The influence of salinity on Mg/Ca in planktic foraminifers – Evidence from cultures, core-top sediments and complementary Δ18O

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Abstract

The Mg/Ca ratio in foraminiferal calcite is one of the principal proxies used for paleoceanographic temperature reconstructions, but recent core-top sediment observations suggest that salinity may exert a significant secondary control on planktic foraminifers. This study compiles new and published laboratory culture experiment data from the planktic foraminifers Orbulina universa, Globigerinoides sacculifer and Globigerinoides ruber, in which salinity was varied but temperature, pH and light were held constant. Combining new data with results from previous culture studies yields a Mg/Ca-sensitivity to salinity of 4.4 ± 2.3%, 4.7 ± 1.2%, and 3.3 ± 1.7% per salinity unit (95% confidence), respectively, for the three foraminifer species studied here. Comparison of these sensitivities with core-top data suggests that the much larger sensitivity (27 ± 4% per salinity unit) derived from Atlantic core-top sediments in previous studies is not a direct effect of salinity. Rather, we suggest that the dissolution correction often applied to Mg/Ca data can lead to significant overestimation of temperatures. We are able to reconcile culture calibrations with core-top observations by combining evidence for seasonal occurrence and latitude-specific habitat depth preferences with corresponding variations in physico-chemical environmental parameters. Although both Mg/Ca and Δ18O yield temperature estimates that fall within the bounds of hydrographic observations, discrepancies between the two proxies highlight unresolved challenges with the use of paired Mg/Ca and Δ18O analyses to reconstruct paleo-salinity patterns across ocean basins. The first step towards resolving these challenges requires a better spatially and seasonally resolved Δ18Osw archive than is currently available. Nonetheless, site-specific reconstructions of salinity change through time may be valid.

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1. INTRODUCTION

The oxygen isotopic composition (Δ18Oforam) and Mg/Ca ratios of planktic foraminifer tests are among the most commonly applied proxies for reconstructing past ocean temperature. The theoretical basis for Δ18O in marine carbonates as a temperature proxy is rooted in the temperature-dependent bonding characteristics of oxygen isotopes (Urey, 1947). Application of the Δ18Oforam proxy in sediment and laboratory studies requires accounting for variations in the oxygen isotopic composition of seawater (Δ18Osw), photosynthetic
activity in symbiont-bearing species, and marine carbonate chemistry (for a summary, see Bernis et al., 1998). In contrast, the mechanism underlying the temperature sensitivity of Mg/Ca is not as well understood. The substitution of Mg$^{2+}$ into marine calcites is thermodynamically favored at higher temperatures (Chave, 1954; Mucci, 1987; Oomori et al., 1987; Koziol and Newton, 1995), but the observed temperature response in foraminiferal calcite is much larger than predicted by theory (i.e. 9% per °C versus 1–3% per °C, Lea et al., 1999; Anand et al., 2003). In addition, planktic foraminifers discriminate heavily against the incorporation of Mg$^{2+}$ into their calcite skeletons, such that their Mg/Ca ratio is 1–2 orders of magnitude lower (e.g., Lea et al., 1999) than inorganically precipitated calcite (Oomori et al., 1987). The discrepancy between theory and observations indicates that the empirical relationship is influenced by additional environmental parameters and/or physiological vital effects.

Laboratory culture experiments that isolate the effects of individual environmental parameters have been used to identify secondary controls on Mg/Ca uptake into planktic foraminifer tests. For instance, Lea et al. (1999) observed a negative relationship between seawater-pH and Mg/Ca uptake, although it was later determined that this effect is greater at lower-than-modern seawater-pH (Russell et al., 2004). Laboratory culture experiments have also established that salinity exerts a small effect on Mg/Ca, which increases by 4–8% per salinity unit (Nürnberg et al., 1996; Lea et al., 1999; Ksakürek et al., 2008; Duenas-Bohórquez et al., 2011). Recent core-top sediment studies, however, suggest that the Mg/Ca sensitivity to salinity is much greater than that measured in culture experiments, up to 59% per salinity unit (Ferguson et al., 2008; Mathien-Blard and Bassinot, 2009; Arbuszewski et al., 2010). Although data by Ferguson et al. (2008) have been questioned due to the presence of a Mg-rich post-depositional calcite precipitate on Mediterranean foraminifer tests (Hoogakker et al., 2009; Mathien-Blard and Bassinot, 2009), the comprehensive study by Arbuszewski et al. (2010) suggests a large 27% sensitivity to salinity for the tropical planktic foraminifer Globigerinoides ruber where ambient salinity exceeds 35. This latter assessment was based on a comparison of Mg/Ca and δ18O_foram data obtained from the same samples of pooled foraminifera tests, in which δ18O_foram compositions appeared to agree with mean annual SST (Arbuszewski et al., 2010). Arbuszewski et al. (2010) quantified the salinity effect by calculating ‘Mg-excess’: i.e. that part of the Mg/Ca-signal that deviates from δ18O_foram-temperature estimates. They also derived an independent Mg/Ca sensitivity to temperature of 4.8 ± 0.8% per °C, which is ~50% of the temperature sensitivity observed in culture experiments and less than 20% of their inferred salinity control.

In this study we present data from a suite of new culture experiments to verify and extend previous experimental results used to establish the salinity dependence of foraminiferal Mg/Ca. Because our new data corroborate previous laboratory results, we present a detailed analysis of alternative ecophysiological explanations for the core-top sediment results of Arbuszewski et al. (2010) and Mathien-Blard and Bassinot (2009), which is based on known temperature, salinity and biological effects on these proxies. Instead of a strong salinity effect on Mg/Ca, we find that both Mg/Ca and δ18O_foram-derived temperatures of G. ruber are consistent with its preference for growth during the warm summer season at higher latitudes.

2. METHODS

2.1. Planktic foraminifer culturing

The temperate-subtropical Orbulina universa and tropical Globigerinoides sacculifer and G. ruber (pink) were cultured at the Wrigley Institute for Environmental Studies (WIES) on Santa Catalina Island, California, in July/August 2008, and at the University of Puerto Rico’s Marine Sciences Center on Isla Maguayez (MSCIM) during March and April 2010, respectively. The experiments are the same as described in Allen et al. (2011, 2012). Juvenile foraminifers were hand-collected by SCUBA divers either 3 (WIES) or 13 km (MSCIM) offshore and at 3–5 m water depth. Immediately after collection foraminifers were brought to the laboratory, where each individual was identified and its largest test dimension measured by light microscopy. If the foraminifers did not already hold prey in their spines, they were fed a 1-day old brine shrimp (Artemia salina). Specimens were then transferred into individual culture jars that contained the experimental seawater. Jars were sealed with Parafilm® and tight-fitting lids to prevent gas exchange and evaporation.

