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journal homepage: [www.elsevier.com/locate/epsl](http://www.elsevier.com/locate/epsl)On the fidelity of shell-derived  $\delta^{18}\text{O}_{\text{seawater}}$  estimatesJennifer Arbuszewski<sup>a,\*</sup>, Peter deMenocal<sup>a</sup>, Alexey Kaplan<sup>a</sup>, E. Christa Farmer<sup>a,b</sup><sup>a</sup> Lamont-Doherty Earth Observatory of Columbia University, Route 9W, Palisades, NY 10964, USA<sup>b</sup> Hofstra University, Dept. of Geology, Hempstead, NY 11549, USA

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## ABSTRACT

Paired foraminiferal Magnesium/Calcium ratio and oxygen isotope analyses are widely used to estimate surface ocean  $\delta^{18}\text{O}_{\text{seawater}}$ , a robust proxy for surface salinity. We assess the fidelity of shell-derived  $\delta^{18}\text{O}_{\text{seawater}}$  estimates for the surface-dwelling foraminifer *Globigerinoides ruber* (white) using an Atlantic meridional coretop transect spanning basin-scale temperature and salinity gradients. Shell-derived and observed  $\delta^{18}\text{O}_{\text{seawater}}$  values are well correlated ( $r^2 = 0.77$ ), but a large systematic bias is observed. Shell Mg/Ca ratios are significantly elevated above values expected from observed and isotopic calcification temperatures in the saline subtropical gyres of both hemispheres. This temperature-independent shell Mg/Ca ratio variability, termed “excess Mg/Ca”, is highly correlated with surface salinity ( $r^2 = 0.77$ ), and the observed salinity dependence ( $27 \pm 4\%$ ) is much higher than indicated by culture studies ( $6 \pm 2\%$ ). Our coretop data are used to develop new Atlantic Basin temperature and salinity calibration equations that are accurate ( $\pm 1.1^\circ\text{C}$  and  $\pm 0.20$ , respectively), precise ( $r^2 = 0.82$  and  $0.81$ , respectively), and verifiable using previously published data. These results are valid for the relatively high salinities of the subtropical Atlantic ( $35.5\text{--}37.3$ ). We discover that inclusion of other published data from lower salinity regions ( $<35$ ) indicates little or no excess Mg/Ca. Taken together, these results point to a strongly non-linear, positive salinity effect on shell Mg/Ca ratios that significantly affects the accuracy of SST and  $\delta^{18}\text{O}_{\text{seawater}}$  estimates in high salinity settings ( $>35$ ).

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## 1. Introduction

Surface ocean salinity gradients reflect general atmospheric circulation and its regulation of net water fluxes into and out of the surface ocean. Tropical surface waters are relatively fresh due to excess rainfall associated with the convergent, ascending limbs of the Hadley circulation (the Intertropical Convergence Zone), whereas the subtropical oceans north and south of the equator are much saltier due to excess evaporation from the dry, descending limbs of the mean Hadley circulation (Fig. 1A). This fundamental link between global atmospheric circulation and surface ocean salinity has led paleoceanographers to search for a reliable and accurate geochemical proxy for surface ocean salinity in order to estimate past changes in ocean salinity and its spatial gradients.

A promising and widely used approach for estimating past changes in surface ocean salinity employs paired Magnesium/Calcium ratio and  $\delta^{18}\text{O}_{\text{shell}}$  analyses of surface-dwelling foraminifer shells to calculate surface ocean  $\delta^{18}\text{O}_{\text{seawater}}$ , a robust proxy for surface ocean salinity (Fig. 1A,B) (Flower et al., 2004; Lund and Curry, 2006; Schmidt, 1999; Schmidt et al., 2004, 2006; Weldeab et al., 2005, 2007). The approach is elegantly simple: the  $\delta^{18}\text{O}$  composition of planktic foraminifer shells records both the local  $\delta^{18}\text{O}_{\text{seawater}}$  and the calcification temperature (through the kinetic fractionation effect),

whereas shell Mg/Ca ratios should mainly record the calcification temperature. Shell  $\delta^{18}\text{O}$  values and Mg/Ca ratio calcification temperature values are substituted into the oxygen isotope paleotemperature equation (Bemis et al., 1998) to solve for  $\delta^{18}\text{O}_{\text{seawater}}$ , providing surface paleosalinity estimates for the distant past.

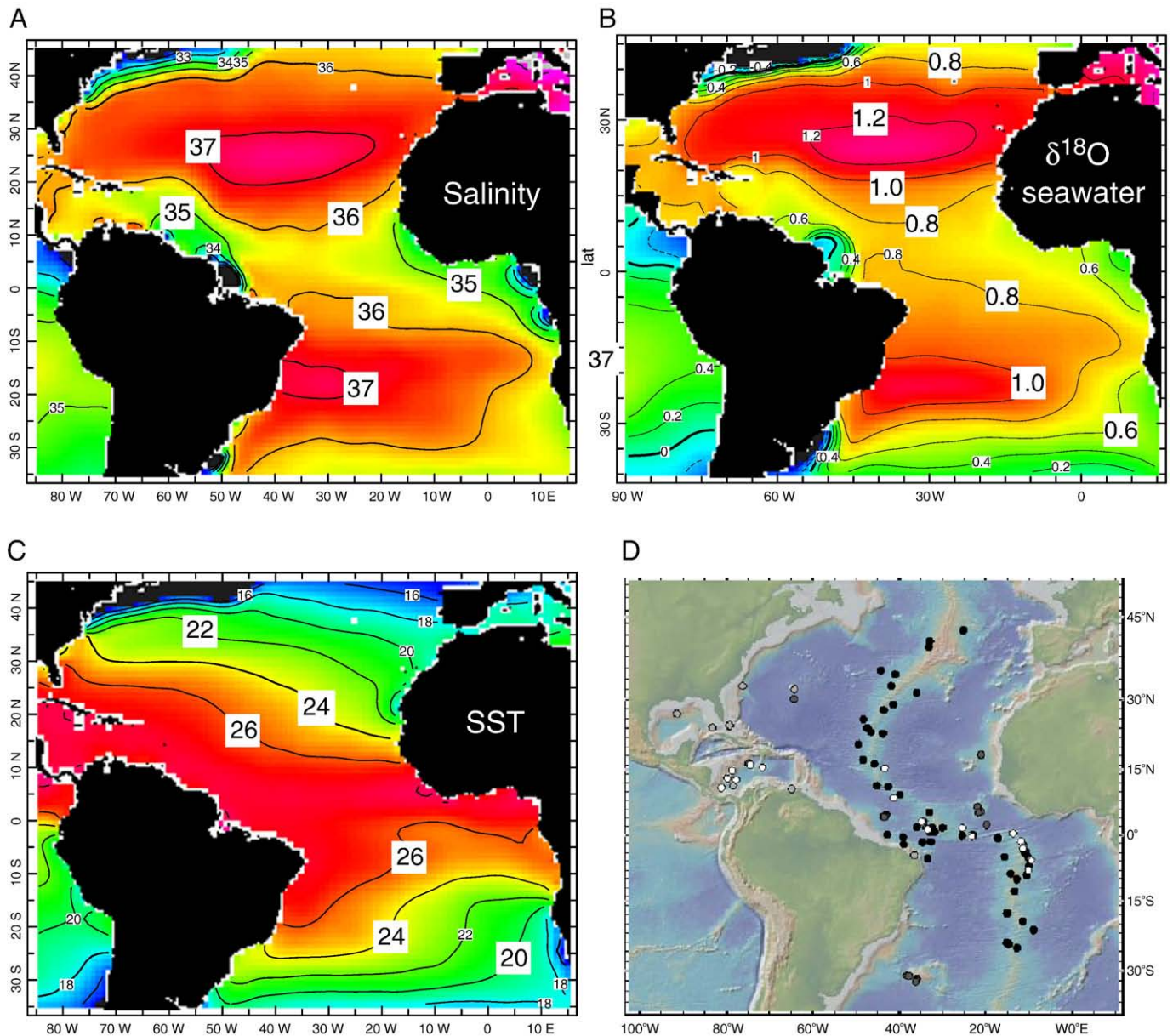
This foraminiferal geochemical proxy for estimating past changes in ocean salinity, has been widely applied (Flower et al., 2004; Lund and Curry, 2006; Schmidt, 1999; Schmidt et al., 2004, 2006; Weldeab et al., 2005, 2007), but it has never been calibrated or verified. We present a rigorous calibration and verification of the shell-derived  $\delta^{18}\text{O}_{\text{seawater}}$  proxy using a meridional transect of coretop samples spanning the large temperature ( $16.7\text{--}27.6^\circ\text{C}$ ) and salinity ( $35.48\text{--}37.28$ ) gradients of the Atlantic basin (Fig. 1A–D). We document a large and systematic bias in this method based on our observations as well as all previously published Atlantic data, which leads to highly inaccurate shell-based  $\delta^{18}\text{O}_{\text{seawater}}$  estimates. This bias is attributed to an open ocean salinity effect on whole shell Mg/Ca ratios that is much larger than observed in culture experiments (Kisakürek et al., 2008; Lea et al., 1999; Nürnberg et al., 1996). This newly quantified salinity effect on shell Mg/Ca compositions permits development of new ocean temperature and salinity equations that are highly accurate, precise, and verifiable with published data.

