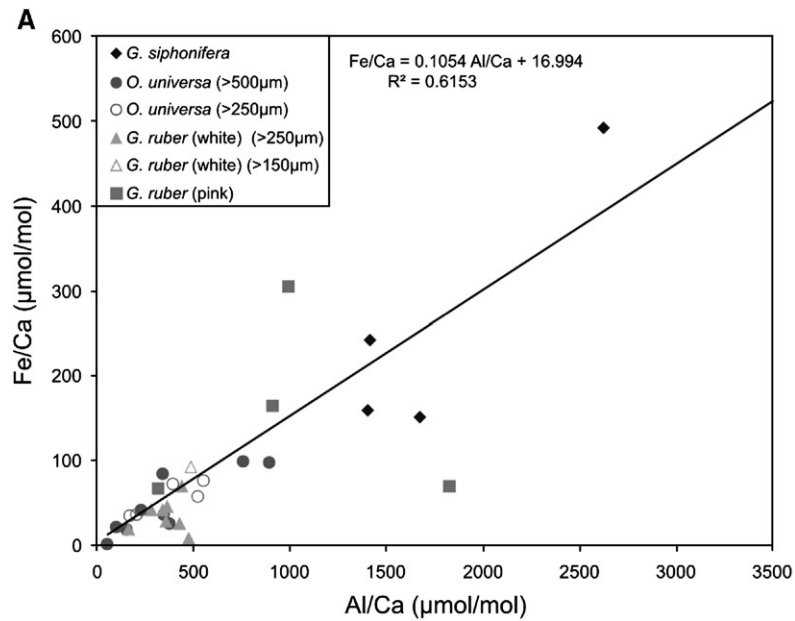


Fig. 3. A) Correlation between Al/Ca and Fe/Ca ratios. The line of best fit is shown and the equation describing the relationship between them. Errors are within symbol size. B) Graph showing Mg/Ca ratios plotted against Al/Ca and Fe/Ca ratios. Lines of best fit are drawn and equations and correlation coefficients for Al/Ca vs Mg/Ca and Fe/Ca vs Mg/Ca are shown. Errors are within symbol size.