The seawater used in these experiments was collected at the dive sites, filtered (0.45 µm), and salinity modified by either adding deionized water to reduce salinity or by partial evaporation under a heat lamp to increase salinity. Salinity was measured with an Orion Star Thermo Scientific conductivity meter (salinity resolution = ±0.1) and ranged between 29.9 and 35.4 in the O. universa experiments, and between 33.0 and 40.0 in the G. sacculifer and G. ruber experiments. In addition to salinity, we also measured alkalinity and pH at the beginning and end of each experiment using a Metrohm 809 open cell autotitrator and pH meter calibrated against NIST buffers and Dickson-certified alkalinity standards. The culture jars were then placed in circulating temperature-controlled water baths, where temperature was kept at 22 ± 0.3 °C in the O. universa experiments and at 26 ± 0.3 °C in the G. sacculifer and G. ruber experiments (Table 1). These conditions are similar to the seawater temperature measured during foraminifer collection at the respective sites. The constancy of the temperature in the baths was monitored by HOBO TidbiT® temperature loggers every 5 min. Because all three species are symbiont-bearing, the baths were illuminated on a 12-h light/dark cycle with cool-white fluorescent lamps, whose output (>300 µmol photons m⁻² s⁻¹) exceeded the light saturation level (Pmax) of the symbionts (Jorgensen et al., 1985; Rink et al., 1998). Light levels were monitored with a Biospherical Instruments QSL-2200 scalar PAR irradiance sensor. Foraminifers were observed daily with a hand lens and fed a freshly hatched brine shrimp every other day until each individual underwent gametogenesis. At that
Table 1
Mg/Ca results from these and previously published culture experiments.

<table>
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<tr>
<th></th>
<th>Salinity (˚C)</th>
<th>Temperature (˚C)</th>
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<th>Analytical uncertainty (mmol/mol)</th>
<th>Mg/Ca_T (mmol/mol)</th>
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Data from this study are based on pooled, culture-grown chambers of 20 G. sacculifer specimens, 50 G. ruber specimens and 15 O. universa specimens. For this study, Duenas-Bohórquez et al. (2011), Kasákůrek et al. (2008), and Lea et al. (1999), the reported analytical uncertainties reflect long-term analytical RSD (2σ), 1 SD of measurements on multiple specimens, 1 SD based on repeat measurements of an in-house standard, and 1 SD of measurements on multiple specimens, respectively. Mg/Ca_T values have been normalized to a single temperature: 26 °C for G. sacculifer and G. ruber (according to Nürnberg et al. (1996) and Kasákůrek et al. (2008), respectively) and 22 °C for O. universa (according to Russell et al. 2004). Mg/Ca_CaT values have been normalized to [CO_3^{2-}] = 200 μmol kg^{-1} according to the equation provided by Russell et al. (2004). For O. universa data from Lea et al. (1999), where carbonate ion concentrations were not reported, [CO_3^{2-}] was calculated from reported pH and alkalinity estimated from the general salinity-alkalinity relationship at Catalina Island of 68 μmol kg^{-1} alkalinity per salinity unit.

2.2. Sample preparation and analysis

The archived foraminifer tests contain chambers that were grown in the ocean prior to collection and chambers that were grown under controlled conditions in the laboratory. Because the juvenile trochospiral test of O. universa is very thin and often gets absorbed entirely as the final spherical chamber is secreted, it contributes ≤5% to the final test weight (Spero and Deniro, 1987) and is thus considered negligible for the bulk test chemistry. In contrast, the G. sacculifer and G. ruber trochospiral test that grew prior to collection may have substantial mass, so the chambers grown in the laboratory need to be isolated from chambers precipitated in the ocean. We accomplished this by amputating all chambers that increased the test size beyond the initial collection measurement with a scalpel. The amputated chambers were then pooled to form individual samples (Spero and Lea, 1993). Each sample thus combines the laboratory-grown chambers of approximately 20 specimens of G. sacculifer, 50 G. ruber and 15 O. universa. O. universa tests were crushed between two glass slides prior to cleaning to expose interior surfaces.

The cleaning procedure followed Russell et al. (2004) and comprised rinsing with MilliQ water to remove fine particles, and two oxidation steps for 30 min with hot...
samples were rinsed 5 times with MilliQ and leached 3 times. Following oxidation, samples were rinsed 5 times with MilliQ and leached 3 times with 0.001 N HNO₃ to remove any re-adsorbed ions.

Elemental analyses of O. universa tests were carried out by Inductively Coupled Plasma Mass Spectrometry (ICP-MS, PerkinElmer SCIEX Elan DRC II) in the Godwin Laboratory at Cambridge University (Yu et al., 2005; Allen et al., 2011) and G. sacculifer and G. ruber samples were analyzed on a Sector-Field Inductively Coupled Plasma Mass Spectrometer (Thermo Scientific Element XR) at Rutgers University (Tali Babila, pers. comm., Allen et al., 2012). Consistency standards were prepared gravimetrically with MilliQ and measured every 3–5 samples (Yu et al., 2005). The long-term relative standard deviation (RSD, 2σ) for Mg/Ca in the Cambridge and Rutgers laboratories is 2.8% and 2.0%, respectively.

3. RESULTS

Table 1 and Fig. 1 present the Mg/Ca ratios of cultured O. universa, G. sacculifer and G. ruber relative to experimental seawater salinity. This compilation combines our new data with previously published culture solution chemistry data by Lea et al. (1999) for O. universa, and by Kissákurek et al. (2008) for G. ruber, as well as laser ablation calibrations and electron micro probe analyses for G. sacculifer by Duenas-Bohórquez et al. (2011) and Nürnberg et al. (1996), respectively. Despite some differences in culturing, cleaning and analytical techniques, the calibrations display consistent patterns in both absolute Mg/Ca values and sensitivity of Mg/Ca to salinity. The following exponential regressions combine published and new culture data, although we restrict the G. sacculifer regression to our new solution chemistry data and the final (19th) chamber laser ablation data by Duenas-Bohórquez et al. (2011). Linear regressions of these data yield similar sensitivities but we prefer exponential regressions, where the percentage change is fixed over the entire Mg/Ca range and the representation of the sensitivity is thus unambiguous.

\[ G. ruber \text{(pink and white): } \frac{\text{Mg}}{\text{Ca}} = 1.29 \pm 0.83 e^{0.033 \pm 0.017} \cdot S, \quad R^2 = 0.80 \]  
(1)

\[ G. sacculifer: \quad \frac{\text{Mg}}{\text{Ca}} = 0.75 \pm 0.34 e^{0.047 \pm 0.012} \cdot S, \quad R^2 = 0.95 \]  
(2)

\[ O. universa: \quad \frac{\text{Mg}}{\text{Ca}} = 1.95 \pm 0.53 e^{0.044 \pm 0.023} \cdot S, \quad R^2 = 0.70 \]  
(3)

These equations indicate a Mg/Ca sensitivity to salinity of 3.3 ± 1.7% per salinity unit for G. ruber, 4.7 ± 1.2% for G. sacculifer and 4.4 ± 2.3% for O. universa (±95% confidence interval). If the 18th chamber data for G. sacculifer (Duenas-Bohórquez et al., 2011) were included, the Mg/Ca sensitivity to salinity in G. sacculifer would be even smaller. Results of Nürnberg et al. (1996) are based on a single chamber per salinity condition and therefore are not included in the regression. Calibrations using only our new data are similar to those including both new and published data (Suppl. Table S1).

Because some previous culture studies performed salinity experiments at slightly different ambient temperatures, we also tested these regressions after normalizing the Mg/Ca ratio of each foraminifer species to a consistent temperature using published temperature sensitivities established in laboratory culture (Table 1). The temperature differences between experiments are small and regressions using original and temperature-normalized Mg/Ca data agree within 95% confidence bounds (Table S1). Because temperature corrections introduce additional uncertainty, we apply regressions using the original data (not temperature-normalized) throughout the rest of the manuscript.

