The effects of temperature, salinity, and the carbonate system on Mg/Ca in *Globigerinoides ruber* (white): a global sediment trap calibration

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Abstract

The Mg/Ca of planktic foraminifera *Globeriginoides ruber* (white) is a widely applied proxy for tropical and sub-tropical sea-surface temperature. The accuracy with which temperature can be reconstructed depends on how accurately relationships between Mg/Ca and temperature and the multiple secondary controls on Mg/Ca are known; however, these relationships remain poorly quantified under oceanic conditions. Here, we present new calibrations based on 440 sediment trap/plankton tow samples from the Atlantic, Pacific and Indian Oceans, including 130 new samples

from the Bay of Bengal/Arabian Sea and the tropical Atlantic Ocean. Our results indicate temperature, salinity and the carbonate system all significantly influence Mg/Ca in *G. ruber* (white). We propose two calibration models: The first model assumes pH is the controlling carbonate system parameter. In this model, Mg/Ca has a temperature sensitivity of 6.0±0.8 %/°C (2σ), a salinity sensitivity of 3.3±2.2 %/PSU and a pH sensitivity of -8.3±7.7 %/0.1 pH units; The second model assumes carbonate ion concentration ($[CO_3^{2-}]$) is the controlling carbonate system parameter. In this model, Mg/Ca has a temperature sensitivity of 6.7±0.8 %/°C, a salinity sensitivity of 5.0±3.0 %/PSU and a $[CO_3^{2-}]$ sensitivity of -0.24±0.11 %/μmol kg^{-1}. In both models, the temperature sensitivity is significantly lower than the widely-applied sensitivity of 9.0±0.6 %/°C. Application of our new calibrations to down-core data from the Last Glacial Maximum, considering whole ocean changes in salinity and carbonate chemistry, indicate a cooling of 2.4±1.6 °C in the tropical oceans if pH is the controlling parameter and 1.5±1.4 °C if $[CO_3^{2-}]$ is the controlling parameter.

Keywords: Mg/Ca; planktic foraminifera; SST; salinity; carbonate chemistry

1. Introduction

Planktic foraminiferal Mg/Ca paleothermometry is one of the most widely applied techniques to reconstruct sea-surface temperature (SST) (e.g. Lea *et al.,* 2000; Weldeab *et al*., 2007; Schmidt and Lynch-Stieglitz, 2011; Mohtadi *et al*., 2014). Fundamental to robust SST reconstruction is accurate knowledge of the relationship between foraminiferal Mg/Ca and temperature, as well as the multiple secondary influences on Mg incorporation into foraminiferal calcite. The substantial biological

mediation of Mg incorporation into foraminiferal calcite necessitates species-specific calibrations (Nürnberg, 1996; Rosenthal *et al*., 1997; Lea *et al*., 1999; Erez *et al*., 2003).

Globigerinoides ruber (white) is the most widely used species for reconstructing tropical and subtropical SST due to its cosmopolitan nature, high abundance, and shallow habitat depth (0-50 m) (Hemleben *et al*., 1989; Schiebel and Hemleben, 2017). Estimates of the sensitivity of Mg/Ca in *G. ruber* (w) to temperature fall between 5-10 % per °C (Table 1), and the most widely-applied calibration has a sensitivity of 9.0±0.6 %/°C (2σ) (Dekens *et al*., 2002; Anand *et al*., 2003). Studies of *G. ruber* (w) grown in laboratory culture, where calcification temperature is well constrained, yield a temperature sensitivity of 8±3 %/°C (Kisakürek *et al.*, 2008).

Since the early development of Mg/Ca paleothermometry, salinity and carbonate chemistry have been known to exert a secondary influence on Mg/Ca (Nürnberg *et al*. 1996; Lea *et al*., 1999). Estimates of the sensitivity of Mg/Ca in *G. ruber* to salinity vary widely. Laboratory culture studies indicate a salinity sensitivity of 3-5 % per salinity unit (Kisakürek *et al.*, 2008; Hönisch *et al.*, 2013), whereas several core-top studies suggest a significantly higher sensitivity of 15-29 %/PSU (Ferguson *et al*., 2008; Arbueszwski *et al*. 2010; Mathien-Blard and Bassinot, 2009), although subsequent work has revised down these core-top estimates (Bousetta *et al*., 2011; Hertzberg *et al.,* 2013; Hönisch *et al.*, 2013). More recently, a Bayesian multivariate fit to core-top data suggested a salinity sensitivity of 3.9±1.2 %/PSU (Khider *et al*., 2015), similar to the results of the culture studies.

Laboratory culture studies show that the carbonate chemistry of seawater, as expressed by pH or carbonate ion concentration ($[CO_3^{2-}]$), significantly effects planktic foraminiferal Mg/Ca. Mg/Ca decreases as pH (and $[CO_3^{2-}]$) increases, with a sensitivity of ~5-10% per 0.1 pH unit (Lea *et al.*, 1999; Russell *et al.*, 2004; Kisakürek *et al.*, 2008; Evans *et al*., 2016). Despite the significant effect of carbonate chemistry observed within culture studies, the influence of carbonate chemistry on Mg/Ca in planktic foraminifera that have calcified under oceanic conditions (i.e. none laboratory-grown) has not been previously investigated.

Here, we assess the relationship between Mg/Ca in *G. ruber* (w) and temperature, salinity, and the carbonate system using samples collected by sediment trap and plankton tow. Sediment trap and plankton tow samples minimise the influence of post-depositional calcite dissolution and/or secondary overgrowth deposition that hinder core-top studies, whilst allowing the analysis of foraminifera that have calcified under oceanic conditions within a well constrained time-period. We have generated new data from a transect of sediment traps located along an isotherm with a strong salinity gradient in the Bay of Bengal and Arabian Sea, which we use to assess the effects of salinity. We have also generated new data from a sediment trap in the tropical Atlantic Ocean, off Mauritania; in these samples, we separated foraminifera by morphotype and into narrow size fractions to assess the effects of biological variability on Mg/Ca. Our newly generated data are combined with all previously published *G. ruber* (w) Mg/Ca data from foraminifera collected by sediment trap and plankton tow. We use climatological data to calculate temperature, salinity, pH and $[CO_3^{2-}]$ at the depth habitat range of *G. ruber* (w) for each of the newly generated and previously published trap/tow samples, and constrain the

individual effects of temperature and salinity, pH and [CO_3^{2-}] on Mg/Ca using subsets of data where covariance between environmental variables is negligible.

2. Materials and Methods

2.1 Arabian Sea and Bay of Bengal sediment trap samples

We utilised 51 samples from sediment trap deployments NBBT09 (17.383°N, 89.700°E; 1450 m water depth), CBBT06 (11.033°N, 84.433°E; 899 m water depth), SBBT09 (5.400°N, 86.767°E; 886 m water depth), and JGOFS AS02-M5 (10.003 °N, 65.005 °E; 2363 m water depth) (Unger *et al*., 2003; Honjo *et al*., 1999) (see supplementary material (SM) and Table S1). These sediment trap deployments form a transect spanning a large salinity gradient (~4 units), with ~no change in mean annual temperature between the sites (Fig. 1). Foraminifera were picked from the 200 to 400 μm size fraction (see SM), and between 5-30 individuals of *G. ruber* (w) *sensu stricto* (Wang [2000]) were used per sample for trace element analysis.

Foraminifera were cleaned following a modified version of the method of Pak *et al*., (2004) and the acidified samples were analysed at Rutgers University using magnetic-sector ICP-MS (Thermo Element XR) (SM). Reproducibility of consistency standards with a Mg/Ca similar to *G. ruber* (w) was 0.03 mmol/mol (0.6%) (2σ). Six of the foraminiferal samples (~12%) were split into replicates and cleaned/analysed separately, with a reproducibility of 0.12 mmol/mol (2.2%) (2σ). The resulting Mg/Ca data are given in Table S2.

2.2 Tropical Atlantic sediment trap samples

We measured Mg/Ca ratios in foraminifera collected by a sediment trap located off Mauritania, in the eastern tropical Atlantic (Fig. 1). The samples were collected in trap deployments CB-7, CB-9, CB-10, CB-12 and CB-13 located at 21.27 °N, 20.75 °W between 705-3610 m water depth (Fischer *et al*., 2016) (SM and Table S1).

We separated the foraminifera from each trap sample by morphotype (Wang [2000]), and into narrow size fractions to assess the potential impact of morphotype and test size on Mg/Ca, resulting in a total of 79 foraminiferal samples. 15-25 individual foraminifera were cleaned following a modified version of the method of Pak *et al*., (2004) and the acidified samples were analysed by ICP-OES (Perkin Elmar Optima 3300 R) at the University of Bremen (SM and Table S2). Reproducibility of our consistency standard was 0.14 Mg/Ca mmol/mol (~2%) (2σ).

2.3 Calculating calcification temperature and salinity

As the vast majority of sediment trap deployments do not have associated continuous in-situ CTD measurements of temperature and salinity, previous studies have used either $\delta^{18}O_{calcite\text{-}water}$ or satellite temperatures (see SM). Here, we calculate temperature/salinity at the depth habitat of *G. ruber* (w) for the time-period represented by each trap/tow sample using WOA13 monthly climatologies (Boyer *et al*., 2013) (Fig. 2). We use Monte Carlo simulation to fully propagate the uncertainty in temperature and salinity relating to habitat depth range, error associated with the climatological mean (a combination of short-term and inter-annual variability), and change in temperature/salinity during the sampling period (SM). Following this

approach, samples from locations/time-periods with significant temperature and salinity variation within upper water-column or substantial short term and/or inter-annual variability are associated with a wide distribution of temperature and salinity; samples from locations/time-periods with a more homogenous upper water-column or less short term and/or inter-annual variability are associated with a narrower distribution of temperature and salinity. These distributions of temperate and salinity are fully propagated as uncertainty in our regressions (section 2.6). All temperature and salinity values reported are for the 0-50m depth range (Hemleben *et al*., 1989; Schiebel and Hemleben, 2017), unless otherwise stated. Hydrographic data for all samples are shown on Figure S1 and given in Table S2.

