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Advancing planktonic foraminifera Mg/Ca thermometry:
a microanalytical perspective

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This thesis represents original work conducted by the author, except where specifically stated and acknowledged, during full-time PhD candidature at the Research School of Earth Sciences, The Australian National University. No part of the thesis has been submitted to another University or institution.

Aleksey Yurevich Sadekov
April 2008

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Abstract

Microanalytical techniques, specifically laser ablation - inductively coupled plasma mass spectrometry (LA-ICPMS) and electron microprobe analysis (EMPA), have been used to determine Mg/Ca compositional variation within and between tests of planktonic foraminifera. Micro-scale characterization of this increasingly widely-used seawater temperature proxy has allowed scrutiny of the factors that limit its applicability as well as the development of new microanalysis-based Mg/Ca proxy calibrations for sea surface temperature and thermocline temperatures.

The variability of Mg/Ca compositions found within and between tests of planktonic foraminiferal species greatly exceeds the possible range of test calcification temperatures using established Mg/Ca-temperature sensitivities. This indicates that factors additional to temperature influence foraminiferal Mg/Ca compositions and raise significant questions about their use as a seawater temperature proxy. The latter are assessed by calibrating the relationship between the Mg/Ca composition of *Globigerinoides ruber* determined by LA-ICPMS microanalysis in core-top and plankton pump samples spanning a range of sea surface temperatures (18.5 – 29.2 °C) from the eastern Indian Ocean. Results demonstrate that despite very large inter- and intra-test compositional variability the pooled mean Mg/Ca compositions for core-top and plankton pump samples forms a strong exponential correlation with mean annual sea-surface temperature. It is further shown that inter-test Mg/Ca variability within core-top samples is a significant source of uncertainty in Mg/Ca seawater temperature estimates and that widely assumed uncertainties in Mg/Ca thermometry may be underestimated. Reasons for the large intra and inter-test Mg/Ca variability are attributed to seasonality ranges over centennial timescales and to a significant

'vital effect' contribution. Statistical methods to minimize effect of these uncertainties on Mg/Ca thermometry are described.

LA-ICPMS to foraminifera Mg/Ca analysis is employed to assess the nature and effects of seafloor alteration on the distribution Mg/Ca within and composition of foraminiferal tests, using several different approaches including a study of core-top samples down a depth transect in the eastern Indian Ocean and, weak acid dissolution under controlled laboratory conditions. Limited evidence is found for selective dissolution of *G. sacculifer* high-Mg calcite and minimal if any discernable dissolution effects are observed on the Mg/Ca compositions of *G. sacculifer* tests above the calcite lysocline. These results are consistent with previous studies of *G. sacculifer,* indicating that the effects of seafloor dissolution on *G. sacculifer* bulk Mg/Ca compositions are small compared to the uncertainty in bulk test compositions that derives from inter-test variability.

New methods for reconstructing paleoseawater temperatures are developed based on LA-ICPMS Mg/Ca microanalysis of *G. ruber, G. sacculifer* and *Pulleniatina obliquiloculata.* The Mg/Ca compositions of individual chambers and of specific tests parts present within *G. rubber* and *G. sacculifer* and *P. obliquiloculata,* in core-top samples are found to correlate best with seawater temperatures at different and specific depths. This provides the basis for developing new Mg/Ca-based methods for reconstructing surface mixed layer and upper thermocline temperatures.

This study illustrates the potential for using novel microanalytical techniques to advance Mg/Ca thermometry, by both providing a framework for better understanding the nature of Mg/Ca dependence on seawater temperature and the effects of complicating factors (e.g. seafloor dissolution, seasonality), as well as providing insight into the underlying biomineralization mechanisms that control Mg incorporation into and the formation of foraminiferal calcite.

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Rationale and background

Mg/Ca thermometry is one of the most rapidly-developing and now widely-used proxies for reconstructing past seawater temperatures. The number of scientific publications related to and using Mg/Ca thermometry has experienced a dramatic increase over the last decade (Fig. 1). This and the growing interest more generally in reconstructing past climate parallels the rise in public awareness of global climate change over recent decades, and the pressing need to better predict future climate change and its associated impacts on societies and environments (Fig. 1). The study of past climates and their evolution presents a powerful approach and perspective to better understand modern climate and future climate scenarios. A crucial step in our understanding of past climates lies in our ability to accurately reconstruct seawater temperatures because the oceans play a major role in driving and modulating global and regional climate change.