## 2. Samples and methods

A meridional transect of 64 Atlantic coretop samples was assembled to test the fidelity of shell-based  $\delta^{18}\text{O}_{\text{seawater}}$  estimates

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**Fig. 1.** (A) Mean annual salinity; (B) mean annual  $\delta^{18}\text{O}_{\text{seawater}}$  (‰, SMOW); and (C) mean annual SST (°C). Data from 2005 World Ocean Atlas and LeGrande and Schmidt (2006); (D) locations of the 64 coretop samples for this study (solid black symbols), as well as locations of coretop samples from Dekens et al. (2002; dark grey symbols), Farmer (2005; white symbols), and other published *G. ruber* Mg/Ca data (see text; light grey symbols).

over a large, ocean-basin-scale  $\delta^{18}\text{O}_{\text{seawater}}$  gradient (Fig. 1C,D). The coretop samples span 43°N to 25°S and were selected from the Lamont Core Repository to satisfy multiple criteria for age control, location, and water depth. Core locations are situated along either flank of the mid-Atlantic ridge to capture open ocean conditions with an average core water depth of 3700 m, well above the 4200 m modern lysocline. Cores were primarily selected based on known or inferred late Holocene coretop ages from stratigraphic age control presented in the CLIMAP, SPECMAP, GLAMAP, or EPILOG core databases (CLIMAP, 1976; Sarnthein et al., 2003; Waelbroeck et al., 2009). *Globorotalia menardii* stratigraphies were used to confirm late Holocene ages for most tropical/subtropical cores (Ericson and Wollin, 1956). Additionally, direct radiocarbon dating and oxygen isotope stratigraphies were developed for a number of cores where dating was uncertain. The planktic foraminifer *Globigerinoides ruber* (white, *sensu stricto*) was selected for analysis because it is known to calcify within the upper mixed layer (0–30 m; (Farmer et al., 2007; Schmidt and Mulitza, 2002)) and Mg/Ca ratio and  $\delta^{18}\text{O}$  temperature

sensitivities have been determined for this species from sediment traps, coretop observations and laboratory culture studies (Anand et al., 2003; Bemis et al., 1998; Dekens et al., 2002; Kisakürek et al., 2008; Lea et al., 2000; McConnell and Thunell, 2005; Schmidt and Mulitza, 2002). Mean annual ocean temperature, salinity, and bottom water ocean carbonate chemistry data were extracted for each core site from the World Ocean Atlas 2005 and GLODAP databases using Ocean Data View (Schlitzer, 2002). Recognizing that salinity is derived from ratios of conductivity and is thus unitless, we avoid use of the common “practical salinity unit” or psu notation (Pilson, 1998; UNESCO, 1981). Surface ocean temperature and salinity at 0 m are only weakly correlated over this entire transect ( $r^2=0.16$ ), providing an optimal dataset for isolating geochemical signatures associated with these two environmental parameters.

Approximately 80–100 *G. ruber* (white) shells were picked from each sample (250–355  $\mu\text{m}$ ), crushed gently (any visible large coarse grains were removed), and split into Mg/Ca and  $\delta^{18}\text{O}$  aliquots then transferred to acid-cleaned vials. Samples were cleaned prior to Mg/Ca analysis by

ICP-OES using an adaptation of the Boyle and Keigwin (1985) and Barker et al. (2003) cleaning protocols, including clay removal with methanol/MilliQ water rinses followed by full reductive and oxidative steps (Barker et al., 2003; Boyle and Keigwin, 1985). We also cleaned a subset of samples using only the clay removal (methanol/MilliQ rinses) step followed by an oxidative cleaning step to investigate potential biases that may have been introduced by including the reductive cleaning (Barker et al., 2003; Yu et al., 2007). Samples for  $\delta^{18}\text{O}$  were cleaned prior to analysis using a series of MilliQ water rinses as a precaution against contamination from infilling of clays and other particulates within the shell chambers. One-sigma sample replicate precision for Mg/Ca ratio and  $\delta^{18}\text{O}$  analyses of these samples were  $\pm 3\%$  and  $\pm 0.04\%$ , respectively.

### 3. Results

#### 3.1. Fidelity of SST estimates derived from shell $\delta^{18}\text{O}$ and Mg/Ca ratios

Calculated  $\delta^{18}\text{O}$  calcification temperatures closely track mean annual SSTs along the sample transect ( $r^2 = 0.65$ ; Fig. 2A), indicating that *G. ruber* (white) is a faithful recorder of mean annual surface ocean conditions. The calcification temperatures were calculated using the Bemis et al. (1998) low-light isotopic temperature equation:

$$T(^{\circ}\text{C}) = 16.5 - 4.80(\delta^{18}\text{O}_{\text{shell}} - (\delta^{18}\text{O}_{\text{seawater}} - 0.27)) \quad (1)$$

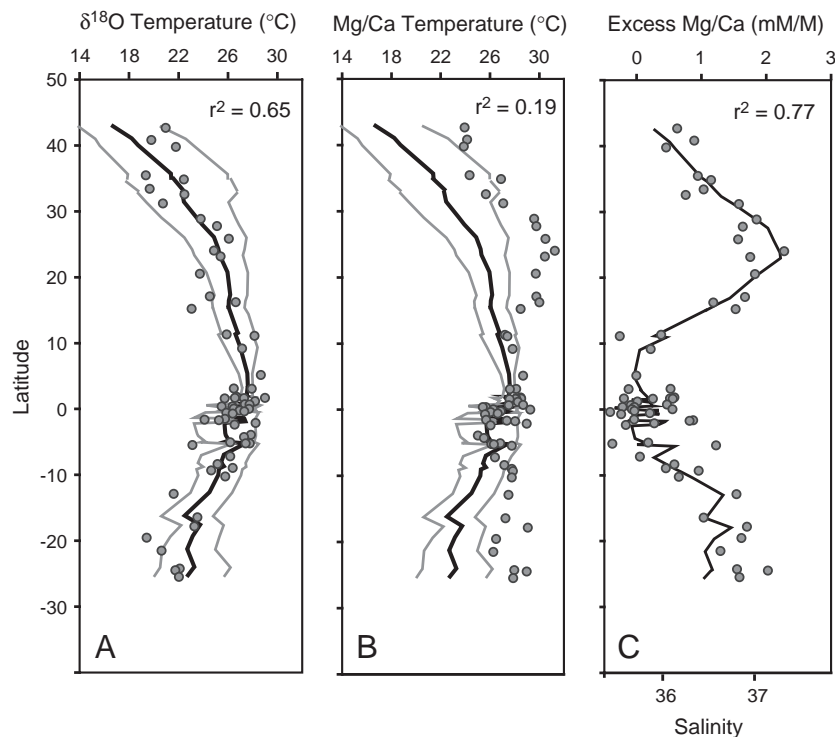
where  $\delta^{18}\text{O}_{\text{shell}}$  is the measured shell isotopic composition (relative to the Pee-Dee Belemnite, PDB) and  $\delta^{18}\text{O}_{\text{seawater}}$  is the seawater isotopic composition (relative to standard mean ocean water, SMOW) (Bemis et al., 1998). The term  $-0.27\%$  corrects for the  $\delta^{18}\text{O}$  difference between SMOW and PDB (Hut, 1987). Over the subtropical–tropical domain represented by this Atlantic transect, a strong linear relationship exists between surface ocean salinity and  $\delta^{18}\text{O}_{\text{seawater}}$

(0–50 m):  $\delta^{18}\text{O}_{\text{seawater}} = 0.238 * \text{Salinity} - 7.69$ ;  $r^2 = 0.66$ ,  $n = 106$ , accessed from the NASA global seawater  $\delta^{18}\text{O}_{\text{seawater}}$  database (Schmidt et al., 1999). Mean annual salinity values at 0 m in the water column are used to compute  $\delta^{18}\text{O}_{\text{seawater}}$  for each core site, and these values are equivalent within error to gridded estimates (LeGrande and Schmidt, 2006). The resulting calcification temperature estimates are most consistent with mean annual surface temperatures from 0 m ( $r^2 = 0.65$ ), and poorer correlations are observed if values are regressed against warm or cool season temperatures ( $r^2 = 0.59$  and  $0.64$ , respectively). Although *G. ruber* is observed to calcify during the warm season in some environments (Fischer et al., 1999; McConnell and Thunell, 2005), particularly in higher-latitude or upwelling regions, our results are most consistent with calcification at mean annual SST values except perhaps for the three coolest, northernmost core locations (Deuser et al., 1981) (Fig. 2A).

Mg/Ca temperature estimates were calculated using the Dekens et al. (2002) Atlantic *G. ruber* equation, which includes a water-depth correction to account for the preferential dissolution of high-Mg shell calcite in undersaturated bottom waters (Rosenthal and Lohmann, 2002):

$$T(^{\circ}\text{C}) = \ln(\text{Mg/Ca} / 0.38) / 0.09 + 0.61 * \text{core depth (km)}. \quad (2)$$

Calculated calcification temperatures using the shell Mg/Ca ratios are surprisingly poorly correlated with mean annual SSTs along this transect ( $r^2 = 0.19$ ; Fig. 2B). The Mg/Ca temperature estimates are also poorly correlated with the shell  $\delta^{18}\text{O}$  calcification temperatures ( $r^2 = 0.09$ ). It is worth noting that an early study also suggested that shell Mg/Ca cannot be explained by temperature alone (Delaney et al., 1985). Here we see that the poor correlation between Mg/Ca temperature estimates and measured annual SST over this large meridional transect is largely driven by elevated Mg/Ca ratios in the high salinity subtropical gyre regions of both hemispheres, resulting in excessively high SST estimates



**Fig. 2.** (A) Mean annual SST (solid black line, 0 m) and monthly maximum and minimum ranges (solid grey lines) for coretop site locations comprising the Atlantic meridional transect. *G. ruber*  $\delta^{18}\text{O}$ -derived calcification temperatures are shown with gray and black symbols ( $r^2 = 0.65$ ) based on the low-light Bemis et al. (1998) equation. (B) Mean annual SST (solid black line) and seasonal ranges (solid grey lines) with *G. ruber* Mg/Ca-derived calcification temperatures (red symbols,  $r^2 = 0.19$ ) based on the Dekens et al. (2002) equation. Note the elevated Mg/Ca SSTs in the subtropics of either hemisphere. (C) Plot of “excess Mg/Ca” (red symbols), calculated as the difference between the measured Mg/Ca and the expected Mg/Ca at  $\delta^{18}\text{O}$  calcification temperatures, compared to mean annual salinity for each core site (solid black line;  $r^2 = 0.77$ ).



for the northern and southern subtropics (Fig. 2B). Surprisingly, Mg/Ca values for the salty subtropical gyre cores are as high as or higher than cores from the warmer tropics. Within the tropical latitude band only (15°N–15°S), Mg/Ca ratio temperatures are actually well correlated with mean annual SSTs, having values that closely match shell isotopic temperatures. This is expected, as the Atlantic dataset used to derive Eq. (2) was largely derived from tropical coretop samples (Dekens et al., 2002). The Mg/Ca-derived SSTs have an equally poor match to observed SSTs when the Anand sediment trap based calibration equation is used (which is similar to the Dekens equation but has no water depth dissolution-correction term) (Anand et al., 2003), indicating that the observed Mg/Ca values are not due to bottom water saturation state.

