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Improved oxygen isotope temperature calibrations for cosmopolitan benthic foraminifera

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Abstract

Despite decades of use as a paleoceanographic proxy, considerable uncertainty still surrounds the temperature dependence of benthic foraminiferal $\delta^{18}O$. Widely applied paleotemperature equations may mix non-equilibrium foraminifera with equilibrium synthetic calcite, resulting in temperature sensitivities that are too large. Warm-water foraminiferal calibrations may give temperature sensitivities that are too small for very cold waters. Here we combine new core top measurements from the Florida Straits and the Arctic Ocean with published data to derive new $\delta^{18}O$:temperature relationships for three groups of benthic foraminifera. We derive a quadratic equation for *Cibicidoides* and *Planulina* that agrees well with equilibrium synthetic calcite, and that should be applicable over all oceanographic temperatures. We find that *Uvigerina* is not at equilibrium and is isotopically heavier than *Cibicidoides* and *Planulina* by 0.47‰, in contrast to the historically used 0.64‰. *Hoeglundina elegans* is further enriched and appears to be slightly heavier than equilibrium aragonite. Finally we discuss the implications of the Florida Straits observations for the hypothesis that benthic foraminifera precipitate their shells from a pH-dependent mixture of bicarbonate and carbonate ions.

1. INTRODUCTION

The oxygen isotopic composition ($\delta^{18}O$) of $CaCO_3$ is arguably the most important chemical tracer in the field of paleoceanography, particularly as preserved in the tests of foraminifera. Urey (1947) first theorized that the fractionation of oxygen isotopes during the precipitation of $CaCO_3$ should be dependent on temperature. Early laboratory experiments with inorganically precipitated $CaCO_3$ (McCrea, 1950) and mollusks (Epstein et al., 1951, 1953) established a temperature sensitivity of about −0.2‰ $\delta^{18}O$ per °C. Emiliani (1955) built upon that foundation and reconstructed upper ocean temperatures over several glacial-interglacial cycles using planktonic foraminifera, recognizing that a global ice volume component of $\delta^{18}O$ must also be subtracted out. Shackleton (1967) argued that the ice volume component could be mostly isolated by measuring $\delta^{18}O$ in deep sea benthic foraminifera, assuming that abyssal temperatures changed little across glacial cycles. Estimates of deep water $\delta^{18}O$ and salinity based on relict sediment pore waters, combined with benthic foraminiferal $\delta^{18}O$, later demonstrated that the glacial deep sea was substantially colder (Schrag et al., 1996) and saltier

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(Adkins et al., 2002) than present, even beyond the ice volume effect. Today planktonic and benthic foraminiferal $\delta^{18}O$ measurements are standard components of most paleoceanographic studies.

Given this long history, it is surprising that considerable uncertainties persist surrounding the $\delta^{18}O$ paleotemperature equations for cosmopolitan benthic foraminifera. Two still widely used paleotemperature equations (one linear, one quadratic) are from Shackleton (1974), who based them on previous inorganic calcite results from just two temperatures within oceanographic ranges (O'Neil et al., 1969; Tarutani et al., 1969) and validated them using benthic *Uvigerina* measurements from three core tops:

$$t = 16.9 - 4.0(\delta_{cp} - \delta_{ws} + 0.2) \quad (1)$$

$$t = 16.9 - 4.38(\delta_{cp} - \delta_{ws} + 0.2) + 0.10(\delta_{cp} - \delta_{ws} + 0.2)^2 \quad (2)$$

where t is temperature in Celsius, δ_{cp} is $\delta^{18}O$ of $CaCO_3$ on the PeeDee Belemnite (PDB) scale, and δ_{ws} is $\delta^{18}O$ of seawater on the Standard Mean Ocean Water (SMOW) scale. Not only are these equations weakly constrained by the data, but it has been suggested that *Uvigerina* does not calcify at isotopic equilibrium with seawater (Bemis et al., 1998), meaning that it would be inappropriate to combine its values with the inorganic data. A better-constrained benthic calibration comes from Lynch-Stieglitz et al. (1999), based on *Cibicidoides* and *Planulina* from Little Bahama Bank between 4 and 26 °C:

$$(\delta_{cp} - \delta_{ws} + 0.27) = -0.21 \pm 0.002t + 3.38 \pm 0.03 \quad (3)$$

Whereas Shackleton's (1974) slope is −0.25‰ per °C in the linear equation and as much as −0.28‰ per °C (at 0 °C) in the quadratic, the Lynch-Stieglitz et al. (1999) slope is only −0.21‰ per °C. The choice of equation at the cold end could therefore impact the magnitude of down-core reconstructed temperature change by more than 30%, with absolute values (after accounting for Shackleton and Opdyke's (1973) canonical taxonomic offset of 0.64‰) differing by up to 2 °C. Duplessy et al. (2002) showed that core top *Cibicidoides* measurements between −1 and 13 °C (adjusted by +0.64‰) appear to agree with Shackleton's (1974) quadratic equation, and they used the −0.28‰ per °C cold-end (<4 °C) linear approximation of that equation to determine the temperature component of glacial deep sea $\delta^{18}O$ measurements.

