# Mg/Ca and Sr/Ca Paleothermometery from Calcareous Marine Fossils

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## Synopsis

The distribution of sea surface and bottom water temperature and salinity is perhaps the best representation of the state of the climate system, as the ocean plays a fundamental role in the evolution of the earth climate. Therefore, determining the past temperature evolution of the ocean is key for understanding Earth's history. This article discusses the four important paleotemperature proxies, namely Mg/Ca in planktonic foraminifera and Sr/Ca in corals as recorders of sea surface temperatures and Mg/Ca in benthic foraminifera and ostracodes as proxies of bottom water temperatures. A clear advantage of these carbonate-based thermometers is that coupling $\delta^{18}O$ and Mg/Ca measurements in foraminifera or Sr/Ca in corals, provides a novel way to adjust for the temperature-dependency of $\delta^{18}O$ and isolate the record of $\delta^{18}O_{water}$, which can then be used to reconstruct local changes in evaporation-precipitation (and by inference salinity) and provide valuable information about changes in continental ice volume.

## Introduction

The distribution of sea surface and bottom water temperature and salinity is perhaps the best representation of the state of the climate system, as the ocean plays a fundamental role in the evolution of the earth climate. Therefore, determining the past temperature evolution of the ocean is key for understanding Earth's history. Although considerable research on magnesium and strontium geochemistry of marine calcareous fossils has been carried out over the past several decades (see review by (Lea, 2003), it was only recent work that cast new light on their potential for reconstructing ocean paleotemperatures. Among the new elemental proxies are Mg/Ca in planktonic foraminifera and Sr/Ca in corals as recorders of sea surface temperatures and Mg/Ca in benthic foraminifera and ostracodes as proxies of bottom water temperatures. Mg, Sr, and Ca have relatively long oceanic residence times, about 13 My for Mg, 5 My for Sr and 1 My for Ca, implying nearly constant Mg-, and Sr- to- Ca ratios in seawater on timescales of $< 1x10^6$ years. A clear advantage of these carbonate-based thermometers is that coupling $\delta^{18}O$ and Mg/Ca measurements in foraminifera or Sr/Ca in corals, provides potentially a novel way to adjust for the temperature-dependency of $\delta^{18}O$ and isolate the record of $\delta^{18}O_{water}$ (Mashiotta et al., 1999), which can then be used to reconstruct local changes in evaporation-precipitation (and by inference salinity) (e.g., Lea et al., 2000) and provide valuable information about changes in continental ice volume (e.g., Lear et al., 2000).

## Thermodynamic effects on Mg and Sr coprecipitation in carbonates

Among the alkaline earth elements, $Mg^{2+}$ and $Sr^{2+}$ form the most important solid solutions with carbonates. Because of the difference in the ionic radii between $Sr^{2+}$ (large) and $Mg^{2+}$ (small), $SrCO_3$ is isostructural with the aragonite crystal cell (orthorombic), whereas $MgCO_3$ is isostructural with calcite (rhombohederal). The Mg/Ca and Sr/Ca ratios in $CaCO_3$ minerals depend on two factors: the Mg/Ca and Sr/Ca activity ratios of ocean water, and the distribution coefficients of Mg/Ca and Sr/Ca between calcite, aragonite and seawater, respectively. These relationships are expressed as $D_{El}=(El/Ca)_{mineral}/(El/Ca)_{seawater}$), where $D_{El}$, is the empirical homogeneous distribution coefficient calculated based on the molar concentration ratios of Mg/Ca and Sr/Ca in calcite, aragonite and seawater, respectively. At equilibrium, the partitioning constant between the two pure mineral phases depends on temperature, as the substitution of Mg into calcite and Sr into aragonite, are both associated with a change in enthalpy or heat of reaction, which is sensitive to temperature. As the substitution of Mg into calcite is an endothermic reaction, the Mg/Ca ratio of calcite is expected to increase with increasing temperature (Rosenthal et al., 1997). In contrast, the substitution of Sr into aragonite is an exothermic reaction, thus the Sr/Ca ratio of aragonite is expected to decrease with increasing temperature.

Based on thermodynamic considerations, Rosenthal et al., (1997) and Lea et al., (1999) proposed an exponential temperature dependence of Mg uptake into calcite of about 3% per °C. This prediction is consistent with experiments of Mg incorporation into inorganically precipitated calcites; inorganic co-precipitation experiments of Sr with aragonite show a weak inverse linear dependence on temperature (see review by Lea, 2003). However, as instructive as these data may be, biologically mediated processes are rarely at thermodynamic equilibrium. For example, foraminifera contain 1-2 orders of magnitude lower Mg than found in marine inorganic calcites. Such offsets suggest that biological processes exert a major influence on the co-precipitation of metals in biogenic carbonates, thus highlighting the need for species-specific empirical calibrations.

## Foraminiferal Mg/Ca paleothermometry

### Temperature Calibrations of Mg/Ca in Planktonic Foraminifera

The temperature dependence of Mg uptake into planktonic foraminiferal tests has been determined using three different approaches: i) Controlled culture experiments in which temperature is fixed independently of other environmental parameters (e.g., light, salinity and *p*H); ii) Measurements of planktonic foraminifera from sediment trap time-series in sites characterized by significant seasonal variability in sea surface temperature (SST); iii) Analyses of fossil foraminifera obtained from surface sediments, typically from core tops. At present, Mg/Ca calibrations are expressed as an exponential dependence of temperature in the form: Mg/Ca (mmol mol$^{-1}$)= $B\ e^{AT}$

Where *A* and *B* are the exponential and pre-exponential constants, respectively, and T is temperature in °C. Justification for the choice of exponential fit to the empirical data comes primarily from the thermodynamic prediction of exponential response. In this relationship, the exponential constant reflects the Mg/Ca response to a given temperature change (in mmol mol$^{-1}$ per °C), implying increased sensitivity with temperature. The pre-exponential constant determines the absolute temperature.