### 3.2. “Excess Mg/Ca” and salinity

The origin of these systematic offsets between the  $\delta^{18}\text{O}$  and Mg/Ca temperature estimates can be explored by calculating “excess Mg/Ca”, which quantifies temperature-independent Mg/Ca variability. Excess Mg/Ca is defined as the difference between the measured shell Mg/Ca ratio and the expected Mg/Ca ratio at the  $\delta^{18}\text{O}_{\text{seawater}}$ -corrected  $\delta^{18}\text{O}$  calcification temperature. It is calculated by substituting into the Mg/Ca temperature Eq. (2) the isotopic temperature given by Eq. (1), with the  $\delta^{18}\text{O}_{\text{seawater}}$  obtained for each sample location from its modern relationship with salinity based on the global  $\delta^{18}\text{O}_{\text{seawater}}$  database (Schmidt et al., 1999) and then solving for the shell Mg/Ca ratio expected at the observed isotopic temperature. This “excess Mg/Ca” represents residual, temperature-independent shell Mg/Ca variability, with positive values indicating shell Mg/Ca ratios that are higher than expected from shell  $\delta^{18}\text{O}$ -derived SSTs:

$$\text{“Excess Mg/Ca” (mmol/mol)} = \text{Measured Mg/Ca} - \text{Expected Mg/Ca at } \delta^{18}\text{O SST.} \quad (3)$$

The “excess Mg/Ca” observed in our transect dataset (red symbols in Fig. 2C) is well correlated with surface ocean salinity ( $r^2 = 0.77$ ). There is an equally high correlation between excess Mg/Ca ratios and surface alkalinity ( $r^2 = 0.77$ ) due to the dominant control of salinity on tropical–subtropical alkalinity gradients (Lee et al., 2006). The “excess Mg/Ca” values approach zero in the lower salinity tropics, indicating that the isotopic and Mg/Ca ratio SST estimates converge on the same value, which is consistent with the fact that the Mg/Ca calibration equation is based on tropical cores (Dekens et al., 2002). In the higher salinity subtropical gyres, excess Mg/Ca ratios are consistently and significantly elevated by up to 1–2 mmol/mol above values expected from  $\delta^{18}\text{O}$  calcification temperatures, leading to temperature estimates that can be biased by several degrees Celsius (Fig. 2B,C).

Excess Mg/Ca values are uncorrelated with surface nutrient  $[\text{PO}_4]$  content, surface water  $[\text{CO}_3^{2-}]$ , water depth, or bottom water carbonate saturation ( $\Delta\text{CO}_3^{2-}$ ) ( $r^2 = 0.02, 0.02, 0.01$ , and  $0.01$ , respectively). Additionally, we explored other combinations of variable calcification season and water depth between 0 and 50 m but none significantly reduced or eliminated the observed “excess Mg/Ca” and its correlation with surface salinity. We calculated excess Mg/Ca using the warmest and coolest monthly SSTs and their associated salinity and  $\delta^{18}\text{O}_{\text{seawater}}$  values at each core site for 0 m, as well as at 50 m and 0–50 m average values. None of these alternate scenarios significantly reduced excess Mg/Ca. We did not explore depths below 50 m because global  $\delta^{18}\text{O}$  calibration studies for this species confirm that calcification occurs between 0 and 30 m (Farmer et al., 2007; Schmidt and Mulitza, 2002). Despite extensive investigation, we found no physically consistent way to reconcile the shell  $\delta^{18}\text{O}$  and Mg/Ca values using available temperature calibration equations without including a significant salinity effect correction for shell Mg/Ca compositions.

### 3.3. “Excess Mg/Ca” and shell cleaning protocol

We examined whether the Mg/Ca cleaning protocol influenced the observed excess Mg/Ca. A subset of coretop samples spanning the full salinity range was repicked and cleaned using only the clay removal and oxidative protocol (Barker et al., 2003) to investigate the possibility that the excess Mg/Ca signal may be an artifact of the cleaning method, particularly due to known preferential removal of Mg during the reductive step. As demonstrated in several previous studies, shells from samples cleaned using the full oxidative–reductive protocol had Mg/Ca ratios that were consistently about 8–9% lower than the oxidative-only cleaned samples. This difference can be attributed to additional etching and Mg loss from the more aggressive cleaning (Barker et al., 2003; Rosenthal et al., 2004; Yu et al., 2007). However, there is no salinity-related bias in the Mg/Ca ratios between these two cleaning methods.

### 3.4. Excess Mg/Ca and shell-derived $\delta^{18}\text{O}_{\text{seawater}}$ calculations

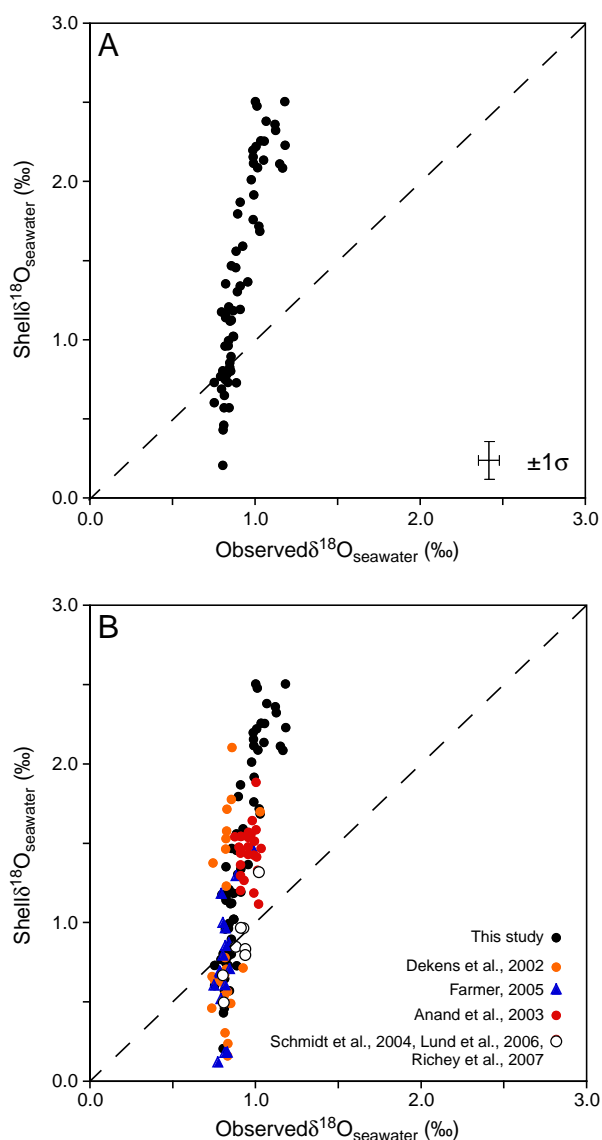
The large salinity effect on shell Mg/Ca compositions directly impacts shell-derived  $\delta^{18}\text{O}_{\text{seawater}}$  estimates (Fig. 3A,B). The shell-derived  $\delta^{18}\text{O}_{\text{seawater}}$  values are estimated by substituting the measured shell  $\delta^{18}\text{O}$  values and the Mg/Ca-derived temperatures (Eq. (2)) into the following equation (derived from (Bemis et al., 1998) low-light  $\delta^{18}\text{O}$  paleotemperature equation):

$$\delta^{18}\text{O}_{\text{seawater}}(\text{SMOW}) = \delta^{18}\text{O}_{\text{shell}}(\text{PDB}) + ((T(^{\circ}\text{C}) - 16.5) / 4.8) + 0.27. \quad (4)$$

The Atlantic *G. ruber* (white) shell-derived  $\delta^{18}\text{O}_{\text{seawater}}$  estimates are compared to observed surface water  $\delta^{18}\text{O}_{\text{seawater}}$  values in Figure 3A (Schmidt et al., 1999). The correlation between observed and shell-derived  $\delta^{18}\text{O}_{\text{seawater}}$  values is remarkably tight ( $r^2 = 0.77$ ) but in high salinity (high  $\delta^{18}\text{O}_{\text{seawater}}$ ) environments the shell-derived estimates are much higher than expected (Fig. 3A). At low salinities (low  $\delta^{18}\text{O}_{\text{seawater}}$ ) the Mg/Ca and  $\delta^{18}\text{O}$  temperature estimates converge near the values expected from coretop, sediment trap, and culture experiment studies. As salinity increases, excess Mg/Ca also increases, and this is the underlying cause for the observed divergence of Mg/Ca and  $\delta^{18}\text{O}$  temperatures (Fig. 2A–C). This same salinity effect on shell Mg/Ca ratios leads to the divergence of the shell-based and observed  $\delta^{18}\text{O}_{\text{seawater}}$  values evident in Figure 3. These results clearly demonstrate that shell-derived  $\delta^{18}\text{O}_{\text{seawater}}$  estimates produce highly inaccurate values if the large salinity effect on shell Mg/Ca ratios is not accommodated.

This offset between shell-derived and observed  $\delta^{18}\text{O}_{\text{seawater}}$  values is observed in all published Atlantic *G. ruber* (white) coretop data as well (Fig. 3B). To compare ours with previously published data, we compiled a set of published *G. ruber* (white) coretop Mg/Ca and  $\delta^{18}\text{O}$  data from the open (sub)tropical Atlantic, and computed  $\delta^{18}\text{O}_{\text{seawater}}$  values using Eq. (4). The results are shown in Figure 3B, where published data are plotted alongside our Atlantic coretop transect, color-coded by author. These published data are comprised of coretop data from three Caribbean/Gulf of Mexico studies (Lund and Curry, 2006; Richey et al., 2007; Schmidt et al., 2004), the eastern tropical Atlantic (Weldeab et al., 2005), numerous samples from the (sub)tropical Atlantic basin (Dekens et al., 2002; Farmer, 2005), and sediment trap data from the Sargasso Sea (Anand et al., 2003). From this comparison, it is apparent that the salinity influence on shell Mg/Ca (and hence the shell-derived  $\delta^{18}\text{O}_{\text{seawater}}$  value) is also present in published coretop and sediment trap data from the (sub)tropical Atlantic.

