



## RESEARCH ARTICLE

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### Key Points:

- We present new Mg/Ca calibrations for two planktonic species using core tops from the Atlantic
- We derive small salinity effects consistent with culture studies and no significant pH effects
- Our calibrations enhance the confidence in using planktonic Mg/Ca for temperature reconstruction

### Supporting Information:

- Supporting Information S1
- Table S1
- Table S2

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## Influences of Temperature and Secondary Environmental Parameters on Planktonic Foraminiferal Mg/Ca: A New Core-Top Calibration

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**Abstract** The accuracy of the Mg/Ca paleothermometer is contested over the influences of secondary environmental parameters such as salinity and pH. Recent calibrations based on compiled sediment trap and laboratory culture data suggest moderate influences from salinity and pH. Core tops are the best analogues to downcore samples used for paleoceanographic reconstruction with well-constrained environmental parameters and thus can be used to validate sediment trap and laboratory culture calibrations. Here, we calibrate new core-top Mg/Ca data in *Globigerinoides ruber* (white) and *Trilobatus sacculifer* (without final sac-like chamber) with sea surface temperature, salinity, and pH. Part of these coretops were previously used to argue for a large salinity effect on *G. ruber* (w) Mg/Ca (Arbuszewski et al., 2010, <http://10.0.3.248/j.epsl.2010.10.035>). Our new *G. ruber* (w) Mg/Ca data are on average 12% lower than the previous results. Our calibrations yield Mg/Ca-temperature sensitivities of  $8.1 \pm 0.7\%/^{\circ}\text{C}$  for *G. ruber* (w) and  $6.6 \pm 0.8\%/^{\circ}\text{C}$  for *T. sacculifer* (w/o sac), and Mg/Ca salinity effects of  $4.7 \pm 2.4\%/_{\text{‰}}$  for *G. ruber* (w) and  $5.5 \pm 2.3\%/_{\text{‰}}$  for *T. sacculifer* (w/o sac). These results agree well with culture experiments but discount the large salinity effects reported in previous core-top studies. Our data reveal insignificant pH effects on Mg/Ca in both species. Overall, our core-top calibrations for *G. ruber* (w) and *T. sacculifer* (w/o sac) lend strong support to previous calibrations, strengthening our confidence in the use of planktonic Mg/Ca as a reliable proxy for sea surface temperature reconstructions.

**Plain Language Summary** The amount of magnesium in the shell of planktonic foraminifera is an important tool for paleoceanographers to reconstruct sea surface temperature changes in the past. The reliability of this tool has been debated because there are other factors, for example, salinity and pH, that possibly affect the amount of Mg in the planktonic foraminiferal shell. Recently, by growing foraminifera in the laboratory, scientists found that the influence of salinity and pH are moderate. To validate these results from laboratories, we measured Mg in planktonic foraminiferal shells on the top of marine sediments, where we can estimate the environment the foraminifera lived in while at sea surface. We confirm that Mg in planktonic foraminifera is marginally affected by salinity but cannot detect the influence of pH. Overall, our results enhance the confidence in using Mg in planktonic foraminifera as a tool to reconstruct past changes in sea surface temperature.

## 1. Introduction

Planktonic foraminiferal Mg/Ca is widely used for past sea surface temperature reconstruction (e.g., Elderfield & Ganssen, 2000; Lea et al., 2000). Bulk shell Mg/Ca of planktonic foraminifera correlates with seawater temperatures, as shown by studies based on sediment traps, core tops, and laboratory culturing (Anand et al., 2003; Dekens et al., 2002; Lea et al., 1999; Nurnberg et al., 1996). However, planktonic Mg/Ca is also influenced by several secondary parameters, including deep water saturation state (Brown & Elderfield, 1996; Regenberg et al., 2014; Rosenthal et al., 2000), surface water salinity (Arbuszewski et al., 2010; Gray et al., 2018; Hönisch et al., 2013; Kısakürek et al., 2008), and surface water carbonate chemistry, like pH (Evans et al., 2016; Lea et al., 1999; Russell et al., 2004).

Low deep water saturation state ( $\Delta[\text{CO}_3^{2-}]$ , defined as the difference between in situ  $[\text{CO}_3^{2-}]$  and the saturation  $[\text{CO}_3^{2-}]$ ) may cause partial dissolution of planktonic foraminiferal calcite, which lowers planktonic Mg/Ca and leads to underestimation of temperatures (Brown & Elderfield, 1996; Regenberg et al., 2014; Rosenthal et al., 2000). The influence of partial dissolution on Mg/Ca can be corrected by empirical

correlations between Mg/Ca decrease and deep water  $\Delta[\text{CO}_3^{2-}]$  (Brown & Elderfield, 1996; Regenberg et al., 2014).

The influence of salinity on Mg/Ca has been debated during the last decade, due to discrepant results derived from different methods. Laboratory culture studies show weak salinity effects of 3–6% Mg/Ca per practical salinity unit (‰ hereafter) on planktonic Mg/Ca (Dueñas-Bohórquez et al., 2009; Gray & Evans, 2019; Hönisch et al., 2013; Kısakürek et al., 2008; Lea et al., 1999). A recent sediment trap study also obtained a small salinity effect of ~3‰ (Gray et al., 2018). In contrast, core-top studies have suggested much stronger salinity effects ranging from 15‰ to 30‰ for Mg/Ca in *Globigerinoides ruber* (w) (Arbuszewski et al., 2010; Ferguson et al., 2008; Mathien-Blard & Bassinot, 2009). Previous studies have attempted to reconcile these contrasting salinity sensitivities between core-top and laboratory culture studies by examining the early diagenesis of foraminiferal shells (Hoogakker et al., 2009; Kontakiotis et al., 2011). Notably, Hertzberg and Schmidt (2013) and Hönisch et al. (2013) reanalyzed data from Arbuszewski et al. (2010) and found that by refining estimates of calcification temperature and restricting dissolution correction to the region with poor preservation can partially discount the strong salinity effect. However, the large salinity effect derived from the Atlantic core tops (Arbuszewski et al., 2010) has remained.

A significant influence of sea surface pH on planktonic Mg/Ca has been suggested by laboratory culture experiments, which showed decreasing Mg/Ca with increasing pH over a large range spanning ~1 pH unit (Evans et al., 2016; Gray & Evans, 2019; Kısakürek et al., 2008; Lea et al., 1999; Russell et al., 2004). A pH effect on *G. ruber* Mg/Ca has also been observed in sediment traps (Gray et al., 2018). However, the pH effect may not be ubiquitous with a weaker effect at pH close to the modern ocean value for *Globigerina bulloides* and *G. ruber* (Kısakürek et al., 2008; Russell et al., 2004) and even absent in the case of *Trilobatus sacculifer* (Allen et al., 2016). Possible influence of pH is yet to be tested by core-top studies.

