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Paleoceanography and Paleoclimatology

COMMENTARY

10.1029/2018PA003517

Key Points:

- All species of planktonic foraminifera are characterized by a temperature sensitivity of ~6% per °C and salinity sensitivity of ~4% per PSU
- Modeled regional salinity variations during the LGM are small, and salinity does not pose a major problem for the Mg/Ca paleothermometer
- Most species have a high sensitivity to pH which can bias SSTs; we present “MgCaRB,” a protocol to accurately account for pH down-core

Supporting Information:

- Supporting Information S1
- Data Set S1

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Nonthermal Influences on Mg/Ca in Planktonic Foraminifera: A Review of Culture Studies and Application to the Last Glacial Maximum

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Abstract Planktonic foraminiferal Mg/Ca is one of the most widely applied sea surface temperature proxies. While the influence of salinity on Mg/Ca has led the accuracy of Mg/Ca-temperatures to be questioned, the effect of seawater carbonate chemistry (pH) is seldom accounted for down-core. Using published data sets, we review controls on Mg/Ca in laboratory cultures of planktonic foraminifera *Globigerinoides ruber* (white), *Trilobatus sacculifer*, *Globigerina bulloides*, and *Orbulina universa*. All are characterized by a temperature sensitivity of ~6% per °C and a salinity sensitivity of ~4% per salinity unit; all except *T. sacculifer* are sensitive to carbonate chemistry (–5 to –9% per 0.1 pH units). We demonstrate the down-core manifestation of these sensitivities using data spanning the last deglaciation and an Earth System Model forced with last glacial maximum conditions. While the effects of salinity are relatively minor, seawater carbonate chemistry exerts a large bias on Mg/Ca temperature if unaccounted for; however, as local pH changes beyond the effect of atmospheric CO₂ are relatively small across most of the ocean (less than ±0.05 pH units, 2σ), atmospheric CO₂ can be used to accurately correct Mg/Ca temperatures. We present protocols to correct Mg/Ca for pH down-core using either atmospheric CO₂ or (preferably) boron isotopes in a new software package “MgCaRB.”

Plain Language Summary The ratio of magnesium to calcium (Mg/Ca) in the shells of foraminifera (single-celled marine organisms) is sensitive to temperature, and as such can be used to reconstruct past climate changes. However, both the salinity and the acidity (pH) of seawater are also known to influence the concentration of Mg in foraminiferal shells, but the extent to which this is the case is debated. We review experiments in which foraminifera were grown under carefully controlled laboratory conditions to examine how sensitive Mg/Ca is to salinity and pH and apply these findings to data from the last ice age. We find that although salinity and pH can bias Mg/Ca-derived temperature, these effects can (and should) be corrected for. Thus, Mg/Ca remains a useful tool to understand past changes in Earth's climate.

1. Introduction

The ratio of Mg to Ca (Mg/Ca) in the tests of planktonic foraminifera is one of the most widely applied methods used to reconstruct sea surface temperature (SST). While a multitude of laboratory culture, sediment-trap, and core-top studies have demonstrated that Mg/Ca is highly sensitive to temperature (e.g., Anand et al., 2003; Elderfield & Ganssen, 2000; Nürnberg et al., 1996), it has nonetheless been recognized since the conception of the proxy that Mg incorporation is not purely a function of temperature (Clarke & Wheeler, 1922; Lea et al., 1999; Nürnberg et al., 1996). Largely through careful laboratory cultures, it has since been demonstrated that principal among these secondary controls are salinity and seawater carbonate chemistry (usually expressed as pH or [CO₃²⁻]; e.g., Hönisch et al., 2013; Lea et al., 1999; Nürnberg et al., 1996; Russell et al., 2004). On longer timescales (>1 Ma), changes in the seawater Mg/Ca ratio must also be considered (e.g., Evans & Müller, 2012).

Following the publication of several studies documenting a large salinity effect on Mg/Ca (15–60% per salinity unit; Arbuszewski et al., 2010; Mathien-Blard & Bassinot, 2009), the use of the proxy has declined sharply, with ~50% fewer publications using planktonic foraminiferal Mg/Ca since 2011 (Google Scholar data, as of November 2018). This decline is perhaps indicative that confidence in the Mg/Ca paleothermometer has

decreased. However, such a large salinity influence is at odds with the modest salinity sensitivity of ~4% per salinity unit suggested by laboratory cultures (e.g., Hönisch et al., 2013; Nürnberg et al., 1996). In contrast, the effect of seawater carbonate chemistry, repeatedly demonstrated in laboratory culture (e.g., Evans et al., 2016; Russell et al., 2004), has largely been ignored in paleo-applications and was only recently demonstrated in nonlaboratory grown foraminifera for the first time (Gray et al., 2018).

