Zinc concentrations in benthic foraminifera reflect seawater chemistry

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Abstract. We have measured Zn/Ca ratios in two taxa of Holocene-aged benthic foraminifera from throughout the world's oceans. Zn/Ca is controlled by bottom water dissolved Zn concentration and, like Cd/Ca and Ba/Ca, by bottom water saturation state with respect to calcite. Measurements on "live-collected" foraminifera suggest that the saturation effect occurs during growth and is not a postdepositional artifact. Zn/Ca could be a sensitive paleoceanographic tracer because deep water masses have characteristic Zn concentrations that increase about tenfold from the deep North Atlantic to the deep North Pacific. In addition, since Zn/Ca responds to a different range of saturation states than Cd/Ca, the two may be used together to evaluate changes in deep water carbonate ion (CO3^2-) concentration.

1. Introduction

Much of our knowledge of the past distribution and circulation of deep water masses has been derived from carbon isotopic (δ13C) and trace metal concentration (Cd/Ca, Ba/Ca) measurements of benthic foraminiferal shells [e.g., Boyle and Keigwin, 1982; Curry and Lohmann, 1982; Curry et al., 1988; Duplessy et al., 1988; Lea and Boyle, 1990; Boyle, 1992; Oppo and Lehman, 1993; Sarnthein et al., 1994]. δ13C and Cd/Ca-based reconstructions of Last Glacial Maximum (LGM) deep circulation agree on a gross scale but differ significantly in certain details. For example, δ13C suggests that the deep glacial Southern Ocean was more nutrient-rich than the Pacific [Curry et al., 1988], while Cd/Ca measurements fall between Atlantic and Pacific values, like today [Boyle, 1992]. Several mechanisms have been proposed to explain such discrepancies, including air-sea exchange [Charles et al., 1993; Lynch-Stieglitz and Fairbanks, 1994], foraminiferal microhabitat effects [Mackensen et al., 1993], and bottom water undersaturation with respect to calcite [McCorkle et al., 1995]. The extent to which these mechanisms operate is not well understood, however, and there is a clear need for additional deep water nutrient tracers. Ba/Ca is one such tracer, though its applicability is complicated by an apparent glacial increase in Ba flux from Atlantic sediments [Martin and Lea, 1998].

We propose that benthic foraminiferal zinc concentration (Zn/Ca) is well suited to be a sensitive paliceirculation tool. Zn is an essential micronutrient for many marine organisms, second only to Fe among the biologically important trace metals [Bruland et al., 1991; Morel et al., 1994; Sunda and Huntsman, 1995]. This contributes to the nutrient-like character of its dissolved vertical profile in seawater, with near-zero concentrations in most surface waters and maximum values below ~1000 m depth [Bruland et al., 1978]. Zn has a deeper regeneration cycle than Cd [Boyle et al., 1976; Bruland, 1980] and is more efficiently removed from surface waters than Ba [Chan et al., 1977]. The overall distribution of dissolved Zn is very similar to that of Si, with correlation between the two elements at r² = 0.98 in global deep waters [Bruland et al., 1978; Martin et al., 1989; Bruland, 1980; Bruland and Franks, 1983; Martin et al., 1990; P. Yeats and J. Dalziel, unpublished data, 1997] (Figure 1). This strong covariance is believed to be due to their similar patterns of biological uptake and regeneration, mainly by diatoms, not to the relatively unimportant incorporation of Zn into biogenic opal [Collier and Edmund, 1984]. Zn concentrations range from <1 nmol kg⁻¹ in the deep North Atlantic (P. Yeats and J. Dalziel, unpublished data, 1997) to >10 nmol kg⁻¹ in the deep North Pacific [Martin et al., 1989]. There is a particularly large (~sevenfold) increase between the deep North Atlantic and the deep South Atlantic [Martin et al., 1990], much larger than the corresponding Cd and Ba gradients [Boyle, 1988; Lea and Boyle, 1989]. This suggests that Zn may be a very sensitive tracer of the glacial-interglacial interactions between North Atlantic Deep Water (NADW) and southern source deep waters such as Circumpolar Deep Water (CPDW) and Antarctic Bottom Water (AABW).