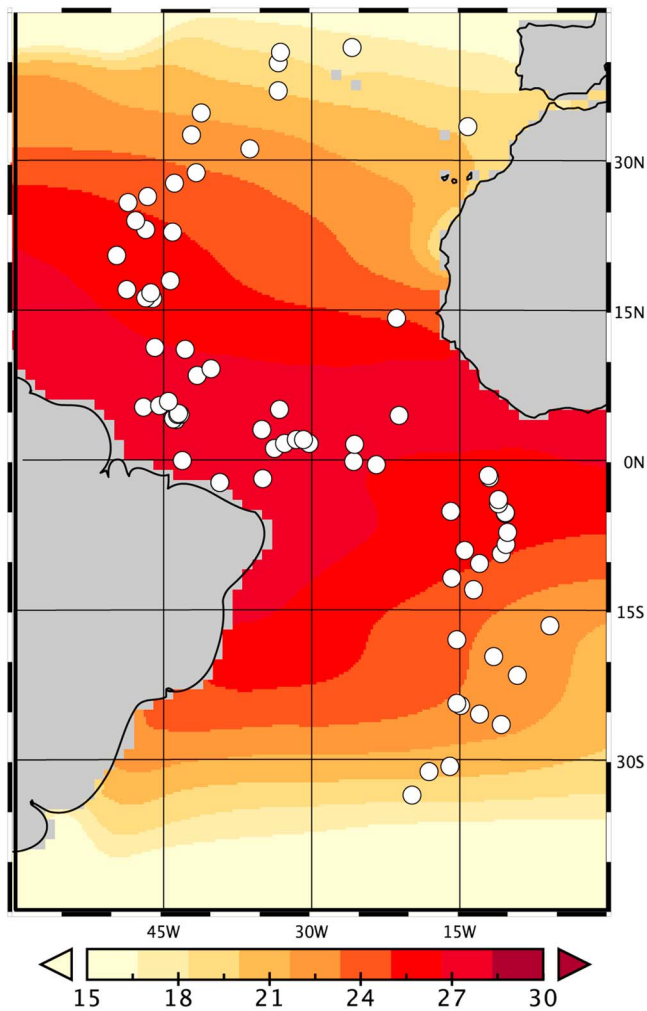
Core-top material provides the best analogue to downcore samples used for palaeoceanographic reconstructions; thus, establishing consistent salinity and pH effects across core-top, laboratory culture, and sediment trap samples is critical to improve our confidence in the Mg/Ca proxy. Previous studies used compiled core-top data to investigate secondary effects on planktonic Mg/Ca (Khider et al., 2015; Saenger & Evans, 2019). However, these studies based on compiled datasets have to consider nonenvironmental factors such as shell morphology, size fraction, and cleaning methods, which potentially compromise the capability of calibration models to resolve influences that are minor compared to that of temperature. Moreover, samples compiled by these studies have covarying temperature and salinity changes, complicating investigate of sensitivities of any individual parameter. Here, we revisit the Atlantic core-top samples previously used by Arbuszewski et al. (2010), which are unique in that their temperature and salinity do not covary. We have measured Mg/Ca in two symbiont-bearing mixed-layer species, *G. ruber* (white, *sensu stricto*) and *T. sacculifer* (without the final sac-like chamber) from these core tops. Part of samples was used by Arbuszewski et al. (2010), providing an opportunity to crosscheck Mg/Ca reproducibility from different studies/labs. Based on these new data, we quantify temperature sensitivity and secondary influences from salinity and pH on Mg/Ca.

## 2. Materials and Methods

### 2.1. Materials and Cleaning Procedure

*G. ruber* (w) and *T. sacculifer* (w/o sac) shells were picked from 56 core tops along the Mid-Atlantic Ridge between 35°S and 45°N, and water depths between 1.7 and 5.2 km (Figure 1). All core tops are from the late Holocene in age according to previous studies, with 18 samples verified by radiocarbon dates and the remaining samples by oxygen isotope stratigraphy and carbonate content (Table S1 in the supporting information; Arbuszewski et al., 2010; Cléroux et al., 2013). We assume all core tops are younger than 6 kyr and investigate the impact of their age uncertainties on calcification temperature and salinity estimates (see section 2.3).

For each sample, about 50 shells were picked from the 250–355  $\mu\text{m}$  size fraction. The narrow size was chosen to minimize potential size effects on Mg/Ca (Elderfield et al., 2002). All *G. ruber* (w) samples were cleaned following the procedure including both oxidative and reductive steps (Barker et al., 2003; Boyle & Keigwin, 1985). Of the 56 *T. sacculifer* (w/o sac) samples, 15 were split into two subsamples and cleaned with both oxidative and reductive steps while the remaining 41 were cleaned by the procedure excluding the reductive step. Briefly, foraminiferal shells were crushed between precleaned glass slides, transferred to



**Figure 1.** Location of core tops against annual mean temperature from WOA2018 (Locarnini et al., 2018).

500- $\mu$ L precleaned PP vials, and then repeatedly rinsed with Milli-Q water and methanol (3–5 times with each reagent). At this stage, shell fragments in vials were checked under a microscope using dark and light backgrounds in turn. If foreign particles are observed, fragments and particles were transferred to a dimple space in a precleaned glass slide, where foreign particles were removed manually using a single-haired brush. This differs from previous procedures that remove foreign particles after the oxidative cleaning step which may cause some dirty particles bleached and unidentifiable. We minimize this possibility by removing particles before the oxidative step. Once free of visible foreign particles, fragments were transferred into new precleaned PP vials for oxidative and reductive cleaning steps, following procedures described previously (Barker et al., 2003; Boyle & Keigwin, 1985). After these cleaning steps, shells were weak acid leached, Milli-Q H<sub>2</sub>O rinsed, and then dissolved in 0.1 M HNO<sub>3</sub> for Mg/Ca analysis.