Here we review the controls on Mg/Ca in planktonic foraminifera grown in culture studies and demonstrate the effect of the resulting sensitivities to temperature, salinity, and pH with down-core data spanning the last deglaciation and an Earth System Model forced with last glacial maximum (LGM) conditions. We show that while salinity and seawater carbonate chemistry do exert an influence on Mg/Ca and should therefore be accounted for, corrections for these nonthermal influences may be accurately applied in order to produce more robust temperature estimates.

2. Constraining the Controls on Planktonic Foraminiferal Mg/Ca Using Laboratory Cultures

To assess the sensitivity of foraminiferal Mg/Ca to temperature, the carbonate system, and salinity, we compile the data of the four species for which all three variables have been studied in laboratory culture: *Globigerinoides ruber* (white), *Orbulina universa*, *Trilobatus sacculifer*, and *Globigerina bulloides* (Allen et al., 2016; Dueñas-Bohórquez et al., 2009; Evans et al., 2016; Hönisch et al., 2013; Kisakürek et al., 2008; Lea et al., 1999; Russell et al., 2004). We use the results of laboratory cultures because these uniquely allow environmental parameters to be independently varied, are free from taphonomic effects, and allow comparison of foraminiferal Mg/Ca to in situ measurements of environmental parameters. For each species, a multivariate least-squares regression was performed using all cultures for which temperature, salinity, and carbonate chemistry measurements were available. Our approach differs from the usual treatment of culture data as we consider all experiments conducted on each species together in one regression model (see Supporting Information S1).

While there is currently no definitive theoretical or experimental basis regarding which carbonate system parameter(s) planktonic foraminifera Mg/Ca should be related to, most studies attribute the effect to either pH or $[\text{CO}_3^{2-}]$ (e.g., Evans et al., 2016; Russell et al., 2004). Here pH was chosen as the controlling carbonate system parameter for both theoretical/experimental and practical reasons (Supporting Information S1). Due to the tight coupling of surface ocean pH and $[\text{CO}_3^{2-}]$ in response to changes in atmospheric CO_2 , using $[\text{CO}_3^{2-}]$ rather than pH would not radically alter the main conclusions of this study.

The data were fit using an exponential function to yield the following equations (see Figures 1a–1c). For *G. ruber* (white),

$$\text{Mg/Ca} = \exp(0.036(S-35) + 0.064T - 0.87(\text{pH}-8) - 0.03). \quad (1)$$

Residual Standard Error (RSE) = 0.68.

For *T. sacculifer*,

$$\text{Mg/Ca} = \exp(0.054(S-35) + 0.062T - 0.24). \quad (2)$$

RSE = 0.51. Note, the pH sensitivity is insignificant in this species and was omitted (see Table S1).

For *G. bulloides*,

$$\text{Mg/Ca} = \exp(0.036(S-35) + 0.064T - 0.88(\text{pH}-8) + 0.15). \quad (3)$$

RSE = 0.61. Note, the generic salinity sensitivity has been assumed in this equation as no studies under varying salinities have been performed for this species (see Table S1).

For *G. bulloides*, including one outlier (the highest temperature data point),

$$\text{Mg/Ca} = \exp(0.036(S-35) + 0.10T - 0.84(\text{pH}-8) - 0.71). \quad (4)$$

RSE = 0.67. Including this high temperature data point increases the residual standard error and results in a temperature sensitivity substantially higher than observed in any other cultured species.