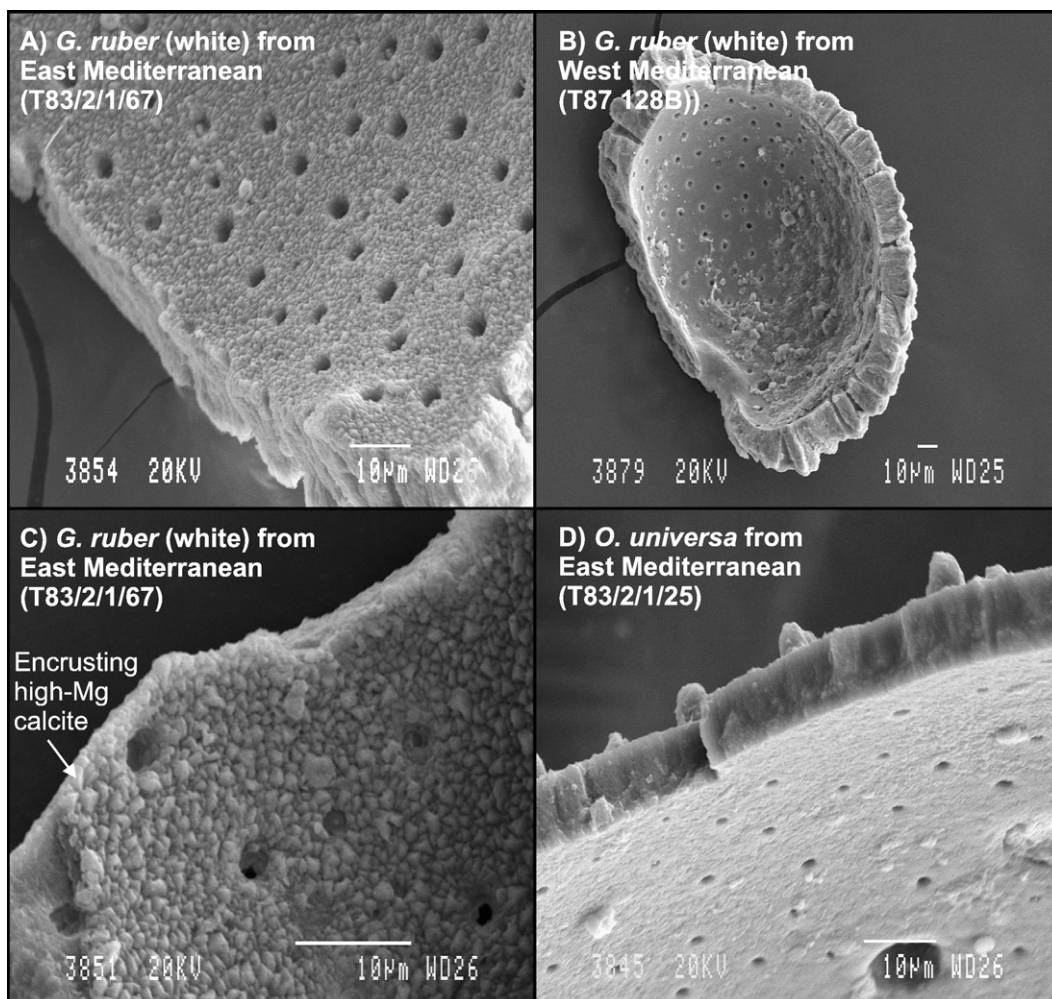


Fig. 4. A+C) SEM image of the interior of a *G. ruber* (white) from an eastern Mediterranean core (T83/2/1/67) with a coating of secondary inorganic high-Mg calcite. B) SEM image of the interior of a *G. ruber* (white) chamber from a western Mediterranean core (T87 128B) with a less developed coating of secondary high-Mg calcite. D) SEM image of an *O. universa* from an eastern Mediterranean core (T83/2/1/25).

Mediterranean foraminifera are not explained by high Mg/Ca overgrowths.

#### 4. Results

Results for all trace element ratios are summarised in Table 1 (and in more detail in Supplementary Table 1). No significant relationship between temperature or salinity and trace metal ratio are observed, except for Mg/Ca. Mg/Ca ratios are higher than expected from previous studies (Fig. 1) ranging from 3.60 mmol/mol to 13.31 mmol/mol with species averages ranging from 4.81 mmol/mol for *G. siphonifera* to 6.43 mmol/mol for *O. universa*. Where Mg/Ca values were obtained for two difference size fractions, ratios are always higher in the larger fraction. The difference is more marked in

*O. universa* than in *G. ruber* (white), most likely due to their greater depth range (20–50 m for *G. ruber* (white) compared with approximately 50–100 m for *O. universa* (Pujol and Grazzini, 1995)) allowing increased dispersal of differently-sized *O. universa* than is possible with *G. ruber* (white). Mg/Ca values for each species correlate poorly with calcification temperatures, obtained by averaging temperatures over the appropriate seasonal and depth range for each species (Locarnini et al., 2006; Antonov et al., 2006; Pujol and Grazzini, 1995) (Fig. 1). The percentage change in Mg/Ca per °C is between 4 and 40% in our results, in contrast with accepted percentage changes in other calibrations of 8 to 10% (Lea et al., 2000; Elderfield and Ganssen, 2000; Lea et al., 1999; Nürnberg et al., 1996; Anand et al., 2003; Dekens et al., 2002; Russell et al., 2004).