The Mg/Ca of subsamples subjected to both reductive and oxidative steps are on average 2.2% lower than those subjected to oxidative cleaning only (Figure 3B), confirming the influence of the reductive step on Mg/Ca (Yu et al., 2007). This difference is negligible compared to Mg/Ca calibration uncertainties ( $\sim 1$  °C) from previous studies (e.g., Anand et al., 2003). We only consider Mg/Ca of *T. sacculifer* (w/o sac) shells cleaned without the reductive step below.

## 2.2. Mg/Ca Analysis

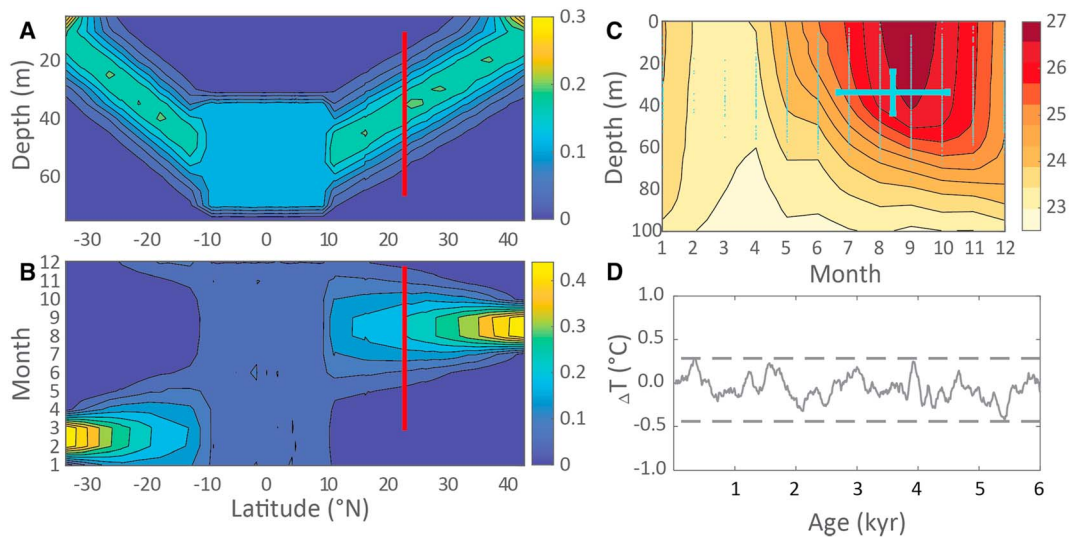
Trace element-to-calcium ratios of dissolved foraminifera shells were measured on a Varian 820 ICP-MS at the Australian National University (ANU), following the method of Yu et al. (2005). The analytical precision for Mg/Ca is better than 2% (2 standard deviation,  $2\sigma$  hereafter). Other trace element ratios, including Fe/Ca, Mn/Ca, and Al/Ca, were used to monitor contamination from Fe/Mn hydroxide coatings and to test the effectiveness of clay removal. Our Mg/Ca shows no correlation with Fe/Ca, Mn/Ca, or Al/Ca, suggesting negligible influence from contamination phases on Mg/Ca (Tables S3 and S4).

Two carbonate reference materials, BAM RS3 and CMSI 1767 (Greaves et al., 2008), were analyzed to test the accuracy of Mg/Ca measurements. Our measured Mg/Ca values for BAM RS3 and CMSI 1767 are  $0.80 \pm 0.02$  mmol/mol ( $n = 3$ ,  $2\sigma$ ) and  $5.58 \pm 0.08$  mmol/mol ( $n = 4$ ,  $2\sigma$ ), respectively, which are within 1.4% ( $2\sigma$ ) of accepted values (Greaves et al., 2008). To test possible bias between laboratories, we measured Mg/Ca values for two in-house calibration standard solutions and two carbonate reference materials (BAM RS3 and CMSI 1767) at both ANU and Lamont-Doherty Earth Observatory of Columbia University (LDEO). In addition, nine newly prepared dissolved foraminiferal samples reported in the study of Arbuszewski et al. (2010) were measured in both laboratories. For these samples, Mg/Ca results from ANU and LDEO agree within 0.16 mmol/mol, except for one standard solution (3.02 mmol/mol at ANU versus 2.81 mmol/mol at LDEO; Figure 2). This suggests negligible analytical bias in Mg/Ca measurements between ANU and LDEO.

## 2.3. Calcification Temperature and Salinity Estimation

For the Atlantic core tops, monthly hydrological temperature and salinity data were extracted from the World Ocean Atlas 2018 data set at a resolution of 5 m in the upper 100-m seawater (Locarnini et al., 2018; Zweng et al., 2018). We notice only a weak correlation ( $r^2 < 0.2$ ) between temperature and salinity for our samples, favorable for using these samples to investigate sensitivities on Mg/Ca from temperature and salinity.

Unlike laboratory cultures where the calcification environment can be controlled and measured, calibrations based on core-top samples may suffer from uncertainties in estimating environmental parameters