To our knowledge, there are only two published benthic foraminiferal Zn/Ca measurements, 3.0 ± 0.4 μmol mol⁻¹ for Pyrgo and 37.3 ± 0.4 μmol mol⁻¹ for Unio (Boyle, 1981), and the higher value is certainly contaminated. We have therefore carried out a "core top calibration" to show that benthic foraminifera reflect bottom water dissolved Zn levels. This follows in the path of previous core top studies of Cd/Ca [Hester and Boyle, 1982] and Ba/Ca [Lea and Boyle, 1989]. We further show that Zn/Ca, like
\[ y = 0.052x + 0.786 \quad r^2 = 0.980 \]

\[ [\text{Zn}] \text{ (nmol kg}^{-1}\text{)} = 0.052[\text{Si}] + 0.79 \]

Degree of calcite saturation, defined by
\[ \Delta \text{CO}_3^2- = [\text{CO}_3^2-]_{\text{in situ}} - [\text{CO}_3^2-]_{\text{saturation}} \]

was calculated at each calibration site from nearest GEOSECS measurements of alkalinity, $\Sigma$CO$_2$, temperature, and salinity (for Brazil margin multicore sites, alkalinity, $\Sigma$CO$_2$, and salinity were again measured directly (D. McCorkle and G. Eisheide, unpublished data, 1999)). As recommended by United Nations Educational, Scientific, and Cultural Organization (UNESCO) [1987], the main thermodynamic equations are from Millero [1979], Mucci [1983], and Dickson and Millero [1987]. The resulting $\Delta$CO$_3^2-$ values are significantly offset from those calculated by GEOSECS [Bainbridge, 1981, Broecker et al., 1982; Weiss et al., 1983] mainly because of a difference in the pressure effect on calcite solubility. The offset is therefore a function of water depth, and ranges from about +6 $\mu$mol kg$^{-1}$ at 1660 m to -8 $\mu$mol kg$^{-1}$ at 4556 m.

3. Results and Discussion

3.1. Zn/Ca Core Top Calibration

Measured Holocene C. wuellerstorfi and Uvigerina Zn/Ca values range between 1.22 and 5.84 $\mu$mol mol$^{-1}$ (Figure 2a and Table 1). The data correlate generally well with predicted seawater Zn concentrations ($r^2=0.67$, $p<0.001$), indicating that these taxa do reflect overlying Zn levels. Lowest Zn/Ca values are found in the North Atlantic (mean of 1.8 $\pm$0.5 $\mu$mol mol$^{-1}$), intermediate values are found in the tropical and South Atlantic (2.8 $\pm$0.6 $\mu$mol mol$^{-1}$), and highest values are found in the Indian and Pacific (4.4 $\pm$0.7 $\mu$mol mol$^{-1}$), following the expected pattern. All but three of the Mn/Ca ratios in these samples are below 30 $\mu$mol mol$^{-1}$, and there is no evidence of Zn contamination related to MnCO$_3$ overgrowths [Boyle, 1983].

Note, however, that many of the Pacific, Indian, and deepest South Atlantic Zn/Ca data (from waters with Zn $>$4 nmol kg$^{-1}$) fall below the trend suggested by the other Atlantic data. This pattern is expected if apparent Zn partition coefficients, defined by

\[ D_{Zn} = (Zn/Ca)_{\text{seawater}}/(Zn/Ca)_{\text{core}} \]

are decreased in waters that are near or below saturation with
Table 1. Zn/Ca Ratios of Holocene Benthic Foraminifera

<table>
<thead>
<tr>
<th>Core</th>
<th>Depth, cm</th>
<th>Latitude</th>
<th>Longitude, m</th>
<th>GEOSECS Estimate, μmol kg⁻¹</th>
<th>Zn/Ca, μmol mol⁻¹</th>
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<td>All13-765</td>
<td>3</td>
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<td>57 38</td>
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<td>38°39'W</td>
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<td>3300</td>
<td>168 -5</td>
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</tbody>
</table>

\(\Delta CO_2^+\) was recalculated from GEOSECS measurements of alkalinity, \(\Delta CO_2\), temperature, and salinity (see text).