To test the accuracy of the temperature estimates generated by this approach we used the WOA13 monthly climatological temperature to predict the temperatures at the only trap site with continuous CTD coverage, located within the Sargasso Sea (SM and Fig. S2). The result demonstrates that the differences between the CTD temperatures and climatological temperatures are normally distributed around a mean of ~0 ($p > 0.88$) (Fig. S2). Thus, while the use of climatological temperature may result in random error (noise) in the calibration, it does not lead to systematic error (inaccuracy) in the calibration. In section 3.9, we discuss how much of the noise results from the use of climatological temperature.

2.4 Estimation of carbonate system parameters

As there is no carbonate chemistry database with a sufficient temporal, spatial and depth resolution to provide carbonate system estimates in the depth habitat of *G. ruber* (w), we first generated monthly carbonate system parameter estimates for each

trap/tow site throughout the upper water-column. This is achieved by combining the gridded GLODAPv2 dissolved inorganic carbon (DIC) and alkalinity (Alk) data for the interior ocean (Key *et al*., 2015; Lauvset *et al*., 2016) with monthly DIC and Alk estimates for the surface ocean, calculated using the monthly pCO_2 climatologies from the Landschützer *et al*. (2014a, b) gridded database and estimates of alkalinity from the algorithms of Lee *et al*., (2006). Monthly values for DIC and Alk throughout the upper ocean were then obtained by interpolating between the surface value and the seasonally invariant ocean interior value using density. pH and [CO_3^{2-}] were calculated from DIC and Alk using the OCMIP2 routines (SM).

To obtain pH and [CO_3^{2-}] for the time interval represented by each sample at the habitat depth of *G. ruber* (w), the monthly gridded values were interpolated using the method described above for temperature and salinity, with Monte-Carlo simulation to account for the uncertainty in the estimates relating to habitat depth and sampling interval (SM and Fig. 2). All pH and [CO_3^{2-}] values reported are for the 0-50m depth range, unless otherwise stated. pH and [CO_3^{2-}] estimates for all samples are shown in Figure S2, and are given in Table S2.

2.5 Compilation of sediment trap/plankton tow data

The compilation of previously published data comprises 310 data points from 16 sediment trap/plankton tow sites in the Atlantic, Pacific and Indian oceans (Fig. 1, SM and Table S1). All Mg/Ca data, along with the original reference for the Mg/Ca data, size fraction, and morphotype are given in Table S2. When combined, our newly generated Mg/Ca data (130 samples) and the compilation of previously-published data comprise 440 sediment trap/plankton tow samples from 20 sites in Atlantic,

Pacific and Indian basins. Within the dataset temperature, salinity, pH (seawater scale) and [CO_3^{2-}] range from 18.4 to 29.1 °C, 32.6 to 36.7 PSU, 7.99 to 8.12 pH units, and 191 to 252 μmol/kg, respectively (Fig. S1). The variation in temperature within the dataset is mainly driven by seasonal variability at each site, whereas the variation in salinity is mainly driven by the location of the sites in differing oceanic regions. Variations in pH and [CO_3^{2-}] are driven by both seasonal variability and regional differences; this essentially decouples the temperature, salinity and pH/[CO_3^{2-}] variation within the dataset; however, there is covariance between temperature and salinity (r= -0.63), temperature and pH (r= -0.68), salinity and pH (r= -0.67), salinity and [CO_3^{2-}] (r= -0.52), and pH and [CO_3^{2-}] (r= -0.55) (Fig. S1).

2.6 Regression analysis

We first analyse the global dataset before taking subsets of this dataset to circumvent covariance between predictor variables, and better constrain the sensitivity of Mg/Ca to temperature, salinity and the carbonate system. Coefficients are from linear and non-linear least-squares regression. Confidence intervals are derived from bootstrapping (Efron, 1979), and we account for the uncertainty in predictor variables (T, S, pH, [CO_3^{2-}]) with Monte-Carlo simulation. Following this approach, the uncertainty associated with the T, S, pH and [CO_3^{2-}] estimate of each sample is fully propagated through to the uncertainty associated with the derived sensitivities. All confidence intervals reported are $\pm 2\sigma$, unless otherwise stated. Additional regression results are given in Table S3.

3. Results and Discussion

3.1 Arabian Sea/Bay of Bengal and Tropical Atlantic data

228 All newly generated Mg/Ca data are shown on Figure 3. Within the Arabian Sea/Bay
229 of Bengal dataset temperature, salinity, pH and [CO_3^{2-}] range from 26.6 to 29.1 °C,
230 32.58 to 36.49 PSU, 7.99 to 8.05 pH units, and 191 to 246 µmol/kg, respectively (Fig.
231 S1); Mg/Ca ranges from 4.68 to 6.67 mmol/mol (Fig. 3). These data are discussed in
232 detail in section 3.4, where we use the data to constrain the effect of salinity on
233 Mg/Ca.
234
235 Within the newly generated tropical Atlantic dataset temperature, salinity, pH
236 and [CO_3^{2-}] range from 20.4 to 23.7 °C, 36.47 to 36.70 PSU, 8.06 to 8.07 pH units,
237 217 to 232 µmol/kg (Fig. S1); Mg/Ca ranges from 3.00 to 5.57 mmol/mol (Fig. 3).
238
239 *3.2 Biological variability*
240 Before investigating the environmental controls on Mg/Ca, we first assess the
241 potential influence of mophotype and test size on Mg/Ca. To explore whether there is
242 a significant difference in Mg/Ca between the *sensu stricto* and *sensu lato*
243 morphotypes of *G. ruber* (w) (Wang, 2000) we focus on the newly generated data
244 from the tropical Atlantic, where Mg/Ca was analysed on both the *sensu stricto* and
245 *sensu lato* morphotypes from the same sediment trap cup. A Student's T test shows no
246 significant difference in mean Mg/Ca of the two morphotypes (p = 0.21; n =32)
247 (Figure S3). A combined analysis our or newly generated data with previously
248 published data from the Indian Ocean (Mohtadi *et al*., 2009) demonstrates there is no
249 significant difference in the mean, or variance, of Mg/Ca in the two morphotypes
250 across the Atlantic and Indian basins (Fig. 4a).
251

252 Test size is also known to influence Mg/Ca in *G. ruber* (w) (Friedrich *et al*.,
253 2012). To assess the possible effects of test size we utilise our newly generated
254 dataset from the tropical Atlantic, in which foraminifera were separated into narrow
255 size fractions. While Mg/Ca generally increases with increasing test size, ~33% of the
256 samples do not show an increasing trend with test size (Fig. 4). Overall, there is no
257 significant difference in mean Mg/Ca in the 150 to 425 μm size range, however the
258 variance in the 300-425 μm size fraction is significantly higher than the 150-250 μm
259 size fraction (Fig. S4). Excluding the 33% of data that do not show a Mg/Ca increase
260 with test size, the data appear to fall on similar trend line of ΔMg/Ca, with a slope of
261 0.35 mmol mol^{-1}/100 μm (Fig. 4e). The samples showing no trend are not related to a
262 particular season or year, and within the same cup sample the *sensu sticto* and *sensu*
263 *lato* morphotypes often show differing trends. Comparing the slope of the relationship
264 between Mg/Ca and test size and the slope of temperature change with depth in the
265 water-column during the interval of time represented by the trap sample shows no
266 significant relationship (Fig. 4f); this likely indicates the relationship between Mg/Ca
267 and test size is not due to changing environmental conditions within the water-column
268 and differing habitat-depths of each size fraction. A recent study suggested that the
269 size of planktic foraminifera may influence the biomineralisation response to
270 changing carbonate chemistry (Henehan *et al*., 2017). While it is possible that the
271 sensitivity with which Mg/Ca responds to an environmental variable (T, S, pH, [CO_3^{2-}
272]) may also be affected by size, it is not possible to test this hypothesis with the newly
273 generated tropical Atlantic data due to the limited range in environmental variables at
274 this site (Fig. S4). Our results suggest that while test size can clearly influence Mg/Ca,
275 the relationship between test size and Mg/Ca is likely to vary not only temporally at
276 sites (Fig. 4c and 4d), but also between sites, and cannot be systematically corrected

for. We will return to test size in section 3.9 in a discussion of potential sources of noise within the calibration.

3.3 Global calibration

When our newly generated Mg/Ca data are combined with all previously published Mg/Ca from sediment traps/plankton tows (section 2.5), Mg/Ca within the dataset ranges from 2.57 to 6.94 mmol/mol and generally increases with temperature (Fig. 5). Regressing Mg/Ca against only temperature results in a temperature sensitivity of 5.3±0.4 %/°C ($p < 10^{-16}$) (Eq. S1). This is significantly lower than the widely-applied 9.0±0.6 %/°C sensitivity of the calibration of Dekens *et al.* (2002)/Anand *et al*. (2003) (Fig. 5). Throughout the text, we refer to the 'multi-species' equation of Anand *et al*. (2003), as this is by far the most widely applied calibration. Incorporating salinity into the regression model results in a slightly higher temperature sensitivity of 6.2±0.5 %/°C ($p < 10^{-16}$) and a salinity sensitivity of 3.3±1.2 %/PSU ($p < 10^{-7}$) (Eq. S2). The slight increase in the temperature sensitivity is due to the negative covariance of temperature and salinity within the dataset.

Next, we add the carbonate system parameters into the regression model, assuming it is either pH or [CO_3^{2-}] (and not both) that influences Mg/Ca. Incorporating pH (seawater scale) into the regression model results in a temperature sensitivity of 5.3±0.6 %/°C ($p < 10^{-16}$), a salinity sensitivity of 4.7±1.2 %/PSU ($p < 10^{-12}$), and a pH sensitivity of -15.2±5.4 %/0.1 pH units ($p < 10^{-9}$) (Eq. S3). The slight change in temperature and salinity sensitivity is due to the covariance of pH with temperature and salinity within the dataset. Substituting [CO_3^{2-}] for pH results in a temperature sensitivity of 7.5±0.6 %/°C ($p < 10^{-15}$), a salinity sensitivity of 7.8±1.6

%/PSU ($p < 10^{-16}$), and a [CO_3^{2-}] sensitivity of -0.35±0.12 %/µmol kg^{-1} ($p < 10^{-9}$) (Eq. S4). Again, the increase in temperature and salinity sensitivities from is due to the covariance of [CO_3^{2-}] with salinity (and salinity with temperature).