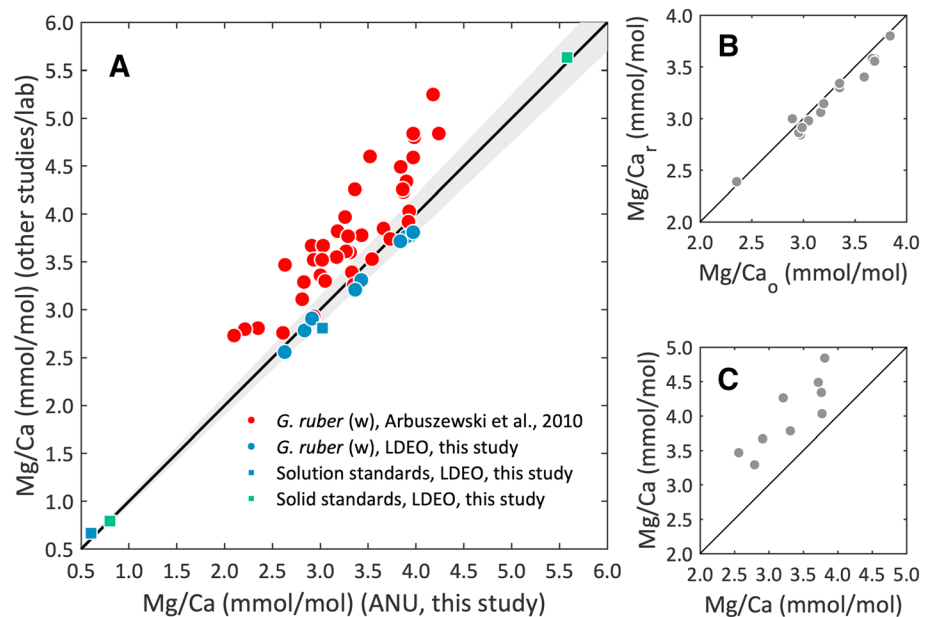


**Figure 2.** Meridional distribution of assumed calcification depth (A) and seasonality (B) at studied core-top sites. Uniform distribution of calcification depth and seasonality is assumed for core-top sites between 10°S and 10°N. In the extratropical Atlantic, the average calcification depth is assumed to shoal toward high latitudes and the distribution of calcification depth is assumed to be Gaussian. When the randomly generated calcification depth is negative, it is forced to 0 m. This is the reason why the highest probability density of calcification depth is at 0 m at the southmost and northmost sites, and in this case, the depth distribution is not Gaussian. In the extratropical Atlantic, the average month of occurrence is assumed to be August–September and February–March in the north and south Atlantic, respectively. The month of occurrence is also assumed to be Gaussian, with the standard deviation diminishing to the high latitudes to represent strong seasonality. The red bars in (A) and (B) indicate the core-top site (V16-206), which is chosen as an example for estimation of calcification temperature as shown in (C) and (D). Panel (C) is the contour of the monthly seawater temperature in the upper 100 m. Cyan cross indicates 1-sigma range of assumed calcification depth and month of occurrence at this site. Cyan dots are 10,000 randomly generated depth-month combinations, for which seawater temperatures are derived. Panel (D) is the temperature variability at this core-top site in the CCSM3 model (Liu et al., 2009). As there is no radiocarbon date available for this site, the temperature (salinity) variation (indicated by two dashed lines) is assumed to be the range of temperature (salinity) during the last 6 kyr. Ten thousand randomly generated temperature variations are applied on top of the seawater temperatures of 10,000 depth-month combinations. The median within the 15.9–84.1 percentile of the 10,000 iterations is the calcification temperature with 1-sigma range. Calcification salinity is estimated in the same way.

associated with foraminifer habitat and seasonality. We first estimate temperature and salinity of both species and propagate the corresponding uncertainties using their known depth habitat and seasonal preference at the core-top sites. Following field observations from sediment traps and plankton tows (Jonkers & Kučera, 2015, 2017; Tolderlund & Bé, 1971; Žarić et al., 2005), we parameterize depth and seasonal preferences of these species at each core-top sites (Figures 2A and 2B). We divide our core tops into “equatorial” (between 10°S and 10°N) and “extra-equatorial” (north of 10°N and south of 10°S) regions, according to the annual mean temperature at 0 m (Figure 1). We assume a uniform calcification depth between 30 and 70 m and no seasonality in the equatorial Atlantic. Outside the equatorial Atlantic, the average calcification depth is assumed to be normally distributed and to shoal from 50 to 10 m toward the northmost and southmost sites, and seasonality to be biased toward summer months (Hertzberg & Schmidt, 2013; Hönisch et al., 2013; Jonkers & Kučera, 2015, 2017; Tolderlund & Bé, 1971; Žarić et al., 2005).

Because our core-top samples are not exactly from the modern time sediment (i.e., age = 0 year), we use model output from a fully coupled atmosphere-ocean general circulation model Community Climate System Model version 3 (CCSM3; Liu et al., 2009) to evaluate the possible variability of temperature and salinity owing to the age uncertainty of each core-top sample. We extracted 10-year mean annual temperature anomalies during the last 6 kyr at model grid points adjacent to each core-top site. For core-top samples with radiocarbon ages, we defined the age-related temperature/salinity bias as the range of temperature/salinity anomaly between the radiocarbon-dated age and today. For all other sites, the temperature/salinity age bias was defined as the range of temperature/salinity anomaly during the last 6 kyr. The resulting age bias for temperature is mostly within 0.8 °C and for salinity within 0.5‰ (Figure S1).

For each core-top site, 10,000 depth-season combinations were randomly generated, and corresponding hydrological temperature and salinity values as well as their uncertainties were estimated. Ten thousand random uniformly distributed age-related temperature/salinity biases are generated and added to



**Figure 3.** (A) Comparison of Mg/Ca between different studies and labs. Green squares, blue squares, and blue circles represent results for solid carbonate standards, solution standards, and dissolved foraminiferal solutions, respectively. Red circles show foraminiferal samples measured by this study and Arbuszewski et al. (2010). The solid line with shading is the 1:1 line with  $\pm 2\%$  analytical uncertainty. (B) Comparison between *Trilobatus sacculifer* (w/o sac) Mg/Ca cleaned with both reductive and oxidative steps ( $Mg/Ca_r$ ) and oxidative step only ( $Mg/Ca_o$ ). (C) Comparison between *Globigerinoides ruber* (w) Mg/Ca measured in this study at LDEO and by Arbuszewski et al. (2010). LDEO = Lamont-Doherty Earth Observatory of Columbia University; ANU = Australian National University.

estimates of temperature/salinity variability based on calcification depths and seasonality. The medians and  $1-\sigma$  ranges of both temperature and salinity of 10,000 iterations combine information about varying calcification depths, seasonality, and core-top age uncertainty and represent the best estimates of calcification temperature and salinity with fully propagated uncertainties. The resulting calcification temperature and salinity estimates are only very weakly correlated ( $r^2 = 0.11$ ) for our core-top samples.

#### 2.4. Sea Surface pH and Deep Water Carbonate Saturation Estimation

We used the Global Ocean Data Analysis Program database Version 1.1 (Key et al., 2004) to calculate carbonate chemistry parameters based on total alkalinity, dissolved inorganic carbon (DIC), anthropogenic  $CO_2$ , phosphate concentration, and silicate concentrations estimated for each core-top site. We removed anthropogenic  $CO_2$  from DIC to obtain preindustrial DIC levels (Sabine et al., 2004) and calculated sea surface pH and deep water  $\Delta [CO_3^{2-}]$  using  $CO_2$ sys v2.1 (Lewis et al., 1998) with the same dissociation constants as used in Yu and Elderfield (2007).

Uncertainty in pH is difficult to constrain due to poor data coverage. The pH uncertainty associated with core-top age is negligible based on assumptions of no significant change in air-sea  $pCO_2$  difference and a 20 ppm  $pCO_2$  decrease (late Holocene  $pCO_2$  variability), which would raise sea surface pH from 0.011 to 0.022 at our core-top sites. The exact pH change depends on in situ pH ( $r^2 = 0.96$ ) and is 1 order magnitude smaller than the pH variability revealed by our core tops. Accordingly, pH uncertainty due to core-top age will only marginally affect the detection of potential influence of pH on Mg/Ca. For both species, pH is significantly correlated with salinity ( $r^2 = 0.39$ ) but not with temperature ( $r^2 = 0.10$ ).