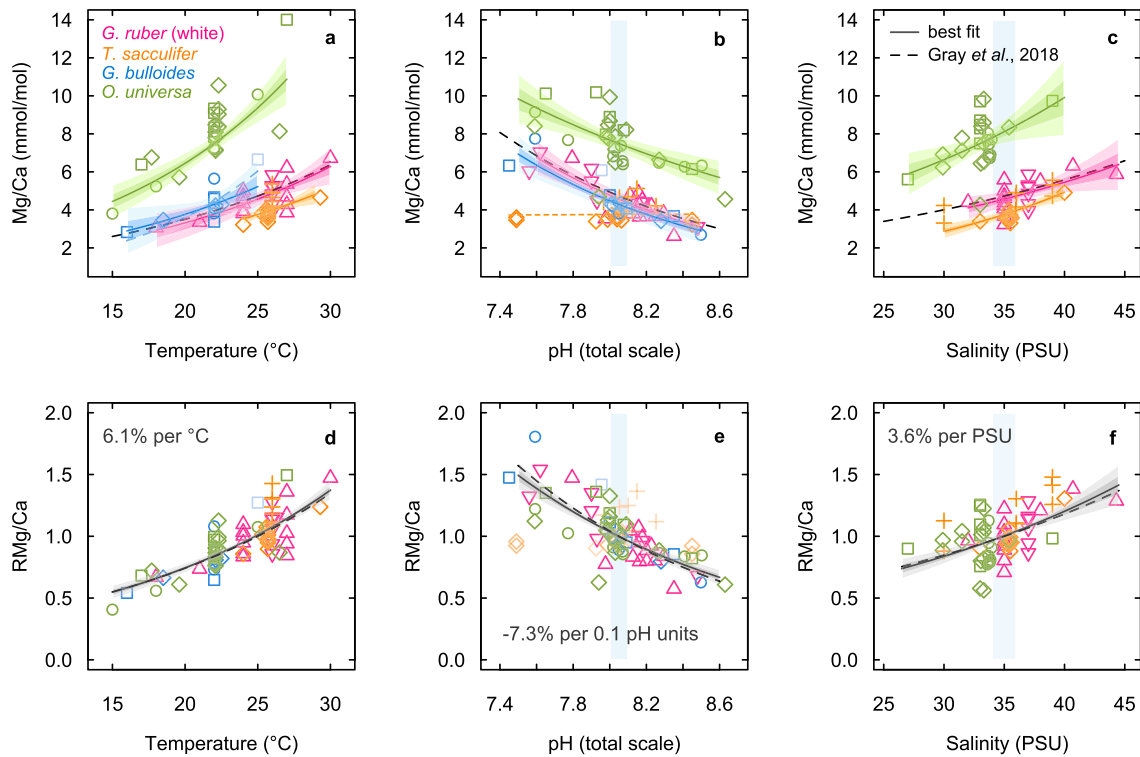


Figure 1. The effect of temperature (a and d), pH (b and e), and salinity (c and f) on Mg/Ca in planktonic foraminifera grown in laboratory culture. Data from different studies are represented by the symbols: Lea et al. (1999), squares; Russell et al. (2004), circles; Kisakürek et al. (2008), triangles; Dueñas-Bohórquez et al. (2009), crosses; Hönisch et al. (2013)/Allen et al. (2016), diamonds; Evans et al. (2016), inverted triangles. In each panel, we show data from all culture experiments conducted on each species normalized for the other variables using the sensitivities from the multivariate regressions (i.e., in the temperature panel, the data from the salinity and pH experiments are also shown normalized to a constant salinity and pH). Each data point represents an average of multiple individual foraminifera; the spread of the data is indicative of how well the other variables are described by the multivariate regression, as well as any inherent noise. Solid lines show the best fit to data from the multivariate regression with 68% and 95% confidence intervals. The black dashed line is the *G. ruber* (white) sediment trap calibration of Gray et al. (2018). The gray boxes show ± 1 PSU and ± 0.05 pH units, the typical 2σ variation expected about the mean surface ocean changes in salinity and pH during the LGM (section 4). In the lower panels (d–f), data are shown as a ratio to the \sim midpoint of the normalized Mg/Ca value in the data set, allowing us to compare the sensitivities of the different species together. The *T. sacculifer* data are not included in the multispecies pH regression, and these data are indicated by faint symbols in (e). The outlying *G. bulloides* data point is shown in faint blue. This data point is not included in the regressions. The *G. bulloides* Mg/Ca-temperature relationship including this data point is shown by the dashed blue line in panel (a).

For *O. universa*:

$$\text{Mg/Ca} = \exp(0.040(S-35) + 0.075T - 0.50(\text{pH}-8) + 0.48). \quad (5)$$

RSE = 1.15.

Where T is temperature in degrees Celsius, S is salinity in practical salinity units (PSU), and pH is on the total scale. See Table S1 for coefficient significance and uncertainty, as well as notes.

Converting the Gray et al. (2018), *G. ruber* (white) sediment-trap calibration into this form (with pH on the total scale) yields the following equation:

$$\text{Mg/Ca} = \exp(0.033(S-35) + 0.060T - 0.83(\text{pH}-8) + 0.10). \quad (6)$$

RSE = 0.50.

This analysis demonstrates that all four species have indistinguishable Mg/Ca-temperature and Mg/Ca-salinity sensitivities, being characterized by a $6.1 \pm 0.01\%$ (2σ) increase per degree Celsius and a $3.6 \pm 0.01\%$ increase per PSU when the data from all species are combined (Figures 1d and 1e and Supporting Information S1). The temperature and salinity sensitivities from all cultured species are in excellent agreement with the global sediment trap study of Gray et al. (2018). In contrast to the

apparently universal temperature and salinity sensitivities, the response to carbonate chemistry appears to be species-specific; while *G. ruber*, *O. universa*, and *G. bulloides* are all characterized by a negative Mg/Ca-pH relationship with a sensitivity of -5 to -9% per 0.1 pH unit increase, in good agreement with the global sediment trap study of Gray et al. (2018), the culture data of Allen et al. (2016) show only a very minor response of *T. sacculifer* Mg/Ca to any carbonate system parameter. It is beyond the scope of this study to examine the basis of these sensitivities, which remain poorly understood, but see, for example, Bentov and Erez (2006) and Evans et al. (2018) for a discussion of possible mechanisms. We note the form of the relationship between Mg/Ca and pH may also be more complex than an exponential function (Evans et al., 2016), although Mg/Ca-derived temperatures are insensitive to the function form in the Pleistocene.