Several key features stand out from these regressions. Firstly, temperature, salinity and pH/[CO_3^{2-}] all have a significant influence on Mg/Ca, with temperature exerting the greatest influence. Secondly, the widely-applied calibration of Dekens *et al.* (2002) and Anand *et al*. (2003) does not accurately describe the sediment trap/plankton tow data (Fig. 5). Thirdly, the sensitivity of Mg/Ca to salinity is significantly lower than the estimates derived from coretop studies (Ferguson *et al*., 2008; Arbueszwski *et al*., 2010; Mathien-Blard and Bassinot, 2009). Finally, the covariance between predictor variables (temperature, salinity, pH, [CO_3^{2-}]) is influencing the results of the regressions. In most instances this influence is relatively minor; however, a more significant difference is seen when [CO_3^{2-}] is incorporated into the regression model.

In the next three sections, we address the issue of covariance to more accurately constrain the sensitivity of Mg/Ca in *G. ruber* (w) to temperature, salinity, and the carbonate system. To constrain the sensitivity of Mg/Ca to salinity (section 3.4) and temperature (section 3.5), we take subsets of the global dataset where covariance between predictor variables is reduced. We test the derived sensitivities from these subsets of data for the influence of covariance by re-running the regression models, each time including in an additional predictor variable; when the inclusion of additional predictor variables does not change the resulting sensitivity, the influence of covariance is demonstrated to be negligible.

327

328 *3.4 Sensitivity of Mg/Ca to salinity*

329 To assess the sensitivity of Mg/Ca to salinity we focus on our new data from
330 the Arabian Sea and Bay of Bengal. Regressions of the entire Arabian Sea/Bay of
331 Bengal dataset demonstrate that covariance of predictor variables is influencing the
332 results (SM). To better constrain the sensitivity of Mg/Ca to salinity, we take a subset
333 of the Arabian Sea/Bay of Bengal dataset from a more limited temperature range (28
334 to 29 °C; Fig. 3) and exclude two samples with pH <8.00 to reduce the variation in
335 pH (n = 29, ~60% of Arabian Sea/Bay of Bengal dataset). We opt for this temperature
336 range as the mean annual temperature at all four sites is ~28.5 °C, thus maximising
337 amount of data within the subset. Within the subset there is very little variation in
338 temperature (<0.9°C) or pH (0.005 units), and a large range in salinity (3.50 PSU),
339 making it ideally suited to assess the Mg/Ca sensitivity to salinity (if pH is the
340 controlling carbonate system parameter). Using this subset of data and regressing
341 Mg/Ca against salinity only results in a salinity sensitivity of 3.3±2.2 %/PSU (p <
342 0.01) (Fig. 3),

343

344 $$Mg/Ca = 1.75 \pm 1.81 \times \exp(0.033 \pm 0.022 \times S) \quad (1)$$

345

346 (RSE=0.30); incorporating both temperature and pH into the regression model results
347 in an identical salinity sensitivity of 3.3±2.2 %/PSU (p < 0.001), indicating no effect
348 of covariance between predictor variables on the results. This result agrees well with
349 the culture study of Hönisch *et al.*, (2013), which suggested a salinity sensitivity of
350 3.3±1.7 %/PSU for *G. ruber*, and is significantly lower than the coretop based

estimates of Ferguson *et al*. (2008), Arbueszwski *et al*. (2010), and Mathien-Blard and Bassinot (2009).

Due to the strong covariance of salinity and [CO_3^{2-}] within the Arabian Sea/Bay of Bengal dataset (r= 0.96), it is not possible to constrain the effect of salinity if [CO_3^{2-}] is the controlling carbonate system parameter unless some assumption of the sensitivity of Mg/Ca to [CO_3^{2-}] is made (see section 3.6); substituting [CO_3^{2-}] for pH within the regression model results in insignificant terms for both salinity and [CO_3^{2-}].

3.5 Sensitivity of Mg/Ca to temperature

To constrain the sensitivity of Mg/Ca to temperature, we take a subset of the global dataset with significantly lower variation in salinity (<0.6 PSU) and where the covariance between temperature and salinity (r = -0.09), and temperature and pH (r = -0.34) is considerably reduced. We opt for this salinity/pH range (36.1 to 37.0 PSU/8.06 to 8.12 pH units) as it gives the greatest number of data points (n = 215, ~50% of the global dataset), while ensuring the maximum range in temperature (7.5 °C) and the least covariance between predictor variables. The subset of data comprises three previously published datasets (Anand *et al*., 2003; Haarmann *et al*., 2011; Babila *et al*., 2014), and the newly generated data from the tropical Atlantic (Fig. 6).

Regressing Mg/Ca against temperature results in a temperature sensitivity of 6.0±0.8 %/°C ($p < 10^{-15}$),

$$Mg/Ca = 1.08 \pm 0.25 \times \exp(0.060 \pm 0.008 \times T) \quad (2)$$

(RSE=0.45) (Fig. 6). Adding salinity and pH into the regression model results in an identical temperature sensitivity of 6.0±0.7 %/°C ($p < 10^{-15}$), indicating no influence of covariance between temperature and salinity, and temperature and pH, on the results. Substituting pH for [CO_3^{2-}] results in a lower sensitivity of 5.4±0.9 %/°C ($p < 10^{-15}$); however, temperature and [CO_3^{2-}] covary within the subset of data (r = 0.67). Consequently, this subset of data cannot be used to constrain the sensitivity of Mg/Ca to temperature if [CO_3^{2-}] is the controlling carbonate system parameter unless a sensitivity to [CO_3^{2-}] can be assumed (see section 3.6).

We performed an 'extreme jacknife' of the temperature regression to assess whether the resulting temperature sensitivity is being significantly biased by any one of the constituent datasets (SM). This test assesses whether the temperature sensitivity given in Eq. 2 is biased by: (a) the Mg/Ca of a particular dataset being significantly influenced by another factor that is not accounted for in the regression model, or (b) a systematic offset between the habitat depth temperature in the time-period covered by the trap samples at a particular site and the 0-50 m depth climatological temperature at that site; the results demonstrate that no one particular dataset is significantly biasing the results (Fig. 6b).

A key finding of our study is that the temperature sensitivity of 6.0±0.8 %/°C given in Eq. 2 is significantly lower than the widely-applied 9.0±0.6 %/°C sensitivity of Dekens *et al*. (2002)/Anand *et al*. (2003); it is clear from Figure 6 that the calibration of Dekens *et al*. (2002)/Anand *et al*. (2003) does not accurately describe

401 the dataset. Assuming a 0-25m habitat depth for this subset results in a lower
402 temperature sensitivity of 5.2±0.8 %/°C (Eq. S5). The residual standard error of this
403 fit is, however, substantially higher than using a habitat depth of 0-50 m. The lower
404 temperature sensitivity in Eq. 2 compared to the 9.0±0.6 %/°C sensitivity in the
405 calibration of Dekens *et al*. (2002)/Anand *et al*. (2003) is therefore not dependent on
406 the assumed habitat depth of *G. ruber* (w). Forcing the temperature sensitivity to a
407 higher value (i.e. 9%/°C) increases the residual standard error of fit (Fig. S7). Our
408 results do not support the relationship between Mg/Ca and temperature suggested by
409 Dekens *et al*. (2002)/Anand *et al*. (2003).
410
411 Regressing only the data from Anand *et al.*, (2003) against climatological
412 temperature results in a temperature sensitivity of 7.0±1.2 %/°C (Eq. S6). Therefore,
413 the data of Anand *et al.*, (2003) do not support a temperature sensitivity of 9%/°C
414 when climatological temperature, rather than $\delta^{18}O_{calcite\text{-}water}$ temperature, is used. Note
415 that temperature and pH covary almost perfectly in the dataset of Anand *et al*., (2003)
416 (r=-0.98), which may be the cause of the slightly higher apparent temperature
417 sensitivity in this dataset (see section 3.7 for further discussion on temperature-pH
418 covariance). Anand *et al*. (2003) pointed out that the $\delta^{18}O_{calcite\text{-}water}$ temperatures used
419 in their study were ~3 °C warmer than the measured CTD temperatures of the upper
420 1m of the water column during the winter months of the study period. The authors
421 suggested this may have been due to a sampling bias associated with warm-core
422 eddies. Our compilation demonstrates the data of Anand *et al*. (2003) are not
423 exceptional.
424

425 Now we will revisit the possible cause of this discrepancy by assessing the
426 application of different $\delta^{18}O_{calcite\text{-}water}$ calibrations, looking at the effects of $[CO_3^{2-}]$ on
427 $\delta^{18}O_{calcite}$ (Spero *et al*., 1997), and exploring the potential for variability in the
428 salinity-$\delta^{18}O_{water}$ relationship (SM). As Figure S9 shows, the choice of $\delta^{18}O_{calcite\text{-}water}$
429 calibration makes little difference to the problem, with the seasonal range predicted in
430 $\delta^{18}O_{calcite}$ always ~0.5‰ greater than the range observed in foraminiferal $\delta^{18}O_{calcite}$.
431 Applying the $[CO_3^{2-}]$-$\delta^{18}O$ relationship of Spero *et al*., (1997), the seasonal variability
432 of $[CO_3^{2-}]$ in the Sargasso Sea can only explain 10% (~0.05‰) of this discrepancy
433 (Fig. S10).
434
435 With choice of $\delta^{18}O_{calcite\text{-}water}$ calibration and carbonate chemistry changes
436 unable to adequately account for the discrepancy, we now assess the potential for a
437 systematic seasonal change in the salinity-$\delta^{18}O_{water}$ relationship; this could result in a
438 substantially larger change in $\delta^{18}O_{water}$ than suggested by the modest seasonal change
439 in salinity. LeGrande and Schmidt (2006) state that current salinity-$\delta^{18}O_{water}$
440 relationships are only applicable at a regional level, and these relationships may
441 change seasonally. Although no obvious seasonal cycle is apparent in the very limited
442 number of $\delta^{18}O_{water}$ measurements from the region, the data do display variability of
443 the magnitude required to explain the discrepancy (±0.7 ‰) (Fig. S11). A systematic
444 seasonal change in $\delta^{18}O_{water}$ would therefore seem the most likely cause of the
445 discrepancy in $\delta^{18}O_{calcite}$, and explain why it is observed in multiple planktic
446 foraminiferal species simultaneously (Anand *et al*., 2003).
447
448 *3.6 Sensitivity of Mg/Ca to the carbonate system*

