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:

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

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

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:

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

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 measure-

ments 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-
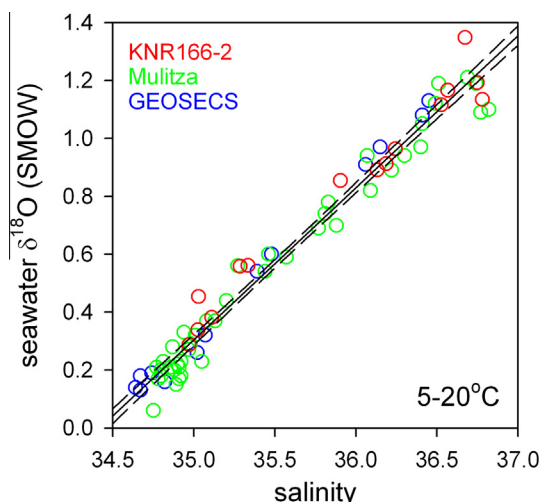
Fig. 1. Seawater $\delta^{18}O$ and salinity measurements from Florida Straits (red) and from nearby stations over the same temperature range (green, blue). Linear fit is Eq. (4) with 95% confidence intervals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tion to the same temperature range as our samples (5–20 °C). Omitting three of the KNR166-2 measurements as 2σ outliers yields the relationship:

$$\delta_{ws} = -18.09 + 0.5255S \quad (4)$$

where S is salinity ($r^2 = 0.97$). Resulting seawater $\delta^{18}O$ values range from 0.26‰ to 1.17‰ at the sites where we have foraminiferal observations, with an estimated uncertainty of ±0.06‰ (1σ).

Total alkalinity and dissolved inorganic carbon (DIC) were measured at 24 KNR166-2 multicore sites as described by Marchitto et al. (2007). For sites where the Niskin bottle pre-tripped or where alkalinity and DIC were not measured, these parameters were estimated using our observed second-order polynomial relationships with salinity ($r^2 = 0.98$ and 0.95, respectively). pH and saturation coefficients (Ω) for calcite and aragonite were calculated using CO2SYS v.2.1 (Lewis and Wallace, 1998), using the first and second dissociation constants of carbonic acid from Hansson (1973) and Mehrbach et al. (1973) as refit by Dickson and Millero (1987). Resulting pH values range from 7.85 to 8.07 on the seawater scale, with an estimated uncertainty of ±0.03 (1σ). We do not attempt to remove the influence of anthropogenic CO_2 addition (ocean acidification) as was done by Lear et al. (2010) at these sites. If we did then the pre-anthropogenic pH values would be roughly 0.05 to 0.1 higher, with the largest corrections in the highest pH waters (Sabine et al., 2004).

2.2. Arctic Ocean

C. wuellerstorfi (>250 μm) were picked from the top 1 cm of 27 box cores collected between 893 and 3482 m water depth in the Pacific sector of the Arctic Ocean during USCGC *Polar Star* cruises P-1-92-AR, P-1-93-AR, and

P-1-94-AR (Table A2). Six of the P-1-94-AR core tops were radiocarbon dated and yielded ages of 1790 to 3790 cal yr BP (Darby et al., 1997; Hoffmann and McManus, 2007; Hoffmann, 2009). Of 115 stable isotope measurements made on individual tests we omit four with $\delta^{13}C < 1.0$‰, plus one with a $\delta^{18}O$ value >0.5‰ higher than the mean of its core, as these were likely mixed in from glacial-age sediments. Bottom water temperatures and salinities were estimated using the US Navy hydrographic database and span ranges of −0.6 to −0.2 °C and 34.92 to 34.96, respectively. Seawater $\delta^{18}O$ was estimated using a regression against salinity derived from 117 Pacific sector Arctic measurements (Schmidt et al., 1999) and spans a range of 0.31–0.36‰, with an estimated uncertainty of ±0.07‰ (1σ).

2.3. Analytical procedures

Foraminiferal $\delta^{18}O$ measurements were made at the Woods Hole Oceanographic Institution on a Finnigan MAT252 with a Kiel II carbonate device and on a Finnigan MAT253 with a Kiel III carbonate device (Ostermann and Curry, 2000). Calibration to the Vienna PDB scale was done using the NBS-19 standard. Long-term $\delta^{18}O$ reproducibility of NBS-19 is ±0.07–0.08‰ (1σ).

Seawater $\delta^{18}O$ was measured at the Georgia Institute of Technology on a GV Isoprime with Multiprep device relative to Vienna SMOW and an internal lab standard. $\delta^{18}O$ reproducibility of the internal standard analyzed at the same time as the samples was ±0.02 (1σ).

2.4. SMOW-PDB conversion

Since it is the isotopic fractionation between $CaCO_3$ and seawater that is temperature dependent, if the $\delta^{18}O$ of both the solid (δ_c) and the liquid (δ_w) are measured together and referenced to the same standard, then the $\delta^{18}O$ difference ($\delta_c - \delta_w$) need not be expressed relative to any standard. This was the case for the pioneering work of Urey's group (e.g., Epstein et al., 1951, 1953) who measured both phases relative to the PDB standard. In more recent practice, $CaCO_3$ $\delta^{18}O$ is measured relative to another $CaCO_3$ standard like NBS-19 that is referenced to PDB, while seawater is measured relative to a water standard that is referenced to SMOW (Craig, 1961). Hence it became necessary to convert one $\delta^{18}O$ scale to the other, and Shackleton (1974) followed the lead of Urey's group and converted seawater $\delta^{18}O$ from the SMOW scale to the PDB scale. That conversion is based on the small isotopic difference between CO_2 liberated from PDB $CaCO_3$ and CO_2 equilibrated with SMOW, under established conditions (e.g., Friedman and O'Neil, 1977; Coplen et al., 1983), and is meant to mimic the $\delta^{18}O$ value that would have been obtained if the seawater had been measured relative to PDB. A small problem arises because the value for that difference has been refined over time: Shackleton (1974) used 0.2‰ (Craig, 1965) whereas the currently accepted value is 0.27‰ (Hut, 1987) and is used here. This evolution does not bias the current application of the older equations, as long as the correction that was in use at the time the equation was developed (0.2‰ in the case of Shackleton (1974)) is employed. It