Culture calibrations are available for a limited number of species including, *G. sacculifer* (Nürnberg et al., 1996), *O. universa* (Lea et al., 1999; Russell et al., 2004), *G. bulloides* (Lea et al., 1999; Mashiotta et al., 1999), and *N. pachyderma* (d) (Langen et al., 2005) (Figure 1A). Combined, the available experiments suggest a temperature sensitivity of 9.7±0.9% change in Mg/Ca per °C, thus providing the strongest direct evidence for temperature control on planktonic foraminiferal Mg/Ca, much in the same way inorganic experiments supported the thermodynamic expectations. The sediment-trap based multi-species calibration of Anand et al., (2003) from the Sargasso Sea (Figure 1B) is in good agreement with culture calibrations, suggesting a temperature sensitivity of 9±0.3% per °C. Anand et al., (2003) derived calcification temperatures for the different planktonic species from paired $\delta^{18}O$ measurements rather than use estimates from the local hydrography. The latter might be associated with significant errors due to the uncertainty about the exact calcification depth. The multiple-species core top calibration of Elderfield and Ganssen, (2000), re-evaluated by Rosenthal and Lohmann, (2002) suggests temperature sensitivity of 9.5±0.5% per °C (Figure 1C). The good agreement between the multi-species calibrations provides robust evidence that the temperature signal imprinted during the test formation is reliably transferred into the sediment, thus supporting the use of planktonic foraminifera Mg/Ca for paleotemeprature reconstructions, despite evidence for significant post-depositional diagenetic alteration.

Offsets in Mg/Ca among individual species observed in both culture and field trap calibrations stress the need for single-species calibrations. Although there is significant variability among the different equations, the median exponential value of the 14 currently available calibrations is 8.6±1.6% per °C (average 8.3±1.6%). Although, in a few cases the estimated temperature sensitivity seems to be significantly lower, the general agreement in the exponential constants (A) among calibrations, suggests that the ~9±1% per °C is arguably a robust feature of planktonic foraminifera. The pre-exponential constants (*B*) differ significantly among calibrations, for both same and different species. This high variability reflects a combination of several factors including intra- and inter-species variability (Anand et al., 2003; Elderfield and Ganssen, 2000), variable diagenetic overprints (Rosenthal and Lohmann, 2002), and methodological biases among laboratories (Rosenthal et al., 2004). It follows, that the accuracy of Mg/Ca thermometry is much better in estimating relative changes in seawater temperatures than absolute temperatures.

### Inter-species and Intra-species variability

Inter-species variability in Mg/Ca is generally correlated with their calcification depth. Accordingly, shallow mix-layer dwellers (e.g., *G. ruber* and *G. sacculifer*) have high Mg/Ca, whereas deep dwellers (e.g., *G. tumida* and *G. dutertrei*), are characterized by relatively low Mg/Ca (Rosenthal and Boyle, 1993). However, although it is common to assign planktonic foraminifera specific calcification depths, it is also well known that many species continue to calcify while migrating vertically through the water column and some species such as *G. sacculifer*, also add an outer calcite crust prior to reproduction (aka “gemetogenic crust”) at depths significantly deeper (and colder) than their principal habitat depth. These processes are likely to cause significant variability in the Mg distribution within and among foraminifera tests, which should be linked to changes in calcification temperature. It follows, that the “whole test” Mg/Ca composition of the test, most commonly used for temperature reconstructions, represents a weighted average of calcite layers formed at different depths/temperatures. This is less of an issue for the shallow, mixed-layer species of *G. ruber* and *G. sacculifer* and more critical for deep species such as *N. dutertrei*, *G. tumida* and *G. trancatulinoides*.

Studies using high spatial resolution analytical methods, reveal large compositional variability within individual chambers and within the test as a whole. Compositional differences in Mg/Ca, observed in sequentially precipitated test layers, are apparently consistent with the extent of vertical migration experienced by the different species during their adult life; shallow dwelling species (e.g., *G. ruber*) tend to have a more homogeneous composition than deep-dwelling species (e.g., *N. dutertrei*) thus suggesting that temperature exerts significant control on intra-test variability (Eggins et al., 2003). Likewise, the observation of low Mg/Ca outer-wall layers on *G. sacculifer* tests (Eggins et al., 2003) is consistent with the calcification of gametogenic calcite at deeper and colder depths, in contrast with previous results (Nürnberg et al., 1996). The pattern of Mg/Ca variation is, however, significantly different between symbiont-bearing and symbiont-free species. Tests of symbiont-bearing foraminifera show cyclic variations between high and low Mg/Ca layers within individual chambers, which are largely absent from symbiont-free species (Sadekov et al., 2005). This variability cannot simply be attributed to changes in ambient temperature, but is more likely due to biological effects on the co-precipitation of Mg in foraminiferal calcite (Sadekov et al., 2005).

