Refining *Globigerinoides ruber* Mg/Ca paleothermometry in the Atlantic Ocean

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**A B S T R A C T**

The Mg/Ca ratio of the planktonic foraminifera *Globigerinoides ruber* (white) has become a widely used proxy for reconstructing sea surface temperature (SST), as numerous studies have shown that temperature is the primary control on Mg/Ca ratios in foraminiferal calcite. However, a recent study of core-top sediments across an Atlantic meridional transect suggests that salinity might have a stronger control on foraminiferal Mg/Ca ratios than previously thought. By analyzing Mg/Ca ratios and δ¹⁸O values in *G. ruber* (white), Arbuszewski et al. (2010) found a 27% increase in *G. ruber* Mg/Ca ratios per 1 salinity unit increase for seawater salinities above 35.5. Here, we use shell weight analyses and SEM images from a subset of the core-tops used in the Arbuszewski et al. (2010) study across a narrow depth range (3197–3733 m) to show that *G. ruber* shells from the equatorial region are highly dissolved compared to those from the subtropical North and South Atlantic gyres, significantly impacting their Mg/Ca-SSTs. Shell weights from the higher-productivity equatorial region of the Atlantic are on average 20% and 15% lower than those from the oligotrophic North and South Atlantic gyres, respectively. Given the large preservation gradient along the transect studied by Arbuszewski et al. (2010), application of a single dissolution-corrected Mg/Ca-SST calibration equation (Dekens et al., 2002) on cores from the subtropical gyres and the equatorial region is not appropriate. When regional differences in preservation are considered, as well as realistic habitat depths and calcification seasons for *G. ruber* in temperate latitudes, we find a strong correlation between observational SSTs and calculated *G. ruber* Mg/Ca-SSTs in core-top samples spanning 43°N to 25°S in the Atlantic. In addition, our re-calibrated Mg/Ca-SSTs are more strongly correlated with isotopic calcification temperatures across the transect than originally reported by Arbuszewski et al. (2010). This study provides evidence that regional differences in preservation, rather than salinity, significantly affects *G. ruber* Mg/Ca-SSTs in the Atlantic, and supports culturing experiments that found salinity only has a minor influence on foraminiferal Mg/Ca ratios.

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1. Introduction

Numerous culturing, core-top, and sediment trap studies have shown that temperature is the primary control on Mg/Ca ratios in foraminiferal calcite (e.g. Anand et al., 2003; Barker et al., 2005; Cléroux et al., 2008; Dekens et al., 2002; Hastings et al., 1998; Kisakürek et al., 2008; Lea et al., 1999; Nürnberg et al., 1996), and calibrations of this relationship have been applied successfully to the paleo-record to reconstruct ocean temperatures across a wide range of time periods (e.g. Koutavas et al., 2002; Lea et al., 2000; Oppo et al., 2009; Schmidt et al., 2012a). In addition, paired Mg/Ca temperatures and δ¹⁸O calcite (δ¹⁸O c) measurements on surface-dwelling planktonic foraminifera are often used to reconstruct past δ¹⁸O seawater (δ¹⁸O sw) variability, a robust proxy for sea surface salinity (e.g. Schmidt et al., 2006; Schmidt and Lynch-Stieglitz, 2011; Weldeab et al., 2007). A number of secondary controls on foraminiferal Mg/Ca ratios have been identified from culturing experiments, including pH, carbonate ion concentration, and salinity; however, these studies suggest that their influence is small in comparison to temperature (Hönisch et al., 2013; Kisakürek et al., 2008; Lea et al., 1999; Nürnberg et al., 1996; Russell et al., 2004).

While laboratory culturing studies have suggested an influence of salinity on foraminiferal Mg/Ca ratios of up to 5–8% per salinity unit (Hönisch et al., 2013; Kisakürek et al., 2008; Lea et al., 1999; Nürnberg et al., 1996), recent studies on core-top foraminifera from high-salinity regions suggest an influence of salinity ranging from 15 to 30% per salinity unit (Arbuszewski et al., 2010; Ferguson et al., 2008; Mathien-Blard and Bassinot, 2009). As the average sensitivity of Mg/Ca ratios to changes in temperature is ~9% per degree Celsius (Anand et al., 2003; Dekens et al., 2002; Lea et al., 1999), in the case of a large salinity effect, the use of foraminiferal Mg/Ca ratios as a temperature proxy may be greatly...
hamstered, as the salinity effect would overshadow any temperature change.

Ferguson et al. (2008) measured Mg/Ca ratios on planktonic foraminifera from the high salinity Mediterranean Sea and noted a significant bias on Mg/Ca ratios for seawater salinities above 36. For the surface-dwelling planktonic foraminifera *Globoigerinoides ruber* (white), they determined an influence of salinity on Mg/Ca ratios of ∼15–30% per salinity unit increase, depending on the size fraction measured (Ferguson et al., 2008). However, subsequent studies have concluded that foraminifera shells from the Mediterranean Sea appear to be affected by post-depositional diagenetic alteration, adding high-Mg overgrowths under CaCO₃-supersaturated conditions in pore-waters (Boussetta et al., 2011; Hoogakker et al., 2009; Kontakiotis et al., 2011; Sabbatini et al., 2011).