does, however, mean that the older equations will have slightly biased intercepts when directly compared to equations that use the 0.27‰ correction to calculate $\delta_c - \delta_w$. For the purpose of plotting we revise Shackleton's Eqs. (1) and (2) by quantity $\delta_{cp} - \delta_{ws} + 0.2$ and then adding 0.07 to both sides. All published data are similarly plotted as $\delta_{cp} - \delta_{ws} + 0.27$. All equations are given with δ_c on the PDB scale and δ_w on the SMOW scale, for clarity and to facilitate their application for paleoceanography.

2.5. Regressions

Linear regressions for foraminifera are calculated using the reduced major axis (RMA) method, using a Matlab script provided by Ed Peltzer of MBARI. We use RMA because the uncertainty in the temperature at which the foraminifera grew is likely comparable to the uncertainty in $\delta_c - \delta_w$, especially considering that some core top foraminifera may not be modern. In contrast to ordinary least squares (OLS) fitting, RMA simultaneously minimizes the misfit of data in both the x and y directions, and results in a symmetric equation (i.e., the independent and dependent axes are interchangeable). In all cases below, OLS linear regression is within the 1σ uncertainty of the RMA fit. For quadratic fits we use OLS in the absence of an established method for RMA.

3. RESULTS AND DISCUSSION

3.1. Florida Straits

$\delta_c - \delta_w$ is strongly anti-correlated with temperature for all five benthic foraminiferal species analyzed (Fig. 2). *P. ariminensis* and *P. foveolata* are isotopically indistinguishable from *C. pachyderma* (with the exception of one or
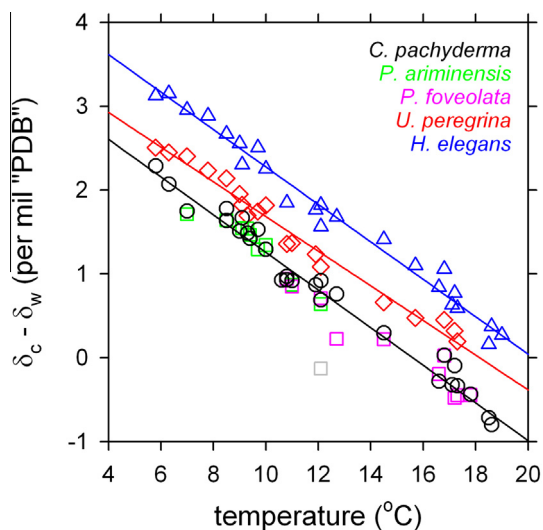

Fig. 2. Florida Straits benthic foraminiferal $\delta^{18}O$ difference from seawater on the PDB scale, vs. bottom water temperature. Lines are RMA linear regressions, Eqs. (5)–(7). Gray point is a 3σ outlier excluded from the regression.

two outliers), and we follow Lynch-Stieglitz et al. (1999) in lumping the *Cibicidoides* and *Planulina* measurements together in the following discussion. There are clear isotopic offsets between the remaining taxa, with *H. elegans* > *U. peregrina* > *Cibicidoides* and *Planulina*. After omitting a single *P. foveolata* measurement that is a >3σ outlier, we arrive at the following equations based on RMA regression:

$$Cibicidoides + Planulina : (\delta_{cp} - \delta_{ws} + 0.27)$$
$$= -0.225 \pm 0.006t + 3.50 \pm 0.07 \tag{5}$$

$$U.peregrina : (\delta_{cp} - \delta_{ws} + 0.27)$$
$$= -0.207 \pm 0.007t + 3.75 \pm 0.08 \tag{6}$$

$$H.elegans : (\delta_{cp} - \delta_{ws} + 0.27)$$
$$= -0.223 \pm 0.007t + 4.51 \pm 0.09 \tag{7}$$

where uncertainties are $\pm 1\sigma$. Temperature explains 97%, 98%, and 98% of the $\delta_c - \delta_w$ variance in each equation, respectively. All three slopes are within the 2σ combined uncertainties of each other. In the following sections we compare the Florida Straits observations to other comparable data sets.

3.2. *Cibicidoides* and *Planulina* compilation

The most extensive published data set of *Cibicidoides* and *Planulina* core top $\delta^{18}O$, with seawater $\delta^{18}O$ estimated using salinity, is from the nearby Little Bahama Bank (Slowey and Curry, 1995; Lynch-Stieglitz et al., 1999). Their foraminiferal measurements were made in the same laboratory as the new measurements presented here. We show the Little Bahama Bank data as single-species averages from each core top, including the three species analyzed in the Florida Straits plus *Cibicidoides cicatricosis*, *Cibicidoides corpulentis*, *Cibicidoides kullenbergi*, *Cibicidoides robertsoniensis*, and *C. wuellerstorfi* ($n = 92$) (Fig. 3). These core tops span a temperature range of 4.1–25.6 °C, thus expanding our observations at both the warm and cold ends.