## Secondary non-temperature effects

### *Salinity and pH effect*

Culture studies show a weak positive relationship between planktonic foraminiferal Mg/Ca and seawater salinity (Lea et al., 1999; Nürnberg et al., 1996) and an inverse dependence on *p*H (Lea et al., 1999; Russell et al., 2004). Over a large salinity gradient, the effect is about 7±4% change in Mg/Ca per salinity unit (SU), for *G. sacculifer* and *O. universa* (Lea, 2003). In both species, Mg/Ca ratios decrease by about 7±6% per 0.1 *p*H (Lea et al., 1999; Russell et al., 2004). Given a temperature sensitivity of ~9% per °C, the salinity effect translates to an uncertainty of about 0.3-1°C for a change of 1 SU and –0 to -1.2°C per 0.1 *p*H unit. However, caution must be taken when applying these relationships. First, no discernible changes are seen at salinity changes of <3 (Nürnberg et al., 1996). And second, the errors in both relationships are relatively large.

### Dissolution effects

Core top studies along bathymetric transects, indicate a systematic decrease in Mg/Ca ratios of planktonic foraminifera with increasing depth, independent of the overlying sea surface temperatures, thereby suggesting that foraminiferal Mg/Ca is altered by post-depositional dissolution on the seafloor driven by the depth-dependent decrease in carbonate saturation levels (Dekens et al., 2002; Rosenthal et al., 2000). The systematic decrease in Mg/Ca ratios of planktonic foraminifera is likely caused by preferential dissolution of Mg-rich calcite, which might be more susceptible to dissolution (Brown and Elderfield, 1996). The preferential dissolution of Mg-rich chamber calcite, formed in warm surface waters, shifts the test's bulk Mg/Ca toward the composition acquired in colder, thermocline waters (Rosenthal et al., 2000). The decrease in Mg/Ca with depth is higher in nonspinose, thermocline dwelling species (e.g., *G. tumida and N. dutertrei*) than in spinose, shallow dwelling species (*G. ruber and G. sacculifer*), in accord with the larger range of temperatures over which the deep dwellers calcify (Brown and Elderfield, 1996; Dekens et al., 2002).

Besides temperature, dissolution is the main cause for the observed variance in Mg/Ca data. Various approaches have been offered to account for dissolution effects on Mg/Ca. Lea et al., (2000) and Dekens et al., (2002) proposed that combining core top measurements of the magnitude of the depth-dependent decrease of Mg/Ca with independent estimates for past shifts in lysocline depth, can provide an estimate as to the potential error in Mg/Ca-based temperature estimates due to dissolution effects. Applying this approach on two Pacific records, they suggest a potential error of 0.5°C in their estimates of the tropical Pacific glacial-interglacial temperature amplitude. This approach, however, does not quantify the dissolution effects on specific samples, which might respond more to changes in pore-water chemistry than shifts in lysocline depth. Taking a different approach, Rosenthal and Lohmann, (2002), suggested that the relationship between size-normalized test weight and the dissolution driven decrease in Mg/Ca, could be used for correcting down core Mg-based temperature estimates for dissolution effects. While this method is very attractive, as it directly addresses dissolution effects experienced by a particular sample, further studies have demonstrated that the test size-weight relationship is not strictly a function of dissolution, as initially thought, but also depends on the [$CO_3$] content of seawater in which they grow (Barker and Elderfield, 2002). Thus, the initial test weight must be known in order to correct Mg/Ca ratios for dissolution effects.

### ***Temperature Calibrations of Mg/Ca in Benthic Foraminifera***

The temperature calibration for benthic species is at present somewhat uncertain. The first calibration was based on the species *Cibicidoides pachyderm*a from a shallow bathymetric transect in Little Bahama Banks (LBB) spanning a temperature range of 5-18°C (Rosenthal et al., 1997). Subsequent core-top calibrations (Lear et al., 2002; Martin et al., 2002) showed that the temperature sensitivity of *Cibicidoides* Mg/Ca agrees with the calibration of Rosenthal et al., (1997) and is essentially identical with the ~10% increase in Mg/Ca per °C observed in planktonic foraminifera. Similar temperature sensitivity was observed in other benthic species including *Planulina spp., Oridorslis umbunatus* and *Melonis spp*. Lear et al., (2002) whereas other species *Uvigerina spp*. and *Planulina aremenensis*, exhibited significantly lower sensitivity of about 6% per °C.

While these observations lend further support to the dominant effect of temperature on foraminiferal Mg/Ca, there are still a few important questions about the accuracy of these calibrations. Most importantly, it has been questioned whether samples from LBB have been compromised by diagenetic calcite overgrowths enriched in Mg. Ongoing research efforts, at the time of this writing (January 2006), provide new insights on benthic foraminiferal Mg/Ca. New calibration studies of *C. pachyderma* from depth transects in the Florida Strait and Great Bahama Banks, where the problem of diagenetic calcite overgrowth is rather minimal, suggest a relatively low, linear dependence of Mg/Ca over a temperature range of 6-19°C (e.g., Curry and Marchitto, 2005). Thus, there is a growing body of evidence to suggest that the temperature sensitivity of benthic foraminiferal Mg/Ca is significantly lower than initially thought, and more similar with that reported for *Uvigerina spp*.