Reported Zn/Ca errors are ±1σ on mean or mean of two to three measurements. From a total of 87 Zn/Ca measurements, three were judged to be significantly contaminated (values much higher than replicates) and were not included in the means.

Supplemented by our own unpublished stable isotope data.

With respect to calcite, as C. wuellerstorfi Cd and Ba apparent partition coefficients are \cite{McCorkle:1995} Figure 2b shows apparent \(D_{Zn}\) versus \(\Delta CO_2^+\), in waters with \(\Delta CO_2^+\) below -25 μmol kg⁻¹, \(D_{Zn}\) decreases with decreasing saturation. These data can be fitted with a simple two-part linear relationship, allowing us to predict \(D_{Zn}\), from \(\Delta CO_2^+\):

\[
D_{Zn} = 0.15 \Delta CO_2^+ + 5.25 \quad \Delta CO_2^+ < 25 \mumol kg^{-1} \quad (4)
\]

\[
D_{Zn} = 9 \Delta CO_2^+ > 25 \mumol kg^{-1} \quad (5)
\]

The true relationship is likely to be nonlinear, but the present data do not warrant anything more complex than two line segments. Such a simple relationship, which describes the data reasonably well, is preferable to a best fit, which would necessarily change with each new datum added to the calibration. The \(\Delta CO_2^+\) effect on \(D_{Zn}\) appears to extend farther into supersaturated waters than for \(D_{Cd}\), combined Cd/Ca data from Boyle \cite{Boyle:1988, Boyle:1992}, McCorkle \cite{McCorkle:1995}, and our own unpublished results suggest that \(D_{Ca}\) is related to \(\Delta CO_2^+\) below roughly 5 μmol kg⁻¹. Although we have not examined Ba/Ca in detail, the data compiled by McCorkle \cite{McCorkle:1995} imply that \(D_{Ba}\) may be affected over a range of \(\Delta CO_2^+\) similar to that observed for \(D_{Zn}\). There is no additional relationship between \(D_{Zn}\) and water depth or temperature within the range of these data.

Once \(D_{Zn}\) is predicted from \(\Delta CO_2^+\), it can be applied to foraminiferal Zn/Ca to yield an inferred seawater Zn concentration:

\[
Z_{nw} = \frac{[(Zn/Ca)_{foram} / D_{Zn}]}{[Ca]_{Seawater}} \quad (6)
\]

Applying this conversion to the core top data (in a somewhat circular fashion) increases the correlation between foraminiferal and seawater data significantly \cite{McCorkle:1995} (Figure 2c). The remaining scatter in this relationship may be due to uncertainties in estimating bottom water Si and \(\Delta CO_2^+\) from GEOSECS data.
uncertainties in predicting seawater Zn from Si estimates, presence of older foraminifera due to bioturbation and/or lack of latest Holocene sediment, and occasional laboratory contamination. The high correlation in spite of all these factors suggests that Zn concentrations in *C. wuellerstorfi* and *Uvigerina* are relatively precise functions of bottom water Zn and ΔCO$_2$ levels.

### 3.2. ΔCO$_2$ Effect in Live *C. wuellerstorfi*

The observed drops in apparent $D_{Zn}$, $D_{Cd}$, and $D_{Ba}$ in low-ΔCO$_2$ waters may be due to decreased incorporation of these trace metals during growth or to post mortem preferential dissolution of trace metals over Ca [McCarroll *et al.* 1995, Boyle and Rosenthal, 1996]. In the laboratory, neither Zn nor Cd is preferentially lost from benthic foraminiferal calcite as dissolution proceeds beyond the usual cleaning process (Figure 3; see also Boyle [1988] for Cd). This suggests that the measured trace metals are not localized on surfaces or in any other