449 The limited range in pH and [CO_3^{2-}] within the dataset does not allow us to
450 use the same approach used to constrain the sensitivity to salinity and temperature.
451 Instead, to assess the sensitivity of Mg/Ca to pH we perform a multivariate regression
452 using the entire global dataset and prescribe the sensitivity of Mg/Ca to temperature
453 and salinity as 6.0±0.8 %/°C and 3.3±2.2 %/PSU (see sections 3.5 and 3.6). We
454 account for the uncertainty in temperature and salinity sensitivity with Monte-Carlo
455 simulation. This approach results in a pH sensitivity of -8.3±7.3 %/0.1 pH units ($p <$
456 10^{-5}) (Fig. 7),
457
458 $$Mg/Ca = \exp(0.060\pm0.008\times T + 0.033\pm0.022\times S - 0.83\pm0.73\times(pH-8) - 1.07\pm0.80) \quad (3)$$
459
460 (RSE=0.50). The large uncertainty associated with the pH sensitivity in Eq. 3 is
461 primarily due to the very small range in pH within the dataset (~0.13 units). This
462 result is in very good agreement with an exponential fit to the *G. ruber* (w) culture
463 experiments of Kisakürek *et al.,* (2008) and Evans *et al*., (2016), which yields a pH
464 sensitivity of -9.3±4.1 %/0.1 pH units (Eq. S11) (Fig. 7). Our estimate of the
465 sensitivity of Mg/Ca to pH is entirely consistent with the results of the culture data of
466 Kisakürek *et al.,* (2008)/Evans *et al*., (2016).
467
468 If we consider that [CO_3^{2-}] is the controlling carbonate system parameter we
469 must take a different approach than that used to estimate the sensitivity to pH. This is
470 because the salinity sensitivity used to account for the effects of salinity in the
471 regression model is derived from the Arabian Sea/Bengal dataset, in which salinity
472 and [CO_3^{2-}] covary strongly. Furthermore, there is also covariance between [CO_3^{2-}]
473 and temperature in the subset of data used to derive the sensitivity to temperature in

Eq. 2. Instead we must assume a sensitivity to [CO_3^{2-}] and use this assumed sensitivity to [CO_3^{2-}] to calculate a sensitivity to salinity; we can then use the assumed sensitivity to [CO_3^{2-}] and calculated sensitivity to salinity to derive the sensitivity of Mg/Ca to temperature if [CO_3^{2-}] is the controlling parameter.

Regressing the data from the culture experiments of Kisakürek *et al.,* (2008)/Evans *et al*., (2016) against [CO_3^{2-}] results in a sensitivity of -0.24±0.12 %/µmol kg^{-1} (Eq. S12; Fig. S12), within error of the -0.35±0.12 %/µmol kg^{-1} suggested by multivariate regression of the global dataset (Eq. S4). Taking a subset of data from the Arabian Sea/Bay of Bengal dataset from the same temperature range used to calculate the sensitivity to salinity in Eq. 1 (28 – 29 °C), and regressing the data against salinity with a prescribed sensitivity to [CO_3^{2-}] of -0.24±0.12 %/µmol kg^{-1} results in a salinity sensitivity of 5.0±3.0 %/PSU ($p < 0.001$). Incorporating temperature within the regression model results in a very similar salinity sensitivity of 5.1±2.8 %/PSU ($p < 10^{-5}$). Prescribing the salinity sensitivity of 5.0±3.0 %/PSU, and the [CO_3^{2-}] sensitivity of -0.24±0.12 %/µmol kg^{-1} in a multivariate regression of the entire dataset results in a temperature sensitivity of 6.7±0.8 %/°C ($p < 10^{-15}$),

$$Mg/Ca = \exp(0.067\pm0.008\times T + 0.050\pm0.030\times S - 0.0024\pm0.0012\times[CO_3^{2-}] - 1.37\pm1.31) \quad (4)$$

(RSE=0.50), similar to the temperature sensitivity if pH is the controlling parameter (Eq. 3). Regressing the subset of data with very little variation in salinity (< 0.6 PSU) used to calculate the temperature sensitivity in section 3.5 against temperature with a prescribed sensitivity to [CO_3^{2-}] of -0.24±0.12 %/µmol kg^{-1} results in an identical

499 (within error) temperature sensitivity of 7.0±0.9 %/°C. This confirms the temperature
500 sensitivity given in Eq. 4, without necessitating an assumption of the sensitivity to
501 salinity. Application of a lower [CO_3^{2-}] sensitivity, as suggested for *G. ruber* (pink)
502 (Allen *et al*., 2016), has very little effect on the resulting temperature and salinity
503 sensitivities (SM).
504
505 *3.7 Reconciling sediment trap and culture temperature sensitivity estimates*
506 The temperature sensitivities indicated by the sediment trap data, i.e. 6.0±0.8
507 %/°C if pH is the controlling parameter, and 6.7±0.8 %/°C if [CO_3^{2-}] is the controlling
508 parameter, are lower than the temperature sensitivity of 8±3 %/°C inferred from the
509 culturing experiment of Kisakürek *et al.,* (2008) (Fig. 8). One way by which the
510 sediment trap and culture data can be reconciled is if the influence of temperature on
511 the dissociation constant of water ($K_w = [H^+][OH^-]$) is considered. As K_w changes as a
512 function of temperature, the pH of water decreases with increasing temperature by ~-
513 0.015 pH units/°C, without changing the ratio of Alk/DIC (Millero, 1995). Hence, in
514 the culture experiments of Kisakürek *et al.,* (2008) temperature and pH covary
515 perfectly ($r > 0.99$), with a 0.18 pH unit decrease from coldest to warmest sample. If
516 the culture data of Kisakürek *et al.,* (2008) are normalised to a pH of 8.05 (the mean
517 value within the sediment trap dataset) to remove the internal shift of pH due to
518 temperature, using a pH sensitivity of -8.3 %/0.1 pH units derived from the sediment
519 trap dataset (Eq. 3), the Kisakürek *et al.,* (2008) data suggest a lower temperature
520 sensitivity of 6.3±1.9 %/°C ($p < 0.01$) (Fig. 8),
521
522 $$Mg/Ca = 0.97 \pm 0.50 \times \exp(0.063 \pm 0.019 \times T) \quad (5)$$
523

(RSE=0.36; n=5), in excellent agreement with the temperature sensitivity indicated by the sediment trap dataset if pH is the controlling carbonate system parameter (Eq. 3; Fig. 8). Using the pH sensitivity of -9.3±4.6 %/0.1 pH units suggested by the pH experiments to normalise the culture data instead, results in an identical (within error) temperature sensitivity of 6.2±1.9 %/°C ($p < 0.01$). Accounting for the influence of temperature on the dissociation constant of water (K_w) within the culturing experiments thus allows the culture and sediment trap datasets to be reconciled if pH is the controlling carbonate system parameter. If [CO_3^{2-}] is the controlling carbonate system parameter, the sediment trap and culture data cannot be reconciled as the ratio of Alk/DIC (and thus [CO_3^{2-}]) is not changing in the temperature experiment of Kisakürek *et al.,* (2008). Based on our current understanding of foraminiferal calcification mechanisms (e.g. Erez *et al*., 2003; de Nooijer *et al.*, 2009), Evans *et al.,* (2016) argued that pH is the carbonate system parameter that influences foraminiferal Mg/Ca (SM), and recent work has revealed foraminifera actively pump protons during calcification (Toyofuku *et al*., 2017). Our results provisionally support this inference, as this would allow the sediment trap and culture data to be reconciled.

3.8 Proposed calibrations

We propose the following calibration for the conversion of *G. ruber* (w) Mg/Ca to temperature if pH is the controlling carbonate system parameter,

$$Mg/Ca = \exp(0.060\pm0.008\times T + 0.033\pm0.022\times S - 0.83\pm0.73\times(pH-8) - 1.07\pm0.80) \quad (3)$$

(RSE=0.50), and the following calibration if [CO_3^{2-}] is the controlling carbonate system parameter,

549

550 $Mg/Ca = exp(0.067 \pm 0.008 \times T + 0.050 \pm 0.030 \times S - 0.0024 \pm 0.0012 \times [CO_3^{2-}] - 1.37 \pm 1.31)$

551 (4)

552

553 (RSE=0.50). As discussed above, we suggest that pH is most likely to be the
554 controlling carbonate system parameter as this allows the reconciliation of the culture
555 experiment and sediment trap datasets, but further culturing work is needed to test this
556 assertion.

557

558 *3.9 Sources of noise within the calibration*

559 Significant noise can be seen in the sediment trap Mg/Ca dataset (Fig. 8),
560 with ~30% of the variance unaccounted for by T, S and the carbonate system. Here
561 we assess how much of this noise relates to (i) the use of climatological temperature
562 and (ii) different size fractions within the dataset.

