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On the fidelity of shell-derived $\delta^{18}O_{seawater}$ estimates

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ABSTRACT

Paired foraminiferal Magnesium/Calcium ratio and oxygen isotope analyses are widely used to estimate surface ocean $\delta^{18}O_{seawater}$, a robust proxy for surface salinity. We assess the fidelity of shell-derived $\delta^{18}O_{seawater}$ 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 $\delta^{18}O_{seawater}$ 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 ± 4%) is much higher than indicated by culture studies (6 ± 2%). Our coretop data are used to develop new Atlantic Basin temperature and salinity calibration equations that are accurate (±1.1 °C and ±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 (35.5–37.3). 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 $\delta^{18}O_{seawater}$ estimates in high salinity settings (>35).

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 $\delta^{18}O_{shell}$ analyses of surface-dwelling foraminifer shells to calculate surface ocean $\delta^{18}O_{seawater}$, 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 $\delta^{18}O$ composition of planktic foraminifer shells records both the local $\delta^{18}O_{seawater}$ and the calcification temperature (through the kinetic fractionation effect), whereas shell Mg/Ca ratios should mainly record the calcification temperature. Shell $\delta^{18}O$ values and Mg/Ca ratio calcification temperature values are substituted into the oxygen isotope paleotemperature equation (Bemis et al., 1998) to solve for $\delta^{18}O_{seawater}$, 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 $\delta^{18}O_{seawater}$ proxy using a meridional transect of coretop samples spanning the large temperature (16.7–27.6 °C) and salinity (35.48–37.28) 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 $\delta^{18}O_{seawater}$ 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 $\delta^{18}O_{seawater}$ estimates

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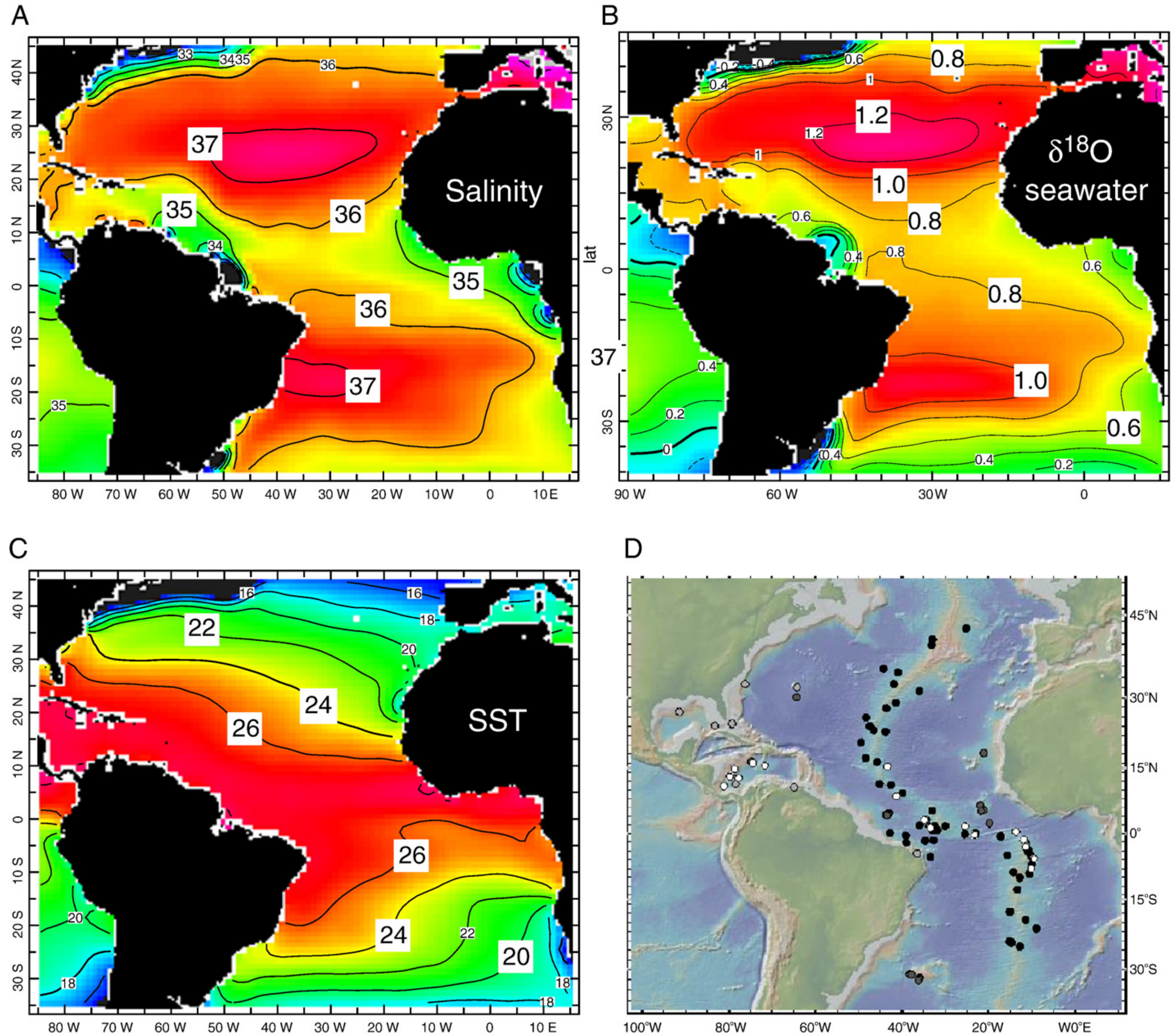

Fig. 1. (A) Mean annual salinity; (B) mean annual $\delta^{18}O_{seawater}$ (‰, SMOW); and (C) mean annual SST (°C). Data from 2005 World Ocean Atlas and LeGrande and Schmidt (2006); (D) locations of the 64 coretop samples for this study (solid black symbols), as well as locations of coretop samples 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 $\delta^{18}O_{seawater}$ 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 $\delta^{18}O$ 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 μm), crushed gently (any visible large coarse grains were removed), and split into Mg/Ca and $\delta^{18}O$ aliquots then transferred to acid-cleaned vials. Samples were cleaned prior to Mg/Ca analysis by