## Inferring seawater $\delta^{18}O$ and salinity

The $\delta^{18}O$ composition of calcareous marine fossils reflects both the temperature and the isotopic composition of seawater in which the shell or skeleton was formed. The $\delta^{18}O$ of modern surface water reflects the hydrological balance between evaporation and precipitation (E/P), i.e., the surface salinity. Over longer time scales, seawater $\delta^{18}O$ is also a function of the extent of continental ice sheets. Paired $\delta^{18}O$ and Mg/Ca measurements in foraminifera, allow to adjust for the temperature-dependency of carbonate $\delta^{18}O$ and isolate the record of $\delta^{18}O_{water}$, which can then be used to reconstruct local changes in E/P and by inference salinity (e.g., Lea et al., 2000; Mashiotta et al., 1999) and provide valuable information about changes in continental ice volume (e.g., Lear et al., 2000). Furthermore, paired measurements on the same samples also allow for the determination of temporal leads and lags between variations in seawater temperature and the build-up or erosion of continental ice sheets, which is fundamental for understanding climate change. Indeed, the application of this method has already led to important findings despite the short time since Mg-paleothermometry appeared on the paleoceanographic arena. Perhaps the most important are records from the western equatorial Pacific warm pool (WPWP) that shed new light on the long-standing question of tropical cooling during glacial periods (e.g., de Garidel et al., 2005; Lea et al., 2000)) (Figure 2). Among the most significant findings that come from these studies are: 1) Sea surface temperature (SST) in the WPWP was ~3°C cooler during glacial periods than at present; 2) During glacial termination, changes in equatorial SST lead by ~3000 years the northern hemisphere deglacial record. This and other record highlight the great potential in this new method; and 3) Except for glacial-interglacial variability, WPWP sea surface temperature and salinity were stable throughout the Pleistocene, at the time of major Northern Hemisphere glaciation. The $\delta^{18}O_{water}$ record is a good example for the usefulness of the new method. It suggests that surface water in the WPWP was fresher during glacial intervals, and also that there is a a long term freshening of the WPWP, thus pointing out to significant variations in the distribution of tropical temperatures and salinity both on orbital and longer time scales (de Garidel et al., 2005).

## Ostracode Mg/Ca paleothermometry

Studies over the past decade have provided strong evidence for the dependence of ostracode Mg/Ca on temperature (Dwyer et al., 2002; and references therein) and demonstrated its utility for paleoceanography (e.g., Dwyer et al., 1995). Ostracodes are bivalved crustaceans that grow via a process of molting. Ostrcodes excrete an exosekelton known as a carapace that in some taxa consists of 80-90% calcite and the rest of chitin and proteins. Tests of adult specimens, used in paleoceanography, are flat, typically 0.5-1 mm in length and weigh between 20 and 200 microgram, thus providing a good target for geochemical analyses. Temperature calibrations are currently available for two marine, epifaunal benthic ostracodes, the deep-sea genus *Krithe* and shallow marine/estuarine genus *Loxoconcha* (Dwyer et al., 2002; Dwyer et al., 1995), both long-lived genera known since the Cretaceous. Mg/Ca ratios in these genera are significantly higher than in deep-sea benthic foraminifera. Based on core top calibrations, Dwyer proposed a linear relationship between *Krithe* Mg/Ca and temperature, with a slope of $0.95\pm0.15$ mmol mol$^{-1}$ per °C. which can also be described by an exponential dependence of 6% per °C (Figure 3).

In principle, the factors controlling the coprecipitation of Mg and its preservation in ostracode tests are similar to those discussed for foraminifera. There are however, significant differences in both Mg/Ca ratios, and the temperature sensitivity between the two ostracode genera and among species (Dwyer et al., 2002). There are also significant ontogenic effects, which can be minimized by studying only tests of the adult stage (Dwyer et al., 2002). Culture studies show no discernible salinity effects, and dissolution experiments suggest that the effect of post-depositional dissolution on the test composition are minimal (Dwyer et al., 2002). Ostracode Mg/Ca has been used successfully for reconstructing the history of bottom water temperatures through the Pliocene and Pleistocene (e.g., Dwyer et al., 1995).

## Coralline Sr/Ca paleothermometry

### Temperature Calibrations of Sr/Ca in corals

The variability of skeletal Sr/Ca in hermatypic coral skeletons has been shown in many studies to be highly correlated with monthly or seasonal variations in water temperature. Early studies have indicated that the Sr/Ca in coral skeletal aragonite is primarily regulated by water temperature (Beck et al., 1992) with more Sr incorporated in coral skeleton at lower temperatures as discussed above. The relationship obtained in these studies is of the form:

$(Sr/Ca)_{coral}$ (mmol mol$^{-1}$) = B + A(SST)

where sea surface temperature (SST) is given in °C, and the slope A=-0.062 mmol mol-$^{1}$ per °C (Beck et al., 1992). These initial observations are supported by more recent studies showing strong correlations between near-monthly coral Sr/Ca and surface water temperature (e.g., Alibert and McCulloch, 1997; Linsley et al., 2000; Linsley et al., 2004; Marshall and McCulloch, 2002) (Figure 4). Generally the slope of the Sr/Ca-SST relationship is similar for near-monthly coral Sr/Ca and monthly SST (Table 1). Despite the success of the coral Sr/Ca paleo-thermometer at many sites, these and other studies have also revealed potential complicating factors that can limit the use of this tracer. Some of these factors-uncertainties are summarized below.

### Secondary non-Temperature effects

#### *Disequilibrium offset*

Although in Porites corals, the slope of the Sr/Ca-temperature relationships, derived at different sites with different individual corals, is generally the same, the intercepts of the linear relationship are significantly different among sites even for coral analyzed on the same type of instrument. Marshall and McCulloch (2002) working with Porites corals from the Great Barrier Reef attribute this effect to be, in part, due to the disequilibrium Sr/Ca offset in corals. Similar to the $^{18}O/^{16}O$ in corals, the skeletal Sr/Ca is out of equilibrium with seawater Sr/Ca. The different intercepts for coral Sr/Ca-SST relationships, thus, reflect the fact that the disequilibrium offset can vary between corals of the same species even in close proximity. For the genus Porites, the similarity of the slopes of the Sr/Ca-SST relationships (Table 1) indicates that Sr/Ca can be used to accurately reconstruct paleo-water temperature as long as adequate site and coral specific temperature calibration is carried out. For fossil corals lacking a site-specific calibration, the consistent Sr/Ca-SST slope, but potentially different intercept implies that only relative changes in SST over time can accurately be reconstructed (+/- 0.5°C). In all cases, however, for an individual coral Sr/Ca record to be an absolute temperature proxy the degree of disequilibrium offset must be constant in that coral. This is generally the case for corals sampled along the maximum growth axis.

