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Does the Mg/Ca in Foraminifera Tests Provide a Reliable Temperature Proxy?

Sarah Clark

Abstract: The Mg/Ca in foraminifera shells is commonly used as a proxy to estimate ocean temperatures in Earth’s past. However, studies have shown that both dissolution and salinity influence the Mg/Ca in shells of tropical foraminifera, which can cause paleotemperature estimates to be inaccurate. We measured Mg/Ca in shells of *Globigerinoides ruber* and *Globigerinoides sacculifer* from core tops in the eastern equatorial Pacific. We compared our results with global core top data, which paleotemperature equations have been calibrated and published. We find that Mg/Ca values range greatly at the same surface ocean temperature. We also find that salinity and dissolution do not affect the relationship between Mg/Ca and temperature. In analyzing the carbonate ion concentration of the water at 30m, we find that this might be affecting the relationship between Mg/Ca and temperature, which could be affecting the accuracy of the Mg/Ca proxy.

Introduction: The relationship between Mg/Ca and temperature has been well established in literature, and is commonly used as a reliable temperature proxy. Foraminifera—single-celled amoebas with shells composed of calcium carbonate—are commonly used as sea surface temperature (SST) indicators because of the chemistry of their shells. Foraminifera use the ions in their habitat water to create their shells. However, depending on the conditions of the water, foraminifera will use a magnesium ion instead of a calcium ion to make their shells. Therefore, foraminifera are excellent indicators of environmental change because the ratio of magnesium to calcium in their shells can be measured to estimate the environmental conditions that they lived in.
Equations have been calibrated to estimate SST using the Mg/Ca data. However, the equations that have been calibrated from these studies are not compatible with one another, and are often region specific. A single global equation needs to be calibrated for the proxy so that a single standard and method can be used that is not region specific.

Proxies are necessary to estimate climate conditions in the past, so it is very important to have a reliable proxy. We can analyze the reliability of the Mg/Ca temperature proxy by comparing the data from modern deep sea core top samples to modern satellite data. In this paper we will analyze [1] Does the Mg/Ca in Foraminifera test provide a reliable temperature proxy? [2] If not, then what conditions could affect the relationship between Mg/Ca and temperature? [3] How does this affect the development of the Mg/Ca temperature proxy?

**Methods:** We used *G. sacculifer, G. ruber sensu lato,* and *G. ruber sensu stricto* (figure 1) to analyze SST. We used sacculifers and rubers because they live at the sea surface, between 0 and 30 meters. Sacculifers and rubers are also commonly used for SST estimates, and were also used by Dekens et al. who we compare our data with.

(Figure 1)

The core tops were collected from the eastern equatorial Pacific Ocean (EEP), ranging from 10°N and 30°S, 70°E and 120°W. The EEP was ideal for this study because the measured satellite SST (figure 2) and sea surface salinity (SSS) (figure 3) data shows steep gradations.
The SST and SSS data were collected from the World Ocean Atlas 2005. The data was measured at 30 meters below the sea surface, and was measured seasonally as well as annually. All the data collected has been averaged over decades so that periodic climate changes do not affect the overall climate in a region.

(Figure 2)

(Figure 3)
Before picking the samples, we washed each sample individually in a sieve with distilled water. The samples were rinsed with a wash bottle in perpendicular patterns until the water ran clear through the sieve. Clusters of sediment and microfossils were lightly crushed with a finger and then rinsed to provide a more thorough cleansing of sediment and residue. After rinsing, the sample was then gathered and rinsed into a beaker, and then dried at 60-80°C.

We picked individuals of *G. sacculifer* and of two morphotypes of *G. ruber* (sensu lato and sensu stricto) in 66 core top samples. Only 8 out of 66 core top samples yielded enough numbers for analysis. An average of 22 individuals was picked per morphotype sample, however, samples ranged from 10 individuals to 42 individuals. The samples were then measured using a micrometer. I picked both rubers and sacculifers within the size fraction of 250-350 microns. We used the same size range for both species as Dekens et al. (2002).

<table>
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<th>Cruise</th>
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<th>Longitude</th>
<th>Water Depth</th>
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<th>Salinity 30m</th>
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</table>

Our samples were analyzed by Jeroen Greneveld at the University of Bremen in Germany. The cleaning process was performed by Jeroen, using Barker et al.’s procedure, with the exception of the step of picking out alien particles. The samples underwent ultrasonic cleaning alternated with washes in deionized water (Seralpur) and methanol. An oxidizing step
was used, and neutralized with multiple Seralpur washes. The samples were transferred into clean vials and a weak acid leach (0.001 M QD HNO3) was applied. The samples were dissolved in 0.075 M QD HNO3 after being centrifuged for 10 minutes (6000 rpm) to exclude any remaining insoluble particles from the analyses. The samples were diluted with Seralpur before analysis with an ICP-OES (Perkin Elmer Optima 3300RL with autosampler and ultrasonic nebulizer U-5000 AT (Cetac Technologies Inc.)) at the Department of Geosciences, University of Bremen. Stability of the Mg/Ca measurements was monitored by analysis of an in-house artificial standard solution with Mg/Ca ratio of 2.90 mmol/mol (long-term standard deviation of 0.026 mmol/mol or 0.91%). The analyses of an international limestone standard (ECRM752) were well within the error of its reported Mg/Ca ratio of 3.75 mmol/mol [Greaves, Caillon et al., 2008]. Analytical precision based on three repetitions per analysis of Mg/Ca for G. inflata was 0.23%, while reproducibility based on replicate samples (n = 47) was ± 0.12 mmol/mol (1, ca. 3.8%).