A second study by Mathien-Blard and Bassinot (2009) measured Mg/Ca ratios on *G. ruber* (white) across a wide range of salinities from the Atlantic, Pacific, and Indian Oceans and noted a salinity bias on Mg/Ca ratios of ∼15% per salinity unit increase. For samples from the high salinity regions of the Atlantic Ocean, Mathien-Blard and Bassinot (2009)’s calculated Mg/Ca-sea surface temperatures (SSTs) were significantly elevated above isotopic calcification temperatures, in some cases by as much as ∼2.5°C (Fig. 1). However, the difference between their calculated Mg/Ca-SSTs and isotopic calcification temperatures is only weakly correlated with sea surface salinity. In addition, prior to Mg/Ca analysis, their *G. ruber* samples were cleaned using the method of Barker et al. (2003), which includes only an oxidative step for removal of organic matter. Cleaning protocols that also include a reductive step to remove metal oxides have been shown to reduce shell Mg/Ca ratios by ∼7–15% (e.g. Arbuzzewski et al., 2010; Barker et al., 2003; Pena et al., 2005; Rosenthal et al., 2004).

Reducing the Atlantic Mg/Ca ratios measured by Mathien-Blard and Bassinot (2009) by 10% (a value commonly applied when comparing reductively vs. non-reductively cleaned samples, e.g. Arbuzzewski et al., 2010; Schmidt et al., 2012b) puts most of their calculated Mg/Ca-SSTs within a ±1°C range of isotopic calcification temperatures (Fig. 1), similar to their reported ±1°C uncertainty on calculated Mg/Ca-SST estimates. Therefore, it does not appear that there is a large salinity bias on the Atlantic core-tops studied by Mathien-Blard and Bassinot (2009).

Most recently, a study by Arbuzzewski et al. (2010) found a 27% increase in *G. ruber* (white) Mg/Ca ratios per salinity unit increase for seawater salinities above 35.5. Their study is based on measurements of 64 core-top *G. ruber* (white) Mg/Ca ratios across an Atlantic meridional transect spanning from 43°N to 25°S, including samples from both the high salinity subtropical Atlantic gyre regions and the lower salinity Equatorial Atlantic region (Fig. 2). Arbuzzewski et al. (2010) found that *G. ruber* Mg/Ca ratios from the high salinity subtropical gyres are significantly elevated above values expected from observed and isotopic calcification temperatures. In addition, they noted that their calculated core-top Mg/Ca-SSTs were weakly correlated with observed temperatures across the transect ($r^2 = 0.19$), attributing the poor correlation to elevated Mg/Ca ratios in the high salinity subtropical gyre regions, resulting in excessively high SST estimates for the northern and southern subtropics (Arbuzzewski et al., 2010).

![Fig. 1. Plot of the difference between calculated Mg/Ca-SSTs and isotopic calcification temperatures versus sea surface salinity for the Atlantic Ocean core-tops used in the study by Mathien-Blard and Bassinot (2009). The original data are plotted in blue, while the data with a 10% Mg/Ca reduction are plotted in pink. Note that the 10% Mg/Ca reduction puts most of their calculated Mg/Ca-SSTs within a ±1°C range of isotopic calcification temperatures, similar to their reported ±1°C uncertainty on calculated Mg/Ca-SST estimates (Mathien-Blard and Bassinot, 2009). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image1)

![Fig. 2. Map indicating the locations of core-tops analyzed by Arbuzzewski et al. (2010) (blue dots). Locations outlined in red indicate core-tops analyzed in the current study for shell weights and SEM imaging. Numbers next to outlined locations correspond to core names as follows: (1) VM27-261, (2) VM19-301, (3) VM16-206, (4) RC13-188, (5) RC24-11, (6) RC24-16, (7) RC24-17, (8) VM16-36, (9) RC8-23. Latitudes, longitudes, and core depths can be found in Table 1. Map created with Ocean Data View (Schlitzer, 2013). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image2)
In this paper, we closely examine the study of Arbuszewski et al. (2010), focusing on a number of assumptions that were made that led to their conclusions. In their study, Arbuszewski et al. (2010) converted all of their measured Mg/Ca ratios to SST using a single dissolution-corrected Mg/Ca:SST calibration equation (Dekens et al., 2002) that includes a water-depth correction factor to account for the loss of high-Mg foraminiferal calcite due to dissolution. Here, we use shell weight analyses and scanning electron microscope (SEM) imaging to assess the assumption that all of the G. ruber shells used in the study by Arbuszewski et al. (2010) were subject to dissolution, and whether or not a single calibration equation should be used across the range of latitudes and depths of the core-tops used by Arbuszewski et al. (2010). In addition, we evaluate the observational data chosen by Arbuszewski et al. (2010) that was used to compare with their calculated Mg/Ca-SSTs, as this data assesses how well calculated core-top Mg/Ca-SSTs reconstruct modern oceanographic conditions. Taking all of these factors into account, we conclude with a re-evaluation of the proposed large salinity effect on G. ruber Mg/Ca ratios that was determined by Arbuszewski et al. (2010).

2. Materials and methods

2.1. Description of geochemical data

The previously published geochemical data referred to throughout this paper were reported by Arbuszewski et al. (2010). In the Arbuszewski et al. (2010) study, a suite of 64 core-top sediment samples spanning from 43°N to 25°S along the Mid-Atlantic Ridge were analyzed for δ18O and Mg/Ca ratios (Fig. 2). In brief, 80–100 specimens of G. ruber (white, sensu stricto) were picked from each sample from the 250–355 μm size fraction, crushed, and split into aliquots for Mg/Ca and δ18O analyses (Arbuszewski et al., 2010). After removal of clays, and full reductive and oxidative cleaning steps, samples were analyzed for Mg/Ca ratios on an ICP-OES (Arbuszewski et al., 2010). Samples for δ18O analyses were also cleaned in rinses of ultra-pure water prior to analysis (Arbuszewski et al., 2010).

Stratigraphic quality for each core-top was assessed using a variety of methods, including radiocarbon dating, age control from the CLIMAP, GLAMAP, SPECMAP, EPILOG, or MARGO databases, or δ18O, CaCO3 or Globorotalia menardii stratigraphies (Arbuszewski et al., 2010).