4. DISCUSSION

4.1. Mg/Ca sensitivity to salinity

The three foraminifer species studied in laboratory experiments incorporate different amounts of Mg into their tests, but the effect of salinity, i.e. 3–5% per salinity unit, is consistent among the three species. This suggests that the process causing the salinity dependence is proportional to the Mg content of the shell. Importantly, the salinity effects observed in the laboratory are at least 5x smaller than the 27% sensitivity to salinity inferred from G. ruber tests from Atlantic sediments (Arbuszewski et al., 2010) (Fig. 2). To investigate the cause of this disagreement, we first consider whether culture experiments may have overlooked a larger sensitivity to salinity due to limitations in the experimental design.

Although the experimental seawater modification should concentrate all ions equally with increasing salinity, seawater evaporation at elevated temperature may lead to the degassing of some CO₂, thus lowering the total concentration of dissolved inorganic carbon (DIC) and changing the relative concentrations of alkalinity to DIC. For example, in the G. ruber experiments alkalinity increased by 426 µmol kg⁻¹ between low and high salinity treatments, but DIC only by 313 µmol kg⁻¹ (Allen and Hönisch, 2012; Allen et al., 2012). This corresponds to a [CO₂]⁺ increase with salinity in the culture experiments by 81 µmol kg⁻¹, an effect that would not be observed in the natural ocean under conditions of constant temperature, pressure and acidity. Because Russell et al. (2004) observed a negative relationship between Mg/Ca in O. universa and the symbiont-barren Globigerina bulloides when [CO₂]⁺ falls below 200 µmol kg⁻¹, the experimental variation in [CO₂]⁺ could have caused a bias. No Mg/Ca-[CO₂]⁺ calibrations have been published for G. sacculifer and G. ruber, and we therefore tested the effect of [CO₂]⁺ by normalizing the O. universa Mg/Ca data to [CO₂]⁺=200 µmol kg⁻¹, using the equation of Russell et al. (2004). The Mg/Ca sensitivity to salinity in O. universa then increases to 6.6 ± 2.5%. Because the uncertainties in our O. universa
culture data (Fig. 1) are relatively large and the carbonate ion effect is not very well resolved below 200 μmol kg⁻¹ (Russell et al., 2004), we consider this adjusted sensitivity the upper bound of the salinity influence, which is still much smaller than the 27% sensitivity observed for G. ruber from core-top sediments.

Synergistic effects may exist between temperature and the Mg/Ca sensitivity to salinity. It is plausible that the

Fig. 1. Results from laboratory culture calibrations of Mg/Ca versus salinity in three species of planktic foraminifers. Closed symbols indicate new data presented herein, where each data point represents a solution chemistry analysis of pooled culture-grown chambers of 15–50 individual foraminifers. Similarly, G. ruber data by Kısakürek et al. (2008) were measured by solution chemistry on 2–6 pooled specimens. Globigerinoids saccular data by Duenas-Bohórquez et al. (2011) were measured on multiple individual chambers by laser ablation; data by Nürnberg et al. (1996) are based on repeat microprobe measurements of one chamber per sample. Error bars represent the analytical uncertainties reported by original studies, as listed in Table 1. Culture temperatures differ slightly between studies and are indicated in the legend. The larger temperature ranges for G. ruber and G. sacculifer experiments have little effect on the regressions (Table S1).

Fig. 2. Excess Mg/Ca in G. ruber tests from sediment trap and core-top observations (grey symbols), and Mg/Ca ratios from laboratory cultures (black symbols). Excess Mg/Ca is defined as the part of the Mg/Ca signal that cannot be explained by average annual SST and δ¹⁸Osw at the core sites (Arbuszewski et al., 2010). The grey line defines the linear regression through Arbuszewski’s core-top data across the salinity range 35–37; the black line is the regression through the combined G. ruber culture data of this study and Kısakürek et al. (2008).
mechanism responsible for lowering [Mg] in the calcifying fluid is reduced under higher Mg activities in seawater, resulting in even greater Mg incorporation at higher temperatures under elevated salinity. Testing such effects would require an experimental design where both salinity and temperature are varied systematically, but such experiments have not yet been conducted. The existence of a synergistic temperature-salinity effect cannot be ruled out at this time; however, in the absence of a theoretical basis or empirical evidence for such an influence on Mg/Ca we will assume that temperature-salinity amplifications do not play a significant role here.

We therefore conclude that the design of the culture experiments is unlikely to have caused underestimation of the salinity effect on Mg/Ca, and that the culture data cannot be reconciled with the core-top data in this way.

4.2. Comparison with core-top sediments

Recognizing that geochemical data from core-top sediments are subject to multiple uncertainties, Arbuszewski et al. (2010) and Mathien-Blard and Bassinot (2009) established comprehensive core-top data sets of Mg/Ca and δ18O_foram in tests of the tropical-subtropical, symbiont-bearing G. ruber. To gain insight into the controls on these temperature pressures, both studies compared Mg/Ca and δ18O_foram from the same samples and assumed that the oxygen isotopic composition recorded in G. ruber tests can be used as a reference for evaluating the Mg/Ca temperature computation (e.g., Mulitza et al., 1998; Peet et al., 2002; Schmidt and Mulitza, 2002). Here we follow a different approach and do not try to align the proxies with mean annual SST, but rather apply experimentally determined sensitivities to these proxies in order to compare the difference between proxy estimates and oceanographic data, and to assess the ecophysiology of G. ruber. From now on we will refer to Mg/Ca temperatures estimates as ‘Mg/Ca-Ts’ and to δ18O_foram temperature estimates as ‘δ18O_foram-Ts’.

To identify which parameter(s) could be responsible for the observed Mg/Ca difference in salinity sensitivity between cultured and core-top specimens, we review the calibrations and assumptions applied by Arbuszewski et al. (2010) and Mathien-Blard and Bassinot (2009). Both studies assumed that G. ruber lives in the surface ocean (0–50 m), but each made different choices regarding foraminifer size, dissolution correction and δ18O_ws estimation. For instance, Arbuszewski et al. (2010) analyzed tests in the 250–355 μm size class, cleaned them following the procedures outlined by Boyle and Keigwin (1985/1986) and Barker et al. (2003) including a reductive cleaning step, applied a depth-dependent dissolution correction (Dekens et al., 2002) to their Mg/Ca-Ts, and used a linear regression for Atlantic sea surface salinity (SSS) and δ18O_ws data (Schmidt et al., 1999) to estimate the local sea surface δ18O_ws. In comparison, Mathien-Blard and Bassinot (2009) selected tests in the 250–315 μm size class, cleaned them following the procedure of Barker et al. (2003) (i.e. without a reductive cleaning step), applied a Mg/Ca temperature calibration without dissolution correction (Anand et al., 2003), and selected local sea surface δ18O_ws from the gridded data set of LeGrande and Schmidt (2006). The equations used for translating foraminiferal δ18O_foram to temperature yield relatively similar results, where Arbuszewski et al. (2010) used the low light equation established for O. universa (Benis et al., 1998) and Mathien-Blard and Bassinot (2009) the Uvigerina equation of (Shackleton, 1974). Following Arbuszewski et al. (2010), Mg/Ca data from Mathien-Blard and Bassinot (2009) were reduced by 10% to account for the lack of a reductive cleaning step. In the following discussion we will first evaluate the effect of the depth correction on Mg/Ca, then infer potential depth habitats from Mg/Ca-Ts, followed by an evaluation of the choice of δ18O_ws and the δ18O_foram-temperature equation. We conclude our assessment with an analysis of seasonal habitat preferences of G. ruber.