Here we present new benthic foraminiferal $\delta^{18}O$ measurements from four calcitic taxa (*Cibicidoides pachyderma*, *Planulina ariminensis*, *Planulina foveolata*, *Uvigerina peregrina*) and one aragonitic taxon (*Hoeglundina elegans*) picked from the tops of 31 multicores that were collected in the Florida Straits in 2002 (Supplementary Table A1). These core sites span a temperature range of 5.8–19.0 °C, and seawater $\delta^{18}O$ is well constrained. We also present *Cibicidoides wuellerstorfi* measurements from 27 Arctic Ocean core tops, to extend the data set below 0 °C (Table A2); and previously unpublished *H. elegans* measurements from the same collection of Little Bahama Bank sediments used by Lynch-Stieglitz et al. (1999) (Table A3). We combine these data with previously published measurements in an attempt to resolve the outstanding discrepancies between the paleotemperature equations discussed above. For the most part we limit our consideration of published data to those that were measured against the marble standard NBS-19 (Friedman et al., 1982), as is the case for all unpublished data that we present. Direct calibration against NBS-19 minimizes the likelihood of significant interlaboratory offsets (Coplen, 1996). In Section 3.2 we discuss the implications of including published data that were not measured against NBS-19.

2. MATERIALS AND METHODS

2.1. Florida Straits

Benthic foraminifera (>250 μm) were picked from the 0–1 cm slice of multicores collected from 31 sites in the Florida Straits during R/V *Knorr* cruise KNR166-2 (Table A1). Thirteen of these multicore tops were radiocarbon dated: five post-dated the mid-20th century period of nuclear bomb atmospheric testing (fraction modern >1) and the remaining eight were all younger than ~3000 cal yr BP (Lund and Curry, 2004, 2006; Marchitto et al., 2007). $\delta^{18}O$ was measured on the following species: *C. pachyderma* (cf. *C. floridanus* [Poag, 1981]), *P. ariminensis*, *P. foveolata*, *U. peregrina*, and *H. elegans*. Most of the $\delta^{18}O$ measurements were made on small aliquots taken from samples consisting of ~5–20 crushed and homogenized foraminifera, with the bulk of each sample being used for trace metal analyses presented by Marchitto et al. (2007) and Bryan and Marchitto (2008). At some sites additional $\delta^{18}O$ measurements were made on single specimens of *C. pachyderma*; in those cases the value plotted here is the simple average between the multi-specimen analysis and the mean of the single specimens.

Seawater samples were collected at KNR166-2 multicore sites using a Niskin bottle mounted to the multicorer frame and rigged to trip at the seafloor. Salinity was measured on the bottle samples so that each multicore site could be matched to the nearest of 55 KNR166-2 CTD casts, providing precise bottom water temperatures which span a range of 5.8 to 19.0 °C. At 13 of the 31 multicore sites this method was not possible because either the bottle failed to trip (4 sites), the bottle tripped above the seafloor (7 sites), or the salinity profile was too invariant to provide an unambiguous match to a CTD (2 sites). In these cases salinity and temperature were derived from nearby CTDs as described previously (Marchitto et al., 2007; Bryan and Marchitto, 2008).

Seawater $\delta^{18}O$ was measured at 18 KNR166-2 multicore sites, including four sites where foraminifera were not analyzed. Because of pre-tripping only nine of the bottles provide direct measures of bottom water $\delta^{18}O$ at sites where we have foraminiferal $\delta^{18}O$, but all 18 are potentially useful for developing a regression against salinity that can be applied to the rest of the foraminiferal sites (Fig. 1). To corroborate our observations we combine them with paired $\delta^{18}O$ and salinity measurements from the two nearest GEOSECS stations with subsurface data (Ostlund et al., 1987) and from 10 western Atlantic stations between 15 and 20°N measured by S. Mulitza (Schmidt et al., 1999), limiting the data selec-