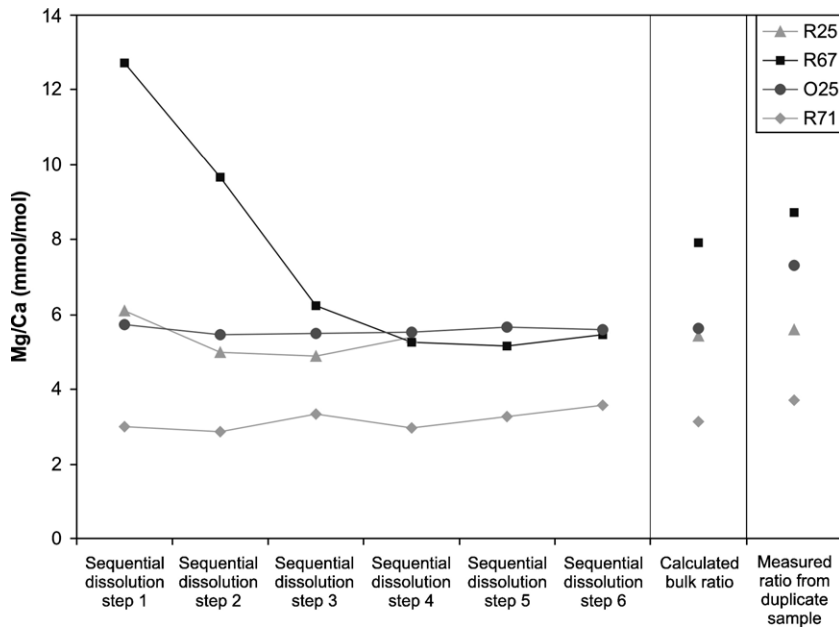


Fig. 5. Mg/Ca ratio of sequential dissolution steps of samples of *G. ruber* (white) from the Eastern Mediterranean (shown as R67 and R25 from cores T83/2/1/67 and T83/2/1/25 respectively) and from the central Mediterranean (shown as R71 from core T87 71B) and also *O. universa* from the Eastern Mediterranean (shown as O25 from core T83/2/1/25). Also shown is the calculated bulk dissolution Mg/Ca ratio, which would have been measured if the sample had not been dissolved sequentially, and a previous bulk Mg/Ca ratio of a sample from the same core. The bulk dissolution Mg/Ca ratio is lower than the previous bulk Mg/Ca ratio since the foraminifera picked for sequential dissolution analyses were smaller in size. Error bars at  $2\sigma$  are within symbol size.

Correlations between Mg/Ca ratios and calcification salinities, again calculated by averaging data (Antonov et al., 2006) for the appropriate seasonal and depth range of each species (Pujol and Grazzini,

1995), are generally more significant than with calcification temperatures (Fig. 6A). Percentage increases per psu range from 15% in *O. universa* (>500  $\mu\text{m}$  fraction) to 59% in *G. siphonifera*, much higher than