2.2. Core selection and sample processing

To examine the preservation differences of the foraminifera in the core-tops analyzed by Arbuszewski et al. (2010), we performed shell weight analyses and SEM imaging on G. ruber (white), the same species of planktonic foraminifera used for the Mg/Ca and δ18O analyses, on a subset of the same cores used by Arbuszewski et al. (2010). We obtained a different set of core-top samples from cores across a narrow depth range (~3.2 to ~3.7 km) from the North, Equatorial, and South Atlantic (Table 1). This depth range was chosen as it contained the greatest number of cores in the three regions, and the range is above the ~4 km lysocline depth (Berger, 1968; Jones et al., 1984), enabling us to examine preservation differences that may be driven by factors other than the ΔCO2−3 (defined as [CO2−3]in situ − [CO2−3]saturation) of bottom waters. Three cores from the North Atlantic, four cores from the Equatorial Atlantic, and two cores from the South Atlantic satisfied these constraints and had enough sample material remaining close to the top of the cores. Samples were first rehydrated with deionized water, disaggregated on an orbital shaker table for 6 h, and then wet-sieved through a 63 μm mesh. The remaining >63 μm fraction was then dried in an oven overnight at 50°C.

2.3. Shell weight analyses

Shell weight analyses were performed on the core-top samples following the procedure outlined in Broecker and Clark (2002). When available, 50 shells of G. ruber (white, sensu stricto) were picked from the 300–355 μm size fraction and weighed in triplicate on a Mettler Toledo MX5 microbalance. To avoid potential bias in shell selection, G. ruber shells were picked upon first encounter on a gridded picking tray. Performing shell weight analyses on a narrow size fraction of foraminifera minimizes size related weight differences (e.g. Barker et al., 2004; Beer et al., 2010a, 2010b; Broecker and Clark, 2001). Therefore, simply reporting average shell weights on samples used for geochemical analyses, which are often from a ~100 μm size fraction range (e.g. Arbuszewski et al., 2010), is insufficient for assessing potential dissolution using this method. In addition, when picking foraminifera for geochemical analyses, there is a bias to select only the ‘best-looking’ shells (i.e. those that might not have any evidence of dissolution), thereby influencing the average shell weights reported for foraminifera used for geochemical analysis. We attempted to sonicate samples prior to shell weight analyses to remove any residual fine debris; however, due to the frail nature of the samples from the tropical Atlantic, the foraminifera broke up or were damaged immediately upon sonication. As even minor loss of shell material during sonication would have major implications for the shell weights, the decision was made to not sonicate any of the samples. We assume that as all samples underwent the same initial sample washing process, any offset due to residual fine debris would be constant among samples.

2.4. Scanning electron microscopy imaging

Representative shells of G. ruber were selected from the same subset of samples used for shell weight analyses to obtain SEM images. Shells were mounted on SEM stubs using adhesive tape.
and sputter-coated with gold. Images were obtained using a JEOL JSM-6400 with a 5 kV accelerating voltage at the Microscopy and Imaging Center at Texas A&M University.

3. Results

3.1. Shell weight analyses

The results from the shell weight analyses on G. ruber are summarized in Table 1. Average shell weights from the North Atlantic sites range from 21.3 µg to 23.1 µg, with an average of 22.5 µg, while average shell weights from the South Atlantic sites range from 20.6 to 21.4 µg, with an average of 21.0 µg. Average shell weights from the Equatorial Atlantic are significantly lower, ranging from 18.4 µg to 19.6 µg, with an average of 17.9 µg. Triplicate measurements of each core-top sample yielded the same weight each measurement, indicating that the reported average shell weights are highly precise. We estimate the standard error of our measurements to be about ±0.5–0.7 µg, in agreement with a prior study of the natural variability of a population of G. ruber (white) shells from the South China Sea (Regenberg et al., 2013), and the average shell weights obtained from cores RC24-16 and RC24-17, recovered from nearly identical locations (Table 1). In comparison to the North Atlantic sites, South Atlantic sites are on average 6% lower, while Equatorial Sites are 20% lower than North Atlantic sites. Broecker and Clark (2002) found only a ~4% reduction in average shell weights due to sonication of samples to remove residual fine debris. Therefore, it is unlikely that the shell weight differences between the three regional sites are an artifact of not sonicating the samples prior to weighing them.

3.2. SEM imaging

SEM images were obtained for whole shells of G. ruber from a subset of the core-tops used in the shell weight study (Fig. 3, Panel I). Overall, shells from the North and South Atlantic exhibit excellent preservation, while those from the Equatorial Atlantic display significant loss of shell material. Further magnified images show evidence of dissolution pits and loss of surface structure on shells from the Equatorial Atlantic (Fig. 3, Panel II), especially in comparison to those from the North and South Atlantic (Fig. 3, Panel III). Although the three study regions exhibit some range of shell preservation, the shells chosen for SEM imaging exhibit features common to most of the G. ruber shells in each sample.

4. Discussion

4.1. Preservation differences across the Atlantic basin

Based on the results of our core-top shell weight study, and as indicated by the SEM images on the same G. ruber shells, G. ruber shells from the North and South Atlantic exhibit a much higher degree of preservation than those from the Equatorial Atlantic across the same range of depths between the three regions. These findings are in line with previous studies from the Equatorial Atlantic that found evidence for significant dissolution of G. ruber along depth transects from the Caribbean and Western and Eastern Equatorial Atlantic at sites well above the lysocline depth (Dekens et al., 2002; Regenberg et al., 2006; Rosenthal et al., 2000; Rosenthal and Lohmann, 2002). There have been fewer studies examining preservation along depth transects in the North and South Atlantic; however, Dekens et al. (2002) found no evidence for dissolution of G. ruber shells above the lysocline on the Rio Grande Rise in the South Atlantic. Given that our shell weights from the North Atlantic are slightly higher than those from the South Atlantic, we interpret our results to indicate that G. ruber shells from the North and South Atlantic sites have undergone little dissolution.