In Table S1, we present a multi-species equation that could be used as a reference for species for which insufficient calibration data are currently available. However, this multi-species equation should only be used to reconstruct relative temperature changes, and due to the apparently species-specific response of Mg/Ca to pH, it should be applied with caution. As all species have the same temperature and salinity sensitivity within uncertainty, in Table S1 we present a further set of species-specific equations where the “generic” temperature and salinity sensitivities were prescribed in the regression model, and the pH and “intercept” terms were allowed to vary. Given the considerably smaller uncertainty in the generic temperature and salinity sensitivities (due to the increased sample size relative to the single-species regressions), these equations considerably reduce the uncertainty in calibrated Mg/Ca-SSTs.

In common with previous studies utilizing culture data, we find only a minor sensitivity of Mg/Ca to salinity in planktonic foraminifera (Dueñas-Bohórquez et al., 2009; Hönisch et al., 2013; Kisakürek et al., 2008; Lea et al., 1999; Nürnberg et al., 1996). This finding is at odds with some core-top studies which have suggested a much higher ~ 15 – 60% per PSU sensitivity to salinity (Arbuszewski et al., 2010; Ferguson et al., 2008; Mathien-Blard & Bassinot, 2009). As discussed in detail in Hönisch et al. (2013) and Hertzberg and Schmidt (2013), this discrepancy arises through the way that core-top data have been treated in some studies, either through inappropriate correction for dissolution or incorrect assumption of calcification depth/season. Furthermore, a “residual salinity” signal has been induced in some studies by forcing a Mg/Ca-temperature relationship that does not accurately describe these foraminifera through a dataset in which temperature and salinity covary (Khider et al., 2015). In certain settings, such as parts of the Mediterranean, the role of high-Mg diagenetic overgrowths must also be considered (cf. Ferguson et al., 2008; Hoogakker et al., 2009). Because there is good reason to disregard the high salinity sensitivity observed in some core-top studies and the agreement between the salinity sensitivity observed in culture, the global sediment-trap study of Gray et al. (2018; Figure 1), and the more recent core-top study of Khider et al. (2015), we recommend that the culture salinity sensitivities be applied down-core. As we demonstrate below, given the regional salinity variations expected in most of the ocean over glacial-interglacial cycles (less than ± 1 PSU, 2σ), a salinity sensitivity of $\sim 4\%$ per PSU does not pose a major problem for the Mg/Ca paleothermometer.

Recently, Gray et al. (2018) demonstrated that the widely used Mg/Ca-temperature sensitivity of $\sim 9\%$ per $^{\circ}\text{C}$ (e.g., Kisakürek et al., 2008) does not accurately describe a global set of sediment-trap *G. ruber* (white) samples when the combined impact of temperature, pH, and salinity are separated from each other. The principal reason for this discrepancy is that increasing temperature decreases the pH of water by ~ 0.015 pH units per degree Celsius, via its effect on K_{W} (the dissociation constant of water). As a result, planktonic foraminiferal species which are sensitive to pH will have a higher “apparent” Mg/Ca sensitivity to temperature than the direct thermal effect. That is, keeping all else constant, increasing temperature by 1°C will result in an $\sim 9\%$ increase in Mg/Ca; $\sim 6\%$ of this is the “direct” thermal effect, and the remainder is due to the effect of temperature on pH and pH on Mg/Ca (see Gray et al., 2018). However, it is important to deconvolve the direct thermal effect and the temperature-pH effect as temperature is not the only control on pH; over glacial cycles surface ocean pH increases by ~ 0.12 pH units with the lowering of atmospheric CO_2 (see section 4). Failing to account for this pH change would result in a substantial bias to Mg/Ca-SSTs (see sections 3 and 4 below).

The results of the multivariate regressions of the culture data described above demonstrate that the other planktonic species with a Mg/Ca-pH sensitivity, *O. universa* and *G. bulloides*, are also characterized by a Mg/Ca-temperature sensitivity of $\sim 6\%$ per $^{\circ}\text{C}$ when the effect of temperature on pH is accounted for. It is

therefore important to consider the impact of the carbonate system and the temperature-derived influence on K_W on Mg/Ca reconstructions from these three species. In contrast, there is no evidence for a large pH effect on *T. sacculifer* Mg/Ca (see Figure 1 and Table S1 and Allen et al., 2016), which appears to be an exception in this respect based on the available data. However, *T. sacculifer* is nonetheless also characterized by a Mg/Ca-temperature sensitivity of ~6% per °C, which provides additional evidence that it is the interaction of temperature and pH that results in the higher apparent sensitivities of the other species considered here. Specifically, because pH exerts at most a minor control on *T. sacculifer* Mg/Ca, there is no mechanism by which temperature-driven pH change can impact the temperature sensitivity of this species. The direct thermal Mg/Ca-temperature sensitivity of foraminifera that are sensitive to pH is the same, but the overprint of K_W -derived pH changes results in different apparent temperature sensitivities.