4.2.1. Depth correction on Mg/Ca

The depth correction applied by Arbuszewski et al. (2010) is based on the longstanding observation that Mg/Ca in planktic foraminifer tests is prone to partial dissolution in the sediment (Savin and Douglas, 1973; Lorens et al., 1977; Russell et al., 1994; Brown and Elderfield, 1996; Rosenthal et al., 2000; Rosenthal and Lohmann, 2002; Dyez and Ravelo, 2013). Arbuszewski et al. (2010) used the approach of Dekens et al. (2002), who assessed dissolution using specimens picked from core-top sediments along several depth transects. Dekens et al. (2002) performed a multivariate best-fit analysis and derived a Mg/Ca-temperature calibration for G. ruber that has subsequently been verified by the sediment trap calibration of Anand et al. (2003) but the Dekens calibration includes a depth correction for samples obtained deeper than 2.8 km in the Atlantic Ocean. We reevaluate this depth correction applied to G. ruber and G. sacculifer based on the depth transects studied by Dekens et al. (2002). Fig. 3 shows the original Mg/Ca data, which display relatively constant Mg/Ca values in the Atlantic Ocean, where a significant decrease in Mg/Ca is only observed in the deepest cores of the Ceara Rise (at 4.4 km water depth) and the Sierra Leone Rise (at 5.1 km water depth). Similar observations have been made by Rosenthal and Boyle (1993), who studied Mg/Ca in the same three foraminifer species from the Sierra Leone Rise and observed no change in Mg/Ca above 4.5 km water depth. In contrast, Regenberg et al. (2006) found clear evidence for decreasing Mg/Ca in Caribbean core-tops >3000 m water depth. Because the Caribbean is an enclosed basin, we focus our evaluation on open ocean records here.

The depth-corrected Mg/Ca-Ts for G. ruber and G. sacculifer from Dekens et al. (2002) are shown in the lower panels of Fig. 3 as a deviation from local SST: i.e. ΔTdepth corrected = TT_Mg/Ca depth corrected – SST. All depth-corrected data in the Atlantic (i.e. water depths >2.8 km but above 4.4 km) produce higher temperature estimates than sediments unaffected by dissolution from <2.8 km water depth. Furthermore, Mg/Ca-Ts from the deepest cores (>4.5 km water depth) are cooler than the shallowest samples from the same transect, indicating the applied correction is too small. This observation is
consistent with estimates of carbonate saturation ($\Delta$CO$_3^{2-}$, upper panels in Fig. 3), which indicate that bottom water is in fact supersaturated down to $\sim$4.4 km and thus suggest favorable conditions for calcite preservation. It appears that the dissolution correction applied to Atlantic cores results in: (1) temperature overestimates for water depths between 2.8 and 4.4 km, and (2) temperature underestimates for the deepest cores ($>$4.4 km). Based on these observations we suggest that a depth correction may not be appropriate here. Establishing and applying a depth correction at these sites requires independent verification of actual dissolution, for instance by scanning electron microscopic examination of test surface structures and size-normalized shell weights.

The Atlantic latitudinal transect of Arbuszewski et al. (2010) encompasses 64 sediment cores, of which only two cores are from a water depth shallower than 2.8 km, and four cores from water depths $>$4.4 km. It follows from above that the dissolution-corrected Mg/Ca-Ts for the majority of cores in this transect likely exceed actual calcification temperatures, whereas the four deepest cores may underestimate calcification temperature. To address this potential artifact, we apply the multispecies temperature equation of Anand et al. (2003):

$$\text{Mg/Ca} = 0.38 \times (\text{SST} - 0.09)$$

and remove the need for making any depth correction for dissolution by excluding the four sediment cores $>$4.4 km water depth, and a small number of additional cores (VM22-202, VM26-100, VM26-102 and VM27-161) which are from $>$4.3 km depth and bathed in undersaturated or nearly undersaturated ($\Delta$CO$_3^{2-} = -7.5$ to $+3.2 \mu$mol kg$^{-1}$) bottom waters (Arbuszewski et al., 2010).

By omitting the depth correction entirely, it is possible that some temperatures are now underestimated. Better verification of the preservation state is clearly warranted.
but here we focus on the open ocean observations described in Fig. 3, which suggest little or no dissolution in sediment cores <4.4 km water depth. As noted previously by Arbuszewski et al. (2010), the shape of the calcification temperature profile with latitude changes little when the depth correction is omitted; however, each temperature estimate is on average ~2°C cooler than the depth-corrected temperature estimates (Fig. 4a and b).

4.2.2. Foraminiferal depth habitat and salinity normalization

Because Arbuszewski et al. (2010) correct their data for dissolution, some of their Mg/Ca-Ts exceed the highest sea surface temperatures reported in oceanographic data bases (Fig. 4a), leading them to conclude that this offset may be explained by salinity. However, after eliminating the dissolution correction (Fig. 4b) and normalizing Mg/Ca to S = 35.4 using Eq. (1) (Fig. 4c and d), we find G. ruber Mg/Ca-Ts fall within or below the bounds of maximum summer SST, which means that these temperature estimates are matched seasonally and/or vertically in the water column. Using the seasonally resolved WOA 2009 database in Ocean Data View (ODV, Schlitzer, 2012), we now take the uncorrected Mg/Ca-Ts, normalized to SSS = 35.4 using Eq. (1), and find which seasons and water depths are recorded by matching Mg/Ca-Ts and observations at each core site.

Fig. 5a shows Mg/Ca-based growth temperatures occur only during the warmest summer/fall months and in the upper water layers at subtropical to temperate latitudes. In contrast, the low-latitude data indicate that Mg/Ca-based growth temperatures are matched throughout the year at different water depths. We suggest that these observations reflect how the habitat depth and season of maximum flux of G. ruber varies with latitude. Averaging these habitat depth estimates and plotting them versus mean annual sea surface salinity yields a negative correlation (Fig. 5b), where G. ruber appears to live closer to the sea surface in high-salinity environments (i.e. mid-latitudes) but may live as deep as 60 m in low salinity environments (i.e. near the equator). This result provides an alternative to the hypothesis that Mg/Ca covaries with salinity (Arbuszewski et al., 2010).

The inferred seasonal occurrence is consistent with seasonal plankton net observations by Tolderlund and Bé (1972) at Atlantic Stations Delta (44°N, 41°W), Echo (35°N, 48°W) and Bermuda (32°06′N, 64°39′W), where G. ruber occurs only in August and September at the northernmost station Delta and from March through December at Echo and Bermuda. Furthermore, the depth habitat preferences are in agreement with plankton net observations that place G. ruber in the upper 10 m of the water column at Echo (Tolderlund and Bé, 1972), but with occurrences in deeper tows at Bermuda and the Sargasso Sea (Tolderlund and Bé, 1972; Fairbanks et al., 1980; Deuser, 1987) or throughout the upper 75 m in the central equatorial Pacific (Watkins et al., 1998). To the best of our knowledge no such data are available for the equatorial Atlantic, but because hydrographic conditions near the equator are comparable between the Pacific and Atlantic, for now we assume that the equatorial Pacific depth habitat (Watkins et al., 1998) is also representative for the Atlantic.