Dissolution of foraminiferal calcite can occur within the water column, at the sediment–water interface, and/or within the sediment column as a result of low in situ carbonate ion concentrations (Berger et al., 1982). Based on CaCO3 budgets for the global open ocean, Milliman et al. (1999) estimated that as much as 60–80% of calcite dissolution can occur in the upper 500–1000 m of the water column, well above the lysocline depth. Within the water column and at the sediment–water interface, the rain rate of organic matter (Jahnke et al., 1994; Martin and Sayles, 2006) and the ΔCO2 of deep water (Berger, 1968), which is primarily a function of the relative age of bottom waters, are the main controls on calcite dissolution. At and below the seafloor, dissolution is controlled by the flux and rain rate of calcium carbonate, bottom water chemistry, and the metabolic respiration of organic carbon within sediments (e.g. Archer et al., 1989; de Villiers, 2005; Emerson and Bender, 1981). Martin and Sayles (2006) created a model of coupled organic matter oxidation and calcite dissolution and showed that metabolic dissolution is likely to be significant at all bottom water carbonate saturation levels and can result in dissolution of up to 50% of the CaCO3 rain at the depth of the calcite saturation horizon. Most of these factors affecting dissolution vary not only spatially with latitude and depth within the water column, but they can also change temporally.

For all nine locations where shell weight analyses were performed, bottom water ΔCO2 values are roughly equal (Table 1), yet the large differences in shell weights between the three regions indicate that there is likely another factor controlling the dissolution differences between the sites. A number of studies have shown that even for locations where bottom waters are supersaturated with respect to carbonate ion concentration, significant calcite dissolution can occur at the sediment–water interface and within the sediment column due to enhanced productivity in the overlying water column (Archer et al., 1989; de Villiers, 2005; Emerson and Bender, 1981). Metabolic CO2 generated from the oxidation of organic carbon can drive porewater carbonate ion values below calcite saturation levels, leading to dissolution (Archer et al., 1989; Emerson and Bender, 1981; Hales and Emerson, 1996, 1997).

To assess the possibility that productivity differences may be the cause of the dissolution differences among the three regions, we plotted the average shell weights for the nine sites on a map of surface chlorophyll concentrations inferred from ocean color measurements from the SeaWiFS project (http://seawifs.gsfc.nasa.gov) (Fig. 4). A number of studies have shown that surface chlorophyll concentrations correlate well with primary productivity, and thus are a good first order approximation of primary productivity by marine phytoplankton (e.g. Frazel and Berberian, 1990; Huot et al., 2007). Although not all of the organic matter produced in the upper water column will descend to the sediments, the general pattern of regions with high (low) surface chlorophyll concentrations match locations for which prior studies have measured high (low) surface sediment organic carbon concentrations (e.g. Mollenhauer et al., 2004; Premuzic et al., 1982). Sites in the North and South Atlantic with the highest average shell weights fall within the oligotrophic gyre regions, while the Equatorial sites fall within the high-productivity equatorial upwelling zone (Fig. 4). Additionally, between the core-tops from the Equatorial Atlantic, those with the lowest average shell weights fall directly within the regions of highest surface water productivity. Therefore, it is likely that productivity differences are the main discriminating factor of preservation differences between the three sites. While the North and South Atlantic sites are both within the low productivity oligotrophic gyre regions, South Atlantic sites have lower average shell weights than North Atlantic regions. This is likely due to
Fig. 3. SEM images of representative *Globigerinoides ruber* (white) shells from the North, Equatorial, and South Atlantic. Panel I: Whole shell images of *G. ruber* (white) from the Equatorial Atlantic (A&B from core RC24-11, C from core RC24-17), South Atlantic (D from core VM16-36), and North Atlantic (E&F from core VM27-261, G from core VM16-206, H from core VM19-308). Panel II: Further magnified images of features from shells from the Equatorial Atlantic (A&B correspond to region outlined in Panel I-A image; C&D correspond to regions outlined in Panel I-B image; all are from core RC24-11). Panel III: Further magnified images of shell surface images from shells from the North Atlantic (A corresponds to region outlined in Panel I-E image, core VM27-261; B corresponds to region outlined in Panel I-G image, core VM16-206). Overall, shells from the North and South Atlantic exhibit much better overall preservation than those from the Equatorial Atlantic.
4.2. Dissolution and Mg/Ca ratios in Globigerinoides ruber

G. ruber is one of the most susceptible species of planktonic foraminifera to dissolution (e.g. Adelseck, 1978; Berger, 1968; Thunell and Honjo, 1981), an issue that has major implications for using the Mg/Ca ratio of this species to estimate past SST. The partial dissolution of G. ruber shells can significantly bias Mg/Ca ratios due to the heterogeneous distribution of Mg within the shell and the higher solubility of Mg-rich calcite (Brown and Elderfield, 1996; Dekens et al., 2002). Laser ablation and electron microprobe mapping studies have shown that G. ruber shells contain Mg-enriched surface veneers (Bolton et al., 2011; Eggoins et al., 2003; Sadekov et al. 2005, 2008), so any loss of the surface structure of the shell due to dissolution would considerably impact the shell’s Mg/Ca ratio, yielding calibrated SSTs lower than they should be. This is likely true for the Equatorial Atlantic sites in our study, as the SEM images we obtained on shells from these locations show significant loss of surface layers (Fig. 3, Panel I-A-B, Panel II-A-D).