Typical deep sea temperatures remain unrepresented however, so we turn to two additional data sets. Keigwin (1998) reported *Cibicidoides* and seawater $\delta^{18}O$ from 21 near-core-top Holocene samples collected in the northwest Pacific, some of which had been previously presented by McCorkle and Keigwin (1994) (Fig. 3). NBS-19 was used by Keigwin to reference the calcite data to PDB, as is done here. Keigwin (1998) described their *Cibicidoides* as probably being mostly *C. mundulus*, which is a sometimes synonym for *C. kullenbergi*. These samples span a temperature range of 1.5–2.3 °C. The final data set comprises unpublished Arctic Ocean *C. wuellerstorfi* measurements from 27 core tops spanning a temperature range of −0.6 to −0.2 °C, described in Section 2.2 (Fig. 3).

Combining the Florida Straits, Little Bahama Bank, northwest North Pacific, and Arctic Ocean data sets ($n = 187$) yields the RMA linear equation:

$$(\delta_{cp} - \delta_{ws} + 0.27) = -0.224 \pm 0.002t + 3.53 \pm 0.02 \tag{8}$$

with $r^2 = 0.99$. The slope of Eq. (8) is indistinguishable from that of the Florida-only Eq. (5) and significantly different (by >10σ) from Shackleton's (1974) Eq. (1) linear
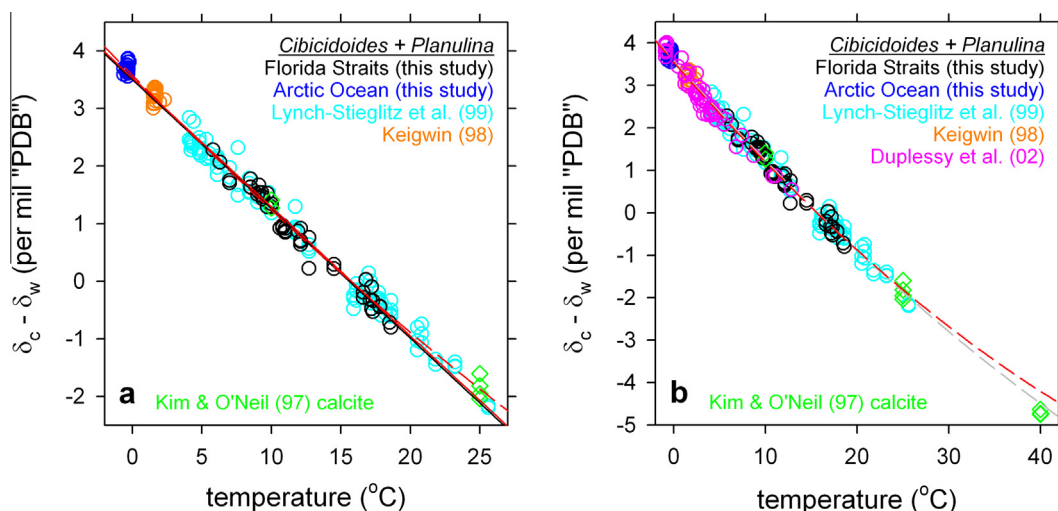
Fig. 3. (a) Compiled *Cibicidoides* and *Planulina* $\delta^{18}O$ difference from seawater on the PDB scale, vs. bottom water temperature. Also shown are synthetic calcite data from Kim and O'Neil (1997) (green diamonds). Lines are: RMA linear regression for the Florida Straits data (Eq. (5), black); RMA linear regression for all foraminiferal data (Eq. (8), solid red); and OLS quadratic regression for all foraminiferal data (Eq. (9), dashed red). (b) Same as (a) but adding data from Duplessy et al. (2002) and extending into warmer waters. Dashed red line is Eq. (12), and Eq. (9) is shown in dashed gray for reference. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

slope of −0.25‰ per °C. It is slightly steeper than the Lynch-Stieglitz et al. (1999) Eq. (3) slope of −0.21 ± 0.002.

There is perhaps a faint hint of curvature in the data, and fitting the combined data with an OLS quadratic equation gives:

$$(\delta_{cp} - \delta_{ws} + 0.27) = -0.245 \pm 0.005t + 0.0011 \pm 0.0002t^2 + 3.58 \pm 0.02 \tag{9}$$

again with $r^2 = 0.99$. The cold-end slope of quadratic Eq. (9) is −0.25‰ per °C below 0 °C, which is equal to the Shackleton (1974) Eq. (1) linear slope but smaller than his Eq. (2) value of −0.28 that was recommended by Duplessy et al. (2002) for use below 4 °C. At 25 °C the quadratic slope is −0.19‰ per °C, compared to −0.21 for Eq. (2). The exact temperature solution to Eq. (9) is:

$$t = \frac{0.245 - \sqrt{0.045461 + 0.0044(\delta_{cp} - \delta_{ws})}}{0.0022}$$

Although we are dealing with organisms that must exert tight controls on their biomineralization, insight into the correct form of the paleotemperature equation (linear vs. curved) might be gained from theoretical considerations and from inorganic experimental data. At equilibrium and under ideal conditions, the standard Gibbs free energy for any chemical reaction is equal to the negative product of the gas constant, the temperature in Kelvin (T), and the natural log of the equilibrium constant. For an isotopic exchange reaction the equilibrium constant is the fractionation factor α (the isotopic ratio in one phase relative to the other), and hence from first principles $\ln \alpha$ should be a linear function of T^{-1}. At high temperatures the quantum mechanical behavior of vibration theoretically causes $\ln \alpha$ to approach zero proportionally to T^{-2} (Bigeleisen and Mayer, 1947). A plot of α (or equilibrium $\delta_c - \delta_w$) against temperature should therefore be curved over all tempera-