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**Figure 2.** (opposite) (a) Zn/Ca ratios in Holocene benthic foraminifera *C. wuellerstorfi* (squares) and *Uvigerina* app. (diamonds), versus bottom water dissolved Zn concentrations estimated from GROSECBS dissolved Si measurements and the global deep water Zn:Si linear relationship shown in Figure 1. Core tops are from the North Atlantic (open squares and diamonds), the tropical and South Atlantic (shaded squares and diamonds), and the Indian and Pacific (solid squares and diamonds). Each symbol is a mean of up to three measurements, and error bars are ±1 s of replicates. Dotted line represents the relationship for waters in which the apparent partition coefficient for Zn into benthic foraminiferal calcite ($D_{Zn}$) appears to be unaffected by ΔCO$_2$. i.e., $D_{Zn} = 9$ (estimated from Figure 2b). (b) Apparent $D_{Zn}$ of the samples in Figure 2a versus ΔCO$_2$ calculated from GROSECBS data. Symbols are as in Figure 2a but without error bars. Dotted lines represent a simple two-part linear relationship (see text), not necessarily the best fit to the data. Note that one datum from the North Atlantic plots off the scale ($D_{Zn}$ = 18.6, ΔCO$_2$ = 29). (c) Foraminiferal Zn:Ca, calculated using $D_{Zn}$ derived from the linear relationship in Figure 2b, versus seawater dissolved Zn estimated from GROSECBS Si. Symbols are as in Figure 2a. Dotted line is the 1:1 line, not the best fit.

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**Figure 3.** Results of a progressive dissolution experiment using *Uvigerina* app. from core SH107-67GSC (33-35 cm). Five groups of 45 individuals each were crushed and split into thirds, yielding a total of 15 samples. Each sample was weighed, then subjected to the usual chemical cleaning process, which concludes with a 0.001N nitric acid leach (circles). Two thirds of the samples were then subjected to additional leaches in 0.075N nitric acid (diamonds). Mass loss was calculated by comparing Ca concentrations to original masses. Some of the original mass includes fine sediment inside the foraminifera, so mass loss is an overestimate of shell dissolution. Results indicate no preferential loss of (a) Zn or (b) Cd (relative to Ca) as dissolution progresses. Note that the ordinates are scaled to encompass the full range of modern variability and that the scatter in the data is typical of foraminiferal measurements.
dissolution-prone phase. It is conceivable, however, that dissolution at the seafloor is more effective at selecting for trace metals than the rapid dissolution that occurs in the laboratory. Therefore a better test is to distinguish between increased incorporation and postmortem dissolution to look for the ΔCO₂⁻ effect in living benthic foraminifera. This strategy has been used to infer that ΔCO₂⁻ influences the fractionation of δ^{13}C during benthic foraminiferal calcification [McCorkle et al., 1999].

Zn/Ca was measured in unstained ("dead") C. wuellerstorfi from eight multicores between 1604 and 3885 m depth along the Brazil margin and in stained ("live") C. wuellerstorfi from just three multicores (because of low stained abundances) between 3356 and 3885 m. The ΔCO₂⁻ values of the waters overlying these sites range from -3 to 47 μmol kg⁻¹. Figure 4 shows the Zn/Ca values predicted from bottom water Si, using a constant D_{Zn} of 9 (crosses) and D_{Zn} that varies with ΔCO₂⁻ according to equations (4) and (5) (plusses). Unstained C. wuellerstorfi clearly show the ΔCO₂⁻ effect in the four deepest cores. Stained specimens from 3356 and 3581 m have even lower Zn/Ca values and therefore also show the effect. The stained sample from 3885 m is by far the smallest, and a small contamination (<2σ of process blank [Zn] reproducibility) could explain the difference from its unstained counterpart.