### *Extension rate*

Relatively little is still known about the degree to which biological parameters such as metabolism and calcification rate influence the final Sr/Ca in coral skeleton. However, work in this area is actively proceeding. Shen et al., (1996) and Alibert and McCulloch (1997) find little growth rate effect on Sr/Ca in Porites lutea skeletons accreted in the maximum growth axis and Shen et al., (1996) found no perceptible growth rate effect in Porites at accretion rates between accreting18 and 23 mm/yr. These results are at odds with those of De Villiers et al., (1994), who claimed to find significantly higher Sr/Ca ratios associated with slower skeletal extension rates in *Pavona clavus*. De Villiers et al. (1994) argued that the difference between skeleton accreting at 12 mm/yr and 6 mm/yr is equivalent to 1-2°C based on near monthly calibration with monthly SST. However, as noted by Marshall and McCulloch (2002), because De Villiers et al., (1994) did not sample exclusively along the corals maximum growth axis, this invalidates their calcification rate argument since it is widely known that sampling in off axis sections of Porites skeletons has higher Sr/Ca apparently due to smaller polyp size and lower skeletal density.

### *Monthly Sr/Ca oscillations in coral aragonite*

Using high spatial resolution ion microprobe analyses, Meibom et al., (2003) have found distinct near-monthly oscillations of *Porites lutea* skeletal Sr/Ca with an amplitude greater than 10%. They propose that these "monthly" Sr/Ca oscillations result from metabolic changes that are synchronous with the lunar cycle. As has been previously observed in Porites (Cohen et al., 2001), their study showed that temporally equivalent skeletal elements in Porties can have different Sr/Ca ratios. Some of the skeletal Sr/Ca heterogeneity is apparently due to the presence of night-time and day-time deposited skeletal elements (Cohen et al., 2001). During the night, small equant micron-sized crystals are deposited at the axial spines of the corallites (centers of calcification). Larger needle shaped crystals are formed during the day along all surfaces of the precipitating skeleton. Microprobe analyses of Sr/Ca show that the night-time and day-time skeleton have significantly different Sr/Ca (e.g., Cohen et al., 2001) and that Sr incorporation into the skeleton may be inversely related to calcification rate (Ferrier-Pages et al., 2003).

### *Replication of Long-term Secular Variability in Coral Sr/Ca and Possible changes in Sr/Ca-temperature relationship over time*

One means of potentially separating climate-related Sr/Ca variability from variability induced by biologic or diagenetic processes is to develop replicated coral Sr/Ca series from a specific site or in a specific region. Only limited replication of century-scale and decadal Sr/Ca variability has been completed to date and more replicated multi-century Sr/Ca corals records are needed to assess potential biologic or diagenetic effects on Sr/Ca. In the South Pacific Linsley et al. (in press) present partially replicated annually averaged multi-century long Porites Sr/Ca series from Fiji and Rarotonga. Both sites are in the same climatic zone in the South Pacific and were expected to show generally similar trends. However, there are significant differences between the Sr/Ca series at Rarotonga and also between the long-term Sr/Ca trends at Rarotonga and Fiji suggesting that processes other than temperature may have influenced coral Sr/Ca at one or both of these sites.

In this same study Linsley et al., (in press) (in press) have reported that application of the slope of Sr/Ca-SST relationship derived from near-monthly coral Sr/Ca and monthly SST to the entire annually averaged multi-century Sr/Ca series at both sites results in unrealistically large long-term secular trends in SST. To get the Sr/Ca secular trend and interdecadal amplitude at Fiji and Rarotonga to fit the amplitude of instrumental SST and night time marine air temperature variability from 1870 to 1997 required a scaling of ~0.2 mmol/mol per 1°C whereas the monthly calibrations are 0.053 and 0.065 mmol/mol per 1°C at Fiji and Rarotonga respectively. This 0.2 mmol/mol per 1°C scaling also resulted in a more realistic amplitude of estimated SST changes before 1870. At Fiji, Sr/Ca results for the 20 year period centered on 1660 would indicate a 4°-5°C cooling relative to the late 20th century using the calibration derived from comparison to monthly instrumental SST (Linsley et al., 2004). The apparent amplification of inferred SST changes from coral Sr/Ca prior to the calibration period was previously discussed with respect to interdecadal variability in Sr/Ca from both Fiji and Rarotonga by (Linsley et al., 2004) and may suggest that at these sites the Sr/Ca-SST relationship has not been constant over the last 380 years.

### Coral Sr/Ca Summary

Coral skeletal Sr/Ca seasonal variability has proven to be highly correlated with water temperature at many sites and appears to be a potentially useful tracer in paleoceanographic studies. As noted above, there are however questions/concerns about the accuracy of the coral Sr/Ca thermometer in modern corals that are important since these issues may directly affect interpretation of Sr/Ca data from fossil corals and reports of significant tropical Pacific and Caribbean cooling prior to 10,000 years B.P. (e.g., Beck et al., 1997). Although this tracer clearly has the potential to greatly improve our understanding of oceanic conditions, there remains important work to be done to more fully understand the significance of all modes of Sr/Ca variability in corals.