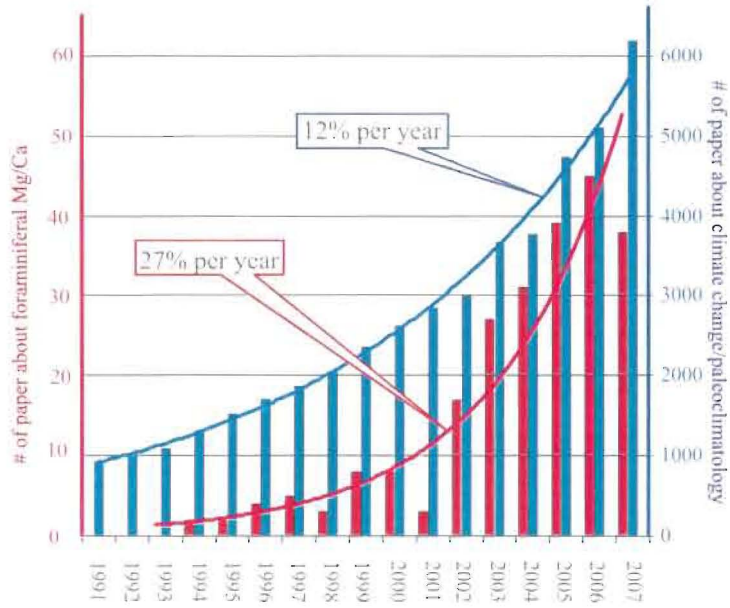

Figure 1.
Number of the publication in scientific journals related to climate change and paleoclimatology (blue) and foraminiferal Mg/Ca thermometry (red). Data was taken from the *Web of Science* database.

Mg/Ca thermometry is based on empirical observations that show the Mg/Ca composition of calcite foraminifer tests (shells) increase systematically with seawater temperature. Foraminifera are unicellular marine organisms that precipitate microscopic calcium carbonate (calcite) tests comprising multiple chambers and growth layers. Planktonic foraminifera inhabit the surface mixed layer and upper thermocline of the oceans, spanning all latitudes from the Arctic to the Southern Ocean. Fossil tests of planktonic foraminifera occur abundantly in deep-ocean sediments and their stable isotopic ($\delta^{18}O$, $\delta^{13}C$) and elemental compositions (Ba/Ca, Sr/Ca, Mg/Ca) are widely employed in paleoceanography to constrain past seawater temperature and properties including salinity and productivity.

In his pioneering work on the magnesium content of foraminifera tests, *Chave* [1954] showed a positive correlation between magnesium concentration and water temperature. This relationship was confirmed by subsequent studies [*Blackmon and Todd*, 1959; *Duckworth*, 1977; *Savin and Douglas*, 1973], but the first calibration and application of foraminiferal Mg/Ca as a proxy for seawater temperature was not published until 1995 by *Nürnberg* [1995]. Since that study the dependence of foraminiferal test Mg/Ca compositions on temperature has been confirmed from core top samples [*Dekens, et al.*, 2002; *Elderfield and Ganssen*, 2000; *Hastings, et al.*, 1998; *Lea, et al.*, 2000; *Rosenthal, et al.*, 1997; *Rosenthal and Lohmann*, 2002; *Rosenthal, et al.*, 2000], plankton net and sediments trap samples [*Anand, et al.*, 2003; *McConnell and Thunell*, 2005; *McKenna and Prell*, 2004], and in laboratory cultures [*Lea, et al.*, 1999; *Mashiotta, et al.*, 1999; *Nürnberg, et al.*, 1996]. An advantage of Mg/Ca thermometry over other paleoseawater palaeothermometers is that Mg/Ca ratio of seawater is nearly constant throughout the ocean and, Mg and Ca have long residence times (~1 Ma for Ca and 10 Ma for Mg) [*Broecker and Peng*, 1982; [*Rosenthal, et al.*, 2000]. Moreover, the Mg/Ca composition of planktonic foraminifer tests is extraordinarily and consistently sensitive to seawater

temperature, increasing by 9±1% per °C.