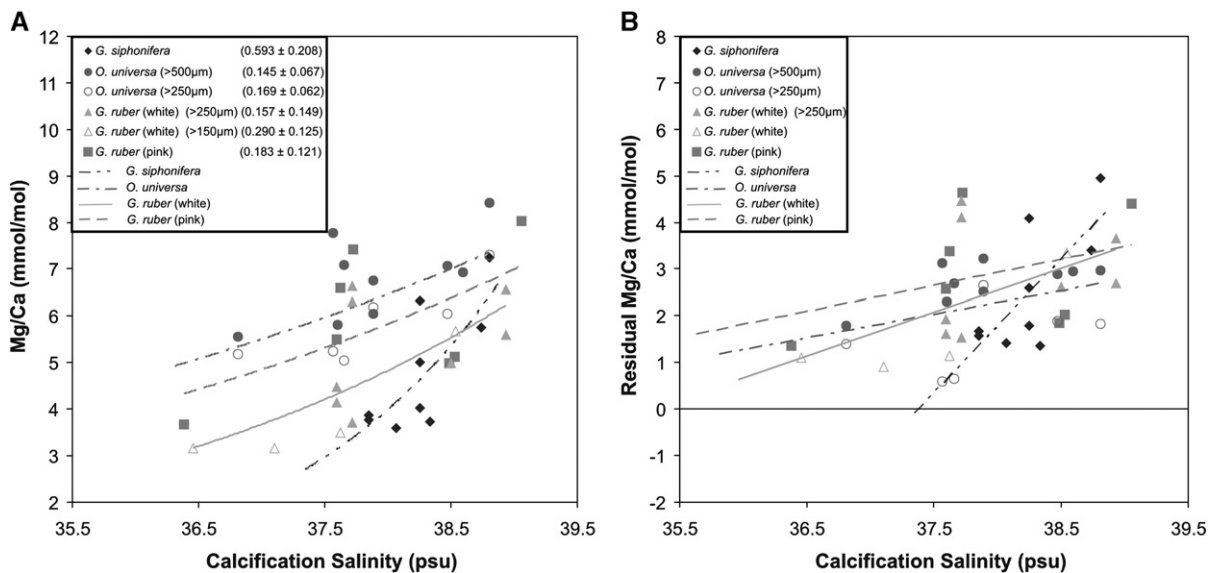


Fig. 6. A) Mg/Ca ratios plotted against calcification salinity. Numbers are the exponential factor of the line of best fit  $\pm$  error quoted at  $2\sigma$ . B) Graph showing residual Mg/Ca plotted against calcification salinity. Residual Mg/Ca is the observed Mg/Ca minus predicted Mg/Ca using the calibration of Russell et al. (2004) for *O. universa* and Anand et al. (2003) for all other species. In both parts, errors are plotted at  $2\sigma$  and are within symbol size. Lines of best fit for each species are also shown.

those predicted by a culture study ( $\approx 4\%$ ) (Lea et al., 1999).

## 5. Discussion

### 5.1. Non-contributing secondary controls on Mg/Ca

Measured Mg/Ca values in Mediterranean foraminifera are higher, for the same temperature, than seen in regions where calibrations have previously been conducted. Our results also exhibit unusually poor correlations between Mg/Ca ratios and calcification temperatures with much greater sensitivity relative to previously published sensitivities (Lea et al., 2000; Elderfield and Ganssen, 2000; Lea et al., 1999; Nürnberg et al., 1996; Anand et al., 2003; Dekens et al., 2002; Russell et al., 2004).

These high Mg/Ca values cannot be explained by contamination by clay minerals or high Mg overgrowths (as detailed in Section 3.4 above). Measured Al/Ca and Fe/Ca ratios rule out any large contribution of Mg from detrital clays. Sequential dissolution experiments indicate that minor high-Mg calcite overgrowths, visible on the inside surface of tests by Scanning Electron Microscopy (but not by optical microscopy), are fully removed by the cleaning process applied to all samples in this study. Differential dissolution of samples also does not offer an explanation for the high Mg/Ca because the depth of the

cores used in the study (296–2654 m) is relatively shallow, and because the high Mg/Ca is observed at all depths (Fig. 7).

An influence of the wide size fractions used in the study on the Mg/Ca ratios across the Mediterranean Sea can also be ruled out. Many planktonic foraminifera species show increasing Mg/Ca ratios with increasing size (Elderfield et al., 2002), as confirmed by the size fractions of *O. universa* and *G. ruber* (white) in this study which show Mg/Ca consistently lower in the smaller size fraction (Fig. 1). If the average size of the foraminifera in the samples increased from west to east across the Mediterranean, this might lead to a measured increase in Mg/Ca. No systematic trend in the size of foraminifera with location was observed during picking in this study, however. More-over, any such trend would impact the different species studied here in opposite directions. Within the 212–500  $\mu\text{m}$  size range investigated in (Elderfield et al., 2002), Mg/Ca increased by 30% in *G. siphonifera* and *O. universa*, increased by 20% in *G. ruber* (white) but decreases by up to 15% in *G. ruber* (pink). There is also a geochemical argument against a size fraction influence on the increasing Mg/Ca across the Mediterranean Sea. In the same study (Elderfield et al., 2002), foraminiferal Sr/Ca ratios decreased consistently with increasing size, an observation that our data supports, especially in *O. universa*, where small size fraction samples contain higher Sr/Ca