Although limited in number, the above data support the theory [Boyle and Rosenthal, 1996; Elderfield et al., 1996] that the relationships between ΔCO₂⁻ and the various partition coefficients are set during growth. Unfortunately, the actual mechanisms of trace metal incorporation into foraminiferal calcite are not well understood. The zeroth-order prediction of a metal's partition coefficient into calcite is based on an ideal solid solution:

\[ D_{\text{ideal}} = K_{\text{sp} \text{(calcite)}} / K_{\text{sp} \text{(metal carbonate)}} \]  

where \( D_{\text{ideal}} \) is a true thermodynamic distribution coefficient and \( K_{\text{sp}} \) is the solubility product for each solid at a given temperature and pressure. At 25°C and 1 bar pressure the ideal distribution coefficients for Zn and Cd are ~210 and 680, respectively [Davis et al., 1987, Zachara et al., 1988]. In the real world, \( D \) will also depend on the activities of the exchange cations in solution and in the solid phase. For example, Crockatt and Winchester’s [1966] inorganic calcite precipitation experiments produced Zn partition coefficients of ~6 at 25°C and 1 bar pressure. Zachara et al. [1988] found that in the laboratory, Zn adsorption onto calcite decreases as Ca²⁺ activity increases, possibly in response to increased calcite solubility.

However, as noted by Morse and Bender [1990] and Elderfield et al. [1996], such inorganic considerations are of limited applicability because of the biological mediation of foraminiferal shell growth. Elderfield et al. [1996] proposed that trace metals are removed by Rayleigh distillation from an internal biomineralization reservoir with a constant fractionation factor \( \alpha \). As the reservoir is consumed, \( D \) (relative to the initial composition of the reservoir, which may or may not be the same as seawater) will move away from \( \alpha \) and approach 1 asymptotically. They further suggested that calcification in undersaturated (low ΔCO₂⁻) waters is accompanied by infrequent flushing of the reservoir, bringing \( D \) toward 1. This model fits qualitatively with core top \( Zn/Ca \) and Cd/Ca data, where \( \alpha >1 \) and \( D_{Zn} \) and \( D_{Cd} \) decrease with decreasing ΔCO₂⁻.

It may also be consistent with McCorkle et al.’s [1993] Bu/Ca data if the biomineralization reservoir contains significantly less Ba than seawater, resulting in an \( \alpha >1 \) despite measured \( D_{Ba} \) values <1 [Lea and Boyle, 1989].

3.3. Application to Paleoceanography

On glacial-interglacial timescales a given core location may fall into one of three ΔCO₂⁻ categories: (1) ΔCO₂⁻ always remains below ~25 μmol kg⁻¹, so neither Zn/Ca nor Cd/Ca are affected by saturation state; (2) ΔCO₂⁻ falls below ~25 μmol kg⁻¹ but remains above roughly 5 μmol kg⁻¹, so only Zn/Ca is affected; or (3) ΔCO₂⁻ falls below ~5 μmol kg⁻¹, and both Zn/Ca and Cd/Ca are affected. Calcite lysoclone reconstructions suggest that LGM [CO₂⁻] was on the order of 5-10 μmol kg⁻¹ higher than today in the deep Pacific and ~10 μmol kg⁻¹ lower than today in the deep Atlantic [e.g., Farrell and Prell, 1989; Broecker, 1995]. If these estimates are reasonably accurate, then case (1) would correspond to a relatively small portion of the world ocean, such as certain regions of the North Atlantic shallower than ~3000 m. Here Zn/Ca and Cd/Ca could be converted directly into inferred Zn_{sw} and Cd_{sw}. Case (2) would be valid over a much larger region of the Atlantic, plus large portions of the Pacific shallower than ~3000 m. In such areas, Cd_{sw} (derived directly from Cd/Ca) could be used to estimate seawater dissolved Zn concentrations by making some assumptions about regional circulation. For example, dissolved Cd and Zn increase proportionally from south to north in the modern deep Pacific, so Zn can be predicted straightforwardly using Cd. In the Atlantic, dissolved Zn and Cd would be related mainly by mixing of NADW (having one Zn/Cd end-member ratio) with Southern Ocean waters (having another Zn/Cd ratio). Once seawater [Zn] is predicted, it could be combined with observed foraminiferal Zn/Ca to yield estimates of ΔCO₂⁻. Paleo-ΔCO₂⁻ values are easily converted to [CO₂⁻]_{in situ} by calculating [CO₂⁻]_{saturation}.  