Paleoceanographic studies that have estimated past changes in  $\delta^{18}\text{O}_{\text{seawater}}$  at core sites in the tropical and subtropical Atlantic have often been confronted by an apparent difficulty in explaining the very large temporal  $\delta^{18}\text{O}_{\text{seawater}}$  changes they observe. Several studies from the Atlantic tropics and subtropics have cited glacial–interglacial,



**Fig. 3.** (A) Observed surface  $\delta^{18}\text{O}_{\text{seawater}}$  compared to foraminifer shell-based  $\delta^{18}\text{O}_{\text{seawater}}$  estimates (derived from *G. ruber* (white) Mg/Ca and  $\delta^{18}\text{O}$  analyses, see text) for the Atlantic transect (40°N–25°S). Although the correlation is high ( $r^2=0.77$ ), the shell-derived data greatly overestimate the  $\delta^{18}\text{O}_{\text{seawater}}$  range due to the excess Mg/Ca effect associated with salinity changes (Fig. 4). (B) Available published Atlantic *G. ruber* (white) Mg/Ca and  $\delta^{18}\text{O}$  data were compiled (see text) and  $\delta^{18}\text{O}_{\text{seawater}}$  values were calculated as in (a). Note the overall agreement between all data, and their consistently higher than observed  $\delta^{18}\text{O}_{\text{seawater}}$  values, indicating that this “excess Mg/Ca” effect is evident in other published data.

millennial-scale, and even century-scale  $\delta^{18}\text{O}_{\text{seawater}}$  changes in excess of 0.4 to 1.0‰ at given core sites after any ice volume effect has been removed (Lund and Curry, 2006; Schmidt et al., 2004, 2006). The amplitudes of these changes are as large as or larger than the entire subtropical–tropical Atlantic  $\delta^{18}\text{O}_{\text{seawater}}$  (or salinity) gradient (e.g. Fig. 1C), which is the reason why the interpretations have been questioned. We suggest here, and demonstrate quantitatively later, that these anomalously large  $\delta^{18}\text{O}_{\text{seawater}}$  changes are due to uncompensated salinity effects on the shell Mg/Ca composition.

### 3.5. “Excess Mg/Ca” signal not due to post-depositional diagenesis

The “excess Mg/Ca” is highly correlated with salinity based on the results of this study and published Atlantic coretop data. In two

studies investigating the origin of very high Mg/Ca ratios published from cores in very high salinity regions of the Eastern Mediterranean and Red Sea (Ferguson et al., 2008; Hoogakker et al., 2009) the surface microstructure of foraminifer shells was examined by Scanning Electron Microscope (SEM) and subhedral high-Mg diagenetic overgrowths were found on the interior chamber walls. Given the very high salinities in these regions, the overgrowths were interpreted to have formed post-depositionally due to  $\text{CaCO}_3$ -supersaturated conditions in interstitial pore waters during early burial (Hoogakker et al., 2009). We obtained detailed SEM images of the inner and outer shell walls of *G. ruber* (white) shells from 11 of our coretop samples (range of 35.6 to 37.3), capturing the full salinity range of our sample set. To remove any sediment from the chambers the individual specimens were cleaned using gentle sonication in methanol and water prior to imaging. Shells were also cleaved with a scalpel and imaged by SEM to inspect the shell wall interior for overgrowths.

We find no evidence of diagenetic coatings in any of our coretop samples, and shells appeared to be pristine and uniform based on detailed SEM micrographs of interior and exterior shell chamber surfaces. Samples with the highest excess Mg/Ca were not different microstructurally compared to shells with little or no excess Mg/Ca (Fig. 4). There are no apparent overgrowths or contaminant phases on the *G. ruber* (white) shells in this set of samples spanning a large range in both salinity and excess Mg/Ca values. The one consistent microstructural difference apparent in these samples is the occurrence of dissolution-related features such as etching and shell thinning due to varying degrees of shell dissolution associated with water depth and bottom water  $\Delta\text{CO}_3^{2-}$ . Thus we conclude that the diagenetic overgrowth mechanism proposed by Hoogakker et al. (2009) does not apply to these open ocean samples. We conclude that the temperature-independent, excess Mg/Ca signal observed in our data, and other published data as well, is most likely recorded within the primary shell structure.

## 4. Discussion

### 4.1. Atlantic *G. ruber* Mg/Ca sensitivity to temperature, salinity, and bottom water $\Delta\text{CO}_3^{2-}$

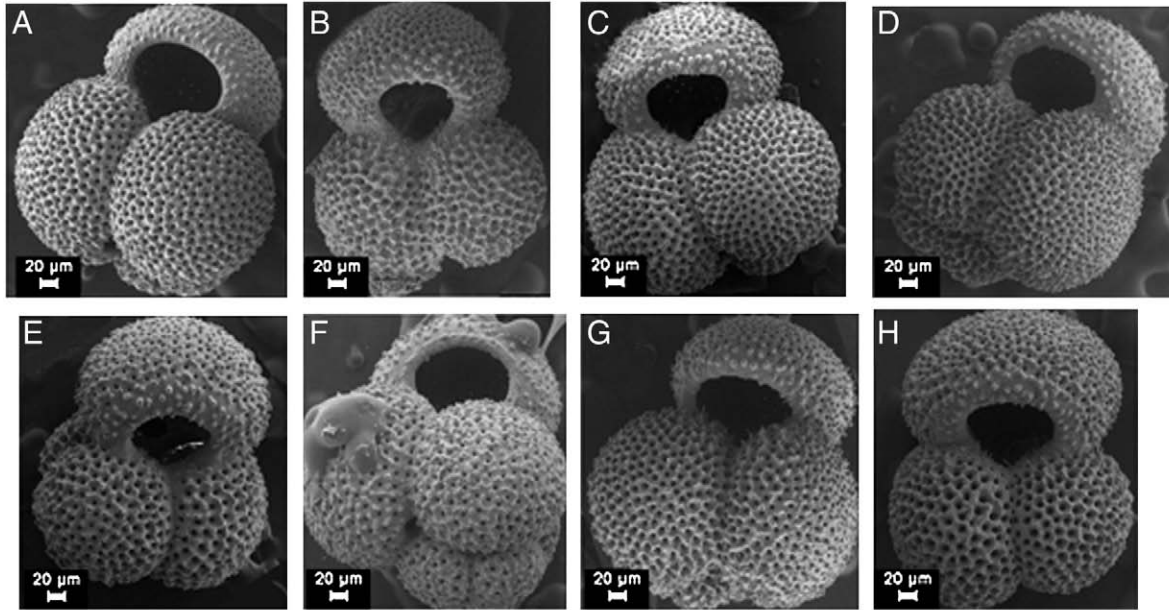
We isolate the separate influences of temperature, salinity, and bottom water  $\Delta\text{CO}_3^{2-}$  on measured shell Mg/Ca compositions using a multivariate regression approach. The close correspondence between *G. ruber* (white)  $\delta^{18}\text{O}$  calcification temperatures and mean annual SSTs (at 0 m) along this transect supports conclusions from basinal (Farmer et al., 2007) and global (Schmidt and Mulitza, 2002) coretop calibration studies that *G. ruber* (white) is a faithful recorder of mean annual conditions in the upper mixed layer (0–30 m) of the tropical and subtropical oceans. Using mean annual SST, salinity, and bottom water  $\Delta\text{CO}_3^{2-}$  of each core site as predictors and  $\ln(\text{Mg/Ca})$  of *G. ruber* (white) as the predictand, a multivariate regression returned the following equation with an  $r^2$  value of 0.82 ( $n=64$ ; 95% confidence limits are indicated for each coefficient value).

$$\text{Mg/Ca (mmol/mol)} = \exp(-9.7 \pm 1.5 + 0.0482 \pm 0.0075 \cdot T + 0.269 \pm 0.039 \cdot S + 0.0046 \pm 0.0015 \cdot \Delta\text{CO}_3^{2-}). \quad (5)$$

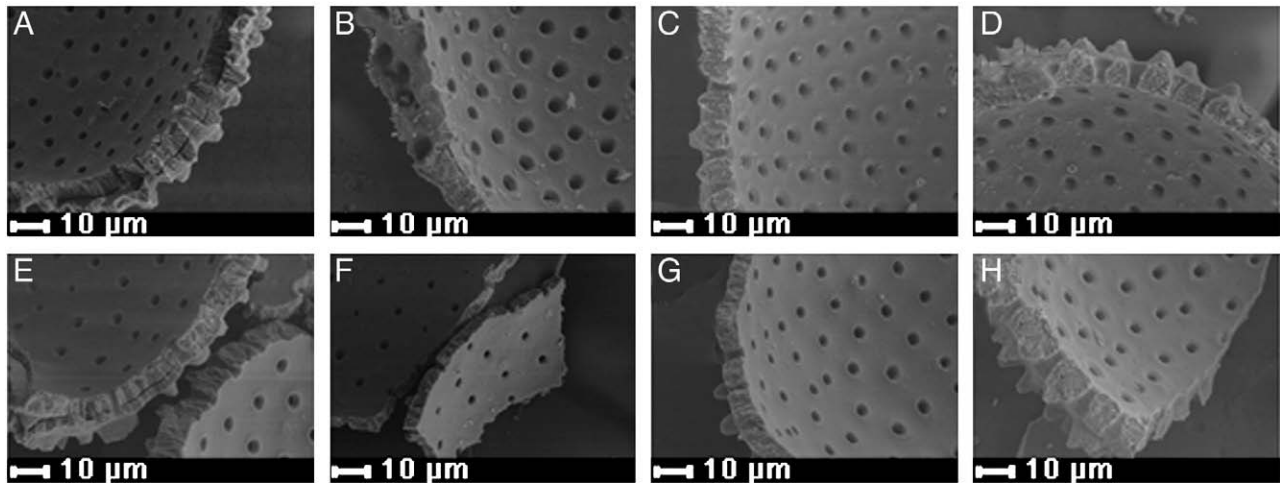
The multivariate fit of our Atlantic Mg/Ca data as functions of  $T$  and  $S$  is shown in Figure 5 (this three-dimensional plot does not show the additional, minor contributions from  $\Delta\text{CO}_3^{2-}$  variability captured in Eq. (5) due to plotting limitations).