Calibration of test Mg/Ca composition changes with seawater temperature are based on empirical relationships observed between Mg/Ca and seasurface temperatures above core-top sediment sample sites, between Mg/Ca and calculated $\delta^{18}O$ calcification temperatures [*Anand, et al.*, 2003; *McKenna and Prell*, 2004], or in laboratory culture experiments [*Lea, et al.*, 1999; *Nürnberg, et al.*, 1996]. The best fit relationship typically has the exponential form

$$Mg/Ca = A \exp(B^{*}T) \qquad (1)$$

where A is pre-exponential constant, B the exponential temperature sensitivity constant, and T is seawater temperature. The exponential increase is consistent with thermodynamic control of Mg incorporation into calcite [*Nürnberg, et al.*, 1996]. Experiments on inorganic calcite precipitation from seawater also indicate that the distribution coefficient for Mg/Ca (K in equation 3) correlates positively with temperature. [*Mucci and Morse*, 1983; *Mucci*, 1987; *Oomori et al*, 1987; *Nürnberg, et al.*, 1996]

$$CaCO_3 + Mg^{2+} \Leftrightarrow MgCO_3 + Ca^{2+} \qquad (2)$$

$$K = [\chi(MgCO_3)/\chi(CaCO_3)] / [\chi(Mg^{2+})/\chi(Ca^{2+}) \qquad (3)$$

where χ is the activity of the component phase in calcite solid solution or ion in seawater.

Despite the growing evidence in support of the exponential temperature dependence of the Mg/Ca composition of foraminiferal calcite, the accuracy and reliability of Mg/Ca thermometry in reconstructing past ocean temperatures remains debated [*Barker, et al.*, 2005; *Barker, et al.*, 2003; *Bentov and Erez*, 2006; *Eggins, et al.*, 2004; *Rosenthal, et al.*, 2004]. Questions surrounding the accuracy and reliability of Mg/Ca thermometry can be grouped into three observation-based

themes:

Theme I: What is the "true" nature Mg/Ca-temperature relationship?

a) The Mg/Ca composition of planktonic foraminifer tests is almost two orders of magnitude lower than in inorganic calcite precipitation from seawater [*Katz*, 1973]. Furthermore, foraminiferal calcite and inorganic calcite have significantly different absolute distribution coefficient (K) values (see equation 3) [*Mucci*, 1987; *Mucci and Morse*, 1983; *Nürnberg, et al.*, 1996]. These differences indicate that Mg incorporation into foraminifer test calcite is subject to additional biological controlling factors (so called "vital effects"), which bias foraminiferal calcite compositions away from inorganic compositions. The cause of this bias remain unknown.

b) "Vital effects" have been shown to be species-specific. For example, *Dekens et al* [2002] showed that for the same temperature range in the tropics, *Globigerinoides ruber* Mg/Ca values are on average 5-15% higher than the Mg/Ca values of *G. sacculifer*, and 49-55% higher than *Neogloboquadrina dutertrei*. Similarly, *Anand et al* [2003] have determined different Mg/Ca-thermometer calibration fits for a wide variety of individual species of planktonic foraminifera. The origin of these different species-specific calibrations has been attributed to differences in intra-test Mg/Ca distribution but is highly speculative given the limited knowledge of the Mg/Ca distribution within tests of different species.

c) Different studies have reported Mg/Ca-seawater temperature calibrations that vary greatly for the same species. For example, calibrations for *Globigerinoides ruber* yielded pre-exponential factors between 0.3 and 0.48, and exponential factors between 0.058 and 0.102

(see *Anand et al.*, 2003) producing temperature estimates that differ by up to 4-5 °C. The reasons for these calibration discrepancies remain unresolved.