Given this agreement between inferred depth habitat and observations, we used ODV (Schlitzer, 2012) to gather summer and winter salinity at 20 and 50 m water depth from WOA 2009 and derive a new set of calcification temperature estimates (Fig. 4c) by omitting the dissolution correction and applying Eq. (1) (i.e. 3.3% sensitivity to salinity) to normalize all Mg/Ca data to S = 35.4, which is typical of tropical Atlantic SSS. We applied summer salinity at 20 m to normalize Mg/Ca data >15°N/S, and averaged annual salinity at 20 and 50 m to normalize Mg/Ca data <15°N/S (Fig. 4c and d and Suppl. material). These Mg/Ca-Ts are now in good agreement with G. ruber’s optimum growth conditions of 23–26.5°C, as observed from plankton studies (Tolderlund and Bé, 1972) and culture experiments (Bijma et al., 1990). This agreement further corroborates that Mg/Ca yields reasonable temperature estimates without requiring a very large (i.e. 27%) sensitivity to salinity. However, because some significant differences remain between Mg/Ca-Ts and δ18O foramin-Ts (Fig. 4c), we now turn to evaluating the δ18O foramin-Ts.

4.3. Translating foraminiferal δ18O foramin to temperature

Arbuszewski et al. (2010) and Mathien-Blard and Bassinot (2009) applied different temperature calibrations for G. ruber

\[
T^*(C) = 16.5 - 4.80(\delta^{18}O_{foram} - \delta^{18}O_{sw} + 0.27),
\]

(5)

\[
T^*(C) = 16.9 - 4.00(\delta^{18}O_{foram} - \delta^{18}O_{sw} + 0.20),
\]

(6)

Eq. (5) (Bemis et al., 1998) has been established for the planktic O. universa grown under low light conditions in laboratory culture between 15 and 25°C, and Eq. (6) (Shackleton, 1974) has been established for the benthic genus Uvigerina, from core-top sediments for temperatures <17°C. Using Eq. (6) to translate δ18O G. ruber data from the Atlantic coretop transects yields on average 0.67°C higher temperatures compared to Eq. (5). It is important to note here that the original Shackleton (1974) equation was a linearization of the O’Neil et al. (1969) quadratic temperature relationship. As such, it is inappropriate for computing tropical temperatures and will always lead to a temperature overestimate at high temperatures. Before we assess the suitability of these calibrations to translate G. ruber δ18O foramin to temperature, we need to consider the effects of the oxygen isotopic composition of seawater and carbonate chemistry on δ18O foramin.

4.3.1. The oxygen isotopic composition of seawater

Estimating temperature from δ18O foramin requires knowledge of δ18O sw (e.g., Urey, 1948; McCrea, 1950; Urey et al., 1951; Bemis et al., 1998). Arbuszewski et al. (2010) estimated δ18O sw from a linear regression between Atlantic SSS and δ18O sw data from the upper 50 m of the water column (δ18O sw = 0.238 × S − 7.69, r² = 0.66, N = 106, Schmidt et al., 1999), whereas Mathien-Blard and Bassinot (2009) selected local sea surface δ18O sw from the gridded data set by LeGrande and Schmidt (Fig. S1a, 2006). The gridded data set of LeGrande and Schmidt (v. 1.1, 2006)
is derived from the same global data base as Schmidt et al. (1999); the authors noted, however, that $\delta^{18}$Osw to salinity relationships are only regionally coherent and may vary on seasonal, annual and inter-annual timescales.

A simple cross plot of the $\delta^{18}$Osw estimates derived from the linear regression versus $\delta^{18}$Osw estimates from the gridded data set of LeGrande and Schmidt (2006) (Fig. S1b) shows that both estimates agree within error ($\pm 0.26$‰ and $\pm 0.15$‰, respectively) but that the $\delta^{18}$Osw values from the gridded data set are consistently greater than estimates from the linear regression in the 16–36°C/S band by about 0.1‰. Although the uncertainty of $\delta^{18}$Osw estimates is large (Fig. S1b), this latitudinal band is where Arbuszewski et al. (2010) found the highest salinity effect and the greatest deviation between Mg/Ca-Ts and $\delta^{18}$Oforam-Ts. In comparison, the study of Mathien-Blard and Bassinot (2009) includes only three samples from this mid-latitude band, and focuses primarily on higher latitudes. This analysis suggests uncertainty in $\delta^{18}$Osw contributes to the discrepancy between $\delta^{18}$Oforam-Ts and Mg/Ca-Ts. $\delta^{18}$Oforam values may be slightly underestimated in the 16–36°C/S band and $\delta^{18}$Oforam temperatures underestimated by up to 0.5°C.

Given that LeGrande and Schmidt (2006) provide a more differentiated and better constrained assessment of regional $\delta^{18}$Osw, we have applied estimates from their gridded data set to the core-top transect of Arbuszewski et al. (2010) (Fig. 4b and c). Using the data library clone at http://granger.ldeo.columbia.edu/expert/%28/data/free/
alexeyk/LeGrandeSchmidt2006/calculated_d18O.nc readfile/d18o/, we gathered $\delta^{18}O$ data for each core site at 0, 20 and 50 m water depth. The local difference in $\delta^{18}O_{sw}$ between these depths is generally <0.02 and in only two cases as large as 0.04. These differences are smaller than the reproducibility of replicate analyses of G. ruber reported by Mathien-Blard and Bassinot (2009), i.e. 0.22 (2$\sigma$), so we use the values at 20 m for all further calculations.

4.3.2. Marine carbonate chemistry effects on $\delta^{18}O_{foram}$

Culture experiments with the planktic foraminifers O. universa and G. bulloides (Spero et al., 1997; Bijma et al., 1999) and G. sacculifer and G. ruber (Bijma et al., 1998) have revealed linearly decreasing $\delta^{18}O_{foram}$ and $\delta^{13}C_{foram}$ with increasing carbonate ion concentration in all four species. In G. ruber the $\delta^{18}O_{foram}$ versus $[\text{CO}_3^{2-}]$ relationship has a slope of $-0.002^{\%}$ per $\text{µmol kg}^{-1}$ (Bijma et al., 1998). We have tested this effect by normalizing all $\delta^{18}O_{foram}$ data to $230 \pm 21$ $\text{µmol kg}^{-1}$ (1$\sigma$), which is the average $[\text{CO}_3^{2-}]$ determined from the GLODAP data set (Key et al., 2004) for these samples and assumed depth ranges (Suppl. material). Our analysis reveals that this normalization contributes little to resolving the discrepancy between Mg/Ca-Ts and $\delta^{18}O_{foram}$-Ts. The total effect across the Atlantic transect is zero on average, but data in the 16–36°N/S band

Fig. 5. (a) Seasonal occurrence and depth of salinity-normalized Mg/Ca-Ts from G. ruber sampled from Atlantic sediments (data from Fig. 4d and hydrographic data from WOA 2009). Based on Mg/Ca records, G. ruber appears to grow only during the warmest summer/fall months in subtropical to temperate latitudes and at shallower depths than in the tropics. (b) Average habitat depth determined in (a) versus annual mean sea surface salinity. The broad negative correlation with SSS hints at a shallower habitat where salinity is high.
are up to 0.5 °C cooler and data >36°N and <16°N/S are up to 0.33 °C warmer than the average (Fig. 4b and Suppl. material). The net effect of this normalization slightly increases the offset between Mg/Ca-Ts and δ¹⁸O<sub>foram</sub>-Ts, except for three samples >36°N, where the offset becomes smaller (Fig. 4b).