563

564 To assess how much noise may be explained by the use of climatological
565 temperatures we simulate synthetic foraminiferal samples using both CTD
566 temperature and WOA13 temperature for the same period of time, and examine the
567 difference expected in Mg/Ca between these samples (SM). We utilise data from the
568 Sargasso Sea, which is the only trap site with continuous CTD data for the time
569 interval covered by the sediment samples, and simulate samples broadly
570 representative of the actual samples analysed by Anand *et al*. (2003) and Babila *et al*.
571 (2014). We then calculate the residual Mg/Ca based on the difference in temperature
572 between the WOA-synthetic foraminiferal samples and the CTD-synthetic
573 foraminiferal samples and compare this to the residual of the measured Mg/Ca data

574 from the Sargasso Sea sediment trap site. The results show that the residual in
575 measured Mg/Ca data is significantly higher than expected based on the uncertainty
576 introduced by using climatological temperature alone ($p < 10^{-7}$) (Fig. S15); however,
577 ~40% of noise can be explained by the use of climatological temperature. If the
578 Sargasso Sea dataset is representative of the wider trap/tow dataset, substantial
579 improvements in the precision of the calibration could be made if in-situ temperatures
580 were collected along with foraminiferal samples.
581
582 Another source of noise may relate to 'biological' variability. One aspect of
583 biological variability that might be constrained is the influence of size fractions within
584 the global dataset. The mean size of foraminiferal sample within the dataset is 300
585 μm, and 95% of samples fall into the 200 to 400 μm range of mean test size. To test if
586 it is possible to systematically correct for variations in test size, we use the
587 relationship between test size and Mg/Ca given in Figure 4e (0.35 mmol mol^{-1}/100
588 μm) to normalise all sediment trap and plankton tow data within the dataset to the
589 same size (300 μm). Regressing the size normalised Mg/Ca against temperature,
590 salinity and pH/[CO_3^{2-}] increases the residual standard error of fit compared to
591 regressions of the uncorrected data. Incorporating test size as a predictor variable
592 within the regression model returns an insignificant coefficient for test size. Thus,
593 while test size variability might be causing much of the noise, such effects cannot
594 easily be corrected.
595
596 **4. Implications for tropical SST during the LGM**
597

598 We apply our new multivariate calibration models to previously published *G.*
599 *ruber* (w) Mg/Ca data from multiple core sites located in the tropical Pacific, Indian
600 and Atlantic Oceans covering the Last Glacial Maximum (LGM) (SM). Applying the
601 calibration given in Eq. 3, which assumes pH is the controlling carbonate system
602 parameter, results in a tropical ocean cooling of 3.5±1.6 °C (2σ, accounting for
603 Mg/Ca variability only) if no change in salinity or pH is accounted for (Fig. 9). If the
604 1.15 PSU whole ocean increase in salinity during the LGM (Adkins *et al*., 2002) is
605 included, the magnitude of cooling increases to 4.2±1.6 °C. However, if a 0.13 unit
606 surface ocean pH increase (SM) is also accounted for, the magnitude of cooling is
607 reduced to 2.4±1.6 °C. This calculation demonstrates that the combined pH and
608 salinity influence in Eq. 3 reduces the inferred temperature change by about a third.
609 We note that while this value is similar to the value (2.3±1.3 °C) obtained using the
610 calibration of Dekens *et al*. (2002)/Anand *et al*. (2003) (Fig. 9), this similarity is not a
611 confirmation of the calibration of Dekens *et al*. (2002)/Anand *et al*. (2003), which has
612 a higher temperature sensitivity and does not account for changes in salinity or
613 carbonate chemistry.
614
615 Applying the calibration given in Eq. 4, which assumes [CO_3^{2-}] is the
616 controlling carbonate system parameter, results in a cooling of 3.1±1.4 °C (2σ) if no
617 change in salinity or [CO_3^{2-}] is considered (Fig. 9). If the 1.15 PSU whole ocean
618 increase in salinity is accounted for, the magnitude of cooling during the LGM
619 increases to 4.0±1.4 °C. However, if a 69 µmol/kg surface ocean [CO_3^{2-}] increase is
620 also included (SM), the magnitude of cooling is reduced to 1.5±1.4 °C. The
621 substantial effect of including the carbonate ion change on the temperature estimate

622 reflects the strong influence of carbonate ion in Eq. 4, where it accounts for a
623 significantly greater weighting than temperature for LGM conditions.
624
625 These scenarios are not intended as a thorough estimation of LGM
626 temperature change, but instead serve only to highlight that salinity and carbonate
627 chemistry have a substantial effect on reconstructed temperature, and the necessity of
628 obtaining regional salinity and pH/[CO_3^{2-}] estimates for robust SST reconstruction
629 using Mg/Ca. In addition to the secondary influences on Mg uptake into foraminiferal
630 calcite, the effects of dissolution (usually expressed as a function of bottom-water
631 carbonate ion saturation, ΔCO_3^{2-}) on Mg/Ca must also be accounted for in
632 temperature reconstructions from fossil foraminifera (Regenberg *et al*., 2014).
633 Uncertainty in reconstructed temperature change from Mg/Ca will therefore be
634 dependent on the uncertainty of the sensitivities of Mg/Ca to temperature, salinity and
635 the carbonate system within the calibration, the uncertainty in past changes in salinity
636 and pH/[CO_3^{2-}], as well as both the uncertainty in relationship between Mg/Ca and
637 dissolution, and the uncertainty in past changes in bottom- (or pore-) water carbonate
638 chemistry.
639
640 **5. Conclusions**
641
642 This study utilises 440 sediment trap/plankton tow samples from 20 sites in
643 Atlantic, Pacific and Indian basins to provide the most comprehensive field based
644 calibration for Mg/Ca in *G. ruber* (white) to date. The temperature sensitivity within
645 our calibration of 6.0% per °C (assuming pH is the controlling carbonate system
646 parameter) or 6.7% per °C (assuming [CO_3^{2-}] is the controlling carbonate system

parameter) is significantly lower than the widely-applied temperature sensitivity of 9% per °C. The significant effects of salinity (with a sensitivity of 3.3% or 5% per PSU, depending on the controlling carbonate system parameter) and carbonate chemistry (with a sensitivity of -8.3% per 0.1 pH units or -0.24% per μmol/kg [CO_3^{2-}]) on Mg/Ca in *G. ruber* (white) complicate the use of Mg/Ca as a paleothermometer.

Applying our calibration model which assumes pH is the controlling carbonate system parameter (we provisionally suggest pH is most likely to be the controlling parameter), without considering changes in salinity and carbonate chemistry, results in a cooling of ~3.5°C during the LGM; if whole ocean changes in salinity and carbonate chemistry are accounted for the cooling is reduced to ~2.3 °C. Applying our calibration model which assumes [CO_3^{2-}] is the controlling carbonate system parameter, without considering changes in salinity and carbonate chemistry, results in a cooling of ~3.1°C during the LGM; if whole ocean changes in salinity and carbonate chemistry are accounted for the cooling is reduced to ~1.5 °C. The substantial influence of salinity and carbonate chemistry on Mg/Ca necessitates independent estimates of salinity and carbonate chemistry for reliable temperature reconstruction. While boron isotopes may offer a viable tool to account for changes in carbonate chemistry, the lack of a quantative salinity proxy currently adds a currently-unquantifiable uncertainty into Mg/Ca-based temperature estimates.

Future efforts to further improve the Mg/Ca paleothermometer should include (i) culture experiments to assess whether it is pH or [CO_3^{2-}] that controls Mg/Ca, and determine the exact form and sensitivity of this relationship (ii) studies to ascertain if the secondary influences on Mg/Ca in *G. ruber* (white) are as pronounced in other

planktic foraminiferal species and, (iii) the development and refinement of an independent salinity proxy.

Acknowledgments

This research was funded by NSF grant NSF-OCE 1260696 awarded to S. Weldeab and D.W. Lea. We thank Ralf Schiebel for discussions regarding foraminiferal ecology, Birgit Gaye for providing sediment trap samples from the Bay of Bengal, Bobbi Conard for sampling archived sediment trap samples from the Arabian Sea, Minda Monteagudo for help in the preparation of foraminiferal samples for trace element analysis, Ryan Bu for assistance with ICP-MS analysis, Siv Lauvset for discussions regarding carbonate chemistry data, and Damian Loher for assistance producing the temporally resolved carbonate chemistry estimates. Conversations with David Evans and Rosanna Greenop helped guide our thinking regarding potential solutions to the problems raised by the influence of carbonate chemistry on Mg/Ca. Insightful comments from the Editor (Heather Stoll), Michael Henehan, and an anonymous reviewer very much improved previous versions of this manuscript.

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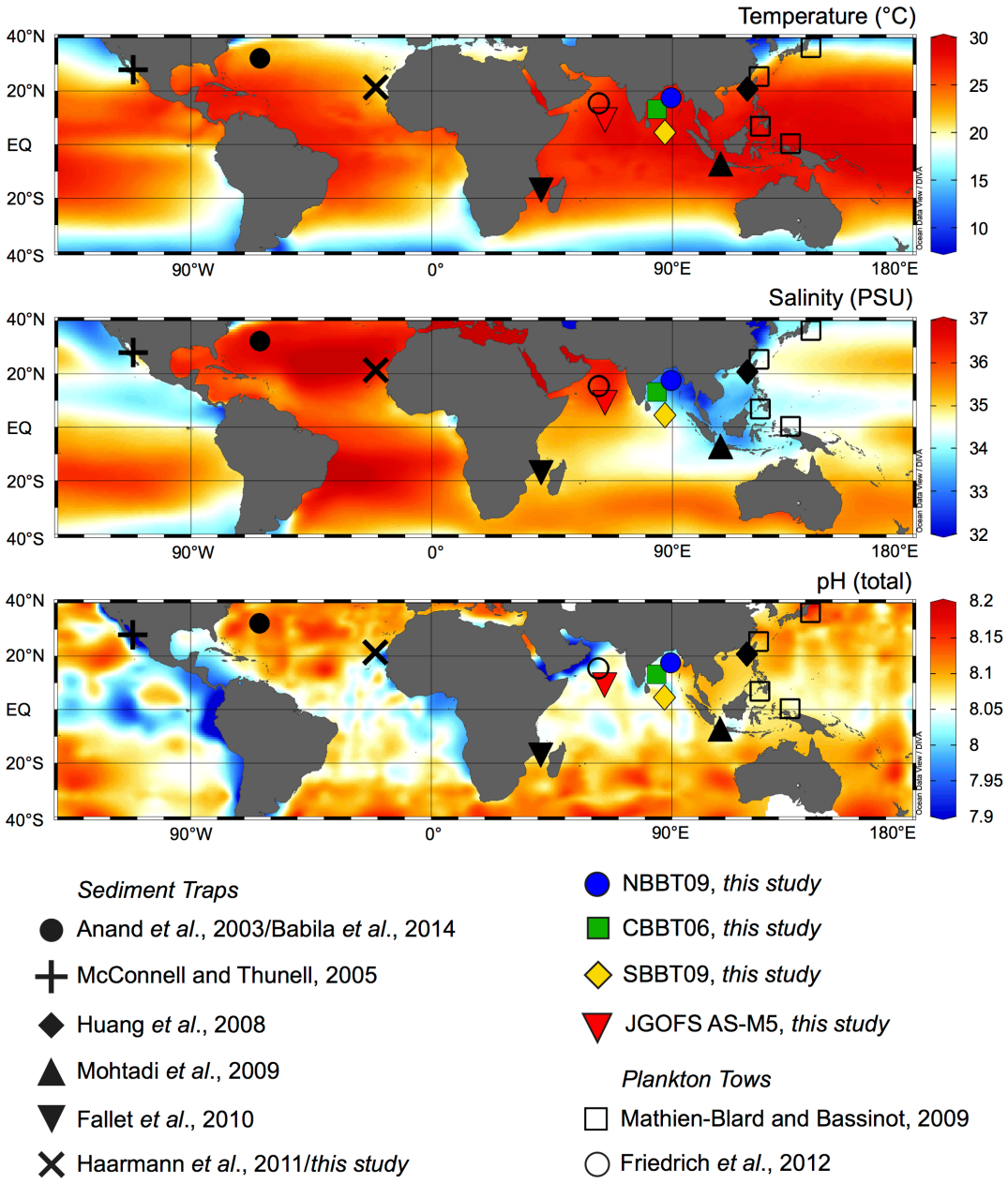
Table 1 Published temperature sensitivities[1] for *G. ruber* (white)[2]