3. Down-core Application to the Last Deglaciation

The covariance between temperature and pH induced by the thermal effect on K_W (as well as the other carbonate and borate disassociation constants) can be overcome by iteratively solving Mg/Ca and either boron isotopes ($\delta^{11}\text{B}$) or atmospheric $p\text{CO}_2$ for temperature and pH (see Supporting Information S1 for how this is done by our MgCaRB script). The boron isotope method is preferred as it results in lower uncertainties (and includes fewer assumptions) than the method using atmospheric $p\text{CO}_2$, which requires equilibrium (or constant disequilibrium) with the atmosphere and alkalinity to be assumed (see section 4). Note, our iterative approach should also result in more accurate estimates of paleo-pH (and thus paleo- CO_2) derived from boron isotopes. We use our MgCaRB script to apply the calibrations for the pH-sensitive species *G. ruber* (white) and the pH-insensitive species *T. sacculifer* to previously published paired Mg/Ca and $\delta^{11}\text{B}$ records spanning the last deglaciation in regions with existing $U^{k'}_{37}$ temperature records. In the Western Tropical Atlantic, we apply the *G. ruber* (white) calibration to the Mg/Ca and $\delta^{11}\text{B}$ record from core GeoB1523-1 (Henehan et al., 2013) and compare the resulting SSTs to the $U^{k'}_{37}$ SST record from core M35003-4 (Rühlemann et al., 1999). In the East Equatorial Pacific, we apply the *T. sacculifer* calibration to the Mg/Ca and $\delta^{11}\text{B}$ record from ODP Site 1238 (Martínez-Boti et al., 2015) and compare the SSTs to the $U^{k'}_{37}$ SST record from ODP Site 846 (Lawrence et al., 2006). Foraminiferal $\delta^{11}\text{B}$ values were converted to $\delta^{11}\text{B}$ -borate using the calibrations of Henehan et al. (2016). For comparison, the same exercise was performed using pH derived from atmospheric $p\text{CO}_2$ instead of the $\delta^{11}\text{B}$ record. Here the ice core $p\text{CO}_2$ stack of Bereiter et al. (2015) was used. In all cases, the Mg/Ca data were salinity corrected by scaling salinity to the sea level curve of Spratt and Lisiecki (2016), although this has only a minor effect on reconstructed SST (see section 4).

The results show that when corrected for pH (using either $\delta^{11}\text{B}$ or $p\text{CO}_2$), the Mg/Ca-SSTs of the pH-sensitive *G. ruber* (white) show a better match to the $U^{k'}_{37}$ -SSTs over deglaciation; uncorrected for pH, the Mg/Ca-SSTs overestimate glacial cooling by ~1.5 °C relative to $U^{k'}_{37}$ (Figure 2). Conversely, if a pH “correction” is forced onto the pH-insensitive species *T. sacculifer* by applying the multi-species calibration (which has a pH sensitivity of -7.3% per 0.1 pH unit) rather than the species-specific *T. sacculifer* calibration (which has no sensitivity to pH), the Mg/Ca-SSTs show a poorer match to the $U^{k'}_{37}$ -SSTs over deglaciation. That is, a species of foraminifera which displays a high Mg/Ca sensitivity to pH in culture shows a better match to $U^{k'}_{37}$ -SSTs over deglaciation when the Mg/Ca-SSTs are corrected for pH, and a species of foraminifera which is insensitive to pH in culture shows a better match $U^{k'}_{37}$ -SSTs over deglaciation when no pH correction is applied. This result indicates the differences in pH sensitivity observed in culture between different species are also apparent in the geological record, validates the application of the culture-based calibrations down-core, and highlights that ignoring the pH effect on Mg/Ca may result in substantial bias (~1.5 °C, see section 4).

4. LGM pH and Salinity Bias in an Earth System Model

We use a state-of-the-art Earth System Model (IPSL-CM5A-MR) forced with preindustrial (PI) and LGM boundary conditions (Braconnot et al., 2012; Dufresne et al., 2013; Taylor et al., 2012) to assess the potential of whole ocean and regional salinity and pH biases on Mg/Ca-SSTs. Modeled changes in salinity and pH were converted to apparent temperature changes using the generic sensitivities given in the results of the culturing experiments (Table S1). The purpose of this exercise is not to try to accurately account for