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## TABLES AND FIGURES

Table 1: Several published monthly Sr/Ca-temperature calibrations for *Porites* corals from the Pacific Ocean (Sr/Ca in mmol mol$^{-1}$ and T °C).

| **Site** | **Species** | **Sr/Ca=B+AT**<br>**B** | <br>**A** | **Reference** | **Method** [a] |
|---|---|---|---|---|---|
| New Caledonia | *Porites lobata* | 10.479 | -0.062 | Beck et al., 1992 | TIMS |
| Hawaii | *Porites lobata* | 10.956 | -0.079 | DeVillers et al., 1994 | TIMS |
| Taiwan | *Porites lobata* | 10.286 | -0.051 | Shen et al., 1996 | TIMS |
| Great Barrier Reef | *Porites sp.* | 10.38 | -0.055 | Alibert & McCulloch,1997 | TIMS |
| Great Barrier Reef | *Porites sp.* | 10.4 | -0.059 | Marshall and McCulloch, 2002 | TIMS |
| Fiji | *Porites lutea* | 10.65 | -0.053 | Linsley et al., 2004 | ICP-AES |
| Rarotonga | *Porites lutea* | 11.12 | -0.065 | Linsley et al., 2000 | ICP-AES |

[a] TIMS= Thermal Ion Mass Spectrometry; ICP-AES= Inductively Coupled Plasma Atomic Emission Spectrometer