Several studies have developed methods to correct foraminiferal Mg/Ca ratios for the effect of dissolution by introducing correction terms into Mg/Ca:SST calibration equations. Dekens et al. (2002) developed separate calibration equations for G. ruber from the Atlantic and Pacific Oceans by adding a water depth-dependent dissolution correction term into the exponent of the calibration equation to account for the preferential dissolution of high-Mg foraminiferal calcite in undersaturated bottom waters. In the Atlantic, their study was based on three core-top depth transects: two sites from the Equatorial Atlantic and one from the South Atlantic. They found no evidence of dissolution at locations on the Rio Grande Rise in the South Atlantic where all cores were taken from above the lysocline (~4 km, Jones et al., 1984), but did find that dissolution significantly impacted G. ruber shells deeper than 3 km at their Equatorial Atlantic sites on the Ceara and Sierra Leone Rises (Dekens et al., 2002). Interestingly, Mg/Ca ratios from the Ceara Rise were offset to higher values than those from the Sierra Leone Rise even though modern observational SSTs at both sites are nearly identical. Dekens et al. (2002) speculated that this offset may be due to differences in the amount of organic matter in the sediments at the two locations, which would lead to differences in the degree of metabolically-induced dissolution. Indeed, the Sierra Leone Rise is located directly within the main high-productivity equatorial upwelling region off Northwest Africa, while the Ceara Rise is further west, away from the high-productivity region. This lends support to our hypothesis that metabolic CO2 generated from the oxidation of organic carbon in sediments is an important, and often times overlooked, driver of calcite dissolution. Based on the limited number of depth transects in the Atlantic, and the core-depths covered within their study, Dekens et al. (2002) concluded that the depth corrections in their calibration equations should only be applied to sediment deeper than ~2.8 km in the Equatorial Atlantic. Regenberg et al. (2006) extended the depth coverage of the Dekens et al. (2002) study to include core-tops from shallower depths from the Caribbean, but came to a similar conclusion regarding the depth at which a water-depth corrected calibration equation for G. ruber should be used (between 2.5 and 3 km).

Rosenthal and Lohmann (2002) developed a calibration equation for G. ruber containing a correction term where the preexponential constant is a function of size-normalized shell weights. Their study was based on a depth-transect from the Sierra Leone Rise in the eastern Equatorial Atlantic, one of the same locations used in the Dekens et al. (2002) study. The main difference between the approaches taken by Dekens et al. (2002) and Rosenthal and Lohmann (2002) is that the correction term developed by Rosenthal and Lohmann (2002) is not static and instead, can change temporally. This is important, especially for productivity-induced diagenetic dissolution, as the factors controlling dissolution in this manner can change with time under different nutrient and upwelling regimes. In addition, correcting for dissolution in this way is a culmination of all dissolution factors, as the final shell weight is the product of any dissolution that may have impacted the shell.

4.3. Conversion of Mg/Ca ratios to sea surface temperature

In their study, Arbuszewski et al. (2010) convert all of their core-top Mg/Ca values (spanning from 43°N to 25°S) to SST using the Dekens et al. (2002) dissolution-corrected Atlantic G. ruber equation:

\[ T (\degree C) = \ln(Mg/Ca/0.38)/0.09 + 0.61 \times \text{core depth (km)} \]  

(1)
However, as discussed in Section 4.2, the study by Dekens et al. (2002) was only able to constrain depth-induced dissolution in the equatorial Atlantic region, cautioning against the use of their dissolution-corrected calibration equation elsewhere. The results of our G. ruber shell weight analyses and SEM imaging of a number of the same cores used in the Arbuszewski et al. (2010) study indicate that there are large preservation differences between sites in the North and South Atlantic versus the Equatorial Atlantic within the same range of core depths. Sites in the North and South Atlantic appear to be only minimally affected by dissolution, at least for the range of core depths we have analyzed here. Therefore, the application of a calibration equation containing a constant dissolution correction results in artificially higher SSTs in the better preserved North and South Atlantic. Across the latitudinal transect of core-tops analyzed by Arbuszewski et al. (2010) from 43°N to 25°S, our results suggest that surface productivity may serve as a good latitudinal indicator of where a dissolution correction should be applied to sediments from cores above the lysocline. If we base our cutoff latitudes on the map of surface chlorophyll concentrations, inferred from ocean color measurements from the SeaWiFS project, as an indicator of regions that should experience a high rain of organic carbon to the sediments, this would fall between 15°N and 7°S (Fig. 4). Thus, we convert all Mg/Ca ratios for core-tops within this latitudinal band to SST using the Dekens et al. (2002) dissolution-corrected calibration equation for G. ruber (Eq. (1)), the same equation that was originally used by Arbuszewski et al. (2010). It is important to note that use of the Dekens et al. (2002) dissolution-corrected calibration equation (Eq. (1)) may not be the best equation to apply in situations where diagenetic dissolution appears to be the controlling dissolution factor, rather than the ΔCO$_2$ of bottom waters. However, as we were not able to obtain samples for all of the core-tops used in the Arbuszewski et al. (2010) study, use of the calibration equation developed by Rosenthal and Lohmann (2002) was not possible as application requires shell weight measurements for each sample, but this is an issue that should be explored in future work.