tures. Experimental inorganic precipitates that are believed to represent equilibrium establish that this curvature is subtle over oceanographically relevant temperatures (McCrea, 1950; O'Neil et al., 1969; Kim and O'Neil, 1997), and this has led some workers to approximate the relationship using linear fits for both benthic and planktic foraminifera (e.g., Shackleton, 1974; Bouvier-Soumagnac and Duplessy, 1985; Bemis et al., 1998; Lynch-Stieglitz et al., 1999). The *Cibicidoides* and *Planulina* $\delta_c - \delta_w$ data compiled here are indistinguishable from the inorganic calcite data of Kim and O'Neil (1997) (Fig. 3), suggesting that these taxa precipitate calcite close to equilibrium, as noted by Bemis et al. (1998). Furthermore the Kim and O'Neil (1997) measurements at 40 °C fall closer to the quadratic fit (Eq. (9)) than to the linear fit (Eq. (8)).

We conclude that although a linear slope of −0.22‰ per °C is a good fit to the *Cibicidoides* and *Planulina* $\delta^{18}O$ observations over the entire investigated temperature range of −0.6 to 25.6 °C, a quadratic fit (Eq. (9)) is more appropriate on the basis of thermodynamic theory and inorganic observations, assuming that these organisms indeed approximate equilibrium. It may be further instructive to compare their $\ln \alpha$ to T^{-1}, as discussed above. The current best estimate of this relationship based on experimental precipitates is from Kim and O'Neil (1997):

$$1000 \ln \alpha = 18.03(1000T^{-1}) - 32.42 \tag{10}$$

where T is temperature in Kelvin. The RMA fit to the compiled *Cibicidoides* plus *Planulina* data is indistinguishable from this (Fig. 4):

$$1000 \ln \alpha = 17.94 \pm 0.12(1000T^{-1}) - 32.18 \pm 0.44 \tag{11}$$

The foraminiferal data are clearly in better agreement with the Kim and O'Neil (1997) equation than with the O'Neil et al. (1969) equation over this temperature range (Fig. 4).
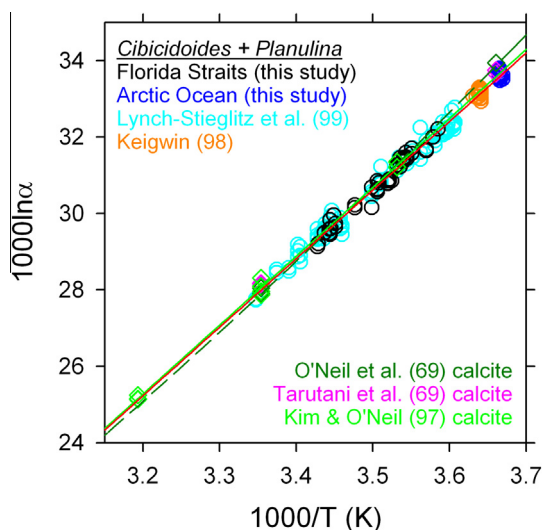
Fig. 4. Compiled *Cibicidoides* and *Planulina* data converted into the fractionation factor α and compared to calcification temperature. Also shown are synthetic calcite data from three studies (diamonds). Lines are: Kim and O'Neil (1997) linear relationship (Eq. (10), light green); RMA linear regression for all foraminiferal data (Eq. (11), red); and O'Neil et al. (1969) quadratic relationship (dashed dark green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

We considered including four additional *Cibicidoides* data sets for which seawater δ^{18}O estimates were available: Belanger et al. (1981) (Atlantic), Graham et al. (1981) (global), Herguera et al. (1992) (Ontong Java Plateau), and Duplessy et al. (2002) (global). Since none of these data sets were measured against NBS-19, we were concerned about possible interlaboratory offsets. To evaluate that likelihood, we added all four data sets to the compilation, and compared each data set to the resulting quadratic equation. Data fell 93% above (Belanger et al., 1981), 89% below (Graham et al., 1981), 100% below (Herguera et al., 1992), and 67% below (Duplessy et al., 2002) the curve (Supplementary Fig. A1). We conclude that at least the first three studies are analytically offset from the bulk of the compilation. Including the Duplessy et al. (2002) data yields ($n = 245$):

$$(\delta_{cp} - \delta_{ws} + 0.27) = -0.250 \pm 0.005t + 0.0014$$
$$\pm 0.0002t^2 + 3.56 \pm 0.02 \quad (12)$$

with $r^2 = 0.99$, which is within 1σ combined uncertainty of Eq. (9) (Fig. 3b). Since the only perceivable offset from Eq. (9) comes at very warm temperatures where there are no foraminiferal observations, we do not consider Eq. (12) to be an improvement over Eq. (9).

3.3. *Uvigerina* compilation

To our knowledge, the only published collection of *Uvigerina* $\delta_c - \delta_w$ that spans a large temperature range is from Grossman and Ku (1986). They presented measurements of *U. peregrina*, *U. curticosta*, and *U. flintii* from modern

surface samples collected along the California Borderland and in the Gulf of Mexico, spanning a temperature range of 2.6–16.9 °C, some of which had been presented by Grossman (1984a,b) (Fig. 5). Measurements were made relative to the NBS-19 standard. We reject two of their 16 averages as $>3\sigma$ outliers relative to the rest of our compilation. Keigwin's (1998) study in the northwest Pacific provides measurements of *Uvigerina* spp. from 26 near-core-top Holocene samples spanning a temperature range of 1.5–2.3 °C, thereby solidifying the cold end of the calibration. We also include the three Indo-Pacific *Uvigerina* spp. core top means from Shackleton (1974) for comparison (Fig. 5).