The validity of this equation can be demonstrated by the inclusion of the other, previously published Atlantic datasets shown in Figure 3B into the regression analysis. The  $T$ ,  $S$ , and  $\Delta\text{CO}_3^{2-}$  coefficients do not change significantly (relative to their errors) when these other published datasets are included into the analysis. If the calibration equation is applied to the previously published Atlantic

## Panel I



## Panel II



**Fig. 4.** Panel I: SEM images of whole *G. ruber* (white) specimens spanning a large range in surface ocean salinity (35.6 to 37.3). Note the absence of any external or internal diagenetic coatings or granular subhedral patches. The scale bars represent 20 µm. Specimens are arranged according to their mean annual salinities: A) RC24-08, SST = 25.75, Salinity = 35.64, B) RC13-190, SST = 27.22, Salinity = 35.66, C) RC24-16, SST = 25.76, Salinity = 35.72, D) V22-174, SST = 25.18, Salinity = 36.32, E) V16-205, SST = 25.99, Salinity = 36.47, F) RC8-18, SST = 23.23, Salinity = 36.54, note: the clumps on the surface of the foram are tape adhesive that could not be removed, G) V14-2, SST = 25.91, Salinity = 37.02, and H) V16-206, SST = 25.26, Salinity = 37.28. Panel II: SEM images of the interior chamber portions of *G. ruber* (white) shells spanning a large range in surface ocean salinity (35.6 to 37.3). The scale bars represent 10 µm. Specimens are arranged according to their mean annual salinities: A) RC24-08, SST = 25.75, Salinity = 35.64, B) RC13-190, SST = 27.22, Salinity = 35.66, C) RC24-16, SST = 25.76, Salinity = 35.72, D) V22-174, SST = 25.18, Salinity = 36.32, E) V16-205, SST = 25.99, Salinity = 36.47, F) RC8-18, SST = 23.23, Salinity = 36.54, G) V14-2, SST = 25.91, Salinity = 37.02, and H) V16-206, SST = 25.26, Salinity = 37.28.

coretop datasets, the correlation between measured and estimated *G. ruber* (white) Mg/Ca remains high ( $r^2 = 0.70$ ;  $n = 112$  (64 LDEO plus 48 other published data)) even though these samples were measured in different labs with slightly different shell cleaning protocols.

The resulting calibration (Eq. (5)) has some notable differences relative to other published calibration studies for this species. The temperature coefficient indicates that shell Mg/Ca increases exponentially by  $4.8 \pm 0.8\%$  per  $^{\circ}\text{C}$ , a value which is significantly lower than the canonical 9% value determined for several Atlantic coretop and sediment trap studies where the salinity effect was not considered for the Mg/Ca temperature calibration (Anand et al., 2003; Dekens et al., 2002; Lea et al., 1999; Nürnberg et al., 1996; Russell et al., 2004). It is important to restate that it was not possible to retain the canonical

Mg/Ca temperature sensitivity of 9% per  $^{\circ}\text{C}$  and simultaneously reconcile the measured  $\delta^{18}\text{O}$  and Mg/Ca ratio data in our study (or others) without dramatically reducing the correlation (Fig. 2C). However, previous coretop studies have not explicitly accounted for the salinity influence on shell Mg/Ca which acts to force any salinity effect into the temperature regression, leading to an apparent increase in the exponential constant. A distinguishing design element of our study is that the correlation between SST and salinity along the sample transect is very weak ( $r^2 = 0.16$ ), providing an optimal statistical basis for isolating the influences of temperature and salinity on shell Mg/Ca ratios.

It is revealing to consider sediment trap calibration studies based on this same species (*G. ruber* (white)), using similar size fractions



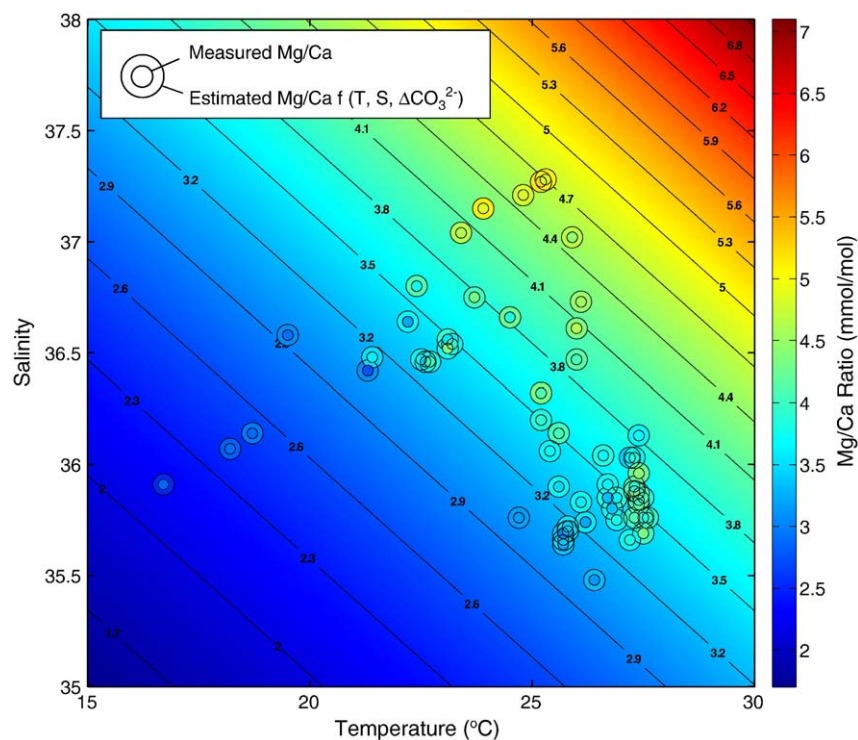
and analytical protocols. There are significant differences in the empirically-derived temperature sensitivity coefficients between the fresher Pacific and the saltier Atlantic regions, and these differences are consistent with our results. In the relatively fresh (salinity of 35.1) Guaymas Basin of the eastern tropical Pacific, McConnell and Thunell (2005) determined that *G. ruber* Mg/Ca values increased by 6.8% per °C. In the saltier waters off Bermuda (salinity of 36.4), Anand et al. (2003) determined a greater temperature sensitivity of 9.0% per °C. Comparison of these two calibration studies reveals that, at a given warm SST value typical of the tropics, the Atlantic samples have 1–2 mmol/mol higher Mg/Ca ratios (Anand et al., 2003; McConnell and Thunell, 2005). This same trend toward higher Mg/Ca ratios in higher salinity waters of the same temperature also exists in *G. ruber* coretop calibration studies from the Pacific, Indian, Atlantic, and Mediterranean basins (Dekens et al., 2002; Ferguson et al., 2008; Lea et al., 2000; Mathien-Blard and Bassinot, 2009). Our temperature coefficient of  $4.8 \pm 0.8\%$  per °C evidently reflects the asymptotic temperature sensitivity of this species over the temperature and salinity ranges of our dataset. As salinity increases, when it is positively correlated with temperature, the apparent temperature sensitivity increases if the salinity effect is ignored (Eq. (5); Fig. 5), and we believe this is why this phenomenon was previously unrecognized.

Culture experiments offer unique opportunities to explore calcification responses to imposed environmental variables and one study utilizing *G. ruber* (white) indicates a temperature sensitivity of  $8 \pm 2\%$  per °C (Kisakürek et al., 2008). This temperature sensitivity is comparable to other culture experiments using other species (Lea et al., 2000; Russell et al., 2004). While the lower limit of this temperature sensitivity is close to the upper range determined for our regression, the two estimates are different. These culture studies are very carefully conducted and the results are robust, yet culture studies

differ significantly from nature in important ways that may affect quantitative comparisons with natural samples. Stresses resulting from growth conditions exceeding natural tolerances are acknowledged in this *G. ruber* culture study and may affect results in unknown ways. In the open ocean, foraminifers are known to exhibit significant variations in the calcifying microenvironment associated with the symbiotic algae (Eggins et al., 2004; Sadokov et al., 2009). Lastly, culture studies have yet to explore how the temperature sensitivity coefficient may vary with salinity.

It should also be noted that even assuming that the 9% value recovered from culture studies is the “true” temperature sensitivity of Mg/Ca ratios, we don’t necessarily expect it to be recovered in the regression procedure that produced estimate (5). Regression coefficients have expected values equal to true slopes only when the predictors are error-free. Therefore, if predictors are affected by random error, the regression coefficients are usually smaller than true slopes: minimizing expected error of prediction forces the slopes down, because smaller slopes inflate predictors’ error less. Because of uncertainty in the actual calcification season and/or depth and coretop ages there is no doubt some error in the predictors of Eq. (5).