Unfortunately, we are unable to constrain the degree of preservation for cores deeper than ∼3.7 km in the North Atlantic and ∼3.6 km in the South Atlantic. Instead, if we assume that the main control on dissolution in these regions is the ΔCO$_2$ of bottom waters, we can use the depth of the lysocline (∼4 km in the Atlantic Ocean, Jones et al., 1984) as the depth below which dissolution is likely going to impact the G. ruber shells in these regions. For core depths above the lysocline north of 15°N and south of 7°S, we convert the Mg/Ca ratios obtained by Arbuszewski et al. (2010) to SST using the multi-planktonic species calibration equation developed by Anand et al. (2003):

$$T (°C) = \ln(\text{Mg}/\text{Ca}/0.38)/0.09$$

(2)

that is based on a sediment trap study from the Sargasso Sea in the subtropical North Atlantic. This equation has been used in many studies to convert G. ruber Mg/Ca ratios to SST, as calibrated core-top Mg/Ca-SSTs using this equation often better reflect modern surface water conditions (e.g. Lund and Curry, 2006; Schmidt and Lynch-Stieglitz, 2011; Schmidt et al., 2012a, 2012b).

Interestingly, this calibration equation is identical to the equation developed by Dekens et al. (2002) without the water-depth dissolution correction term, so in a sense, we are simply using Eq. (1) with no depth correction. For core-top depths that fall below the lysocline, we convert Mg/Ca ratios to SST using the Dekens et al. (2002) calibration Eq. (1). Thus, the main difference between our Mg/Ca-SST conversion and that done by Arbuszewski et al. (2010) is that we do not use a dissolution correction for core-tops above the lysocline north of 15°N and south of 7°S, as we have shown that the G. ruber shells from these areas have been only minimally affected by dissolution.

4.4. Comparison of Mg/Ca-SSTs with observational data

In order to determine how well the calibrated core-top Mg/Ca-SSTs track modern SST, modern observational data must be chosen that best represent the habitat in which the foraminifer was calcified. In the study by Arbuszewski et al. (2010), all core-top Mg/Ca-SSTs (calibrated using Eq. (1), Dekens et al., 2002) were compared to mean annual SST at 0 m water depth derived from the World Ocean Atlas, yielding a poor correlation with an r$^2$ of 0.19 (Fig. 5A). Arbuszewski et al. (2010) noted excessively high SST estimates in the northern and southern subtropics, and attributed this to the high salinities of the subtropical gyres. An “excess Mg/Ca” term was calculated, defined as the difference between the measured shell Mg/Ca ratio and the expected Mg/Ca ratio at the δ$^{18}$O$_{sw}$-corrected δ$^{18}$O calibration temperature (Arbuszewski et al., 2010). The expected Mg/Ca ratios were determined by substituting calculated isotopic temperatures into the Dekens et al. (2002) Mg/Ca-SST calibration equation. Isotopic temperatures were determined with the Bemis et al. (1998) low-light isotopic temperature equation, using measured δ$^{18}$O$_{v}$ values and δ$^{18}$O$_{sw}$ values estimated from a δ$^{18}$O$_{sw}$:salinity relationship derived from the global δ$^{18}$O$_{sw}$ database (Schmidt et al., 1999). When the “excess Mg/Ca” values were compared with mean annual salinity for each core site, a much higher correlation was noted, with an r$^2$ of 0.77 (Arbuszewski et al., 2010). While the “excess Mg/Ca” values were nearly zero in the equatorial region, the highest “excess Mg/Ca” values were found in the higher salinity subtropical gyre regions, with Mg/Ca ratios elevated by up to 1–2 mmol/mol above values expected from δ$^{18}$O calcification temperatures (Arbuszewski et al., 2010). This would lead to Mg/Ca-temperature estimates that can be biased by several degrees of Celsius (Arbuszewski et al., 2010). It is this logic that led Arbuszewski et al. (2010) to conclude that there is a large salinity effect on G. ruber Mg/Ca ratios for G. ruber from regions where salinities are in excess of 35.5.

Here we investigate the assumptions that led to these conclusions by Arbuszewski et al. (2010), and explore an alternative scenario which can greatly improve the correlation between the Mg/Ca-SSTs and modern observational data without a significant influence of salinity on the Mg/Ca ratios. The first assumption, as we have discussed in Section 4.3, is in regards to the calibration equation used by Arbuszewski et al. (2010) to convert their measured Mg/Ca ratios to SST. The second has to do with the observational data chosen to compare their Mg/Ca-SSTs with, mainly in regards to the depth habitat and calcification seasons for G. ruber (white). As stated earlier, Arbuszewski et al. (2010) compared their Mg/Ca-SSTs to the average annual SST at 0 m water depth. However, a number of studies have shown that the preferred depth habitat of G. ruber is ∼30 m, although they can be found in shallower depths, or even depths up to ∼100 m (Bé, 1960; Fairbanks et al., 1980, 1982; Schmucker and Schiebel, 2002). Therefore, comparing core-top G. ruber Mg/Ca-SSTs to temperatures at 0 m depth is not appropriate, and instead, should be compared to temperatures slightly deeper in the water column (30 m).