Reference	Method	Temperature sensitivity (%)*
Lea *et al*., 2000	Coretops, equatorial Pacific	8.9±1.4
Dekens *et al*., 2002	Coretops, multivariate fit accounting for core depth	9±1.5
Anand *et al.*, 2003	Multi-species, sediment trap, Sargasso Sea, $\delta^{18}O$ temperature	9.0±0.6
Anand *et al.*, 2003	250-350 µm, sediment trap, Sargasso Sea, $\delta^{18}O$ temperature	10±2
Anand *et al.*, 2003	350-500 µm, sediment trap, Sargasso Sea, $\delta^{18}O$ temperature	8.5±1.2
McConnell & Thunell, 2005	Sediment trap, Gulf of California, satellite temperature	6.8
Kisakürek *et al.,* 2008	Laboratory cultures	8±3
Mohtadi *et al*., 2009	Sediment trap, Java, satellite temperature	8.4
Mohtadi *et al*., 2009	Sediment trap, Java, $\delta^{18}O$ temperature	6.6
Khider *et al.*, 2015	Coretops, Bayesian multivariate fit accounting for salinity, and bottom water carbonate ion saturation	8.7±0.9

[1]Excluding studies where the temperature sensitivity was assumed

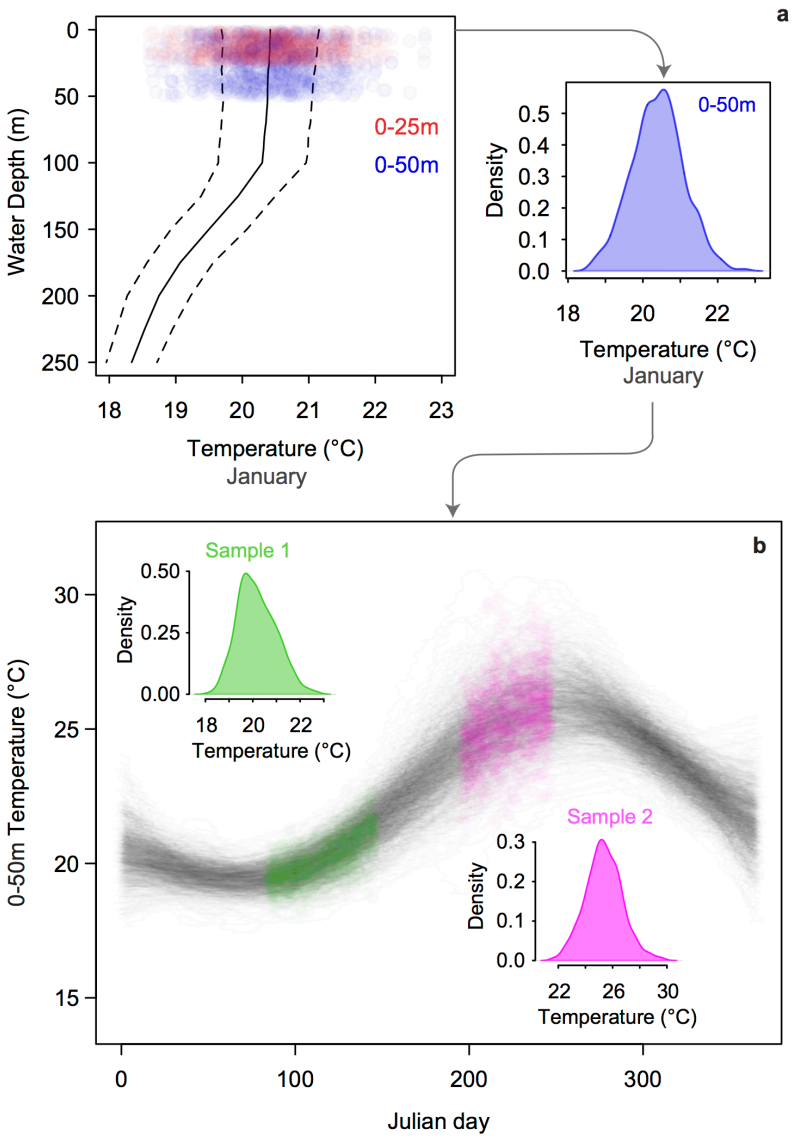
[2]Including one study combining multiple species of planktonic foraminifera

* 95% confidence interval



877

878 **Figure 1** Location of sediment traps (solid symbols) and plankton tows (open symbols) used in this
879 study, overlaid on mean annual SST and SSS at 25m depth from WOA13 (Boyer *et al.*, 2013), and pH
880 at 25m depth from GLODAPv2 (Key *et al.*, 2015; Lauvset *et al.*, 2016). Note, the tropical Atlantic trap
881 site used in this study is located ~120 nm further offshore than that of Haarmann *et al.*, (2011).



882

883 **Figure 2** Calculation of temperature and salinity for time-period represented by each trap sample at
884 habitat depth of *G. ruber* (white) using WOA13 monthly climatologies at each trap site and a Monte-
885 Carlo approach; **(a)** for each month, a random value is drawn from the population of
886 temperatures/salinities from within the specified depth habitat range, accounting for the uncertainty
887 associated with the climatological mean (blue dots = 0-50 m, red dots = 0-25 m) **(b)** a random sample
888 is then drawn from these habitat-depth temperature/salinity populations for each month, and the data is
889 fitted with a GAM (versus Julian day). A day is then randomly drawn from between the open/close
890 date of each trap sample (after adjustment for sinking and calcification time), and the
891 temperature/salinity for that day is calculated based on the GAM fit. This process is repeated 10,000
892 times to fully explore the range in possible calcification temperatures and salinities for each trap
893 sample, accounting for the depth habitat, error associated with the WOA13 monthly climatologies
894 (short term and inter-annual variability), and the period of time represented by each trap sample. The
895 example shown is temperature data for the Sargasso Sea (Anand *et al.*, 2003; Babila *et al.*, 2014). After
896 first generating monthly carbonate chemistry climatologies for each site (section 2.4), the same process
897 is used to calculate carbonate chemistry estimates for each trap/tow sample.
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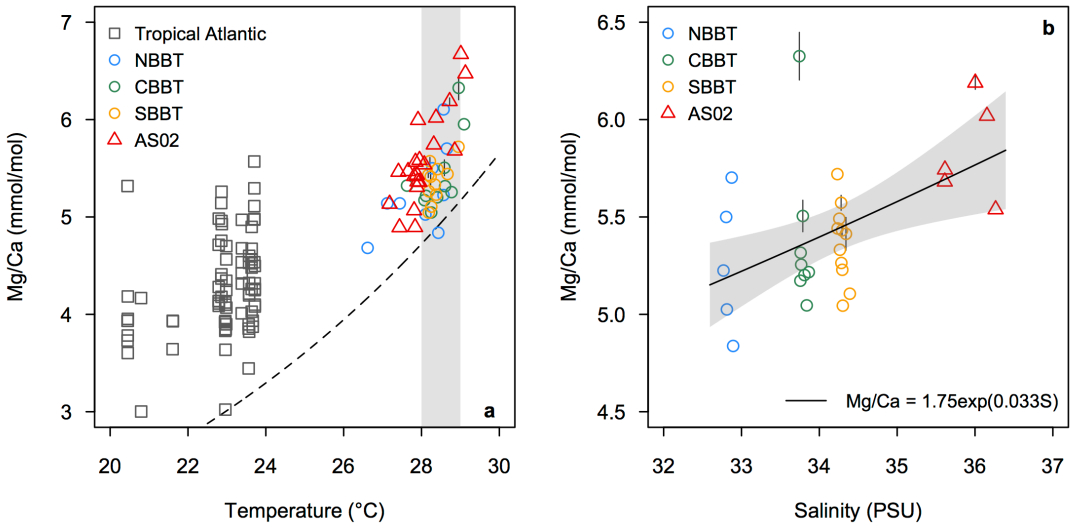
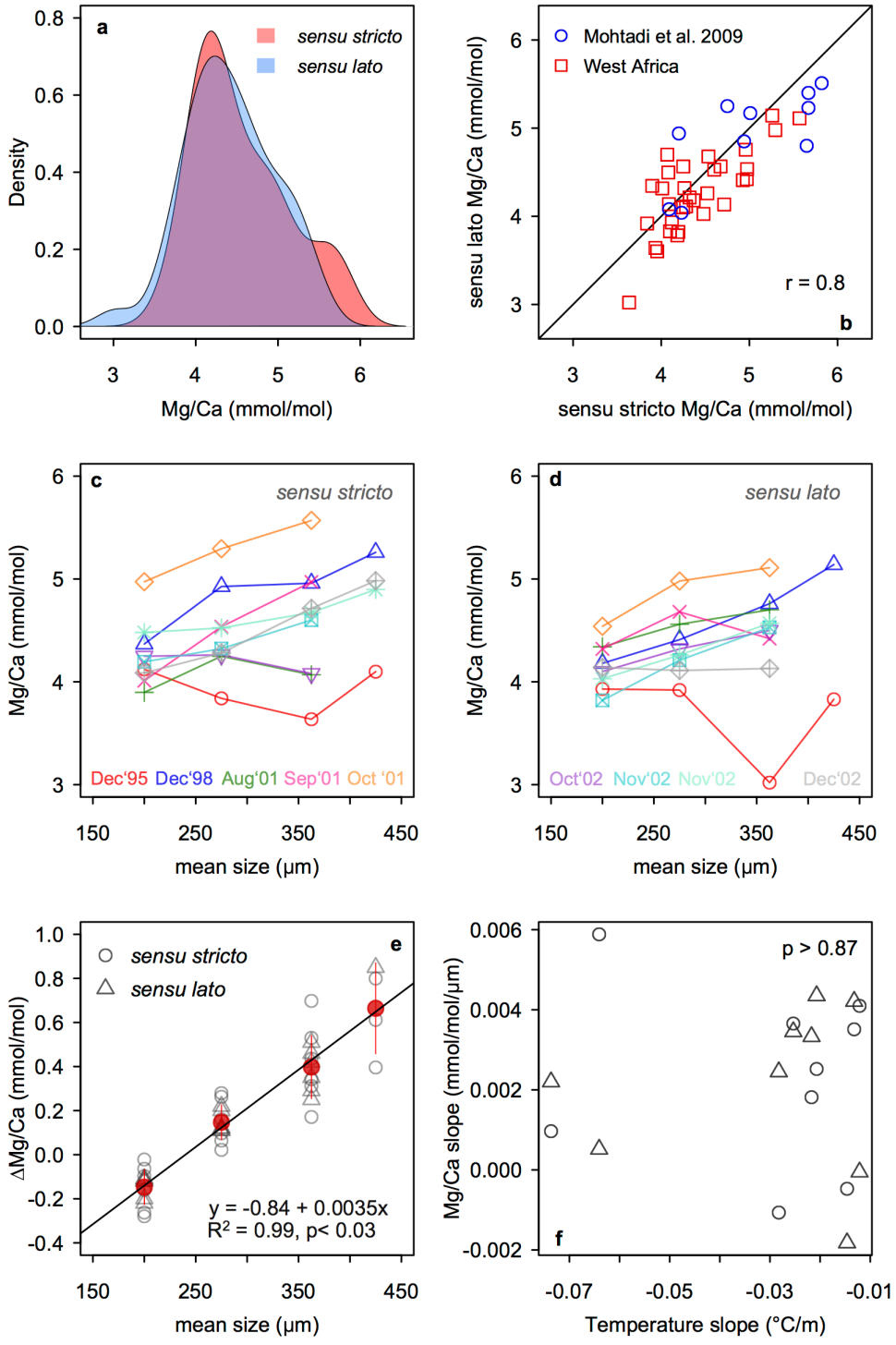