#### 2.5. Regression Analysis

The sensitivities of environmental parameters are assumed to be exponential following previous studies (Anand et al., 2003; Dekens et al., 2002; Gray et al., 2018; Gray & Evans, 2019; Hönisch et al., 2013). The calibration model we test is thus in the following form:

**Table 1**  
Summary of Regression Analysis Between Mg/Ca and Environmental Parameters

	<i>G. ruber</i> (w)					<i>T. sacculifer</i> (w/o sac)				
	$r^2$	RSE			p	$r^2$	RSE		p	
Mg/Ca- <i>T</i>	0.74	0.28	<i>a</i>	$0.41 \pm 0.08$	$2.7E-06$	0.70	0.25	<i>a</i>	$0.57 \pm 0.09$	$1.8E-07$
			<i>b</i>	$0.084 \pm 0.007$	$6.6E-16$			<i>b</i>	$0.069 \pm 0.006$	$1.3E-14$
Mg/Ca- <i>T</i> , <i>S</i>	0.76	0.27	<i>a</i>	$0.42 \pm 0.08$	$2.1E-06$	0.73	0.23	<i>a</i>	$0.56 \pm 0.09$	$9.9E-08$
			<i>b</i>	$0.081 \pm 0.007$	$6.3E-15$			<i>b</i>	$0.066 \pm 0.006$	$4.9E-14$
			<i>c</i>	$0.047 \pm 0.024$	$6.2E-02$			<i>c</i>	$0.055 \pm 0.023$	$2.3E-02$
Mg/Ca- <i>T</i> , <i>S</i> , pH	0.77	0.27	<i>a</i>	$0.62 \pm 0.17$	$1.0E-03$	0.74	0.23	<i>a</i>	$0.44 \pm 0.13$	$1.4E-03$
			<i>b</i>	$0.069 \pm 0.010$	$5.1E-09$			<i>b</i>	$0.074 \pm 0.010$	$2.7E-09$
			<i>c</i>	$0.11 \pm 0.04$	$1.6E-02$			<i>c</i>	$0.015 \pm 0.046$	$3.8E-01$
			<i>d</i>	$-1.35 \pm 0.76$	$8.2E-02$			<i>d</i>	$0.78 \pm 0.79$	$2.4E-01$

Note. The relationship between Mg/Ca and *T*, *S*, and pH is in the form of  $Mg/Ca = a * \exp(b * T + c * (S - 35) + d * (pH - 8))$ . RSE = residual standard error.

$Mg/Ca = a * e^{b * T + c * (S - 35) + d * (pH - 8)}$ . Regression coefficients are derived from nonlinear least squares regression. We report coefficients of determination ( $r^2$ ) and residual standard errors (RSEs) of regression models, and the average  $\pm 1$  standard deviation for each coefficient. To evaluate the significance of Mg/Ca sensitivities to environmental parameters, *p* values are calculated against the null hypothesis that the sensitivity is 0.

### 3. Results

#### 3.1. Mg/Ca Compared With Previous Study

Of the 56 *G. ruber* (w) core tops measured in this study, shells from 39 of them were previously measured and used to argue for a strong salinity effect (Arbuszewski et al., 2010). For these 39 core-top samples, our new *G. ruber* (w) Mg/Ca results, measured at both ANU and LDEO, are on average 12% lower than those reported in Arbuszewski et al., 2010; Figures 3A and 3C). Explaining the higher Mg/Ca in Arbuszewski et al. (2010) requires further investigation but is out of the scope of the current study. We speculate that the slight difference in cleaning procedures, where we manually picked foreign particles before the oxidative cleaning step (see section 2.1), might be responsible for the observed Mg/Ca offset.

#### 3.2. Mg/Ca Calibrations

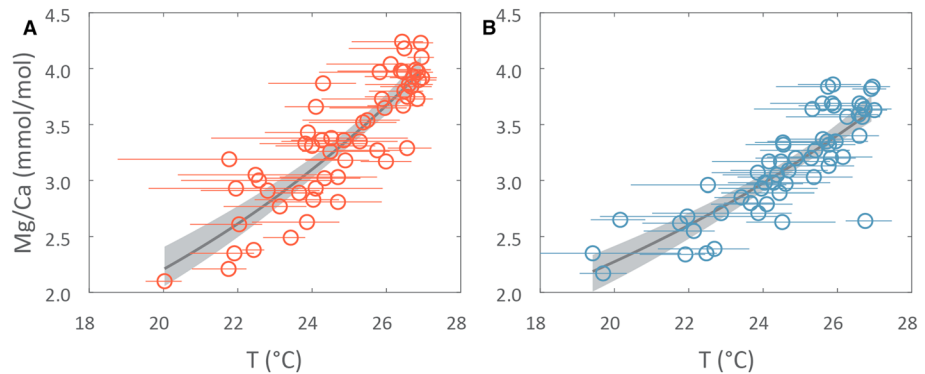
Our regression results are summarized in Table 1. The estimated temperature sensitivity for *G. ruber* (w) Mg/Ca is  $8.4 \pm 0.7\%/^{\circ}C$  ( $1\sigma$ ), if only temperature is included in the regression model. When we further add salinity, the temperature sensitivity remains similar, and the salinity sensitivity is  $4.7 \pm 2.4\%/_{\text{‰}}$  ( $p = 0.06$ ), on the verge of being nonzero at 95% confidence level. When pH is included in the regression model, both temperature and salinity sensitivities change to  $6.9 \pm 1.0\%/^{\circ}C$  and  $11 \pm 4\%/_{\text{‰}}$ , respectively, as the result of strong covariance between salinity and pH ( $r^2 = 0.39$ ). The pH sensitivity is  $-1.4 \pm 0.8\%/0.1$  pH unit ( $p = 0.08$ ).

For *T. sacculifer* (w/o sac), the temperature sensitivity is  $6.9 \pm 0.6\%/^{\circ}C$  if only temperature is considered. When salinity is further included, the regression again shows only a small influence on the temperature sensitivity and yields a salinity sensitivity of  $5.5 \pm 2.3\%/_{\text{‰}}$  ( $p = 0.02$ ). When all three variables (temperature, salinity, and pH) are included, both temperature and salinity sensitivities change, and we obtain a pH sensitivity of *T. sacculifer* (w/o sac) that is not significantly different from 0 ( $p = 0.24$ ).