In addition, sediment trap studies have shown that the largest (and in some cases, only) flux of G. ruber occurs during the warmest months of the year in temperate latitudes (Bé, 1960; Deuser, 1987; Tolderlund and Bé, 1971). This makes sense, as G. ruber is predominantly a tropical species, calcifying throughout the year in the tropics. Thus, given the latitudinal extent of the transect used by Arbuszewski et al. (2010) spanning from 43°N to 25°S, not every core-top G. ruber Mg/Ca-SST value should be compared to average annual temperatures. As the temperate latitudes experience a wider annual range of temperatures, G. ruber Mg/Ca-SSTs for core-tops from these latitudes may appear too warm. Instead, we argue that G. ruber Mg/Ca-SSTs for core-tops from temperate latitudes should be compared to the average temperature of
Fig. 5. Combinations of observational and calibrated Mg/Ca temperatures for core-tops corresponding to the locations in Fig. 2 along the meridional transect. (A) Mean annual temperatures at 0 m water depth (black, solid line) plotted with Mg/Ca temperatures calibrated using the *Globigerinoides ruber* (white) Atlantic Ocean dissolution-corrected calibration equation of Dekens et al. (2002) (blue circles). These are the original observational data and calibrated Mg/Ca temperatures reported by Arbuszewski et al. (2010). Correlation between observed and calibrated temperatures yields an $r^2$ of 0.19. (B) Mean annual temperatures at 30 m water depth between 23°N and 23°S and mean temperatures of the three warmest months of the year at 30 m water depth north of 23°N and south of 23°S (black, broken line) plotted with Mg/Ca temperatures calibrated using the *G. ruber* (white) Atlantic Ocean dissolution-corrected calibration equation of Dekens et al. (2002) (blue circles). Correlation between observed and calibrated temperatures yields an $r^2$ of 0.29. (C) Mean annual temperatures at 0 m water depth (black, solid line) plotted with re-calibrated Mg/Ca temperatures (red squares) using the Mg/Ca ratios originally obtained by Arbuszewski et al. (2010). Mg/Ca ratios for core-tops between 15°N and 7°S (gray shaded region) and core-tops below the lysocline depth outside of this region were calibrated using the Dekens et al. (2002) *G. ruber* (white) Atlantic Ocean dissolution-corrected calibration equation. For core-tops above the lysocline north of 15°N and south of 7°S, Mg/Ca ratios were calibrated using the Anand et al. (2003) multi-planktonic species calibration equation derived from a Sargasso Sea sediment trap study. Correlation between observed and calibrated temperatures yields an $r^2$ of 0.63. (D) Mean annual temperatures at 30 m water depth between 23°N and 23°S and mean temperatures of the three warmest months of the year at 30 m water depth north of 23°N and south of 23°S (black, broken line) plotted with re-calibrated Mg/Ca temperatures (red squares). Correlation between observed and calibrated temperatures yields an $r^2$ of 0.69. Observational data were obtained from the World Ocean Atlas 2005 (Locarnini et al., 2006). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
the 3 warmest months of the year, using ~23°N/S as a cutoff for the temperate latitudes.

Taking these factors into account, we compute correlations between different combinations of the originally calibrated Mg/Ca-SSTs and average annual temperatures at 0 m depth of Arbuszewski et al. (2010), and our re-calibrated Mg/Ca-SSTs and a combination of average annual temperatures at 30 m depth in the tropics and average temperature of the 3 warmest months of the year at 30 m depth in the temperate latitudes (Fig. 5). Correlation of the Mg/Ca-SSTs calculated from only the Dekens et al. (2002) calibration equation with average annual temperatures at 0 m depth yields an $r^2$ of 0.19 (the correlation reported by Arbuszewski et al., 2010) (Fig. 5A), while correlation with our seasonal/depth weighted temperatures is slightly stronger, yielding an $r^2$ of 0.29 (Fig. 5B). Instead, the correlations are greatly improved when using our re-calibrated Mg/Ca-SSTs. We calculated an $r^2$ of 0.63 when comparing our re-calibrated Mg/Ca-SSTs with the average annual temperatures at 0 m depth (Fig. 5C), but the strongest correlation is noted ($r^2 = 0.69$) when comparing our re-calibrated Mg/Ca-SSTs with seasonal/depth weighted temperatures (Fig. 5D). Thus, using a combination of calibration Eq. 1 (Dekens et al., 2002) and Eq. 2 (Anand et al., 2003) is the single factor that has the greatest increase in correlation with observational temperatures. Comparison of our re-calibrated Mg/Ca-SSTs with seasonal/depth weighted observational temperatures further improves the correlation. Although the correlation is not perfect, given the uncertainty in our proposed latitudinal and depth constraints for choice of calibration equation, the uncertainty in stratigraphic control of the core-tops used by Arbuszewski et al. (2010) described in Section 2.1, and the error uncertainty on the measured, Mg/Ca ratios and calibrated Mg/Ca-SSTs ($\pm 1.2^\circ C$, Dekens et al., 2002; $\pm 1.1^\circ C$, Anand et al., 2003), we feel that G. ruber Mg/Ca ratios are a robust proxy for SST, and are not significantly altered in regions of high salinity. In addition, the “excess Mg/Ca” term calculated by Arbuszewski et al. (2010) is based on the assumption that calculated isotopic calcification temperatures are perfect recorders of surface ocean conditions, yet our re-calibrated Mg/Ca-SSTs are more strongly correlated with surface ocean conditions than isotopic calcification temperatures ($r^2 = 0.69$ versus an $r^2 = 0.65$ on their isotopic calcification temperatures, Arbuszewski et al., 2010). Therefore, we believe that the large salinity effect on G. ruber Mg/Ca ratios determined by Arbuszewski et al. (2010) was an artifact of the choice of calibration equation used, whereby using a dissolution-corrected calibration equation for samples that were not affected by dissolution led to artificially high Mg/Ca-SSTs in the subtropical regions. As these samples were from regions with significantly higher sea surface salinities, it appeared that high Mg/Ca-SSTs were related to salinity. In addition, comparison of the Mg/Ca-SSTs from the higher-salinity regions to annual, rather than seasonal SSTs, led these samples to appear even warmer.