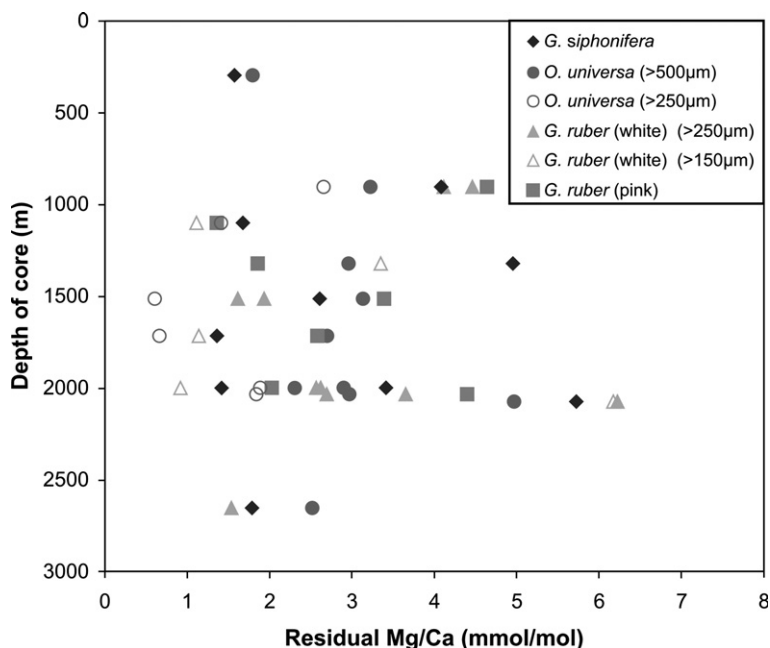


Fig. 7. Residual Mg/Ca plotted against depth of core. Residual Mg/Ca is the observed Mg/Ca minus predicted Mg/Ca using the calibration of Russell et al. (2004) for *O. universa* and Anand et al. (2003) for all other species. Residual Mg/Ca shows no relationship with depth.

ratios than the large fraction samples. But within any one size fraction, our data shows no change in Sr/Ca ratios from the west to the east Mediterranean Sea in any of the species studied.

The unique feature of the Mediterranean Sea is its high salinity. Before considering the possible role of salinity as a secondary control on foraminiferal Mg/Ca, however, we ask whether any other environmental variable might explain the high Mg/Ca ratios observed in the Mediterranean. Nutrient concentrations vary significantly across the basin but are not unusual relative to the open ocean where normal Mg/Ca ratios have previously been observed (Elderfield and Ganssen, 2000; Anand et al., 2003), so gradients in nutrient concentrations are unlikely to explain the increased Mg/Ca ratios in this study. A more plausible candidate is variation in carbonate ion concentration. Salinity and carbonate ion concentration co-vary (because the reaction constants of the carbonate system change with higher salinities (Zeebe and Wolf-Gladrow, 2001)), making it difficult to separate the impact of salinity from carbonate ion concentration on Mg/Ca ratios. Sparse data on pH, alkalinity and total CO<sub>2</sub> in the Mediterranean Sea limit our ability to investigate the effects of this variable on foraminiferal Mg/Ca. Two arguments, however, suggest that carbonate ion concentrations are not the major cause of the high Mg/Ca observed in this study. The first is that estimated carbonate ion concentrations in the Mediterranean (increasing from 170 to 300 μmol/kg eastwards across the basin) (Boyle, 2005), although high for the temperatures at which they are observed, are not significantly outside the range observed in the open ocean (110–280 μmol/kg) (Russell et al., 2004; Takahashi et al., 1980). Secondly, planktonic foraminiferal Mg/Ca ratios have been shown to be constant, or even to decrease, above carbonate ion concentrations of 200 μmol/kg (Russell et al., 2004). It is therefore expected that planktonic foraminifera growing in the Mediterranean Sea would show no significant change in foraminiferal Mg/Ca due to the change in carbonate ion concentrations from the west to the east.