### 4. Discussion

#### 4.1. Temperature Effect

If only temperature and salinity are included in our multivariate regressions, the temperature sensitivities of Mg/Ca are  $8.1 \pm 0.7\%/^{\circ}C$  and  $6.6 \pm 0.6\%/^{\circ}C$  for *G. ruber* (w) and *T. sacculifer* (w/o sac), respectively. These sensitivities are within the ranges derived from the literature using various proxy calibration methods (Allen et al., 2016; Anand et al., 2003; Dekens et al., 2002; Dueñas-Bohórquez et al., 2009; Gray et al.,



**Figure 4.** Correlation between Mg/Ca and calcification temperature for (A) *G. ruber* (w) and (B) *T. sacculifer* (w/o sac). Error bars represent 1-sigma ranges of calcification temperatures. Regression lines are shown with 95% confidence interval.

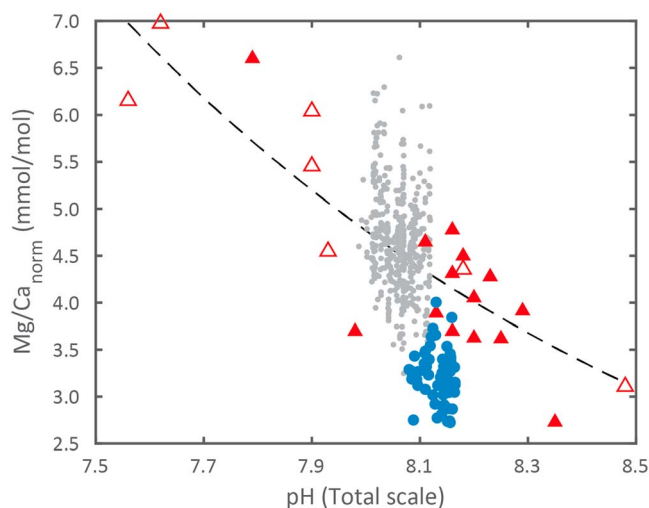
2018; Gray & Evans, 2019; Khider et al., 2015; Lea et al., 2000; McConnell & Thunell, 2005). For both species, the temperature sensitivity would be lowered had the annual mean temperature at 0 m been used ( $4.9 \pm 0.5\%/^{\circ}\text{C}$  for *G. ruber* [w] and  $3.6 \pm 0.5\%/^{\circ}\text{C}$  for *T. sacculifer* [w/o sac]). This is consistent with previous studies and highlights the importance of employing estimates for hydrological parameters to best reflect calcification environments (Hertzberg & Schmidt, 2013; Hönisch et al., 2013).

The derived temperature sensitivities depend on assumptions made when parameterizing calcification depth and seasonality at specific core-top sites. Accordingly, we use the *G. ruber* (w) data set to do several sensitivity tests to examine potential subjectivity of our regression analyses. This includes (1) the latitude used to define equatorial sites and (2) the calcification depth. Field observations show that both calcification depth and seasonality of *G. ruber* (w) differ between the equatorial and nonequatorial regions of the Atlantic (Jonkers & Kučera, 2015, 2017; Žarić et al., 2005). We used  $10^{\circ}\text{S}$ - $10^{\circ}\text{N}$  to define equatorial sites in our main analysis because the annual mean temperature is the highest within this range. We repeat the analyses using latitude ranges of  $7.5^{\circ}\text{S}$ - $7.5^{\circ}\text{N}$  and  $5^{\circ}\text{S}$ - $5^{\circ}\text{N}$  to define the equatorial sites. In both cases, we obtain the temperature sensitivities of  $8.2 \pm 0.8\%/^{\circ}\text{C}$ , statistically identical to the values using  $10^{\circ}\text{S}$ - $10^{\circ}\text{N}$  to define the equatorial Atlantic (our standard case). We used 50 and 10 m as the endmember depths for the equatorial and

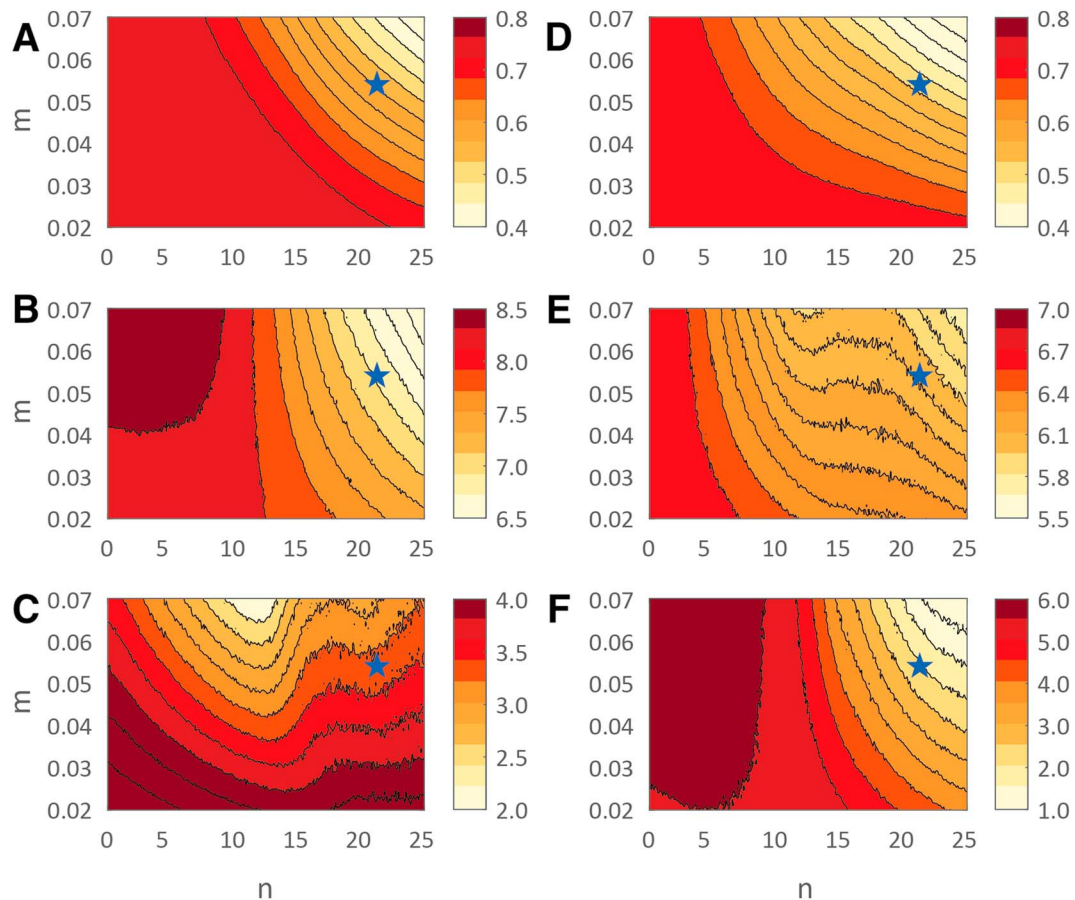
midlatitude regions in the main analyses, because calcification depths have been shown to shoal from equator to higher latitudes in the Atlantic (Hönisch et al., 2013; Jonkers & Kučera, 2017). Given that absolute calcification depths are challenging to pin down, we have considered two additional endmember depth combinations: (1) 30 m (equatorial sites) versus 10 m (northmost/southmost sites) and (2) 30 versus 30 m. In these scenarios, the temperature sensitivity of *G. ruber* (w) Mg/Ca becomes  $8.6 \pm 0.7$  and  $7.7 \pm 0.6\%/^{\circ}\text{C}$ , respectively, which are within the  $\pm 1\sigma$  range of our standard case. Therefore, we believe that the temperature sensitivity is robustly estimated for our core-top samples.