4.4. Remaining differences between Mg/Ca and δ¹⁸O<sub>foram</sub> temperature estimates

Using the <i>O. universa</i> low light equation (Eq. (5)) and gridded δ¹⁸O<sub>sw</sub> to translate the [CO<sub>2</sub>]<sup>−2</sup>-normalized δ¹⁸O<sub>foram</sub> data to temperature yields good agreement with the Mg/Ca-T data north of 15°N (r² = 0.82), but within the 12°N–10°S band the Mg/Ca-Ts fall below annual SST. In contrast, the δ¹⁸O<sub>foram</sub>-Ts tend to exceed annual SST, with several values exceeding the warmest summer temperatures observed in this 12°N–10°S band by up to 1.1 °C (Fig. 4b). South of 10°S the δ¹⁸O<sub>foram</sub>-Ts systematically fall below <i>G. ruber</i>’s optimum growth temperature of 23–26.5 °C (Tolderlund and Bé, 1972; Bijma et al., 1990). Given both annual and summer SSTs of 23–26 °C are observed, it is surprising that <i>G. ruber</i> should prefer to grow at T < 22 °C at these sites. These discrepancies need to be explained, and in the absence of known geochemical effects on Mg/Ca, we will continue to focus on potential uncertainties on the δ¹⁸O<sub>foram</sub> reconstructions, in particular equatorial and South Atlantic δ¹⁸O<sub>sw</sub>, possible mixing with glacial-age foraminifers, and the temperature equation used to translate δ¹⁸O<sub>foram</sub>-Ts.

4.4.1. Insufficient δ¹⁸O<sub>sw</sub> data coverage

The δ¹⁸O<sub>sw</sub> database of Schmidt et al. (1999) has very limited data coverage near core sites in the equatorial and South Atlantic (Fig. S1a). The few available δ¹⁸O<sub>sw</sub> data in those locations were collected close to the African and South American coastlines. This is different in the North Atlantic, where a greater number of data are available closer to the core-top transect. In the South Atlantic it is notable that neither the linear regression of Arbuzewski et al. (2010), nor the gridded data set of LeGrande and Schmidt (2006) yields δ¹⁸O<sub>sw</sub> data higher than 1.02 ± 0.15‰, but the database of Schmidt et al. (1999) does list a few δ¹⁸O<sub>sw</sub> data as high as 1.44 ± 0.05‰ on the western side of the South Atlantic Ocean (Fig. S1a). A 0.4‰ underestimate of δ¹⁸O<sub>sw</sub> translates to a ~2 °C underestimate of growth temperature, which could bring the South Atlantic Mg/Ca-T and δ¹⁸O<sub>foram</sub>-Ts into agreement, but it is unclear how far those higher values may extend eastward. We have tried without success to gain access to water samples and unpublished δ¹⁸O<sub>sw</sub> data that would improve the data coverage near the core transect. The situation near the equator is similar, with the linear regression and gridded data set yielding δ¹⁸O<sub>sw</sub> data in the range of 0.75–0.87‰, whereas measured δ¹⁸O<sub>sw</sub> data range between 0.48‰ and 0.98‰. The lowest data (0.48–0.69‰) are from the eastern equatorial Atlantic, where many of the core sites are located (Fig. S1a). If δ¹⁸O<sub>sw</sub> near south equatorial core sites are overestimated, this would result in δ¹⁸O<sub>foram</sub>-Ts that are too warm. Although this is speculative, it highlights the need for improved characterization of δ¹⁸O<sub>sw</sub>.

4.4.2. Potential mixing with glacial-age foraminifers

In addition to uncertainties in δ¹⁸O<sub>sw</sub>, Lohmann (1995) has reported the mixing of glacial age foraminifers into Rio Grande Rise core-top sediments, where sedimentation rates are as low as 0.5 cm/ky. Similarly, Billups and Spero (1996) showed that a core-top sample from an even higher sedimentation rate core (1.5 cm/ky) in the central equatorial Atlantic at 5°N, 20.5°W (2930 m depth) contained ~20% glacial <i>G. sacculifer</i>. Stott and Tang (1996) made similar observations in equatorial and south Atlantic cores, where individual <i>G. ruber</i> and <i>G. sacculifer</i> from core-top samples had >10% glacial δ¹⁸O values. Although the data shown in Fig. 4 are from sediment cores retrieved somewhat further east of the Rio Grande Rise, they are near the core site studied by Billups and Spero (1996) and Stott and Tang (1996). Given the relatively deep water depths between 3300 and 3900 m of the cores in this database (Suppl. material), it is likely that comparable low sedimentation rates would be found in cores from the South Atlantic gyre. If mixing with glacial age tests is an issue at these core sites, the added ice volume effect on glacial δ¹⁸O<sub>sw</sub> (~+1.1‰) would create a much larger bias on δ¹⁸O<sub>foram</sub>-Ts than on Mg/Ca-Ts. Single test δ¹⁸O<sub>foram</sub> analyses on <i>G. sacculifer</i> and <i>G. ruber</i> suggest this effect could produce an apparent cooling of 0.5–1 °C (Billups and Spero, 1996; Stott and Tang, 1996). In comparison, 2–3 °C lower glacial temperature translates to 18–27% lower Mg/Ca, which is partly compensated by higher glacial salinity by 1 unit or +3–5% Mg/Ca. This leads to an average glacial Mg/Ca ~18% lower than modern, and consequently a diminishing ~0.2 °C apparent cooling if bioturbation mixed 10% glacial tests into core-top sediments.

4.4.3. Light effects on δ¹⁸O<sub>foram</sub> in symbiont-bearing species

To date, no culture calibration has been established for δ¹⁸O<sub>foram</sub> in tests of <i>G. ruber</i>; Arbuzewski et al. (2010) therefore chose an <i>O. universa</i> equation established in laboratory culture under low light conditions (Eq. (5), Bemis et al., 1998), whereas Mathien-Blard and Bassinot (2009) used Shackleton’s (1974) core-top calibration for the benthic foraminifer genus <i>Uvigerina</i> (Eq. (6)). Both calibrations yield relatively similar results but their adequacy for <i>G. ruber</i> has not yet been discussed; we revisit the <i>O. universa</i> equation here.

Bemis et al. (1998) cultured the symbiont-bearing <i>O. universa</i> under two different light intensities: under light-saturating conditions >380 µmol photons m<sup>−2</sup> s<sup>−1</sup> (high light, HL) and below the light compensation level at 20–30 µmol photons m<sup>−2</sup> s<sup>−1</sup> (low light, LL, Eq. (5)) (Rink et al., 1998). The resulting temperature equations differ in their y-axis intercepts, which has been explained by the effect of symbiont photosynthetic activity on elevating the carbonate ion concentration in the foraminiferal microenvironment (Bemis et al., 1998). The HL equation is:

\[
T(°C) = 14.9 - 4.80 \times (\delta^{18}O_{foram} - \delta^{18}O_{sw} + 0.27)
\]  

Bemis et al. (1998) compared these equations to previous calibrations, including a suite of Atlantic <i>G. ruber</i> core-top data from Wang et al. (1995). They noted that where annual SST is warmest, i.e. at the equator, <i>G. ruber</i> data are
best described by the HL equation, and where annual SST <25 °C, G. ruber data are better described by the LL equation. Similarly, Thunell et al. (1999) found good agreement between the HL equation and G. ruber collected from sediment trap material in the Guaymas Basin, Gulf of California. We therefore decided to investigate potential differences in surface-ocean light intensity across the latitudinal transect.