Theme II: What is the nature and origin of intra and inter-test variability in Mg/Ca composition within planktonic foraminifer species? And more specifically, how does this variability affect the reconstruction of seawater temperatures?

a) Planktonic foraminifera from core-top sediment samples show increasing Mg/Ca compositions with increasing test size for many species [*Elderfield, et al.*, 2002]. This size effect corresponds to between a 12-36% increase in Mg/Ca values or 1.5-4.5°C over the full range of test sizes. It has been suggested that this size-dependence may reflect an increase in calcification rate [*Elderfield, et al.*, 2002] or symbiont activity with increasing test size [*Hönisch and Hemming*, 2004]. The origin of the size effect remains unknown.

b) The occurrence of Mg/Ca compositional variation within and between individual foraminiferal tests has been documented since the earliest studies of foraminifer test chemistry [*Emiliani*, 1955; *Krinsley*, 1960]. Studies of the planktonic species *Globorotalia truncatulinoides* by *Lipps and Ribbe* [1967] and *Bender et al.* [1975] documented variations in bulk test Mg contents up to 40% and 120%, respectively. In a detailed investigation of individual *G. truncatulinoides* tests using the electron-microprobe, *Duckworth* [1977] showed that different calcite layers contained Mg/Ca values between 5 and 8 mmol/mol. More recently, direct evidence of Mg/Ca variation within individual foraminifera tests came from studies using electron microprobe and laser ablation ICPMS, which document Mg/Ca variation within and between tests of

up to 120%, which corresponds to an apparent change in calcification temperature of ~15°C [*Brown and Elderfield*, 1996; *Eggins, et al.*, 2003; *Eggins, et al.*, 2004; *Elderfield and Ganssen*, 2000; *Hathorne, et al.*, 2003; *Jha and Elderfield*, 2000; *Lohmann and Rosenthal*, 1993; *McKenna and Prell*, 2004; *Nürnberg, et al.*, 1996; *Puechmaille*, 1994]. The cause of this intra- and inter-test variability in Mg/Ca composition, and in particular the role of termperature in its origin, presents a major uncertainty for the application of Mg/Ca thermometry to seawater temperature reconstructions.

Theme III: How do postdepositional processes, specifically seafloor dissolution, affect test Mg/Ca compositions and, consequently, the accuracy of Mg/Ca thermometry?

a) Numerous studies have documented the presence of detrital minerals, organic matter, and diagenetic-mineral overgrowths on fossil tests. A variety of cleaning methods have been proposed to remove these contaminants from foraminiferal calcite in efforts to analyse the composition of the original foraminiferal calcite. However, these cleaning methods involve the use of chemical reagents that can also dissolve test calcite and modify its Mg/Ca composition. For example, a number of studies have documented a significant and systematic decrease (15 % or ~ 1.5°C) in bulk test Mg/Ca compositions after applying a reductive cleaning process [*Barker, et al.*, 2003; *Rosenthal, et al.*, 2004]. Currently, there is no agreement on what cleaning methods should be used for test cleaning prior to Mg/Ca analysis.

b) A decrease in bulk test Mg/Ca composition with progressive test dissolution has been shown to occur in studies of fossil foraminifer tests from deep-sea sediment samples [*Brown and Elderfield*, 1996;

Dekens, et al., 2002; *Lohmann*, 1995; *Regenberg, et al.*, 2006; *Rosenthal and Lohmann*, 2002; *Savin and Douglas*, 1973]. Partial dissolution of tests can occur in seafloor sediments well above the calcite lysocline and has been shown to produce an approximately 12% decrease in test Mg/Ca composition per kilometre of water depth. This translates into a temperature bias of about -1.3°C per kilometre depth [*Benway, et al., 2003; de Villiers, 2003; Dekens, et al., 2002; Rosenthal and Lohmann, 2002*]. Despite evidence for the effect of seafloor dissolution on foraminiferal test Mg/Ca values, its nature and extent remain controversial.

Aims and outline of this study

The aims of this study are to exploit recent advances in microanalysis techniques, in particular laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS), aided by electron microprobe analysis (EPMA), to:

- improve the understanding of the nature and cause of Mg/Ca variation within and between individual tests of key species of planktonic foraminifera used in palaeoceanography.
- assess the effects of postdepositional dissolution on the distribution of Mg/Ca within foraminiferal test and specific test parts.
- evaluate the effect of intra and inter-test Mg/Ca variability on the accuracy and precision of Mg/Ca thermometry.
- develop new microanalysis-based approaches to reconstructing calcification temperatures of planktonic foraminifera.

These four aims are addressed in each of the four chapters of this thesis, brief descriptions of which are outlined below.