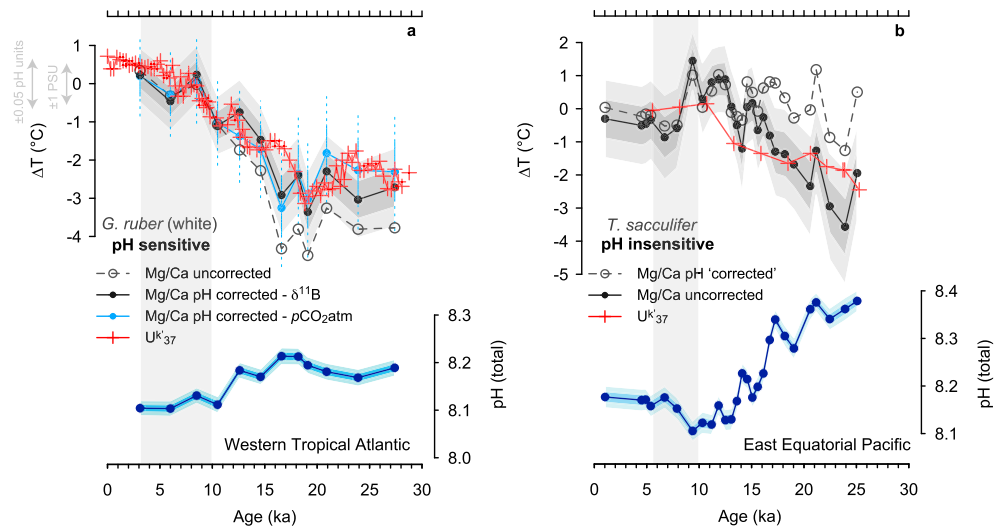


Figure 2. A comparison of alkenone temperatures (red crosses) with Mg/Ca temperatures both corrected and uncorrected for the effect of pH using boron isotopes. All temperature data are shown as a difference from mean Holocene values for the interval in which the Mg/Ca and U^{k}_{37} overlap (light gray shaded box) (a) *G. ruber* (white; a pH sensitive species) in the Western Tropical Atlantic. Temperature and pH were calculated from Mg/Ca and $\delta^{11}B$, solving iteratively using the species-specific equation given in Table S1. Temperature is shown with and without pH correction; note, temperature calculated without correcting for pH overestimates glacial cooling by $\sim 1.5^{\circ}C$. The error envelopes show the combined 1σ and 2σ uncertainty from calibration uncertainty, a $\delta^{11}B$ uncertainty of $\pm 0.23\text{‰}$ (2σ ; Foster et al., 2013), and a salinity uncertainty of ± 1 PSU (2σ). Temperature was calculated from Mg/Ca and pH derived from atmospheric pCO_2 for comparison; the result is indistinguishable from the estimates using $\delta^{11}B$. Mg/Ca and $\delta^{11}B$ data are from GeoB1523-1 ($3.83^{\circ}N$, $-41.62^{\circ}E$, 3,292 m water depth; Henehan et al., 2013). U^{k}_{37} data are from M35003-4 ($12.08^{\circ}N$, $-61.25^{\circ}E$, 1,299-m water depth; Rühlemann et al., 1999). These sites were selected due to their proximity. (b) A similar exercise based on *T. sacculifer* data in the East Equatorial Pacific, a species with no significant Mg/Ca-pH sensitivity. Temperature calculated with the multi-species calibration, which has identical temperature and salinity sensitivities to the *T. sacculifer* calibration, but a pH sensitivity of -7.3% per 0.1 pH unit (rather than zero), is also shown (described as pH “corrected”). As expected from the culture experiments, good agreement with U^{k}_{37} SSTs only arises when *T. sacculifer* is not forced with a high pH sensitivity. Mg/Ca and $\delta^{11}B$ data are from ODP Site 1238 ($-1.87^{\circ}N$, $-82.78^{\circ}E$, 2,203-m water depth; Martínez-Botí et al., 2015). U^{k}_{37} data are from ODP Site 846 ($-3.10^{\circ}N$, $-90.82^{\circ}E$, 3,296 m water depth; Lawrence et al., 2006). The U^{k}_{37} data were calibrated using Conte et al. (2006). Note both U^{k}_{37} records are from sites where the temperature is too low to be substantially impacted by the nonlinearity of U^{k}_{37} (e.g., Tierney & Tingley, 2018). See Supporting Information S1 for a further example using *G. ruber* (white) and an example using *G. bulloides*.

changes in salinity and pH within each region but instead to get an overall sense of how large these regional changes are likely to be, and thus how problematic regional changes in salinity and pH are for Mg/Ca paleothermometry.

Within the model, mean surface ocean salinity increases by 0.7 PSU during the LGM, less than the 1 PSU increase (from the build up of terrestrial ice sheets) the whole ocean is forced with (Figure 3). This relative freshening of the surface is due to the deep ocean becoming disproportionately saline during the LGM (e.g., Adkins et al., 2002; Galbraith & de Lavergne, 2018). Mean surface ocean pH increases by 0.15 units during the LGM; 0.12 pH units of the increase is associated with the lowering of atmospheric CO_2 , and the remainder is due to cooler SSTs.

The 0.7 PSU increase in mean surface ocean salinity biases Mg/Ca-SSTs by only $0.35^{\circ}C$. Furthermore, for most of the open ocean, the local change in salinity (beyond the mean surface ocean change) is small, with 95% of local salinity changes less than ± 1 PSU (Figure S3), equivalent to a temperature error of $\pm 0.5^{\circ}C$. Thus, for most of the open ocean, using the mean LGM surface ocean change of 0.7 PSU scaled to sea level with an uncertainty of ± 1 PSU (2σ) is an entirely reasonable assumption when calculating temperature from Mg/Ca. For coastal regions or semienclosed marginal seas, where local salinity changes are likely to be larger, an estimation of local salinity change is required (e.g., Thirumalai et al., 2016; Weldeab et al., 2007).