Using the Giovanni online data system of the Goddard Earth Sciences Data and Information Services Center (http://disc.sci.gsfc.nasa.gov/giovanni/overview/index.html) to read local photosynthetic active radiation (PAR) and diffuse light attenuation coefficients at 490 nm from SeaWiFS annual data, we determined light intensity at 20 and 60 m water depth at each core site (Fig. S2, Suppl. material). Whereas light intensity at 20 m exceeds 200 μmol photons m⁻² s⁻¹ at all latitudes, light intensity at 60 m water depth falls below 50 μmol photons m⁻² s⁻¹ near the equator. Following photosynthesis measurements by Jorgensen et al. (1985) and Rink et al. (1998), any light level >150 μmol photons m⁻² s⁻¹ exceeds light saturation of the symbiont populations associated with O. universa and G. saccularif and would thus suggest using the HL equation, whereas any light level <50 μmol photons m⁻² s⁻¹ falls near or below light saturation and thus would suggest using the LL equation. Based on this light regime, one would predict the HL equation should produce the best temperature estimates everywhere except for the equator, where using the LL equation would yield better estimates. However, applying the HL equation to extratropical samples yields δ¹⁸O foram-Ts that fall below the optimum growth temperature of G. ruber and even further below Mg/Ca-Ts (Fig. 4c). Assigning the use of the HL and LL equations to samples based on irradiance levels therefore clearly leads to results that are difficult to reconcile (see also Wang et al., 1995; Thunell et al., 1999). Unfortunately, no such light experiments are available for G. ruber. However, applying the O. universa HL equation to the equatorial G. ruber samples decreases δ¹⁸O foram-Ts by 1.6 °C and improves the agreement with Mg/Ca (Fig. 5c). Because the latitudinal light regime provides no support for the use of the HL equation near the equator, we looked for alternative clues as to why application of an equation with a lower y-intercept (i.e. the HL equation) may be warranted at low latitudes.

4.4.4. Size effects on δ¹⁸O foram in G. ruber

Here we focus on the 250–355 μm size fraction chosen by Arbuszewski et al. (2010) for foraminiferal sampling. In a recent test-size study on G. ruber in the Gulf of Mexico, Richey et al. (2012) observed a linear decrease in δ¹⁸O foram with test size that translates to a +0.7–1.2 °C temperature bias per 100 μm size increase. In contrast, the Mg/Ca ratio of G. ruber is constant in small tests and only increased in tests larger than 355 μm diameter, for which the inferred temperature bias is only half as large as in δ¹⁸O foram. Similar observations have been reported by Elderfield et al. (2002); but they observed a gradual increase in both proxies with test size. It is not clear what causes these composition-size relationships but differences in depth habitat and/or seasonal occurrence are likely candidates (Spero et al., 2003; Hönsch and Hemming, 2004; Richey et al., 2012). Importantly, Spero and Lea (1993) observed that the symbiont-bearing G. saccularif grows larger tests with increasing light levels, suggesting that the size effect observed by Richey et al. (2012) may also be related to light levels and that the use of the HL temperature equation on δ¹⁸O foram in larger G. ruber may be more appropriate.

Given the relatively wide size range studied by Arbuszewski et al. (2010) and the higher G. ruber growth rates observed under optimal growth conditions (Bijma et al., 1990), we investigated whether the size distribution within the 250–355 μm fraction varies along the Atlantic core transect. We selected four core-top samples from Arbuszewski’s Atlantic transect, covering 1–40°N, and measured the average sizes of 30 randomly selected G. ruber (sensu stricto) tests under a microscope. Although it should be noted that the original size distribution may have been slightly different from ours (the samples are now already depleted in G. ruber tests), tests from eutrophic regions are on average 80 μm larger compared to higher latitudes (Fig. S3). This size difference hints at a potential bias in test geochemistry. Comparison with the size effect on δ¹⁸O foram observed by Richey et al. (2012) suggests that this size difference could explain about half or more of the difference between the HL and LL equation, and that the use of the HL equation is more appropriate in the 12°N–10°S band (see also Thunell et al., 1999). Given these observations we recommend that paleo- reconstructions should be based on sieve size ranges that are restricted to 50-μm increments (e.g., 250–300 μm, 300–355 μm), so that any involuntary bias towards selecting the largest tests in a sample is minimized.

4.5. Seasonality of G. ruber growth

Our comparison of the Mg/Ca and δ¹⁸O proxies in the North Atlantic shows that agreement between the two proxies can be improved (R² = 0.70) if known geochemical proxy sensitivities are applied (Fig. 6). The benefit of this approach lies in the potential to unravel biological controls that cannot be studied in laboratory culture, where water depth is invariant and foraminiferal reproductive success cannot be quantified. The seasonality of G. ruber growth has been observed with plankton nets at some locations (Tolderlund and Bé, 1972; Watkins et al., 1998), and it can now be corroborated by comparison of core-top proxy temperature estimates with hydrographic observations of mean annual SST (Fig. 7). The proxy deviation from SST is here expressed as ΔT Mg/Ca = Mg/Ca-T – SST and ΔT δ¹⁸O = δ¹⁸O foram-T – SST and yields up to +5 °C in mid latitudes and −3 °C near the equator. Although assumptions of habitat depth and season were part of our approach to normalize proxy records to common salinity and [CO₂⁻], the effect of those normalizations is much smaller (<1 °C, Fig. 4) than the deviation of both ΔT Mg/Ca and ΔT δ¹⁸O from mean annual SST. Despite remaining differences, we suggest that the agreement between the two proxy records is significant and indicates the seasonal preference of G. ruber for warmer summer months at higher latitudes. A similar seasonal bias for G. ruber Mg/Ca
temperatures was also proposed for Caribbean fossil assemblages during glacial cycles (Schmidt et al., 2006).

Near the equator, however, we cannot determine with certainty whether proxy records indicate greater habitat depth, or whether they may be biased by post-depositional dissolution. Applying a dissolution correction only to equatorial samples would further improve the agreement between the Mg/Ca and \(\delta^{18}O_{\text{foram}}\) estimates (Fig. 4d).

4.6. Deconvolving \(\delta^{18}O_{\text{foram}}\) into temperature and salinity contributions

Paleosalinity estimates have been determined by removing the temperature component from \(\delta^{18}O_{\text{foram}}\) records using Mg/Ca-Ts and the ice volume component using global sealevel estimates. Calculated paleo-\(\delta^{18}O_{\text{sw}}\) are then translated to salinity via a modern \(\delta^{18}O_{\text{sw}}\)-salinity relationship (e.g., Flower et al., 2004; Schmidt et al., 2004; Weldeab et al., 2007). Based on the observations made herein, we revisit this approach.