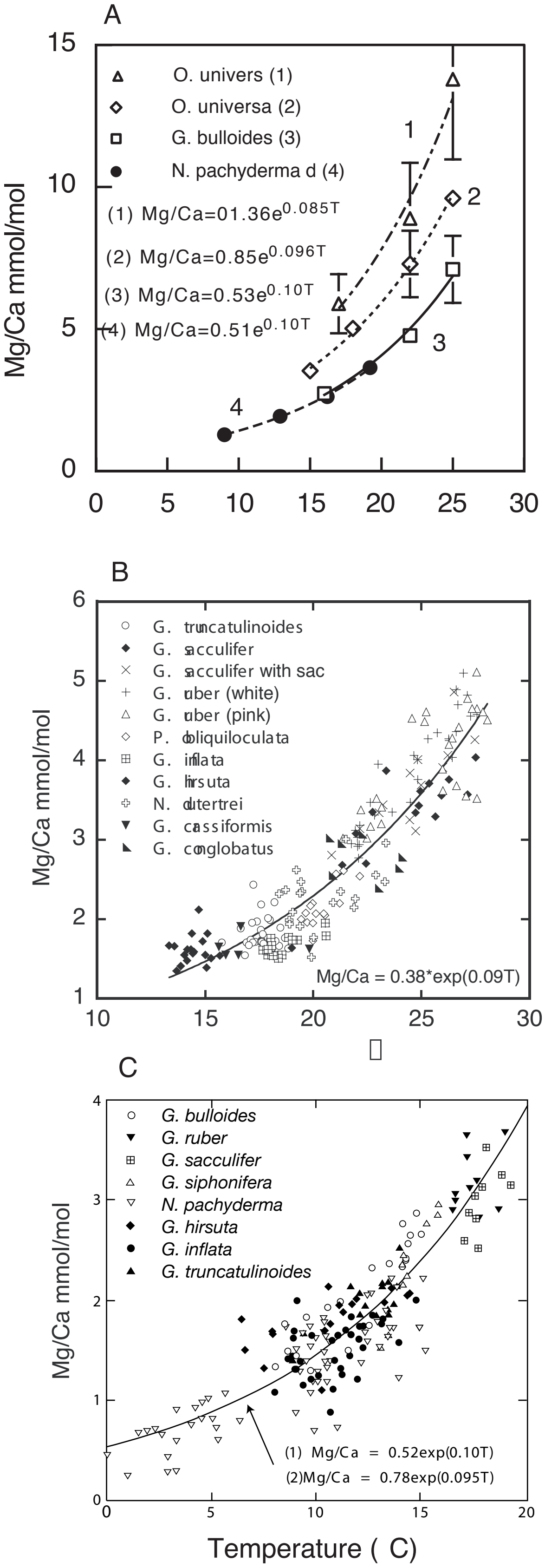
## Figure caption

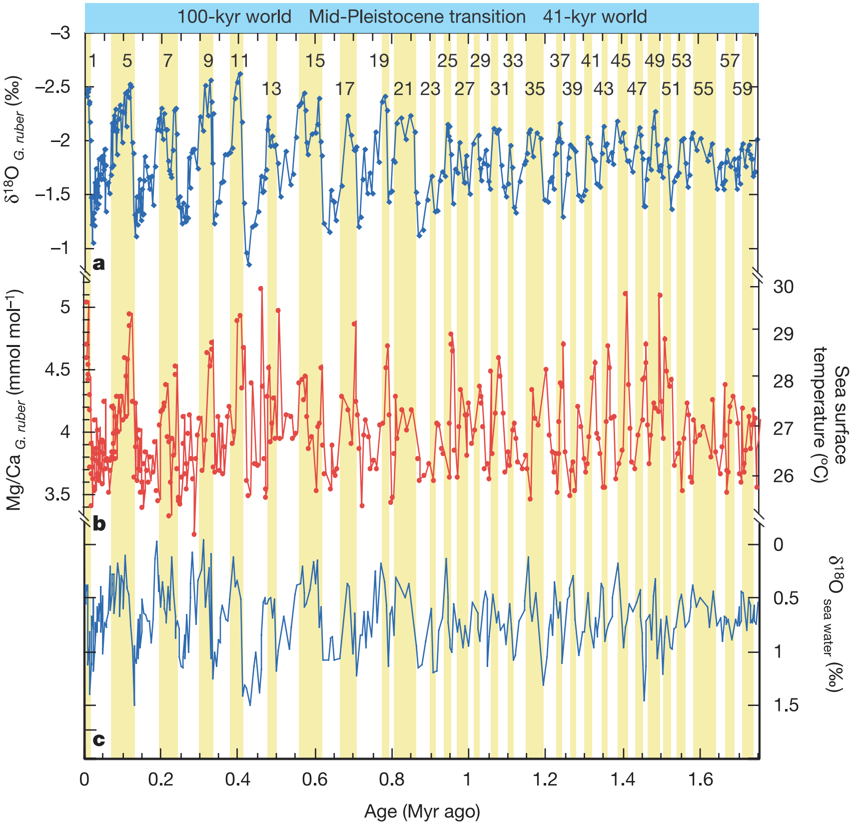
**Figure 1**: Mg/Ca-temperature calibrations based on: (A) Culture experiments (data from 1) (Lea et al., 1999), 2) (Russell et al., 2004), 3) (Lea et al., 1999), 4) (Langen et al., 2005)); (B) Sediment traps from the Sargasso Sea (Anand et al., 2003); (C) Core tops (Elderfield and Ganssen, 2000) (regression line 1 from (Elderfield and Ganssen, 2000), line 2 from (Rosenthal and Lohmann, 2002) based on the same data set).

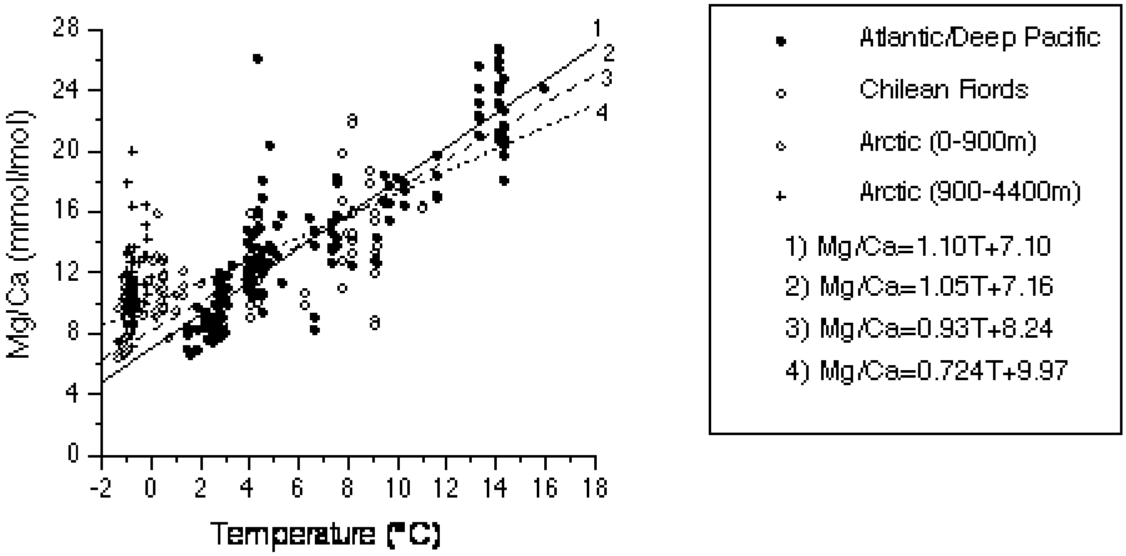
**Figure 2:** Planktonic foraminiferal records (*G. ruber*) from core MD97-2140 in the western equatorial Pacific (Eauripik rise 2° 02N, 141° 46 E, 2547 meter) (de Garidel et al., 2005). (A) $\delta^{18}O$; (B) Mg/Ca-derived SST; and (C) calculated $\delta^{18}O_{sea\text{-}water}$ Interglacial periods are numbered at the top. Note the relatively large galcial0integlacial SST variability (°C), the long-term stability in SST and the shift from 41 to 100 ky dominated periodicity during the mid-Pleistocene.

Figure 3: Various Mg/Ca-temperature calibrations for adult shells of genus *Krithe*. Regression lines are based on samples from 1) Atlantic and central Pacific core tops; 2) Data from regression 1 and core tops from Chilean Fjords; 3) Same as 2 with Arctic core tops between 0-900 m; 4) Same as 3 with Arctic core tops deeper than 900 m. Figure modified from (Dwyer et al., 2002).