Combining these three data sets with the Florida Straits measurements ($n = 62$) yields the RMA linear equation:

$$(\delta_{cp} - \delta_{ws} + 0.27) = -0.231 \pm 0.004t + 4.03 \pm \pm0.03 \quad (13)$$

with $r^2 = 0.98$. The slope of Eq. (13) is significantly steeper than that of the Florida-only *U. peregrina* Eq. (6), but it is within 2σ uncertainty of the *Cibicidoides* plus *Planulina* compilation Eq. (8) slope. We infer from this that Eq. (6) is likely biased due to the smaller number of observations and limited range of temperatures. The OLS quadratic fit to the compiled *Uvigerina* measurements is:

$$(\delta_{cp} - \delta_{ws} + 0.27) = -0.242 \pm 0.015t + 0.0008$$
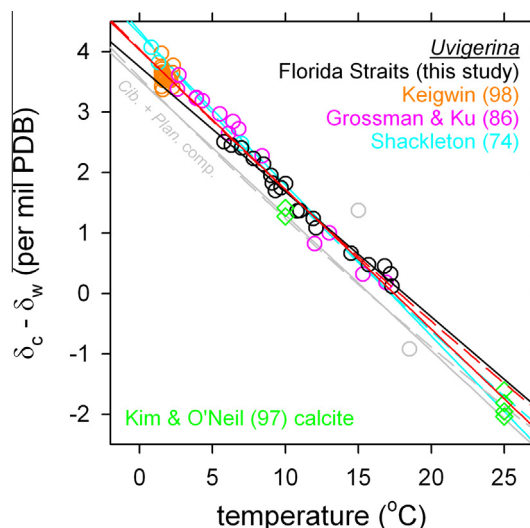$$\pm 0.0009t^2 + 4.05 \pm 0.04 \quad (14)$$

Fig. 5. Compiled *Uvigerina* δ^{18}O difference from seawater on the PDB scale, vs. bottom water temperature. Gray points are 3σ outliers from Grossman and Ku (1986). Also shown are synthetic calcite data from Kim and O'Neil (1997) (green diamonds). Lines are: RMA linear regression for the Florida Straits *Uvigerina* data (Eq. (6), black); RMA linear regression for all *Uvigerina* data (Eq. (13), solid red); OLS quadratic regression for all *Uvigerina* data (Eq. (14), dashed red); Shackleton (1974) linear Eq. (1) (solid cyan); and Shackleton (1974) quadratic Eq. (2) (dashed cyan). The linear and quadratic fits to the compiled *Cibicidoides* and *Planulina* data (Eqs. (8) and (9)) are shown as gray lines for reference. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

again with $r^2 = 0.98$. The cold- and warm-end slopes of Eq. (14) are indistinguishable from those of the *Cibicidoides* plus *Planulina* quadratic Eq. (9). Note, however, that the second order term in Eq. (14) is within uncertainty of zero.

The similarity between the slopes of the *Cibicidoides* plus *Planulina* and *Uvigerina* quadratic equations leads us to conclude that Shackleton's Eqs. (1) and (2) are too steep over most oceanographic temperatures (Fig. 5). We agree with Bemis et al. (1998) that *Cibicidoides* and *Planulina* appear to be closer to isotopic equilibrium (as represented by the Kim and O'Neil (1997) inorganic precipitates) than *Uvigerina*, although scatter in the measurements limits our confidence in this statement (Figs. 3–5).

The canonical value of 0.64‰ for the average isotopic offset between *Uvigerina* and *Cibicidoides*, the so-called "vital effect," was based originally on downcore comparisons back to Marine Isotope Stage 6 at a single site in the deep equatorial Pacific (Shackleton and Opdyke, 1973). Here we calculate this offset as the difference between core top *Uvigerina* $\delta_c - \delta_w$ values and the prediction from *Cibicidoides* plus *Planulina* quadratic Eq. (9). The resulting mean offset is 0.47 ± 0.04‰ ($\pm 2se$, $n = 62$). Keigwin (1998) noted that the Holocene offset in the northwest North Pacific was surprisingly small (~0.4‰), raising the possibility of regional biases. We alternatively calculate the offset based on the Florida core tops only, using the linear *Cibicidoides* plus *Planulina* Eq. (5), which yields a mean value of 0.45 ± 0.06‰ ($\pm 2se$, $n = 19$). The overlap between these several estimates suggests that Keigwin (1998) was not seeing a significant regional bias, but rather that the canonical value is incorrect.

Currently accepted practice is to add 0.64‰ to *Cibicidoides* $\delta^{18}O$ measurements and then apply one of Shackleton's (1974) paleotemperature equations, because *Uvigerina* was thought by Shackleton to calcify at equilibrium with seawater. We have shown that *Cibicidoides* is actually closer to equilibrium, and that 0.64‰ is an overestimate of the *Uvigerina* offset. We therefore suggest that quadratic Eq. (9) be used with unadjusted *Cibicidoides* or *Planulina* $\delta^{18}O$ measurements. In the case of *Uvigerina* $\delta^{18}O$ measurements, we favor Eq. (9) over the *Uvigerina* quadratic Eq. (14) because the former contains three times as many observations. We recommend that *Uvigerina* $\delta^{18}O$ be adjusted to the *Cibicidoides* scale by subtracting 0.47‰. In Section 3.5 we evaluate the suggestion by Bemis et al. (1998) that the inter-species offset might be due to a carbonate ion effect in pore waters that impacts the shallow-infaunal *Uvigerina*.