The line of argument applied in this study uses Mg/Ca to estimate foraminiferal growth temperatures, which were then used to determine \(G. \ ruber\)’s depth and season of growth. The correlations shown in Fig. 7a and b suggest a stronger relationship with latitude for Mg/Ca-Ts than for \(\delta^{18}O_{\text{foram}}\)-Ts. Fig. 4d shows the same differences between the two proxy estimates for individual core sites. We have identified uncertainty in \(\delta^{18}O_{\text{sw}}\) and bioturbation as potential sources for uncertainty in the \(\delta^{18}O_{\text{foram}}\)-Ts. However, determining which proxy may be biased depends on the approach. If we had used \(\delta^{18}O_{\text{foram}}\) instead of Mg/Ca to determine \(G. \ ruber\)’s growth temperature, which is the approach originally taken by Arbuszewski et al. (2010) and Mathien-Blard and Bassinot (2009), we would need to search for parameters that could explain deviations of Mg/Ca-Ts from \(\delta^{18}O_{\text{foram}}\)-Ts. With our current state of knowledge we cannot identify whether one proxy is more or less biased than the other, as both proxies yield temperatures that are observed in the water column at the respective core sites. Arbuszewski et al. (2010) aimed to resolve this issue by performing multi-variate regressions that link mean annual temperature and salinity to Mg/Ca, \(\delta^{18}O_{\text{foram}}\) and \(\Delta CO_2\):

Mean annual SST (°C) = 16.06 + 4.62ln(Mg/Ca) − 3.42\(\delta^{18}O_{\text{foram}}\) − 0.1\(\Delta CO_2\),

(8)

Mean annual SST = 34.28 + 1.97ln(Mg/Ca) + 0.59\(\delta^{18}O_{\text{foram}}\)

(9)

Although the results appear promising when compared to modern hydrographic data, the temperature and salinity sensitivities of Mg/Ca and \(\delta^{18}O_{\text{foram}}\) in these regressions do not agree with observations from laboratory cultures (Eqs. (4)–(7), this study, Bemis et al., 1998; Lea et al., 1999; Ksiksterek et al., 2008), plankton nets (Anand et al., 2003) or core-top calibrations (Shackleton, 1974; Dekens et al., 2002). Furthermore, because both proxies are used in both regressions, neither proxy may subsequently be used independently to verify the regression’s accuracy.

We have tried to reconcile the two proxy estimates, but differences remain (Figs. 4d, 6, and 7) that limit the ability to use paired analyses of Mg/Ca and \(\delta^{18}O_{\text{foram}}\) to reconstruct past salinity (Fig. 8). For instance, a 0.5%\(_{\text{wo}}\) under- or
overestimate in $\delta^{18}O_{sw}$ could erroneously be interpreted as a local salinity difference of $\sim 2.1$ units (Fig. 8b). Such large uncertainties could inhibit mapping attempts of – for example - last glacial maximum (LGM) salinity changes across entire ocean basins. However, $\delta^{18}O_{sw}$ estimates in the equatorial region (i.e. $10^\circ$N$-10^\circ$S) fall closer to observed values than at higher latitudes. This is consistent with DiNezio and Tierney (2013), who recently demonstrated that paired analyses of Mg/Ca and $\delta^{18}O_{foram}$ yield LGM salinity patterns in the Indian Ocean that are consistent with model estimates of how glacial exposure of the Sunda Shelf affects salinity. Furthermore, uncertainties should be reduced for down-core reconstructions at a single site. For example, Saraswat et al. (2013) used paired analyses of Mg/Ca and $\delta^{18}O_{foram}$ to reconstruct deglacial monsoon changes from a sediment core in the southeastern Arabian Sea. Coherency of their reconstruction with Ba/Ca-based riverine runoff estimates and the Hulu Cave precipitation record affirms the efficacy of the $\delta^{18}O_{sw}$ approach on this regional scale. Looking at each temperature proxy individually, the glacial-to-interglacial temperature change for tropical surface ocean reconstructions using Mg/Ca (e.g., Lea et al., 2000; Hönisch and Hemming, 2005; Medina-Elizalde and Lea, 2010), $\delta^{18}O_{foram}$ (e.g., Broecker, 1986; Stott and Tang, 1996), foraminiferal assemblages (CLIMAP, 1976) and alkenones (Bard et al., 1997) all yield last glacial temperatures 1–3 °C colder than during the Holocene, demonstrating the fundamental agreement between different proxy estimates. While this is encouraging, uncertainties of individual temperature proxies often exceed 1 °C, and large spatial and temporal uncertainties remain in local $\delta^{18}O_{sw}$ vs. salinity relationships (paragraphs 4.3.1 and 4.4.1). Thus, paleo-salinity estimation should be approached with caution, and possibly only as deviations (Δ) between time periods rather than quantitative patterns (e.g., DiNezio and Tierney, 2013), until the mechanism(s) for these offsets can be resolved.

5. CONCLUSIONS

The salinity effect on Mg incorporation observed in laboratory-cultured planktic foraminifers is 3–5% per salinity unit. Because glacial salinity was $\sim 3\%$ or $\sim 1$ salinity unit higher compared to the modern ocean, the expected salinity effect on Mg/Ca in glacial foraminifera is an increase of 3–5% or a $+0.3–0.5$ °C temperature bias. In comparison, a 2–3 °C lower glacial temperature causes glacial Mg/Ca to be $\sim 18–27\%$ lower (e.g., Lea et al., 1999; Dekens et al., 2002; Anand et al., 2003). Consequently, temperature should exert the dominant control on planktic foraminiferal Mg/Ca on glacial-to-interglacial timescales.

We conclude, based on the culture data, that the apparently larger salinity sensitivity inferred from sub-tropical Atlantic core-tops with elevated Mg/Ca data (Arbuszewski et al., 2010) is not a direct effect of salinity. Our alternative
hypothesis is that elevated mid-latitude Mg/Ca is caused by the seasonal preference of G. ruber for warm summer conditions in the mid-latitudes, as opposed to annual average conditions near the equator. This hypothesis is supported by the observation that, after omitting the dissolution correction above 4.4 km and excluding data from cores deeper than 4.4 km or close to undersaturation, Mg/Ca-Ts from Atlantic core-top sediments fall predominantly in the range 23–27 °C, which is in good agreement with optimum growth conditions for G. ruber as determined by plankton observations (Tolderlund and Bé, 1972) and culture studies (Bjma et al., 1990). Our analysis underscores the importance of planktic foraminiferal habitat depth, seasonality and dissolution in controlling observed core-top shell chemistry variability and, by extension, the challenge of interpreting down-core records in terms of changes in mean annual surface conditions.

Although our assessment reveals a much-improved agreement between Mg/Ca- and δ18O_foram-Ts compared to earlier studies, some discrepancies remain and their consequences are significant. In particular, reconstructions of surface-ocean salinity using paired δ18O_foram and Mg/Ca data are subject to substantial uncertainties and potential biases. The analysis presented here offers a testable template for interpreting global compilations of core-top G. ruber Mg/Ca and δ18O analyses. To gain greater confidence in such reconstructions, core-top validations like those by Bijma et al. (1990) and Mathien-Blard and Bassinot (2009) would be greatly enhanced by an expanded database of seasonal and vertical plankton abundance through sediment trap arrays and multiple opening and closing nets, direct assessment of the foraminiferal preservation state and the potential impact of bioturbation on pooled geochemical analyses through individual shell analyses. In general, both Mg/Ca and δ18O_foram appear to be reliable indicators of paleotemperatures when seasonality, calcite preservation and uncertainties in modern δ18O_sw are taken into account. More comprehensive observations of modern δ18O_sw (spatially and seasonally) are a vital next step towards resolving discrepancies between the two proxies.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2013.07.028.

REFERENCES


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