### 5.2. Salinity control on Mg/Ca

Having discounted nutrient and carbonate ion controls, salinity remains the most likely environmental factor to explain the unusually high Mg/Ca ratios observed in eastern Mediterranean foraminifera. Indeed, correlations of Mg/Ca with the salinity at which the foraminifera calcified are generally more significant than those with calcification temperatures (Fig. 6A), with percentage

change per psu ranging from 15–59%. Fig. 6B shows residual Mg/Ca (i.e. the deviation from values expected from published temperature relationships (Anand et al., 2003; Russell et al., 2004)) plotted against calcification salinity. These results suggest that salinity is an important control on Mg incorporation in foraminifera in the Mediterranean. It is not clear from these results, however, whether this is also true at salinities lower than 36.5 psu. There are strong indications that high Mg/Ca ratios are also seen in *N. pachyderma* growing in unusually low salinities (~34 psu) at high latitudes in the North Atlantic, Nordic Seas and the Southern Ocean (Meland et al., 2005; Nürnberg, 1995).

Our results agree with previous studies that there is a general trend to increased Mg/Ca ratios at increased salinity but suggest a sensitivity far larger than those found in culture studies (Lea et al., 1999; Nürnberg et al., 1996). The foraminifera species used in this study live comfortably at the salinities present in the Mediterranean Sea, which are well within the tolerance ranges of each species; 27–45‰ for *G. siphonifera*, 23–46‰ for *O. universa* and 22–49‰ for *G. ruber* (Bijma et al., 1990). There is additional field evidence from the literature that a salinity control on Mg incorporation into foraminiferal calcite is observable outside the laboratory and is not unique to the Mediterranean. Mg/Ca in *G. ruber* (white) has been calibrated against temperature in a number of regions, each with slightly different salinity. A general trend to greater Mg/Ca ratios with increasing salinity is observed in these calibrations implying that part of the scatter observed can be accounted for by differing salinity (Fig. 1). A study investigating foraminiferal trace metal concentrations in cores from the Red Sea, where sea level changes have resulted in large swings in salinity, also indicate higher foraminiferal Mg/Ca ratios during glacial times when salinity was high, although it is worth noting that these early analyses were carried out on uncleaned foraminifera (Yusuf, 1980).

Inorganically, the incorporation of Mg into calcite is not well characterised, although Mg is known to inhibit the precipitation of calcite (Davis et al., 2000). The low partition coefficient of Mg in foraminiferal calcite compared to inorganic calcite clearly demonstrates the presence of a strong biological influence on Mg incorporation and high resolution studies using laser ablation have demonstrated just how much compositional heterogeneity exists within a single foraminifer test (Eggins et al., 2003). Reviews of the current state of knowledge (Erez, 2003; Bentov and Erez, 2005) highlight the complex biological pathways and processes that may control trace-element concentrations within foraminifera



tests. During calcification, pockets of seawater are surrounded by cytoplasm and then transported towards the site of calcification. While transported to the site of calcification the composition of the seawater within the pocket, or vacuole, is thought to be modified by the foraminifer. For example the pH of the water increases and therefore the total dissolved inorganic carbon also increases (Erez, 2003). It has been proposed that this is carried out to facilitate the precipitation of calcite. It is also thought that a significant amount of  $Mg^{2+}$  is removed from the parent solution, presumably seawater, with considerable cellular activity of the foraminifera aimed at reducing Mg/Ca ratios of the foraminifer test. The relationships observed between environmental variables and foraminiferal Mg/Ca are therefore expected to be as a result of the variables' influence on the Mg metabolism of the foraminifer (Bentov and Erez, 2006). However the actual mechanisms by which foraminifera reduce and control the Mg concentration of their tests is still not known (Erez, 2003; Bentov and Erez, 2006). One possible mechanism for changing Mg/Ca ratios with salinity is that the process of calcification works differently at these salinities; for example, if vacuolisation of seawater and subsequent ion pumping into these vacuoles is involved (Erez, 2003), then higher salinities might alter this process, allowing the vacuole composition to remain closer to seawater before the onset of calcite precipitation. It has also been proposed that the proportions of primary, Mg-rich, and secondary, Mg-poor, calcite may change under different environmental conditions (Bentov and Erez, 2005). Cryptic species have been shown to exist in many of the world's oceans. There is evidence that 2 different morphotypes of *G. ruber* (white) contain different Mg/Ca ratios, oxygen and carbon isotopes (Steinke et al., 2005). However, in the Mediterranean Sea, only different genotypes of *O. universa* and *G. bulloides* have been identified, not *G. ruber* (white) or (pink) or *G. siphonifera* (Kucera and Darling, 2002). Even if the eastern Mediterranean were inhabited by distinct genetic types of the investigated species, these genetic types would have to have evolved in parallel a different calcification mechanism from their open-ocean counterpart. Although different morphotypes of planktonic foraminifera show different relationships between Mg/Ca and calcification temperature (Steinke et al., 2005), these differences are one order of magnitude too small to account for the enrichment of Mg seen in the eastern Mediterranean specimens.