Figure 3 (a) New Mg/Ca data from the Arabian Sea/Bay of Bengal and the tropical Atlantic, analysed as part of this study, plotted versus climatological temperature (0-50 m, Methods). The calibration of Dekens *et al.,* (2002)/Anand *et al.,* (2003) is shown by the dashed line. The grey box represents data between 28 and 29 °C shown in panel b. Error bars are ±1σ **(b)** Mg/Ca versus salinity in the Arabian Sea/Bay of Bengal. Only samples with a temperature between 28-29 °C (grey box in a), and a pH of > 8.00 are plotted. The best fit to this subset of data is shown by the solid line, with the 95% confidence interval shown in grey. The slightly higher spread in the NBBT data is likely due to the fewer number of individual foraminifera comprising each sample analysed.



911

912 **Figure 4 (a)** probability density of Mg/Ca in *G. ruber* (w) *sensu stricto* and *G. ruber* (w) *sensu lato* (all
913 size fractions) from paired samples **(b)** Mg/Ca in *G. ruber* (w) *sensu stricto* versus Mg/Ca in *G. ruber*
914 (w) *sensu lato* in paired samples. There is no significant difference in mean Mg/Ca or variance
915 between the two morphotypes. Mg/Ca versus mean test size in **(c)** *G. ruber* (w) *sensu stricto* and **(d)** *G.*
916 *ruber* (w) *sensu lato*, with different colors/symbols representing different trap samples **(e)** ΔMg/Ca (the
917 difference relative to the mean Mg/Ca of the 150-250µm and 250-300µm size fraction for each sample)
918 plotted against mean test size, excluding the 33% of data that do not show an increasing trend. Red
919 circles show the mean ΔMg/Ca of both morphotypes for each size fraction. Error bars are ±1σ **(f)** slope
920 of the temperature change in the upper 50m of water column during the time-period represented by
921 each sample (ΔTemperature/Δdepth) versus slope of Mg/Ca-size relationship in each sample
922 (ΔMg/Ca/Δsize) (see SM).

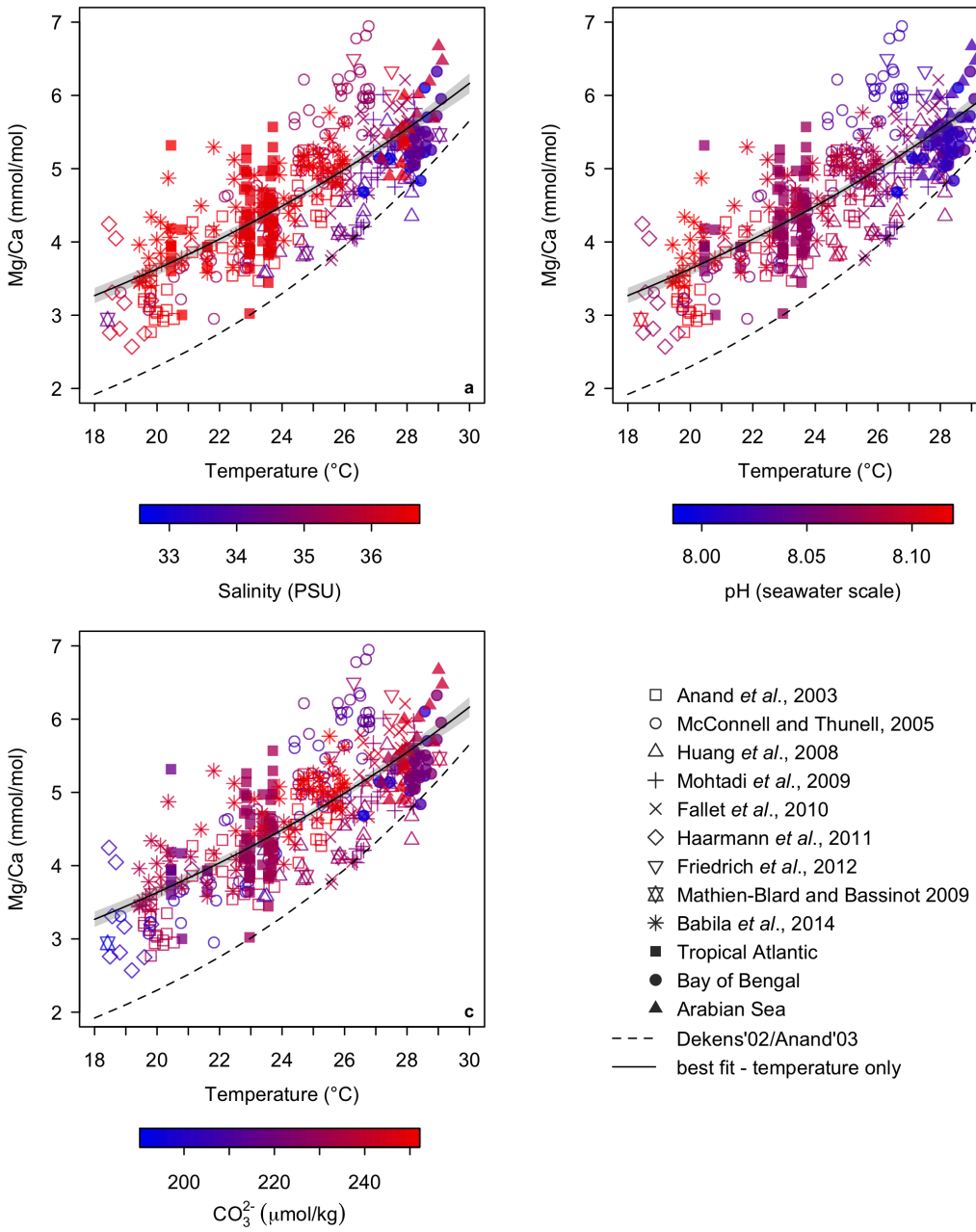


Figure 5 Mg/Ca plotted against temperature climatological temperature (0-50 m, Methods) **(a)** salinity represented by colour **(b)** pH represented by colour, and **(c)** [CO_3^{2-}] represented by colour. The best fit (accounting for only temperature) is shown by the solid line (Eq. S1), with the 95% confidence interval shown in grey. The calibration of Dekens *et al.,* 2002/Anand *et al*., 2003 ('multi-species') is shown by the dashed line.