The influence of salinity on *G. ruber* (white) Mg/Ca ratios deduced from our coretop dataset is significantly higher ( $27 \pm 4\%$  increase per salinity unit) than for foraminifer culturing experiments ( $2\text{--}11\%$  per salinity unit (Dueñas-Bohorquez et al., 2009; Hastings et al., 1998; Lea et al., 1999; Nürnberg et al., 1996)), including a recent culturing study for this particular species, *G. ruber* (white) ( $6 \pm 2\%$  per salinity unit) (Kisakürek et al., 2008). Our high salinity dependence of the Mg/Ca ratio agrees well with a study from the Mediterranean and a recent global coretop and plankton tow study ( $15\text{--}59\%$  and  $\sim 15\%$  per salinity unit change in



**Fig. 5.** The color map shows estimated Mg/Ca based on the equation ( $\text{Mg/Ca} = \exp(-9.7 + 0.0482 \cdot T + 0.269 \cdot S)$ ) for the T–S space shown. Due to plotting restrictions, this color map cannot also show the influence of  $\Delta\text{CO}_3^{2-}$  on shell Mg/Ca values. Each marker represents a pair of values; the color fill of the inner circle indicates the measured shell Mg/Ca while the color fill of the outer circle indicates the estimated Mg/Ca as a function of T, S, and bottom water  $\Delta\text{CO}_3^{2-}$  as described by our new equation ( $\text{Mg/Ca} = \exp(-9.7 + 0.0482 \cdot T + 0.269 \cdot S + 0.0046 \cdot \Delta\text{CO}_3^{2-})$ ). The offset in color between the outer circle and the color map is due to the influence of bottom water  $\Delta\text{CO}_3^{2-}$ . The isolines show values of constant Mg/Ca incremented by 0.3 mmol/mol, the value of the Mg/Ca standard error of our equation, on the color map.

Mg/Ca ratio, respectively) (Ferguson et al., 2008; Mathien-Blard and Bassinot, 2009). In Section 4.6, we combine available  $\delta^{18}\text{O}$  and Mg/Ca datasets from the lower salinity Pacific and Indian Ocean basins to document that this observed pronounced salinity effect on shell Mg/Ca ratios is actually highly non-linear, with little to no excess Mg/Ca (i.e. temperature-independent variability) at the lowest open ocean salinities (salinities of 32–34), and very high excess Mg/Ca at the highest salinities (in excess of 35). Previously published data and our new results presented here demonstrate that the shell Mg/Ca ratios from the more saline Atlantic (sub) tropics are elevated far beyond values expected from their isotopic calcification temperatures.

#### 4.2. Possible mechanism linking salinity and elevated shell Mg/Ca ratios

Biom mineralized shell Mg/Ca incorporation differs from inorganic precipitation in three important ways, each of which underscore the dominant role of biology in regulating foraminiferal shell chemistry (Lea et al., 2003). First, foraminifer biomineralization actively discriminates against Mg, such that the distribution coefficient between shell calcite and seawater is orders of magnitude lower than predicted from the theory or measured in inorganic experiments (Bender et al., 1975; Lea et al., 2003; Nürnberg et al., 1996; Oomori et al., 1987; Zeebe and Sanyal, 2002). Second, the observed exponential temperature-dependence of foraminifer shell Mg/Ca is much greater (6–10% per °C) than inorganic precipitation experiments (3% per °C). Lastly, Mg is heterogeneously distributed in the shell wall, with strong diurnal banding evident in many species (Bentov and Erez, 2006; Elderfield et al., 1996; Hathorne et al., 2003; Kunioka et al., 2006; Sadekov et al., 2005). These considerable differences between biomineralized and inorganic calcification highlight the dominant role of biology in modifying Mg incorporation into biogenic carbonates.

Culture studies have documented that foraminifers grown in higher salinity solutions were more “vital” (Hemleben et al., 1987), exhibiting higher growth rates, heavier shells, with more chambers, and accepting more food than those grown at lower salinities (Hemleben et al., 1987; Nürnberg et al., 1996). From these observations Nürnberg et al. (1996) speculated that “drastically enhanced Mg uptake at high salinity conditions is a direct consequence of increased metabolic activity”, an observation that appears to find support in subsequent studies (Dueñas-Bohorquez et al., 2009). Merging these culture results with recent discoveries from inorganic calcification experiments, a realistic mechanism can be proposed to explain why salinity may affect shell Mg/Ca. Atomic force microscopy of inorganically precipitated calcite shows that the growth rate of calcite increases with increasing ionic strength (i.e. higher salinities) (Stephenson et al., 2009). Incorporation of  $\text{Mg}^{2+}$  ions into the calcite lattice also increased with increasing growth rate in these experiments due to a greater incidence of kink defect sites where  $\text{Mg}^{2+}$  can substitute for  $\text{Ca}^{2+}$  (Stephenson et al., 2009). Kink defects establish lower energy sites for  $\text{Mg}^{2+}$  substitution at ‘step edges’ as calcite layers are added to the host crystal (Stephenson et al., 2008). Hence, we suggest that the salinity-related increases in foraminiferal vitality can promote faster calcification rates and kink defect incidence, which in turn increases  $\text{Mg}^{2+}$  uptake into the calcite lattice.

A recent culture study on *G. sacculifer* isolated the influence of salinity and the carbonate saturation state of seawater and found salinity to be a dominant control on shell chemistry (Dueñas-Bohorquez et al., 2009). They suggest that at higher salinity the concentration of  $\text{Mg}^{2+}$  may be higher in the extracellular parent solution where the cell extracts Mg and may influence the Mg channels and pumps within the cell itself (Dueñas-Bohorquez et al., 2009). Biochemically, it appears salinity has a greater influence on cell function, i.e. cellular Mg transport, than does carbonate saturation state, and this is ultimately recorded in the shell calcite.

#### 4.3. Developing new Atlantic basin equations to estimate mean annual SST and salinity

We develop new equations that accurately and precisely reproduce modern mean annual temperature and salinity using a multivariate (MV) regression approach which exploits the dual sensitivity of shell Mg/Ca ratios and  $\delta^{18}\text{O}$  values to temperature and salinity, with *G. ruber* (white) Mg/Ca ratios,  $\delta^{18}\text{O}$  values, and bottom water  $\Delta\text{CO}_3^{2-}$  as predictors using the same data as presented in Section 4.1. To test the robustness of these new equations, we then verify these equations using published Atlantic basin *G. ruber* (white) Mg/Ca and  $\delta^{18}\text{O}$  data. Bottom water  $\Delta\text{CO}_3^{2-}$  is also included as a predictor as it has been amply demonstrated to influence shell Mg/Ca compositions (Dekens et al., 2002; Rosenthal and Lohmann, 2002). Bottom water  $\Delta\text{CO}_3^{2-}$  was estimated for each core site using the core location and depth coordinates and interpolating the WOCE and GLODAP databases using Ocean Data View.

The approach takes advantage of the dual sensitivity of the shell Mg/Ca ratio and  $\delta^{18}\text{O}$  proxies to temperature, and their shared but separate sensitivity to salinity changes through the strong, modern covariance between salinity and  $\delta^{18}\text{O}_{\text{seawater}}$  in the (sub)tropical Atlantic ( $r^2 = 0.66$ ). An implicit assumption, and limitation, to this approach is that although salinity and  $\delta^{18}\text{O}_{\text{seawater}}$  are well correlated today, the slope and intercept of the correlation were very likely quite different in the past, with large regional variations (Oppo et al., 2007). The purpose of this approach is not to produce a new set of calibration equations to replace earlier studies, but rather to demonstrate how effective this approach is in providing accurate and precise estimates of temperature and salinity based on these new and previously published data – a problem that has plagued all previous efforts (e.g. Fig. 3B). The results of these multivariate regressions to estimate Atlantic SST and salinity are summarized below:

$$\text{Mean Ann SST (}^\circ\text{C)} = 16.06 + 4.62 * \ln(\text{Mg/Ca}) - 3.42 * (\delta^{18}\text{O}_{\text{shell}}) - 0.1 * (\Delta\text{CO}_3^{2-}) \quad (6)$$

$$\text{Mean Ann Salinity (}\text{‰}\text{)} = 34.28 + 1.97 * \ln(\text{Mg/Ca}) + 0.59 * (\delta^{18}\text{O}_{\text{shell}}). \quad (7)$$

The observed Atlantic SST and salinity gradients can be accurately (RMS errors of  $\pm 1.1$  °C and  $\pm 0.23$ , respectively) and precisely estimated ( $r^2 = 0.82$  and  $0.81$ ; Fig. 6A,B) using this multivariate approach. Despite the remarkable skill and robust nature of the coretop calibration, it is important to emphasize again that the multivariate approach works because of the modern covariance between (sub)tropical salinity and  $\delta^{18}\text{O}_{\text{seawater}}$  over the geographic domain of this sample set. It is possible, even likely, that the slope of this relationship changed in the past; this is something the equations cannot resolve but very large (factor of two) slope changes are needed to exceed the RMS error of these equations.

#### 4.4. Verification of calibration equations using published coretop data

The new equations are verified using published coretop and sediment trap data from open ocean sites in the Atlantic basin. We used published raw *G. ruber* (white) Mg/Ca ratio and  $\delta^{18}\text{O}$  data from 48 coretops and sediment trap samples which represent a range of ocean conditions from the Caribbean, Gulf of Mexico, open Atlantic, and sediment traps in the Sargasso Sea (Fig. 1D) (Anand et al., 2003; Dekens et al., 2002; Farmer, 2005; Lund and Curry, 2006; Richey et al., 2007; Schmidt et al., 2004; Weldeab et al., 2005). The results of this verification study demonstrate that using published data with the new calibration equations yields SST and salinity estimates that are equivalently accurate and precise as the original calibration dataset (Fig. 7A,B).



#### 4.5. Application to published downcore data: implications for tropical ocean cooling and $\delta^{18}\text{O}_{\text{seawater}}$ changes at the LGM

One of the primary motivations for the present study was that several published studies suggested very large changes in (sub) tropical Atlantic  $\delta^{18}\text{O}_{\text{seawater}}$  during the LGM and Holocene, even after ice volume effects had been removed. Some of these shifts were equal to or greater than the entire subtropical–tropical Atlantic  $\delta^{18}\text{O}_{\text{seawater}}$  gradient (Fig. 1B), implying exceptionally large changes in salinity and/or changes in the salinity– $\delta^{18}\text{O}_{\text{seawater}}$  slope that were challenging to interpret.