![Figure 4. Zn/Ca in Ross Bengal stained (solid squares) and unstained (open squares) C. wuellerstorfi from Brazil margin multicore tops (R/V Knorr cruise 159-5). Also shown are predicted C. wuellerstorfi Zn/Ca values based on seawater dissolved Si measurements: crosses assume a constant D_{Zn} of 9, while plusses use D_{Zn} that varies with ΔCO₂⁻ (equations (4) and (5)). The predicted values coincide in waters with ΔCO₂⁻ > 25 μmol kg⁻¹. Sample marked with a question mark was by far the smallest ([Ca] ~ 3.8 mM, compared to mean of 17.5 mM) and may be elevated by a slight laboratory Zn contamination.](image.png)
which is a function of pressure, temperature, and salinity, and predicted to change little with time in the deep ocean.

New constraints on paleo-CO$_3^{2-}$ are important for understanding the cycling of CO$_2$ between the atmosphere and ocean and also the preservation of CaCO$_3$ in marine sediments. Lysocline-based estimates could be inaccurate if significant glacial CaCO$_3$ dissolution occurred within CO$_2$-rich pore waters [e.g., Emerson and Bender, 1981; Archer and Matter-Reimer, 1994]. Paleo-pH estimates based on benthic foraminiferal boron isotopes ($\delta^{11}$B) imply that deep Pacific [CO$_3^{2-}$] was actually -100 μmol kg$^{-1}$ higher than today [Sanyal et al., 1995]. This estimate is large enough to explain the entire LGM atmospheric CO$_2$ drop via an increase in ocean alkalinity [Broecker and Peng, 1987; Archer and Matter-Reimer, 1994, Sanyal et al., 1995]. Model results of Sigman et al. [1998], however, imply that it would be difficult to separate the sedimentary lysocline from the calcite saturation horizon by the amount required by the data of Sanyal et al. [1995]. Recently, Broecker and Clark [1999] proposed that the percentage of CaCO$_3$ >63 μm can be used as a proxy for paleo-ΔCO$_3^{2-}$, but this index is also subject to the complications of pore water dissolution.

ΔCO$_3^{2-}$ case (3), which probably holds for much of the Pacific deeper than ~3000 m, is the most complex situation because both $D_{Zn}$ and $D_{Cd}$ are affected. In theory, however, seawater [Zn], [Cd], and ΔCO$_3^{2-}$ can all be estimated by again making assumptions about regional circulation. This concept is illustrated in Figure 5 using a core top sample from the eastern tropical Pacific (KNR73-4PC). The possible pairs of bottom water dissolved Zn concentration and ΔCO$_3^{2-}$ that could produce the measured C. wuellerstorfi Zn/Ca value are plotted as a continuous solid curve. Similarly, the possible pairs of dissolved Cd and ΔCO$_3^{2-}$ that could produce the measured Cd/Ca value are plotted as a dashed curve. The seawater Zn and Cd axes are scaled to each other using two tines: Antarctic deep water entering the South Pacific with estimated [Zn] = 6.3 nmol kg$^{-1}$ and [Cd] = 0.75 nmol kg$^{-1}$ and northeast Pacific deep water with estimated [Zn] = 9.5 nmol kg$^{-1}$ and [Cd] = 0.59 nmol kg$^{-1}$ [Broecker et al., 1982, Boyle, 1988]. Since eastern tropical Pacific deep water can be thought of as an intermediate between these two end-members, the point where the Zn/Ca and Cd/Ca curves intersect corresponds to the inferred trace metal concentrations and ΔCO$_3^{2-}$ above KNR73-4PC. In practice, it is likely that the limited reproducibility of benthic foraminiferal data would result in significant errors, especially for inferred seawater Zn and Cd concentrations. ΔCO$_3^{2-}$ would be less subject to error because it is related to Zn/Ca and Cd/Ca through partition coefficients (i.e., large changes in Zn/Ca and Cd/Ca correspond to relatively small changes in ΔCO$_3^{2-}$; see Figure 5).