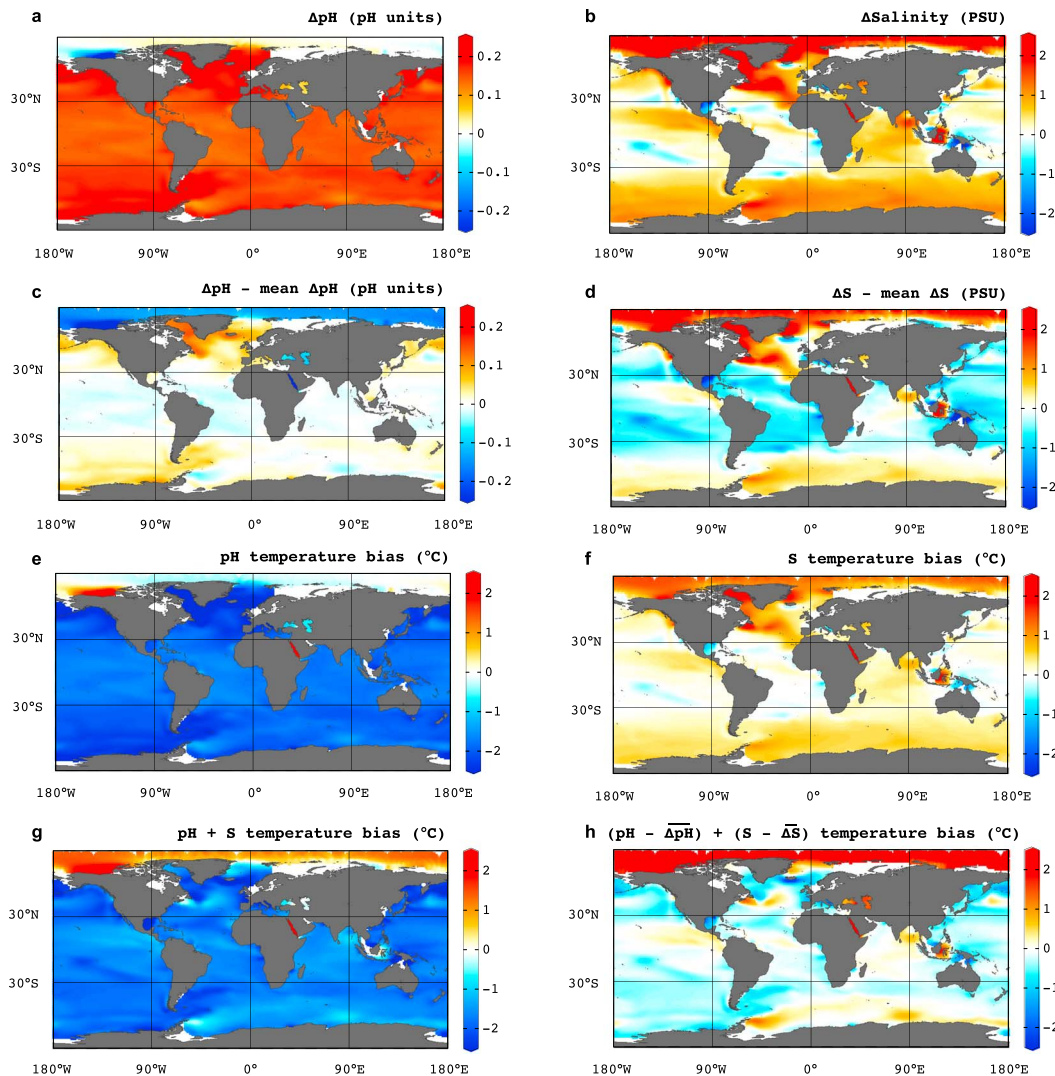


Figure 3. Using a latest generation Earth System Model to examine the extent to which LGM-preindustrial (PI) changes in salinity and pH are likely to bias Mg/Ca-derived SST (a) LGM-PI surface ocean pH difference, (b) LGM-PI surface ocean salinity difference, (c) LGM-PI surface ocean pH difference-mean LGM-PI surface ocean pH difference, (d) LGM-PI surface ocean salinity difference-mean LGM-PI surface ocean salinity difference, (e) temperature bias from LGM-PI pH change (here and throughout, the “generic” temperature, pH, and salinity sensitivities are used), (f) temperature bias from LGM-PI salinity change, (g) temperature bias if the combined LGM-PI pH and salinity change is unaccounted for (h) temperature bias from combined LGM-PI pH and salinity change, corrected for the mean surface ocean change in pH and salinity. Note, while salinity and (particularly) pH changes during the LGM bias Mg/Ca-temperatures, in most of the open ocean the local changes in salinity and pH are small. As such, using the mean surface ocean change in salinity and pH to correct Mg/Ca will accurately remove the salinity a pH bias, resulting in accurate temperatures. Data shown are the mean of the final 50 years of each experiment. See https://pmip3.lscce.ipsl.fr/p3_c5_design/ for experiment details.