3.4. *H. elegans* compilation

H. elegans is one of the few extant aragonitic benthic foraminifera. We are aware of only one extensive collection of published *H. elegans* $\delta_c - \delta_w$, again from Grossman and Ku's (1986) study along the California Borderland and in the Gulf of Mexico, spanning a temperature range of 2.6–20.1 °C (Fig. 6). We reject one of their 26 averages as a $>3\sigma$ outlier relative to the rest of our compilation. We also present previously unpublished average *H. elegans* values from 39 Little Bahama Bank core tops, spanning a temperature range of 4.1–25.6 °C (Fig. 6). Little Bahama Bank
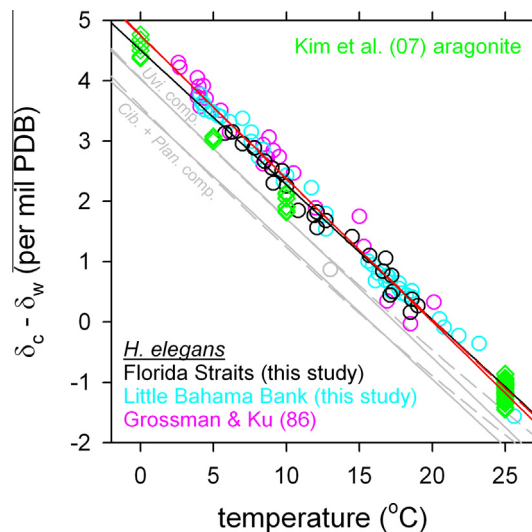

Fig. 6. Compiled *H. elegans* $\delta^{18}O$ difference from seawater on the PDB scale, vs. bottom water temperature. Gray point is a 3σ outlier from Grossman and Ku (1986). Also shown are synthetic aragonite data from Kim et al. (2007) (green diamonds). Lines are: RMA linear regression for the Florida Straits *H. elegans* data (Eq. (7), black); RMA linear regression for all *H. elegans* data (Eq. (15), solid red); OLS quadratic regression for all *H. elegans* data (Eq. (16), dashed red). The linear and quadratic fits to the compiled *Cibicidoides* + *Planulina* (Eqs. (8) and (9)) and *Uvigerina* (Eqs. (13) and (14)) data are shown as gray lines for reference. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

seawater $\delta^{18}O$ was estimated from salinity following Lynch-Stieglitz et al. (1999).

Combining these two data sets with the Florida Straits measurements ($n = 89$) yields the RMA linear equation:

$$(\delta_{cp} - \delta_{ws} + 0.27) = -0.237 \pm 0.003t + 4.75 \pm 0.04 \quad (15)$$

with $r^2 = 0.98$. The slope of Eq. (15) is significantly steeper than that of the Florida-only *H. elegans* Eq. (7), and among the other linear equations presented here it is within 2σ combined uncertainty of only the *Uvigerina* compilation Eq. (13) slope. The OLS quadratic fit to the compiled *H. elegans* measurements is:

$$(\delta_{cp} - \delta_{ws} + 0.27) = -0.243 \pm 0.016t + 0.0003$$
$$\pm 0.0006t^2 + 4.76 \pm 0.08 \quad (16)$$

again with $r^2 = 0.98$. The cold-end slope of Eq. (16) is indistinguishable from that of the *Cibicidoides* plus *Planulina* and *Uvigerina* quadratic Eqs. (9) and (14), while at 25 °C it is steeper (−0.23‰ per °C). Like Eq. (14), the second order term in Eq. (16) is within uncertainty of zero. *H. elegans* appears to be slightly more enriched than most of the inorganic aragonite measurements that are believed to represent equilibrium (Kim et al., 2007) (Fig. 6).

The mean $\delta^{18}O$ offset of *H. elegans* relative to the value predicted by the *Cibicidoides* plus *Planulina* quadratic Eq. (9) is 1.07 ± 0.06‰ ($\pm 2se$, $n = 89$). Calculating this same value using only the Florida Straits data and Eq. (5) gives 1.02 ± 0.06‰ ($\pm 2se$, $n = 24$).

3.5. Test for the influence of pH

Laboratory cultures of the planktonic foraminifera *Orbulina universa*, *Globigerina bulloides*, *Globigerinoides ruber*, and *Globigerinoides sacculifer* demonstrate that shell $\delta^{18}O$ and $\delta^{13}C$ decrease significantly as seawater carbonate ion (CO_3^{2-}) concentration increases, under both constant DIC and constant alkalinity conditions (Spero et al., 1997, 1999; Bijma et al., 1999). McCrea (1950) had observed this effect for $\delta^{18}O$ in rapidly precipitated synthetic $CaCO_3$, and argued that a fast mode of precipitation results in a mineral that captures the $\delta^{18}O$ of the bicarbonate (HCO_3^-) and CO_3^{2-} in solution, in contrast to slow precipitation which achieves solid-state isotopic equilibration with the water. Although biological carbonates were believed to follow the slow, solid-state equilibrium pathway (McCrea, 1950), the Spero et al. (1997, 1999) and Bijma et al. (1999) results may challenge that notion. Spero et al. (1997) noted that *O. universa* closely matches McCrea's rapidly precipitated inorganic $\delta^{18}O$:CO_3^{2-} slope, although the effect in *G. bulloides* is twice as large (perhaps due to a greater influence of respired CO_2 since *G. bulloides* lacks symbionts [J. Bijma, pers. comm. 2013]). The *G. ruber* and *G. sacculifer* slopes bracket the *O. universa* results (Spero et al., 1999).