The initial obstacle to applying the methods proposed for cases (2) and (3) is that end-member trace metal concentrations during the past may have been different from today because of changes in global oceanic inventories or circulation. Although the oceanic residence time of dissolved Zn is poorly constrained, it is probably between a few thousand [Bruland et al., 1994] and

![Figure 5](image-url)  
**Figure 5.** Plot showing the combinations of seawater dissolved Zn, Cd, and ΔCO$_3^{2-}$ that could result in the Zn/Ca (solid curve) and Cd/Ca (dashed curve) values of C. wuellerstorfi from the top of core KNR73-4PC (3681 m, eastern tropical Pacific). The $D_{Zn}$ vs ΔCO$_3^{2-}$ relationship is given by equations (4) and (5). The preliminary ΔCO$_3^{2-}$ vs ΔCO$_3^{2-}$ relationship for sites deeper than 3000 m ($D_{Cd}$ = 0.1 ΔCO$_3^{2-}$ + 2.5 (below ΔCO$_3^{2-}$ - 5 μmol kg$^{-1}$) and $D_{Zn}$ = 3 (above ΔCO$_3^{2-}$ - 5 μmol kg$^{-1}$)) is mainly based upon previously published data [Boyle, 1988, 1992; McCorqule et al., 1995] and subject to change as more high-quality core top data are analyzed. The ordnates are scaled to each other using tines (horizontal dashed lines) that represent Antarctic deep water (GEOSECS station 296) and northeast Pacific deep water (GEOSECS station 347) estimated dissolved Zn and Cd concentrations along the isopycnal corresponding to the water above KNR73-4PC. Note that this scaling is not valid outside of the deep Pacific. The point where the Zn/Ca and Cd/Ca curves intersect represents a unique solution for this core site. Dotted error envelopes are the mean standard deviations of replicate measurements from the core top calibration (±0.12 μmol mol$^{-1}$ for Zn/Ca and ±0.007 μmol mol$^{-1}$ for Cd/Ca). Uncertainties in the equations relating partition coefficients to ΔCO$_3^{2-}$ may introduce additional error. Also plotted for comparison are estimated values of dissolved Zn (triangle), Cd (circle), and ΔCO$_3^{2-}$ from the nearest GEOSECS station (station 340).
a few tens of thousands [Shiller and Boyle, 1985] of years, so glacial-interglacial inventory changes cannot be ruled out. If such variations existed during the past, they would become apparent after many cores are analyzed using a synoptic strategy [Boyle, 1992]. Inventory changes can be distinguishable from 

ACO$_2$ changes because their spatial influences on benthic foraminifera would be very different. Eventually whole-ocean corrections might be applied, such as that used for $\Delta$C$_8$ during the LGM [Duplessy et al., 1988]. Only then could reliable paleo-ACO$_2$ and paleo-[CO$_2$] estimates be made. Even without a detailed assessment of the LGM oceanic Zn inventory, a CO$_2$ increase of the magnitude proposed by Sanyal et al. [1995] (〜100 $\mu$mol kg$^{-1}$) should be easily recognizable using paired Zn/Ca and Cd/Ca measurements.

4. Conclusions

Zn/Ca ratios in C. wuellerstorfi and Uvigerina spp. are controlled by bottom water dissolved Zn concentrations and by saturation state with respect to calcite. Bottom water Zn concentrations are, in turn, mainly controlled by deep circulation and the global oceanic Zn inventory. Benthic foraminiferal Cd/Ca and Ba/Ca are influenced by similar factors [Hester and Boyle, 1982; Boyle, 1980; Lea and Boyle, 1989, 1990; McCorkle et al., 1995], while $\Delta$C$_8$ and Ba/Ca are subject to additional artifacts that complicate their interpretation [Charles et al., 1993; Mackensen et al., 1993; Martin and Lea, 1998]. These various factors can be best separated by employing a multi-tracer approach. With the addition of Zn/Ca, not only can we decipher climatically important deep water circulation changes, but we can also examine changes in bottom water carbonate chemistry. The latter are vitally important to our understanding of the global carbon cycle and atmospheric CO$_2$ levels.

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