Here, we present a case study of a Caribbean basin core VM28-122 (3623 m;  $12\ \mu\text{mol/kg}\ \Delta\text{CO}_3^{2-}$ ) where large ( $\sim 0.8\text{‰}$ ) increases in the local  $\delta^{18}\text{O}_{\text{seawater}}$  were reported for the Last Glacial Maximum (LGM) (Schmidt et al., 2004). We apply our new multivariate equations to the downcore *G. ruber* (white)  $\delta^{18}\text{O}$  and Mg/Ca data. Since shell  $\delta^{18}\text{O}$  reflects both temperature and the local  $\delta^{18}\text{O}_{\text{seawater}}$  (which is a function of global ice volume and local salinity), we first remove the global ice volume signal from the raw  $\delta^{18}\text{O}$  record prior to calculation of SSTs using Eq. (6) (Fairbanks, 1989; Waelbroeck et al., 2002). The  $\delta^{18}\text{O}_{\text{seawater}}$  timeseries is based on applying the modern tropical–subtropical Atlantic salinity– $\delta^{18}\text{O}_{\text{seawater}}$  regression ( $\delta^{18}\text{O}_{\text{seawater}} = 0.238 \cdot \text{Salinity} - 7.69$ ) to the estimated paleosalinity record (Fig. 8B). Our coretop SST, salinity, and  $\delta^{18}\text{O}_{\text{seawater}}$  estimates for this core (27.8 °C, 36.8, and 0.80‰, respectively) closely match the mean annual values at this site (27.7 °C, 35.7, and 0.77‰, respectively; Fig. 8A–C).

For the LGM, our new SST equation returns a value of 24.0 °C, which is 3.8 °C cooler than the late Holocene. This 3.8 °C LGM cooling estimate for VM28-122 is considerably greater than the 2 °C cooling reported in Schmidt et al. (2004) who used the canonical Dekens et al. (2002) Mg/Ca temperature equation. This enhanced tropical cooling is more consistent with a suite of terrestrial and marine paleotemperature estimates that suggest 4–5 °C LGM cooling in the tropics based on groundwater noble gas temperatures, coral Sr/Ca, and tropical snowline changes (Broecker and Denton, 1989; Guilderson et al., 1994; Rind and Peteet, 1985; Stute et al., 1995). A recent study in the Western Pacific Warm Pool that included a salinity effect on foraminiferal Mg/Ca ratios also noted a greater  $\sim 4$  °C cooling during the LGM (Mathien-Blard and Bassinot, 2009).

There is a dramatic reduction in the magnitude of salinity changes since the LGM when the new equations are applied, but the direction of the shift remains (Fig. 9B). Our salinity estimate for the LGM at this site is

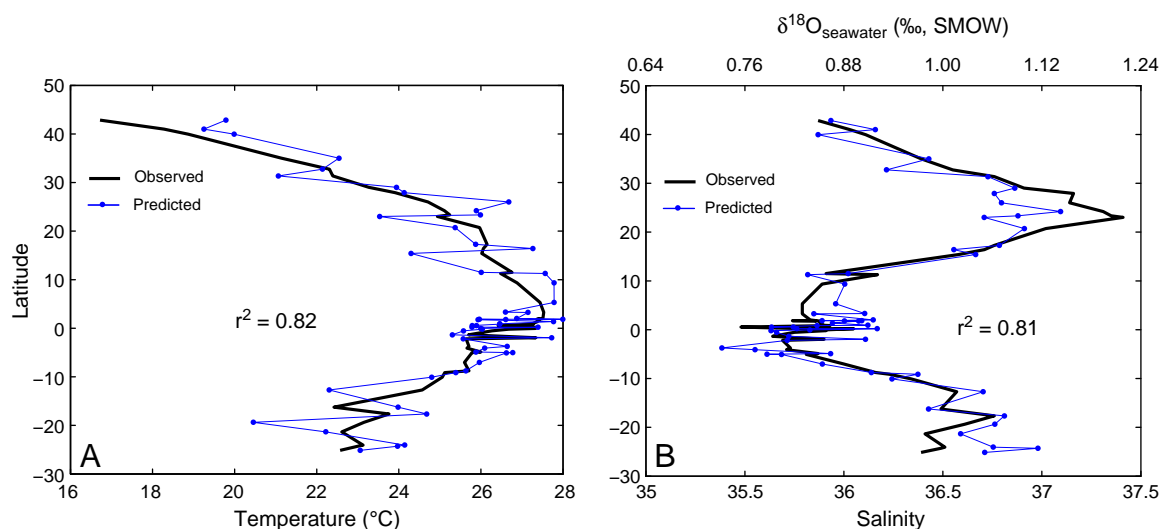
36.2, only 0.5 higher than the modern value, or roughly equivalent to the salinity of the subtropical gyre today (Fig. 1A). This smaller salinity change may be more realistic than the 2.3–2.7 change proposed by Schmidt et al. (2004) which would place glacial salinities around 38, much higher than any modern (sub)tropical Atlantic salinity value today. The  $\delta^{18}\text{O}_{\text{seawater}}$  change is similarly reduced relative to the published estimate; we report an LGM value that is only 0.15‰ higher than the modern value, although it is important to restate that our value relies on the modern  $\delta^{18}\text{O}_{\text{seawater}}$ –salinity relationship. The 0.15‰ increase in LGM  $\delta^{18}\text{O}_{\text{seawater}}$  values we report may be more realistic than the published value of 0.8‰, which is considerably larger than the entire modern  $\delta^{18}\text{O}_{\text{seawater}}$  gradient from the equator to 30°N (Fig. 1B). We suggest this exceptionally high value is due the uncorrected salinity effect on shell Mg/Ca values (Figs. 2 and 3), and we propose that this is the reason the 0.8‰  $\delta^{18}\text{O}_{\text{seawater}}$  change was so challenging to interpret (Schmidt et al., 2004).

Recognizing that the salinity– $\delta^{18}\text{O}_{\text{seawater}}$  relation remains unconstrained for the geologic past, we acknowledge that our calibration effort thus far can only produce reliable SST and salinity estimates if the  $\delta^{18}\text{O}_{\text{seawater}}$ –salinity relation is known to be nearly the same as modern values. However, we have demonstrated that Mg/Ca SSTs based on the canonical equations (Anand et al., 2003; Dekens et al., 2002) cannot produce reliable SST estimates over the large salinity range in the Atlantic basin. We find that the SST and salinity values produced using our new equations lead to surface property values that are less challenging to interpret in the face of other paleoclimate evidence and viable shifts in ocean salinity.

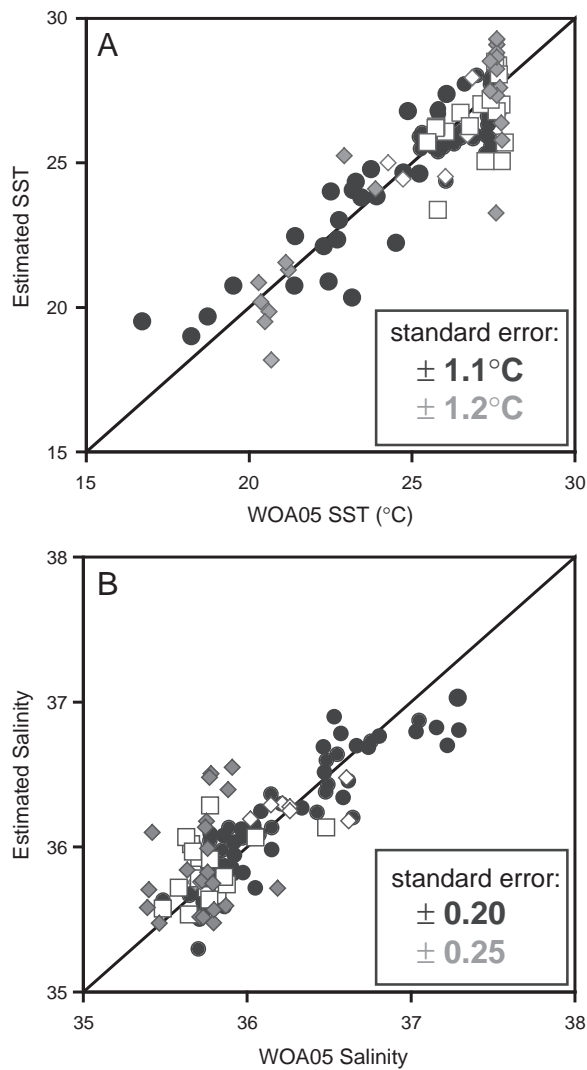
#### 4.6. Non-linear dependence of shell Mg/Ca ratios on salinity

The Atlantic “excess Mg/Ca” results summarized in Figure 2 indicate a large, systematic offset between measured and expected *G. ruber* Mg/Ca ratios related to salinity. Were this regression to be extrapolated to the much lower salinities of the tropical Pacific (33–34), the implied salinity-related offsets to Pacific foraminiferal Mg/Ca ratios would be impossibly large (negative values; Fig. 9).