Building on the work of Usdowski and Hoefs (1993) and Beck et al. (2005), Zeebe (2007) recalculated the $\delta^{18}O$ fractionation factor (α_T) between DIC and seawater as a function of pH. This confirmed that the *O. universa* sensitivity can be explained if this species' calcite, like McCrea's fast precipitates, is formed from a mixture of HCO_3^- and CO_3^{2-} (Zeebe, 1999; 2007). Hence a decrease of $\delta^{18}O$ under high CO_3^{2-} (high pH) conditions is attributed to an increased contribution from CO_3^{2-} (isotopically lighter) relative to HCO_3^- (isotopically heavier).

If benthic foraminifera precipitate their $CaCO_3$ in a rapid (non-equilibrium) mode as proposed for *O. universa*, then past changes in seafloor pH may have left an imprint on the benthic $\delta^{18}O$ record. For example, at the bottom water properties that characterize the Florida Straits, a past pH increase of 0.2 units might masquerade as a 1 °C warming. This mechanism has also been suggested as a possible explanation for the $\delta^{18}O$ offset between *Cibicidoides* and *Uvigerina*, since the latter genus would typically experience lower ambient pH due to its shallow infaunal habitat (Bemis et al., 1998). Furthermore the temperature dependence of α_T predicts a foraminiferal $\delta^{18}O$ temperature sensitivity that is very close to observations, suggesting that the close correspondence between benthic foraminifera and inorganic experiments noted above may not be uniquely diagnostic of slow, solid-state equilibrium precipitation (Zeebe, 2007).

Here we test the applicability of the Zeebe hypothesis to benthic foraminifera using our Florida Straits samples. As described in Section 2.1, total alkalinity and DIC were measured at a subset of the multicore locations, providing excellent estimates of modern seawater pH at each site. Our test begins with the assumption that the HCO_3^- and CO_3^{2-} entering the shell is isotopically equilibrated with seawater at ambient pH. The validity of this assumption depends crucially on the timescale of DIC isotopic re-equilibration with intracellular water, which occurs over hours at seawater pH and higher (Zeebe and Wolf-Gladrow, 2001), although the enzyme carbonic anhydrase may speed the process (Uchikawa and Zeebe, 2012). If this timescale is short relative to the residence time of intracellular DIC, then we must consider isotopic re-equilibration of HCO_3^- and CO_3^{2-} at intracellular pH (Uchikawa and Zeebe, 2012) (see below). If this timescale is long relative to the residence time of intracellular DIC, then we must consider the possible contribution of CO_2 diffusing into the cell and failing to isotopically re-equilibrate with intracellular water. If this CO_2 represents a significant carbon source for the internal HCO_3^- plus CO_3^{2-} calcification pool, then it will drive the $\delta^{18}O$ of that pool higher. This effect could be hypothetically negated if the CO_2 is rapidly protonated from HCO_3^- and CO_3^{2-} in an acidified extracellular microenvironment (Glas et al., 2012) and hence carries the isotopic composition of those two species into the cell.

We modified the MATLAB script from Zeebe (2007) to calculate the fractionation factor (α) for the sum of HCO_3^- and CO_3^{2-} relative to seawater (i.e., α_T minus the very small contributions from CO_2 and carbonic acid). We calculate α at each multicore site as a function of bottom water temperature, salinity, and pH, and then combine it with seawater $\delta^{18}O$ to determine the equilibrium $\delta^{18}O$ of HCO_3^- plus CO_3^{2-}. If benthic foraminifera capture the isotopic composition of that HCO_3^- and CO_3^{2-} at ambient pH and without solid-state backward exchange with water, then the calculated $\delta^{18}O$ values should match the foraminiferal observations.

Since pH and temperature are strongly correlated in the Florida Straits, and since temperature has a much stronger impact on $\delta^{18}O$ over these ranges according to the Zeebe model, we plot the observed and predicted foraminiferal $\delta^{18}O$ values vs. temperature (Fig. 7a). Predicted $\delta^{18}O$ is higher than observations by $\sim1.6‰$ (*H. elegans*) to $\sim2.6‰$ (*Cibicidoides* and *Planulina*) in the middle of the temperature range, which might be explained if bottom water pH values are lower than those actually experienced at the internal site of calcification (assuming sufficient time for isotopic re-equilibration of DIC with intracellular water). As noted previously (Zeebe, 2007), the temperature-dominated predicted slope is close to foraminiferal observations. Given that pH has a relatively small influence on the predicted slope, a comparison of slopes is of limited utility in testing the Zeebe hypothesis.