Chapter 1

Characterization of Mg/Ca distributions in planktonic foraminiferal species by electron microprobe mapping

This chapter reports the distribution of Mg/Ca ratio values within the tests of a range of planktonic foraminifer species, including symbiotic and asymbiotic species. A Cameca SX100 electron microprobe has been employed to map the

distribution of Mg and Ca within the test cross sections. Each of the investigated species is found to display large variations in Mg/Ca composition within individual tests. Symbiotic species display cyclic Mg/Ca compositional banding that is characterized by narrow (<1–3 μm), high-Mg/Ca (typically 8–11 mmol/mol) bands, intercalated between broader low Mg/Ca (typically 1–5 mmol/mol) bands. Symbiont-free species tend to have fewer and broader compositional bands. These may more closely reflect changes in calcification temperature and develop as these species have migrated within the water column.

Chapter 2

Uncertainties in seawater thermometry deriving from intra- and inter-test Mg/Ca variability in *Globigerinoides ruber*

Laser ablation ICPMS microanalysis is used to characterise variations of Mg/Ca composition both within and between individual tests from fossil and live-collected *Globigerinoides ruber* from the eastern Indian Ocean. The extent of inter-test and intra-test compositional variability is shown to exceed that attributable to seasonal and interannual calcification temperature, at any particular sample site. The pooled mean Mg/Ca composition obtained for core top samples between the equator and ~30°S correlate exponentially with mean annual sea surface temperature (Mg/Ca mmol/mol = 0.52 exp(0.076*SST°C), r^2 = 0.99). The inter-test Mg/Ca variability within individual core-top samples is shown to be a source of significant uncertainty in derived Mg/Ca seawater temperature estimates and is notably site specific. It is demonstrated that widely-assumed uncertainties in Mg/Ca thermometry are likely underestimated, and that statistical power analysis in combination with individual test analyses can be used to evaluate the number of tests needed to achieve a target uncertainty for any sample.

Chapter 3

Effects of seafloor and laboratory dissolution on the Mg/Ca composition of *Globigerinoides sacculifer* and *Orbulina universa* tests - a laser ablation ICPMS microanalysis perspective

Laser Ablation ICPMS has been used to investigate the effect of seafloor and artificial test dissolution on test Mg/Ca compositions. Three different approaches are used: 1) the analysis of core-top samples collected at different water depths along a depth transect in the NE Indian Ocean; 2) the analysis of test subjected to laboratory dissolution experiments using weak acid; and 3) the analysis of tests prior to their dissolution and subsequent analysis using a "Flow-through" ICPMS (see more for method in *Haley and Klinkhammer* [2002]). No evidence is found for significant selective dissolution of tests parts that have different Mg/Ca compositions (specifically higher Mg/Ca values) in either *G. sacculifer* and *O. universa* during natural seafloor dissolution above the lysocline or during laboratory dissolution or Flow-Through ICPMS analysis. The integration of these with previously published results for *G. sacculifer,* reveal little if any significant seafloor dissolution affect on the Mg/Ca composition of this species above the calcite lysocline.

Chapter 4

Seawater temperature reconstruction using Mg/Ca microanalysis of *Globigerinoides ruber, G. sacculifer* and *Pulleniatina obliquloculata.*

This study is aimed at understanding the extent and possible nature of differences in Mg/Ca composition between three foraminifer species (*G. ruber G. sacculifer* and *P. obliquiloculata*), and to assess Mg/Ca-temperature calibrations based on LA-ICPMS microanalysis. It is found that differences in intra-test Mg/Ca distributions between species cannot account for the observed differences in species Mg/Ca composition in subtropical to tropical regions. Based on best regression model fits

to depth-temperature profiles at each site, and also the calculated $\delta^{18}O$ calcification temperature of *G. sacculifer* tests, differences in Mg/Ca thermometer calibrations for the different species are attributed to their different preferred habitat depths. A comparison of Mg/Ca calibrations based on preferred depth habitat temperatures indicate that all three species may share a similar or common temperature sensitivity and pre-exponential constant that determines their test Mg/Ca compositions. The potential for reconstructing upper water column temperature profiles using these species and for using the Mg/Ca content of specific internal calcite layers as proxies for seawater temperature is discussed.