#### 4.2. Salinity Effect

For salinity sensitivities, we obtain  $4.7 \pm 2.4\%/‰$  for *G. ruber* (w) and  $5.5 \pm 2.3\%/‰$  for *T. sacculifer* (w/o sac), in good agreement with laboratory culture studies (Dueñas-Bohórquez et al., 2009; Hönisch et al., 2013; Kısakürek et al., 2008; Lea et al., 1999). But, our weak salinity for *G. ruber* (w) is in stark contrast to the anomalous large salinity effect from Arbuszewski et al. (2010). This contrast can be reconciled using our new Mg/Ca data, which are on average 12% lower (section 3.1), and calcification temperature and salinity estimates. Using the subset of data that overlaps with Arbuszewski et al. (2010) and annual mean temperature and salinity at 0 m, the salinity sensitivity would be  $21.5 \pm 3.5\%/‰$ . The



**Figure 5.** *Globigerinoides ruber* (w) Mg/Ca<sub>norm</sub> compared to pH, from core tops (blue dots, this study), sediment traps (gray dots, Gray et al., 2018), and culture studies (filled triangles, Kısakürek et al., 2008; empty triangles, Evans et al., 2016). The dashed curve is the regression line for all culture data.



**Figure 6.** Sensitivity tests for dissolution correction for (A, C, and E) *G. ruber* (w) and (B, D, and F) *T. sacculifer* (w/o sac). In each panel, results are shown with various dissolution corrections including different  $\Delta[\text{CO}_3^{2-}]$  thresholds ( $n$ ) and Mg/Ca deep water  $\Delta[\text{CO}_3^{2-}]$  sensitivities ( $m$ ). The first row are results for  $r^2$  between dissolution-corrected Mg/Ca and calcification temperature and salinity. The second and third rows are results for temperature and salinity sensitivities, respectively. The blue stars represent dissolution correction parameters from Regenberg et al. (2014) for multispecies.

salinity sensitivity reduces to  $17.5 \pm 2.8\%$  when calcification temperature and salinity are used, to  $13.7 \pm 3.2\%$  when Mg/Ca from this study is used, and to  $5.6 \pm 3.2\%$  when both new Mg/Ca and calcification temperature and salinity are used (Figure 4). This result confirms the importance of quantifying calcification environment emphasized by previous studies (Hertzberg & Schmidt, 2013; Hönisch et al., 2013) that were not able to fully discount the strong salinity effect from core tops owing to the biased Mg/Ca data set of Arbuszewski et al. (2010).

Our results show that the salinity effect on *G. ruber* (w) derived from core-top samples is consistent with laboratory culture and sediment trap studies when using our new Mg/Ca data and varying habitat preference of foraminifera. Compared to a recent core-top study based on compiled data set, where no significant salinity can be derived (Saenger & Evans, 2019), our calibrations based on one data set with nonenvironmental factors controlled seems to be better at resolving minor secondary influences. The small salinity effect on *G. ruber* (w) is corroborated by similar results obtained for *T. sacculifer* (w/o sac), which is evaluated from core-top samples the first time. This resolves the longstanding uncertainty surrounding the magnitude of salinity effect and possible discrepancies between different proxy calibration methods. We conclude the salinity effect on Mg/Ca-based downcore temperature reconstructions is not negligible (Gray et al., 2018; Khider et al., 2015) but much smaller than suggested previously (Arbuszewski et al., 2010; Mathien-Blard & Bassinot, 2009).

#### 4.3. pH Effect

The pH sensitivities derived from our multivariate regressions may be biased because of the strong covariance between pH and salinity. This is manifested by large changes in temperature and salinity



sensitivities when pH is included in regression analyses (Table 1). An alternative method to investigate the significance and magnitude of a potential pH effect is to first normalize Mg/Ca to the same temperature and salinity (25 °C and 35‰) using the sensitivities derived from our core-top calibration. For *T. sacculifer* (w/o sac), normalized Mg/Ca ( $Mg/Ca_{norm}$ ) is independent of pH ( $r^2 = 0.00$ ,  $p = 0.74$ ), confirming little pH influence on this species as previously inferred from culture experiments (Allen et al., 2016). For *G. ruber* (w),  $Mg/Ca_{norm}$  is not significantly correlated with pH ( $r^2 = 0.04$ ,  $p = 0.13$ ,  $RSE = 0.27$ , and  $n = 56$ ), although the sensitivity of  $-6 \pm 5\%/0.1$  pH unit is largely consistent with laboratory culture and sediment trap results (Gray et al., 2018; Gray & Evans, 2019).