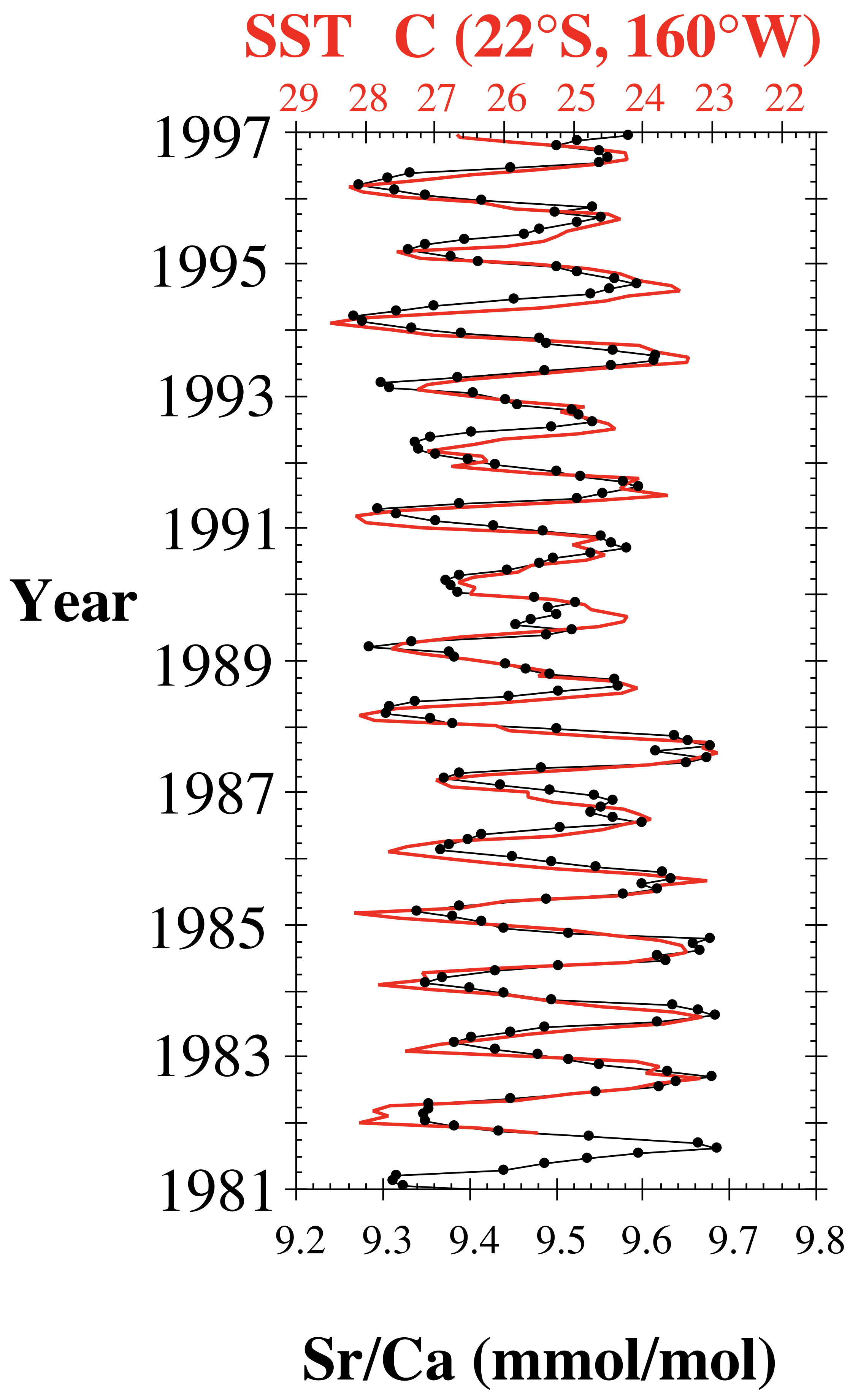
**Figure 4:** Comparison of monthly sea surface temperature (red) for the latitude-longitude grid including Rarotonga in the South Pacific (1° by 1°; centered at 22°S, 160°W) and Sr/Ca measurements (black) analyzed at 1mm intervals in a Porites lutea coral core from Rarotonga. The X-ray positive of the coral core shows the sampling track and annual growth density bands.


A
Mg/Ca mmol/mol
15
10
5
0
0
5
10
15
20
25
30
O. univers (1)
O. universa (2)
G. bulloides (3)
N. pachyderma d (4)
(1) Mg/Ca=01.36e^0.085T
(2) Mg/Ca=0.85e^0.096T
(3) Mg/Ca=0.53e^0.10T
(4) Mg/Ca=0.51e^0.10T
1
2
3
4
B
Mg/Ca mmol/mol
6
5
4
3
2
1
10
15
20
25
30
G. truncatulinoides
G. sacculifer
G. sacculifer with sac
G. ruber (white)
G. ruber (pink)
P. obliquiloculata
G. inflata
G. hirsuta
N. dutertrei
G. crassiformis
G. conglobatus
Mg/Ca = 0.38*exp(0.09T)
C
Mg/Ca mmol/mol
4
3
2
1
0
0
5
10
15
20
Temperature ( C)
G. bulloides
G. ruber
G. sacculifer
G. siphonifera
N. pachyderma
G. hirsuta
G. inflata
G. truncatulinoides
(1) Mg/Ca = 0.52exp(0.10T)
(2)Mg/Ca = 0.78exp(0.095T)


100-kyr world
Mid-Pleistocene transition
41-kyr world
1
5
7
9
11
13
15
17
19
21
23
25
27
29
31
33
35
37
39
41
43
45
47
49
51
53
55
57
59
$\delta^{18}O_{G. ruber}$ (‰)
−3
−2.5
−2
−1.5
−1
a
Mg/Ca $_{G. ruber}$ (mmol mol$^{-1}$)
5
4.5
4
3.5
b
Sea surface temperature (°C)
30
29
28
27
26
$\delta^{18}O_{sea water}$ (‰)
0
0.5
1
1.5
c
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
Age (Myr ago)


28
24
20
16
12
8
4
0
Mg/Ca (mmol/mol)
-2
0
2
4
6
8
10
12
14
16
18
Temperature (°C)
1
2
3
4
● Atlantic/Deep Pacific
○ Chilean Fiords
◇ Arctic (0-900m)
+ Arctic (900-4400m)
1) Mg/Ca=1.10T+7.10
2) Mg/Ca=1.05T+7.16
3) Mg/Ca=0.93T+8.24
4) Mg/Ca=0.724T+9.97

# Comparison of Rarotonga Coral Sr/Ca with IGOSS Satellite SST



X-ray of *Porites lobata*