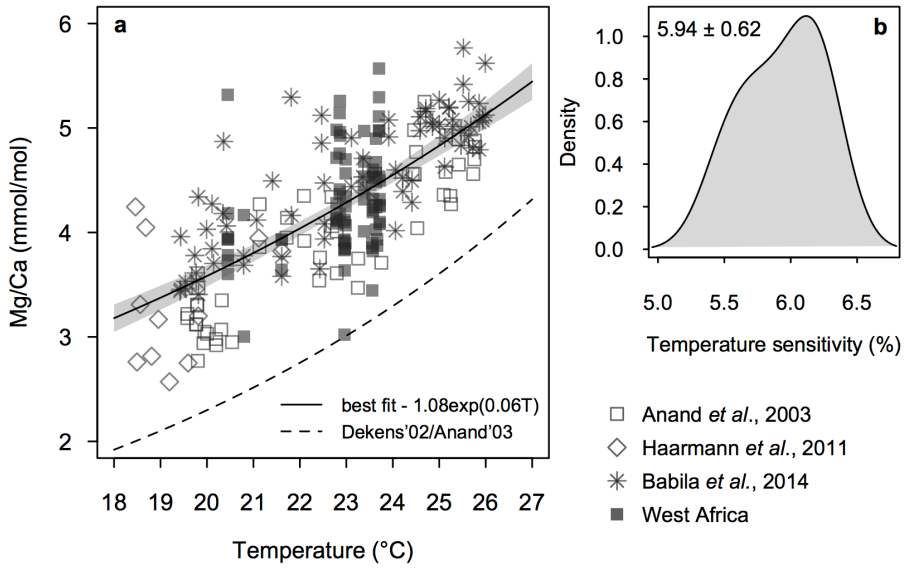


Figure 6 (a) Mg/Ca versus climatological temperature (0-50 m, Methods) from a subset of data with a narrow range in salinity and significantly reduced covariance between temperature and salinity/pH. The best fit to this subset of data is shown by the solid line, with the 95% confidence interval shown in grey. The calibration line of Dekens *et al*., 2002/Anand *et al*., 2003 is shown by the dashed line. Note the calibration line of Dekens *et al*., 2002/Anand *et al*., 2003 does not fit the data of Anand *et al*. (2003) when climatological temperature, rather than the $\delta^{18}O_{calcite}$-$\delta^{18}O_{water}$ temperature, is used. Although the 'multi-species' equation of Anand *et al.* (2003) is plotted here, the same point stands for the *G. ruber* (w) calibrations of Anand *et al.* (2003) **(b)** 'extreme jacknife' of the dataset; each of the constituent datasets was successively removed from the subset of data and the temperature regression was re-run. The results demonstrate that no individual dataset is significantly biasing the results.

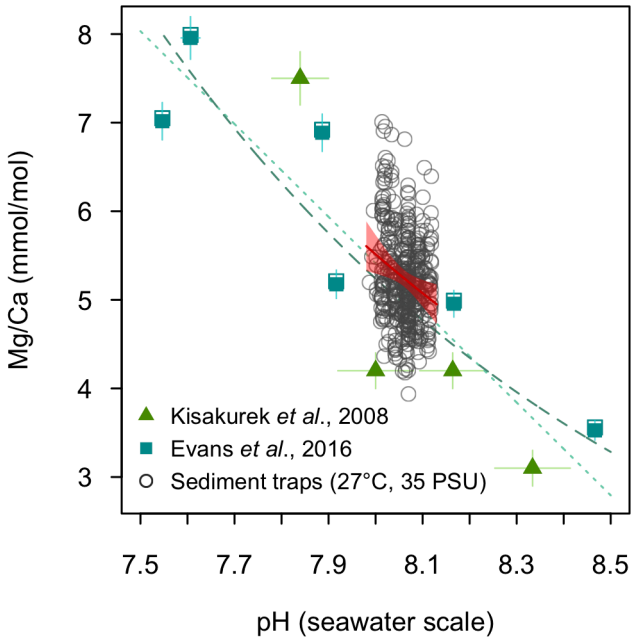


Figure 7 Mg/Ca versus pH (seawater scale), showing both the sediment trap data from this study (normalised to 27 °C and 35 PSU using a temperature sensitivity of 6.0 %/°C and a salinity sensitivity of 3.3 %/PSU) and the data from the culture studies of Kisakürek *et al.,* (2008)/Evans *et al*., (2016). The data of Evans *et al*., (2016) were normalised to 27 °C and 35 PSU using a temperature sensitivity of 6.0 %/°C and a salinity sensitivity of 3.3 %/PSU, and only data from foraminifera cultured at modern seawater Mg/Ca are included. The uncorrected data are shown by the open squares. The data of Kisakürek *et al.,* (2008) were cultured at 27 °C/35 PSU. The best fit to the sediment trap data (exponential) is shown by the solid red line, with the 95% confidence interval shown in red. The best fit to the cultured data is shown by the dashed line (exponential, Eq. S11), and the dotted line (linear). The pH data of Kisakürek *et al.,* (2008)/Evans *et al*., (2016) were converted to the seawater scale. Error bars are ±1σ.

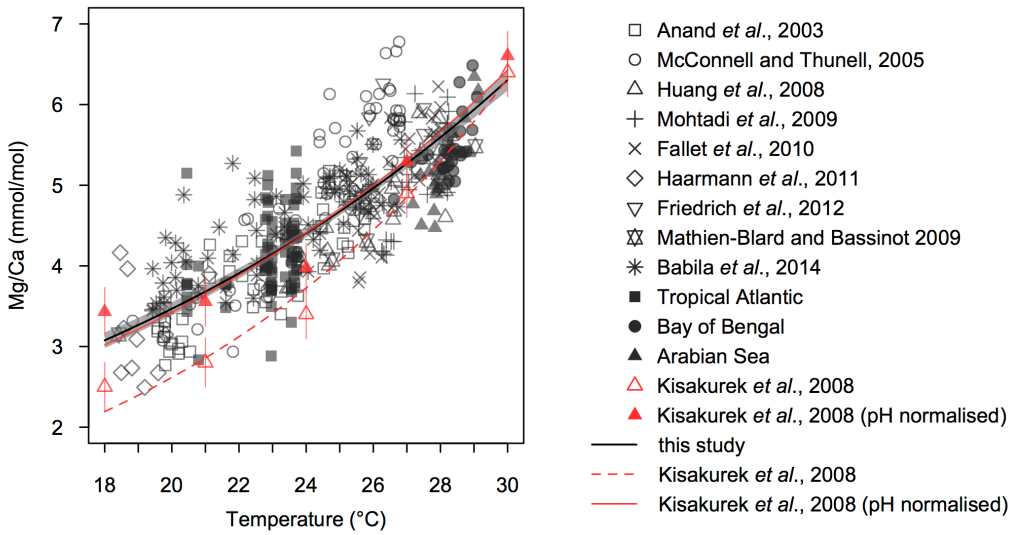


Figure 8 Mg/Ca versus temperature, showing both the sediment trap data from this study and cultured *G. ruber* (white) data of Kisakürek *et al.,* (2008). The sediment trap data are plotted versus climatological temperature (0-50 m, Methods). The sediment trap data have been normalised to a salinity of 35 PSU and a pH of 8.05 units using a 3.3%/PSU salinity sensitivity (Eq. 1) and a -8.3%/0.1 pH unit sensitivity (Eq. 3), respectively. The data of Kisakürek *et al.,* (2008) are shown both uncorrected (open triangles) and corrected (filled triangles) for the effect of pH on Mg/Ca. The calibration line suggested by this study if pH is the controlling parameter (Eq. 3) is shown by the black line (for a salinity of 35 PSU and a pH of 8.05 units), with the 95% confidence interval shown in grey. The dashed red line indicates the best fit to the culture data without correcting for the effect of pH on Mg/Ca. The solid red line indicates the best fit to the culture data after correction for the effect of pH on Mg/Ca (the pH data of Kisakürek *et al.,* (2008) were first converted to the seawater scale). Error bars are ±1σ.

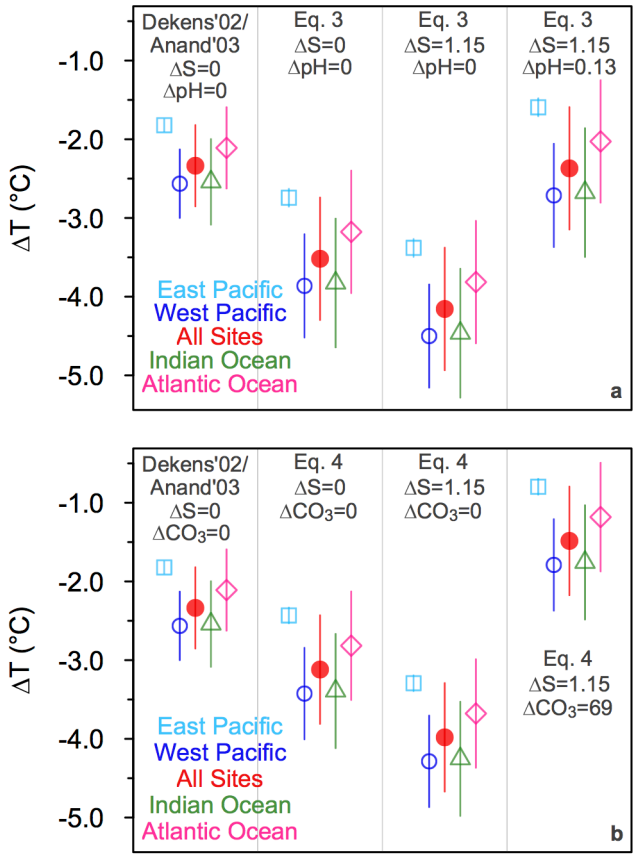


Figure 9 Magnitude of LGM cooling in the tropical ocean using the calibration of Dekens *et al.*, (2002)/Anand *et al.*, (2003) and the calibrations given in this study if **(a)** pH is the controlling carbonates system parameter (Eq. 3) or, **(b)** $[CO_3^{2-}]$ is the controlling carbonate system parameter (Eq. 4). The magnitude of cooling is shown with and without accounting for the whole ocean increase in salinity (1.15 units) and pH (0.13 units)/$[CO_3^{2-}]$ (69 µmol/kg) (supplementary material). Error bars (±1σ) relate only to the standard deviation of the ΔMg/Ca within each region. The true uncertainty of the temperature change is dependent on both the uncertainty of the sensitivities of Mg/Ca to T, S, pH and/or $[CO_3^{2-}]$ within the calibration, and the uncertainty in regional changes in salinity, pH/$[CO_3^{2-}]$, and dissolution during the LGM. Currently, we have very little constraint on regional changes in salinity and pH/$[CO_3^{2-}]$ during the LGM, thus the uncertainty associated with these changes is essentially unquantifiable at present.