From the sediment trap study, a pH effect is significant, but the associated large uncertainty prevents meaningful application (Gray et al., 2018). On the other hand, the trend of decreasing *G. ruber* Mg/Ca with increasing pH is well defined over the pH range from 7.5 to 8.5 in culture experiments ( $r^2 = 0.76$ ,  $p < 10^{-7}$ ,  $RSE = 0.56$ ,  $n = 21$ ; Kısakürek et al., 2008; Evans et al., 2016; Gray & Evans, 2019). However, it is worth noting that *G. ruber* cultured at ambient pH (close to the pH range covered by core tops in this study and sediment trap study of Gray et al., 2018) show similar Mg/Ca values (Kısakürek et al., 2008; Evans et al., 2016; Figure 5). The sensitivity of the pH calibration from culture data heavily relies on the data points with pH outside the ambient range. From a biomineralization perspective, small changes in pH around ambient ocean conditions could be mitigated by foraminifera such that the pH sensitivity within a confined range. Indeed, pH in the calcification environment of symbiont-bearing planktonic foraminifera could be different from ambient seawater pH due to respiration and photosynthesis of symbionts (Eggins et al., 2004; Spero et al., 2015) and proton pumping during calcification (de Nooijer et al., 2014; Zeebe et al., 2008). There is evidence for the modification of internal pH of *G. ruber* by photosynthesis of symbiont from sediment trap observations (Babila et al., 2014). Small changes in ambient pH could probably be overwhelmed by biological processes, resulting little influence on Mg/Ca. Therefore, we suggest that the sensitivity of *G. ruber* (w) Mg/Ca to pH under the late Quaternary surface ocean pH range may need additional studies. Meanwhile, Mg/Ca of *T. sacculifer* (w/o sac), for which a pH effect is absent in both culturing and core-top studies, may be used for temperature reconstructions to circumvent the potential influence of surface seawater pH.

#### 4.4. Dissolution Correction

Postdepositional dissolution can alter planktonic Mg/Ca and potentially bias and introduce noise to the core-top calibration. Partial dissolution occurs in waters that are undersaturated with respect to calcite, resulting in a “kink” in the dissolution correction equation for Mg/Ca, making the response of Mg/Ca to dissolution nonlinear (Regenberg et al., 2014). This nonlinearity prevents the use of multivariate regression from evaluating the dissolution effect. If we correct our Mg/Ca data for dissolution using the relationship of Regenberg et al. (2014) and repeat our regression analyses, new temperature and salinity sensitivities of both species would fall within the 1- $\sigma$  range of values obtained using our standard case (Tables 1 and S2). Nevertheless, poorer regressions (lower  $r^2$  values) are obtained for both species (Table S2), which is surprising given the dissolution correction would be expected to reduce any bias sourced from dissolution. Meanwhile, we notice that dissolution corrections would also introduce some noise due to the scatter associated with the dissolution relationship (Regenberg et al., 2014).

Based on the assumption that the dissolution correction should produce better fits with higher  $r^2$  for core-top calibrations, we set up a sensitivity test to see how a dissolution correction could affect our core-top calibrations. We adopt the form of the dissolution correction from Regenberg et al. (2014):  $\Delta Mg/Ca = m * (n - \Delta[CO_3^{2-}])$ ,  $\Delta[CO_3^{2-}] < n \mu mol/kg$ , where  $m$  is the sensitivity of Mg/Ca to dissolution and  $n$  is the  $\Delta[CO_3^{2-}]$  threshold for initiation of dissolution, both of which are allowed to vary. We apply a range of  $m$  and  $n$  parameter values to correct our core-top Mg/Ca and use the resulting corrected Mg/Ca data in regression analyses with calcification temperature and salinity. Figures 6A and 6B show that the correlation between dissolution-corrected Mg/Ca and temperature-salinity improves as both the deep-water  $\Delta[CO_3^{2-}]$  threshold and the sensitivity of Mg/Ca to the deep-water  $\Delta[CO_3^{2-}]$  are lowered. This suggests the Mg/Ca of *G. ruber* (w) and *T. sacculifer* (w/o sac) in our data set are less affected by dissolution compared to the multispecies correction derived by (Regenberg et al., 2014). As partial dissolution is determined by  $\Delta[CO_3^{2-}]$  of waters surrounding foraminifera shells, both bottom water  $\Delta[CO_3^{2-}]$  and pore-water  $\Delta[CO_3^{2-}]$ , the latter of which is controlled by local remineralization of organic matter, determine carbonate dissolution and Mg/Ca decreases (Martin & Sayles, 1996, 2006). While the empirical relationship of

Regenberg et al. (2014) represents a good average of global data, the extent to which dissolution affects Mg/Ca differs among regions. This is evident from the large variabilities associated with both sensitivities and the threshold values for carbonate dissolution in various regions as summarized in Regenberg et al. (2014). For the Atlantic core tops we worked on, shell weights and SEM images of *G. ruber* (w) from a subset of these samples showed that the extent of dissolution can vary within a narrow bottom water  $\Delta[\text{CO}_3^{2-}]$  range (Hertzberg & Schmidt, 2013).

Moreover, temperature and salinity sensitivities of both species do not vary much, considering regression uncertainties, when different dissolution correction parameters are employed (Figures 6C–6F). Given these observations, we recommend the use of temperature and salinity sensitivities based on the regression results obtained from Mg/Ca data without dissolution correction.

## 5. Conclusion

We present new core-top Mg/Ca data sets from the open Atlantic Ocean for two planktonic species, *G. ruber* (w) and *T. sacculifer* (w/o sac). Following recent advances in understanding about the planktonic Mg-paleothermometer, we reexamine the temperature sensitivity and secondary influences on Mg/Ca using core-top data. The calibrations we derive are as follows:

$$\text{Mg/Ca} = (0.40 \pm 0.07) * e^{(0.083 \pm 0.007) * T + (0.036 \pm 0.023) * (S-35)}, r^2 = 0.79, G. ruber (w)$$

$$\text{Mg/Ca} = (0.56 \pm 0.09) * e^{(0.066 \pm 0.007) * T + (0.056 \pm 0.023) * (S-35)}, r^2 = 0.73, T. sacculifer (w/o sac).$$

The temperature sensitivities obtained for both species are within the published range using different calibration methods. The salinity sensitivities are small, discounting the large salinity effect previously derived by Arbuszewski et al. (2010). Our salinity sensitivities are consistent with results from laboratory culture studies, confirming the minor influence of salinity on planktonic Mg/Ca. No significant pH effect is detected for our core-top data set, but we also encourage further studies (e.g., culturing) to elucidate the magnitude of a pH influence on Mg/Ca within a small pH range. Overall, our calibrations indicate planktonic Mg/Ca is a reliable temperature proxy over glacial-interglacial timescales.

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