We used Dekens et al’s (2002) equation (Mg/Ca = 0.38 exp 0.09[SST – 0.61(core depth KM)]) to calibrate our temperature data from the Mg/Ca. We input our Mg/Ca data into the equation to find the temperature variable. (ln ((Mg/Ca)/0.38)/0.09 = T.

We also analyzed the affect of dissolution in the samples using the Globorotalia menardi Fragmentation Index (MFI). This proxy looks at the dissolution of carbonate, the surface ocean productivity, calcite flux, and dilution by non-carbonate materials. Dissolution is analyzed by counting the number of damaged shells and dividing it by the number of damaged shells plus the number of whole shells. MFI = D/(D + # in A) [damaged parts/ all parts].
We used data collected from Archer et al.’s database to analyze bottom water dissolution and carbonate ion concentration in the water at 30m. This database was established by collecting bottle samples of seawater at different coordinates and depths.

We also know that our core tops are modern sediments because of Loubere et al.’s analysis of oxygen and carbon isotopes from *Neogloboquadrina dutertrei* tests in this region.

**Results:** Due to the amount of upwelling in the EEP and the sensitivity of foraminifera, our temperature range is only about 2°C (23.5-25.5°C). In all three of our morphotypes we see a negative relationship between shell Mg/Ca and SST at 30m instead of the expected positive relationship. The exponential relationship with SST is not as strong in sensu lato (figure 4) and sensu stricto (figure 5), but it is very strong in *G. sacculifer* (figure 6). Under normal conditions this negative relationship between Mg/Ca and SST is thermodynamically impossible.

(Figure 4)
In investigating what could be affecting the relationship between Mg/Ca and SST we analyzed our SSS data. Our SSS data ranges from 34-36 PSU, we found no discernable relationship between salinity and Mg/Ca (figure 7).
We also analyzed dissolution as a factor using MFI, and there is no discernable relationship between the percent of dissolved calcium carbonate and Mg/Ca (figure 8).
Archer’s delta carbonate data was also analyzed for dissolution, there is no discernable relationship between the delta carbonate of the bottom waters and the Mg/Ca (figure 9).

![Coretops in this study](image1)

(Figure 9)

Mg/Ca in *G. ruber* of both morphotypes has a negative relationship with [CO3=] at 30 m water depth. Although we see the same negative trend with Mg/Ca in *G. sacculifer* and [CO3=] at 30m (figure 11), the relationship is stronger for *G. ruber* (figure 10). In our eight sample locations, there is no relationship between SST and [CO3=] at 30m.

![G. ruber (this study)](image2)

(Figure 10)
Discussion: After considering our results, we analyzed the relationships between Dekens’ data and salinity, dissolution, and the carbonate ion concentration at 30m in the same way that we analyzed our own data. We did not compare the Dekens et al. (2002) Mg/Ca data with surface ocean [CO3= ] because in their sample locations, which is true in most places, there is a strong correlation between SST and surface ocean [CO3= ]. Therefore, we could not analyze the affect of sea surface [CO3= ] on Dekens’ SST data.

Despite the negative trend in our data, our data points fall well within the overall trend and range of variability in the Dekens et al. (2002) core top calibration data set (figures 12 and 13).
The Dekens et al. (2002) calibration sample set does not follow a strong exponential relationship with SST (figures 12 and 13). The samples at 27.4°C are especially concerning since they range between 2.4 and 3.7 mmol/mol of Mg/Ca for *G. sacculifer*, and 2.9 to 4.3 mmol/mol for *G. ruber*. This large range of Mg/Ca shows discrepancies in the proxy because the
variability in Mg/Ca cannot be explained by the affect of ΔCO3¯ (figure 14) or SSS (figure 15) (all values from Dekens et al., 2002).

(Figure 14)

The negative relationship between [CO3] at 30m and our Mg/Ca data from *G. ruber* may be an explanation for the negative relationship between our Mg/Ca data and SST because we do not find a relationship between [CO3] at 30m and SST in our samples (figure 16).

(Figure 15)
Spero et al. (1997) reported the strong influence of \([\text{CO}_3^-]\) in habitat waters on \(\delta^{18} \text{O}\) and \(\delta^{13} \text{C}\) of foraminifer tests, so it is very likely that \([\text{CO}_3^-]\) is influencing Mg/Ca in the tests as well.

**Conclusion:** We find a negative, and thermodynamically impossible, relationship between Mg/Ca in *G. sacculifer* and two morphotypes of *G. ruber* and SST in the eastern equatorial Pacific. We find no discernable relationship between our Mg/Ca data and SSS, \(\Delta \text{CO}_3^-\) of bottom waters, or estimates of calcite dissolution in the sediments using MFI. They do not explain the unlikely negative relationship between Mg/Ca and SST. We do find a quantitatively strong but negative relationship between Mg/Ca in *G. ruber* and \([\text{CO}_3^-]\) at 30m water depth which may potentially explain the negative relationship between SST and *G. ruber* in our samples. This is particularly noteworthy since SST and \([\text{CO}_3^-]\) at 30m do not co-vary in our sample locations like they usually do in other locations. More work needs to be done to establish the \([\text{CO}_3^-]\) dependency of Mg/Ca in foraminifer shells, and what affect that might have on determining SST with the Mg/Ca proxy.