We investigate the “excess Mg/Ca”–salinity dependence for lower salinity regions by merging our Atlantic coretop data with previously published coretop and sediment trap data from the lower salinity Pacific and Indian Oceans and the higher salinity Mediterranean. Excess Mg/Ca was calculated as indicated in this study and the same Dekens et al. (2002) and Bemis et al. (1998) equations were used in all cases for

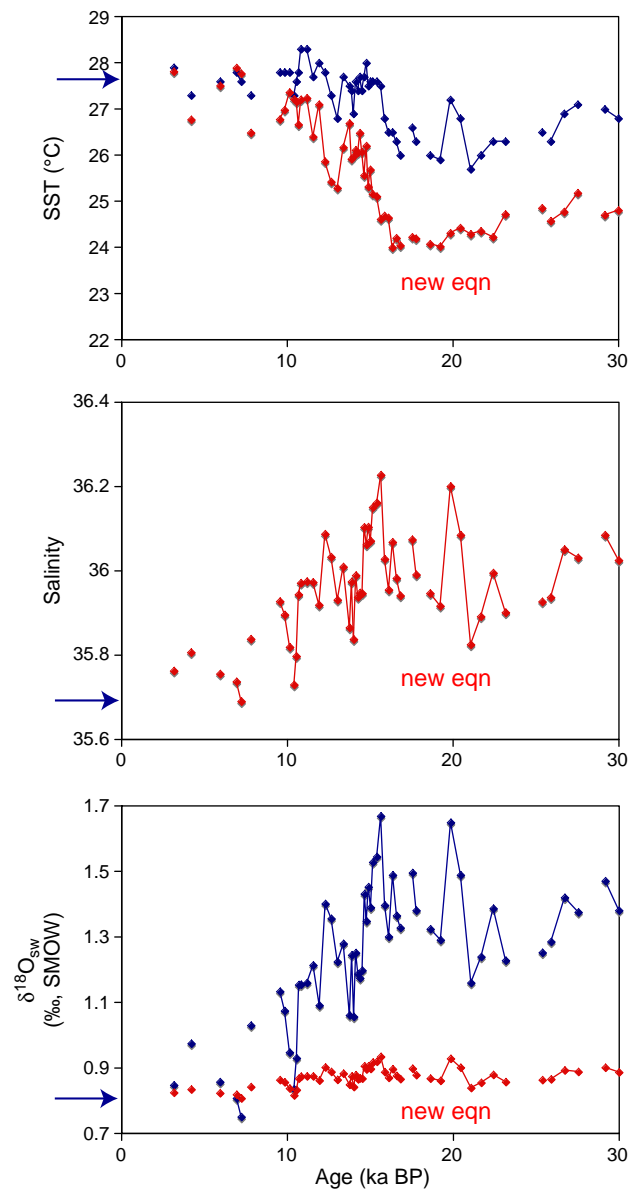


**Fig. 6.** Results of the multivariate regression analysis for estimating mean annual SST and salinity (0 m) as functions of  $\ln(\text{Mg/Ca})$ ,  $\delta^{18}\text{O}$ , and bottom water  $\Delta\text{CO}_3^{2-}$ . Observed (solid black line) and estimated values (blue line and symbols, representing each core location) for mean annual (A) SST ( $r^2 = 0.82$ ,  $\text{RMSE} = \pm 1.1$  °C) and (B) salinity ( $r^2 = 0.81$ ,  $\text{RMSE} = \pm 0.23$ ) for the Atlantic meridional transect ( $n = 64$ ) are shown.



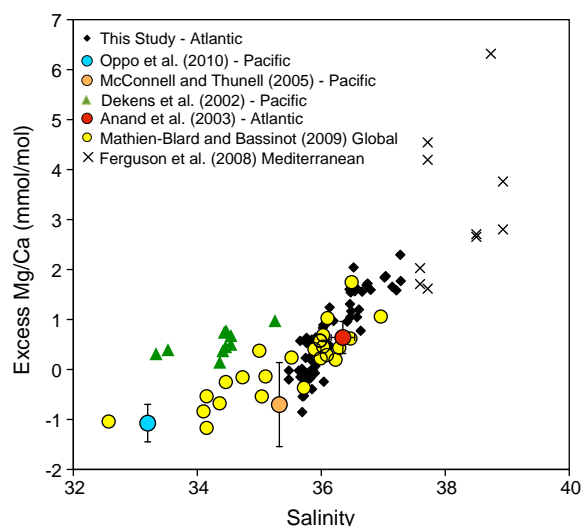
**Fig. 7.** Calibration validation results using published Atlantic *G. ruber* (white) data are shown. The standard errors are shown in grey for our coretop calibration dataset and in red for all published data. (A) Predicted SST against observed SST from the World Ocean Atlas; Atlantic transect samples shown as black dots (standard error =  $\pm 1.1^{\circ}\text{C}$ ), published data shown as gray filled and unfilled symbols (standard error =  $\pm 1.2^{\circ}\text{C}$ ). (B) Predicted Salinity against observed Salinity from the World Ocean Atlas; Atlantic transect samples shown as grey dots (standard error =  $\pm 0.23$ ), published data shown as colored symbols (standard error =  $\pm 0.25$ ).

consistency. To compare datasets using different analytical methods (full vs. oxidation only Mg/Ca cleaning) and different sample types (sediment traps vs. coretop samples) we applied the following sets of adjustments to specific datasets. For studies where only the oxidative cleaning step was used (the McConnell and Thunell (2005) Guymas Basin sediment trap study, the Anand et al., 2003 Bermuda sediment trap study, and the Bassinot and Mathien-Blard (2009) global coretop study), shell Mg/Ca values were reduced by 10% to account for the lower Mg/Ca values associated with full reductive cleaning (Barker et al., 2003; Rosenthal et al., 2004; Yu et al., 2007). No Mg/Ca depth correction was applied to the Bassinot and Mathien-Blard (2009) coretop study and the last century of data from the Oppo et al. (2009) study, as all cores were well above the lysocline. As throughout this study, “excess Mg/Ca” is defined as zero if the isotopic and Mg/Ca temperatures are identical using the canonical equations (Bemis et al., 1998; Dekens et al., 2002). No isotopic data were collected in the Mediterranean coretop study of Ferguson et al. (2008) so we used the SST values at each core site to compute excess Mg/Ca.



**Fig. 8.** Case study showing the applicability of the new equations to paleorecords. (A) SST records calculated using the Dekens et al. (2002) calibration equation (blue line) and the new multivariate equations derived in the present study (red line); modern temperature for core location shown by blue arrow. Note the significant decrease in SST at the LGM and Younger Dryas when the new equations are applied. (B) Salinity record calculated using our new equation shown as red line. The modern salinity for the core location is shown by a blue arrow. (C).  $\delta^{18}\text{O}_{\text{seawater}}$  records calculated using Dekens et al. (2002) Mg/Ca ratio derived T (blue line) and using the new equation from the present study (red line). Prior to calculation of the  $\delta^{18}\text{O}_{\text{seawater}}$ , the ice volume effect was removed from the raw shell  $\delta^{18}\text{O}$  record (Fairbanks, 1989; Waelbroeck et al., 2002). The magnitude of the  $\delta^{18}\text{O}_{\text{seawater}}$  variability since 30 kyr BP is greatly reduced when the new equation is applied. Note the close similarities in structure between the salinity record shown in (B) and the published (blue)  $\delta^{18}\text{O}_{\text{seawater}}$ , indicating that while the magnitude of change is greatly reduced using the new equations the directionality and details of the record remain mostly intact.

The compiled data span a large range of salinity values, ranging from 32 to 40. Considering the entire dataset, it is clear that excess Mg/Ca is non-linearly related to salinity, and that this relationship is evident in many different datasets. Excess Mg/Ca asymptotes to a finite low value at lowest salinities ( $<35$ ), whereas at high salinities ( $>35$ ) excess Mg/Ca values increase rapidly to large positive values. At the highest salinities in the Mediterranean, excess Mg/Ca is extremely high, in the range of 3–7 mmol/mol, as noted by Ferguson et al.



**Fig. 9.** The temperature-independent “excess Mg/Ca” calculated for the Atlantic coretop transect compared to data from other published datasets spanning a large range in salinities from 32 to 40. “Excess Mg/Ca” was calculated as the difference between measured and expected shell Mg/Ca values using the Dekens et al. (2002) Mg/Ca temperature equation and the Bemis et al. (1998) low-light oxygen isotope temperature equation (as for all calculations in this study). Specific corrections to individual Mg/Ca datasets were applied depending on the analytical Mg/Ca cleaning method applied and whether the data were from coretop or sediment trap samples; these are discussed in the text. Note the clearly non-linear relationship between “excess Mg/Ca” and salinity which asymptotes to a low, constant value at low salinities ( $n < 35$ ) and increases to very high values at high salinities.

(2008). Overall, the large and clear trend evident from these datasets argues against the weak 6% per salinity unit Mg/Ca sensitivity to salinity observed in culture experiments. At the same time, this relationship appears to be robust across a broad range of oceanic salinity values.

While we fit a linear relationship between  $\ln(\text{Mg/Ca})$  to salinity for our Atlantic data (Eqs. (5) and (7)), the global data presented in this section point to a non-linear relationship. This relationship contrasts markedly with the interpretation of Bassinot and Mathien-Blard (2009) who proposed that excess Mg/Ca has a simple linear relation with salinity (yellow symbols; Fig. 9). Indeed, non-linear excess Mg/Ca curvature is apparent in their dataset as well. We find that the larger and more comprehensive data compilation presented here, particularly the greater data density at higher salinities, indicates a strongly non-linear dependence of excess Mg/Ca on salinity with a lower, asymptotic effect at low salinities ( $< 35$ ).

## 5. Conclusions

We have identified a large, temperature independent influence on *G. ruber* (white) Mg/Ca ratios that is evidently related to surface ocean salinity and is present in all published coretop and sediment trap datasets from the Atlantic Ocean. Recognizing that shell Mg/Ca ratios and  $\delta^{18}\text{O}_{\text{calcite}}$  are dependent on both sea surface temperature and salinity, we perform a multivariate regression which yields equations for both temperature and salinity that are accurate, precise, and verifiable with published data. This approach allows us to extract and rigorously quantify shell Mg/Ca variability related to surface ocean salinity variations. In a case study to identify potential uses of these new equations, we apply them to raw published downcore records from the Caribbean core VM22-182. The SST and  $\delta^{18}\text{O}_{\text{seawater}}$ /salinity estimates for the last glacial are significantly affected such that new SST estimates agree with values reported from multiple terrestrial and paleoceanographic proxies, and the estimated salinity changes are much more reasonable within the context of likely surface ocean changes. Although the  $\delta^{18}\text{O}_{\text{seawater}}$ -salinity relationship is likely to

have changed in the past, accounting for the salinity influence on shell Mg/Ca ratios appears to lead to more accurate paleo-environmental reconstructions.

Finally, we identify for the first time the strongly non-linear dependence of excess Mg/Ca on salinity based on a global compilation published coretop and sediment trap data along with our Atlantic transect data. This systematic relationship appears to be robust and suggests that it may indeed be possible to develop a single, global equation describing the sensitivity of *G. ruber* (white) shell Mg/Ca ratios on surface ocean temperature, salinity, and bottom water  $\Delta\text{CO}_3^{2-}$ , a problem that has thus far eluded the paleoceanographic community.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at [doi:10.1016/j.epsl.2010.10.035](https://doi.org/10.1016/j.epsl.2010.10.035).

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