The 0.15 pH unit increase in mean surface ocean pH biases Mg/Ca-SSTs by -1.8°C , substantially more than the effect of salinity; the combined effect of the whole ocean change in salinity and pH is to bias Mg/Ca-SSTs by -1.5°C . As the increase in surface ocean pH is predominantly due to the lowering of atmospheric CO_2 , for most of the open ocean the local change in pH (beyond the mean surface ocean change) is relatively small, with 95% of local pH changes less than ± 0.05 pH units (Figure S3), equivalent to a temperature error of $\pm 0.65^{\circ}\text{C}$. Therefore, in most of the open ocean, if no boron isotope record is available SST can be calculated with pH estimated from atmospheric CO_2 (with an uncertainty of approximately ± 0.05 pH units, 2σ), solving iteratively with Mg/Ca to overcome the covariance induced by the thermal influence on pH (see Supporting Information S1). The combined effect of a salinity uncertainty of ± 1 PSU (2σ) and a pH uncertainty of ± 0.05 (2σ) is only $\pm 0.8^{\circ}\text{C}$ (2σ). Including calibration uncertainties, total uncertainty is typically $\sim \pm 1.5^{\circ}\text{C}$ (2σ); with boron isotopes this is reduced to $\sim \pm 1.2^{\circ}\text{C}$.

As well as the secondary controls on the uptake of Mg into foraminiferal calcite, postdepositional dissolution is known to affect the Mg/Ca of foraminiferal tests, and thus Mg/Ca derived temperatures (Brown & Elderfield, 1996; Regenberg et al., 2014). As the calibrations presented in this study are derived from foraminifera that have not undergone dissolution, these calibrations are better suited for reconstructing relative changes in temperature (as in the examples given in section 3), especially at deeper/more undersaturated (with respect to calcite) core sites. To reconstruct absolute temperature, Mg/Ca values must first be corrected back to their primary value, and future work should focus on constraining the effects of dissolution to effectively make this correction (or develop a calibration that explicitly accounts for temperature, pH, salinity, and bottom-water saturation). In reconstructions of both relative and absolute temperature the assumption is usually made that the effects of dissolution have remained constant through time; over glacial-interglacial cycles this assumption is broadly supported in the Indo-Pacific and middepth Atlantic (the locations of the cores used in this study), where changes in bottom water saturation are relatively muted (Yu et al., 2013). However, changes in saturation within the deep and intermediate Atlantic are much larger over glacial-interglacial cycles (Yu et al., 2013). In these locations, and elsewhere further back in time, corrections for changing bottom-water saturation could be made using benthic foraminiferal B/Ca (e.g., Rae et al., 2011).

5. Conclusion

We assess the sensitivity of planktonic foraminiferal Mg/Ca to temperature, salinity, and carbonate chemistry (pH) using previously published laboratory culture experiments. All species of planktonic foraminifera studied are characterized by a Mg/Ca temperature sensitivity of a $6.1 \pm 0.01\%$ (2σ) per degree Celsius and a salinity sensitivity of $3.6\% \pm 0.01\%$ (2σ) per PSU, in good agreement with the sensitivities observed in a global sediment trap study (Gray et al., 2018). Conversely, while *G. ruber* (white), *G. bulloides*, and *O. universa* all display a large influence of seawater carbonate chemistry, with a sensitivity of -5 to -9% per 0.1 pH units, Mg/Ca in *T. sacculifer* appears insensitive to carbonate chemistry. Applying these sensitivities down-core to paired Mg/Ca and boron isotope data spanning the last deglaciation, we find better agreement with $U^{k'}_{37}$ temperatures when the correct species-specific pH sensitivity is used, validating the sensitivities observed in culture. We use a state-of-the-art Earth System Model to assess the potential temperature bias from salinity and pH during the LGM. Given the salinity variations observed within the model in most of the open ocean, a salinity sensitivity of $\sim 4\%$ per PSU does not pose a major problem for the Mg/Ca paleothermometer. The effect of pH is considerably greater than that of salinity, resulting in a large bias in reconstructed temperature if unaccounted for; however, local pH changes beyond the effect of atmospheric CO_2 are relatively small in most of the ocean (less than ± 0.05 pH units, 2σ). The effect of pH can be accurately corrected for by iteratively solving Mg/Ca with either boron isotopes or atmospheric pCO_2 . We present new protocols to make this correction in a software package called “MgCaRB.” Given the secondary influences on Mg/Ca are either small (salinity) or can accurately be corrected (pH), Mg/Ca remains a useful and accurate paleothermometer.

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