In general, the use of foraminiferal Mg/Ca as a palaeotemperature proxy continues to be based on empirical evidence. Until the calcification processes of foraminifera are more fully understood, it is difficult to

propose possible mechanisms for the effect of oceanographic variables, including salinity, on Mg incorporation in foraminiferal calcite.

### 5.3. Implications

A response of foraminiferal Mg/Ca to salinity could have significant implications for the application of Mg/Ca as a palaeothermometer. For example, during the Last Glacial Maximum (LGM) the oceans had an average salinity 1 psu higher than today (Adkins and Schrag, 2001) due to the large amounts of freshwater sequestered in land ice. This increase in salinity would generate higher foraminiferal Mg/Ca ratios, leading to overestimates of LGM temperatures (at least in areas where salinities are higher than 36.5 psu such as the subtropical gyres in the Atlantic, parts of the Caribbean, the Red Sea, parts of the Persian Gulf and Arabian Sea).

An example of the potential significance of salinity for the interpretation of Mg/Ca is provided by records from the Caribbean, a region where calcification salinities range today to >36 psu. Mg/Ca records from sediment cores predict a cooling of Caribbean SSTs by 2.5 °C (Schmidt et al., 2004) at the LGM. Factoring in the effect of a global 1 psu increase in salinity, and a sensitivity of  $\approx 30\%$  per psu for Mg/Ca ratios, the data would represent a LGM cooling of >5 °C. This new SST estimate is more in line with coralline evidence (Guilderson et al., 2001), groundwater palaeotemperatures and palaeosnowlines (Stute et al., 1995), but contradicts estimates made using alkenones (Rosell-Melé et al., 2004) and foraminiferal assemblages (Kucera et al., 2005). This calculation may be oversimplistic, based as it is on results from the Eastern Mediterranean with its extreme and unusual salinity. But it clearly demonstrates that salinity should not be overlooked as a possible variable in controlling foraminiferal Mg/Ca ratios.

## 6. Conclusions

1. Foraminiferal Mg/Ca ratios are unusually high relative to the calcification temperatures at which they are observed in the eastern Mediterranean Sea.
2. These high values cannot easily be explained by contamination by iron-manganese coatings, clay, or overgrowths of high-Mg calcite, and are unlikely to result from elevated carbonate ion concentrations or low nutrient concentrations.
3. The measured Mg/Ca values correlate poorly with calcification temperatures but more significantly with calcification salinities which are unusually high in the



Mediterranean Sea (36–40 psu). Percentage changes in Mg/Ca per psu range from 15–59%, much larger than those observed in cultured foraminifera.

4. Literature evidence supports the general trend to increasing Mg/Ca with rising salinity, although a mechanism for changing Mg/Ca ratios with salinity cannot be proposed with certainty since the calcification process is still poorly understood.
5. These results imply that, particularly for areas of high salinity (> 36 psu) such as the Caribbean, care should be exercised in interpreting planktonic foraminiferal Mg/Ca ratios as entirely controlled by temperature.

### Acknowledgements

We would like to thank Dr. John Arden, Dr. Cees-Jan de Hoog and Dr. Andrew Mason for help in analysing samples and Dr. Angela Hayes for assistance in picking foraminifera. This work was supported with a Natural Environmental Research Council studentship: NER/S/A/2004/12388.

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2007.10.011.

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