Next we calculate the pH required to explain the foraminiferal observations according to the Zeebe model, and plot it vs. bottom water pH (Fig. 7b) and bottom water saturation coefficient (Ω) (Fig. 7c). Inferred calcification pH values range from 8.6 to 9.2 and vary between species (*H. elegans* < *U. peregrina* < *Cibicidoides* and *Planulina*). We note that these values are comparable to internal pH levels measured at the sites of calcification in living *Cibicides lobatulus* (de Nooijer et al., 2009) and *Amphistegina lobifera* (Bentov et al., 2009), and also as inferred from microscale $\delta^{11}B$ measurements on *A. lobifera* shells (Rollion-Bard and Erez, 2010). Although one might expect the aragonitic *H. elegans*, with its lower bottom water Ω range, to require higher internal pH values than the calcitic taxa, Mg^{2+} poisoning of calcite precipitation (Berner, 1975) could necessi-
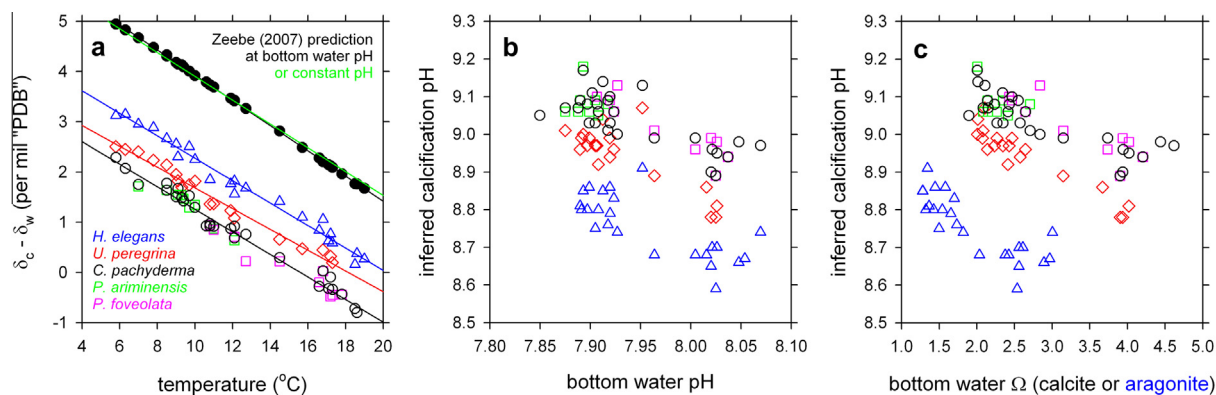
Fig. 7. (a) Florida Straits benthic foraminiferal data as in Fig. 2, compared to predicted values based on the Zeebe (2007) hypothesis that foraminifera precipitate a mixture of HCO_3^- and CO_3^{2-} ions, using bottom water temperature, salinity, and pH in the calculations (filled black circles). Green line is the prediction if pH is held constant at the average value for these sites. (b) Calcification pH required to explain the foraminiferal data according to the Zeebe hypothesis, vs. bottom water pH. (c) As in panel (b) but vs. bottom water saturation coefficient (Ω). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tate higher pH values in those species (Zeebe and Sanyal, 2002) even with active Mg^{2+} removal (Bentov and Erez, 2006). If CO_2 that is at least partially equilibrated with extracellular seawater contributes significantly to the calcification pool, then the Zeebe predictions would be pushed higher, as would the inferred calcification pH values. It is not obvious how this additional carbon source would impact the predicted slope.

We might expect a given species to attain a constant calcification (internal) pH regardless of ambient pH; or for internal pH to span a range of values between ambient and a constant, leading to a positive correlation of the mean internal pH with ambient pH (Rollion-Bard and Erez, 2010); but there is no obvious mechanistic reason for a negative correlation as observed (Fig. 7b). A negative correlation with bottom water Ω (Fig. 7c) would make sense if the Ω variation were dominated by pressure and temperature such that internal pH needs to be higher when solubility is higher (Ω is lower), but here Ω is dominated by bottom water $[CO_3^{2-}]$, i.e., pH (cf. Fig. 7b). Rather, the inverse correlations in Fig. 7b and c could simply be artifacts, given that the predicted slopes have considerable uncertainties (Uchikawa and Zeebe, 2013). The inverse correlations are probably due to the fact that bottom water pH and temperature are strongly correlated, combined with the need for the cold-end (low-pH) predictions to be adjusted to a higher internal pH than the warm-end (high-pH) predictions in order to match observations (cf. the slope differences in Fig. 7a).

We are left with the question of whether the benthic foraminiferal data are better explained by solid-state thermodynamic $CaCO_3$ equilibrium with water, or by the Zeebe model of mixed HCO_3^- and CO_3^{2-} incorporation at some elevated internal pH. We find it compelling that the Cibicidoides and Planulina data are such a good match to the inorganic calcite experiments of Kim and O'Neil (1997), assuming those experiments truly achieved solid-state equilibrium. Yet the apparent departure of Uvigerina from equilibrium demands an explanation. We consider it plausible that Uvigerina represents a mixture of equilibrium calcite

and rapidly-precipitated, isotopically-heavier calcite that drives its $\delta^{18}O$ toward the Zeebe prediction. To the extent that H. elegans is similarly enriched relative to presumed equilibrium aragonite (Kim et al., 2007), an analogous mixture might be present in that species as well. For the Zeebe model to explain 100% of the precipitates, each of the three taxa would need to achieve a different but essentially constant internal pH, largely irrespective of environmental pH.

4. CONCLUSIONS

We have investigated oxygen isotope fractionation by three taxonomic groups of benthic foraminifera as a function of temperature. The most extensive set of observations comes from the combination of Cibicidoides and Planulina, which exhibit a quadratic temperature dependence ranging from −0.25‰ per °C in cold waters to −0.19‰ per °C in warm waters (Eq. (9)), or −0.22‰ per °C over all temperatures if fit with a straight line (Eq. (8)). Absolute values agree well with synthetic calcite precipitated at equilibrium. Uvigerina displays slopes (Eqs. (13) and (14)) that are within uncertainty of Cibicidoides and Planulina, while absolute values are 0.47‰ more enriched. The aragonitic H. elegans linear and warm-end quadratic slopes (Eqs. (15) and (16)) are slightly steeper than for the calcitic taxa, but additional measurements are needed to determine whether or not this difference is real. H. elegans absolute values are enriched over Cibicidoides and Planulina by 1.07‰, and appear to be slightly enriched above equilibrium synthetic aragonite. Finally, with these data we are unable to discern an impact of bottom water pH on benthic foraminiferal $\delta^{18}O$, but we speculate that Uvigerina's (and possibly H. elegans') deviation from equilibrium could be explained by admixture of rapidly-precipitated non-equilibrium $CaCO_3$ that would be subject to a pH influence.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.gca.2013.12.034.

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