4.5. Comparison of Mg/Ca-SSTs with $\delta^{18}O_c$-SSTs

Although we have resolved the issue reported by Arbuszewski et al. (2010) of elevated Mg/Ca-SSTs in the Atlantic subtropics, the offset between Mg/Ca-SSTs and isotopic calcification temperatures ($\delta^{18}O_c$-SSTs) along the transect that was described by Arbuszewski et al. (2010) (Fig. 6A) also requires closer examination. In order to translate G. ruber $\delta^{18}O_c$ measurements into temperature, Arbuszewski et al. (2010) used the equation of Bernis et al. (1998):

$$T \ (^\circ C) = 16.5 - 4.90 \times (\delta^{18}O_c - \delta^{18}O_{sw} - 0.27\%o)$$ (3)

that is based on culturing experiments of the foraminifera *Orbulina universa* grown under low-light conditions. In Eq. (3), $\delta^{18}O_c$ is the measured G. ruber isotopic composition relative to Pee-Dee Belemnite (PDB), $\delta^{18}O_{sw}$ is the seawater isotopic composition relative to standard mean ocean water (SMOW), with the $-0.27\%o$ term correcting for the $\delta^{18}O$ difference between SMOW and PDB (Hut, 1987). In their calculation of $\delta^{18}O_{sw}$ along the meridional transect, Arbuszewski et al. (2010) estimated $\delta^{18}O_{sw}$ based on a single relationship between surface ocean salinity and $\delta^{18}O_{sw}$ (0–50 m) of $\delta^{18}O_{sw} = 0.238^\circ$ salinity – 7.69, created from the NASA global seawater $\delta^{18}O_{sw}$ database (Schmidt et al., 1999). Mean annual salinity values at 0 m in the water column were then used to compute $\delta^{18}O_{sw}$ for each core site along the transect (Arbuszewski et al., 2010).

Comparison of the resulting calcification temperatures with mean annual surface (0 m) temperatures yields an $r^2$ of 0.65, as reported by Arbuszewski et al. (2010). As noted earlier, our re-calibrated Mg/Ca-SSTs are more strongly correlated with surface ocean conditions than isotopic calcification temperatures ($r^2 = 0.69$). Moreover, our re-calibrated Mg/Ca-SSTs are more strongly correlated to $\delta^{18}O_c$-SSTs, with $r^2$ of 0.43 (Fig. 6B), significantly higher than the $r^2$ of 0.09 reported by Arbuszewski et al. (2010), when comparing $\delta^{18}O_{sw}$-SSTs with their Mg/Ca-SSTs that were calculated using only the Dekens et al. (2002) Mg/Ca-SST calibration equation (Fig. 6A).

It is worth noting that correlation of the Arbuszewski et al. (2010) $\delta^{18}O_{sw}$-SSTs with our combination of seasonal/annual temperatures at 30 m depth along the transect yields an $r^2$ value of 0.44, lower than the $r^2$ of 0.65 between calcification temperatures and mean annual surface (0 m) temperatures. This is in contrast to the stronger correlation between Mg/Ca-SSTs and seasonal/annual temperatures at 30 m depth than mean annual temperatures at 0 m depth. We hypothesize that this discrepancy is due to calculation of $\delta^{18}O_{sw}$ values based on a single $\delta^{18}O_{sw}$: salinity relationship across the entire transect that may have removed distinct latitudinal differences in the slope and fresh water end member of the relationship (Fairbanks et al., 1992), and/or may have removed regional seasonal and depth differences in the relationship. See Hönisch et al. (2013) for additional factors that may affect the correlation between the Arbuszewski et al. (2010) $\delta^{18}O_c$-SSTs and observational and Mg/Ca-SSTs.

5. Conclusions

Our results suggest that application of a single dissolution-corrected Mg/Ca-SST calibration equation for G. ruber (Dekens et al., 2002) is not valid across the entire Atlantic Basin given the excellent preservation of shells in the oligotrophic gyre regions. Basin-wide application of a dissolution-corrected calibration equation leads to artificially high Mg/Ca-SSTs in the subtropical gyre regions. However, a dissolution-corrected calibration equation for G. ruber is needed in the high-productivity equatorial upwelling region where there is evidence for significant shell dissolution, even at core depths above the lysocline. In addition, for core depths below the lysocline in the subtropics, a dissolution-corrected calibration equation for G. ruber still appears to be required. It is important to note that the boundaries for application of different calibration equations that we have discussed are a first attempt to do this, and additional work needs to be done to better define the oceanographic locations and conditions under which different calibration equations should be used. Therefore, taking into account usage of appropriate calibration equations and comparison to temperatures based on realistic G. ruber growth seasons and depth habitats, we find invoking a large salinity effect on G. ruber Mg/Ca ratios is unnecessary. We thus are able to reconcile the core top Mg/Ca data reported in Arbuszewski et al. (2010) with culturing experiments that found salinity has only a minor influence on foraminiferal Mg/Ca ratios.
Comparison of isotopic calcification temperatures with Mg/Ca-SSTs. (A) Isotopic calcification temperatures ($\delta^{18}$Oc-SSTs) (green triangles) calculated by Arbuszewski et al. (2010) plotted with Mg/Ca temperatures calibrated using the Globigerinoides ruber (white) Atlantic Ocean dissolution-corrected calibration equation of Dekens et al. (2002) (blue circles). Correlation between isotopic and Mg/Ca temperatures yields an $r^2$ of 0.09 (Arbuszewski et al., 2010). (B) Isotopic calcification temperatures ($\delta^{18}$Oc-SSTs) (green triangles) calculated by Arbuszewski et al. (2010) plotted with re-calibrated Mg/Ca temperatures (red squares) (see Fig. 5C caption for description). Correlation between isotopic and Mg/Ca temperatures yields an $r^2$ of 0.43. Also shown are seasonal/depth weighted observational temperatures (black, broken line).

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