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

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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 $\delta^{18}O$ of foraminiferal calcite it allows deconvolution of temperature and ice-volume signals to infer past ocean temperatures and salinities (assuming the relationship between seawater $\delta^{18}O$ 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.

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

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 $\delta^{18}O$ record, assuming the relationship between salinity and $\delta^{18}O$ 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 μmol/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±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 (~4 °C) in mean-annual sea-surface temperatures (although seasonal ranges are larger, reaching