

## Zinc concentrations in benthic foraminifera reflect seawater chemistry

Thomas M. Marchitto Jr.<sup>1</sup>

Massachusetts Institute of Technology/Woods Hole Oceanographic Institution  
Joint Program in Oceanography, Woods Hole, Massachusetts

William B. Curry and Delia W. Oppo

Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

**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 ( $\text{CO}_3^{2-}$ ) concentration.

### 1. Introduction

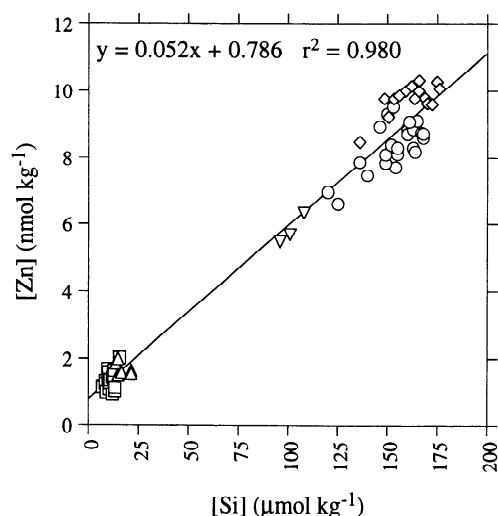
Much of our knowledge of the past distribution and circulation of deep water masses has been derived from carbon isotopic ( $\delta^{13}\text{C}$ ) and trace metal concentration (Cd/Ca, Ba/Ca) measurements of benthic foraminiferal shells [e.g., Boyle and Keigwin, 1982; Curry and Lohmann, 1982; Curry et al., 1988; Duplessy et al., 1988; Lea and Boyle, 1990; Boyle, 1992; Oppo and Lehman, 1993; Sarnthein et al., 1994].  $\delta^{13}\text{C}$  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,  $\delta^{13}\text{C}$  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 somewhat 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 paleocirculation 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  $r^2 = 0.98$  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 Edmond, 1984]. Zn concentrations range from  $<1 \text{ nmol kg}^{-1}$  in the deep North Atlantic (P. Yeats and J. Dalziel, unpublished data, 1997) to  $>10 \text{ nmol kg}^{-1}$  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,  $3.0 \text{ } \mu\text{mol mol}^{-1}$  for *Pyrgo* and  $37.3 \text{ } \mu\text{mol mol}^{-1}$  for *Uvigerina* [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

<sup>1</sup>Now at Lamont-Doherty Earth Observatory, Columbia University, Palisades, New York.



**Figure 1.** Modern relationship between dissolved Zn and dissolved Si concentrations in seawater deeper than 1000 m. Data are from 54°-68°N (squares) (P. Yeats and J. Dalziel, unpublished data, 1997), 34°N (triangles) [Bruland and Franks, 1983], and 61°S (inverted triangles) [Martin et al., 1990] in the Atlantic; and from 33°-37°N (circles) [Bruland et al., 1978; Bruland, 1980] and 40°-56°N (diamonds) [Martin et al., 1989] in the Pacific.

Cd/Ca and Ba/Ca [McCorkle et al., 1995], is influenced by bottom water saturation state with respect to calcite.

## 2. Materials and Methods

We have measured Zn concentrations in the cosmopolitan calcitic benthic foraminifera *Cibicides wuellerstorfi* and *Uvigerina* spp. in 33 Holocene sediment core tops from around the world's deep ocean (>1500 m depth; Table 1). Sediments were verified to be Holocene in age using published benthic and planktonic foraminiferal  $\delta^{18}\text{O}$ , radiocarbon dates, and bulk sediment percent  $\text{CaCO}_3$  (see Table 1). Although some of the cores (such as the deepest AII107 cores from the Vema Channel) contain only ~10 cm of Holocene sediment [Jones et al., 1984], omission of these data does not alter our conclusions. Eight additional multicores from along the Brazil margin (~26°-30°S, ~43°-47°W) were used to compare data from "live" and "dead" *C. wuellerstorfi*. The tops (0-1 cm) of these cores were preserved in a formalin solution and then stained with Rose Bengal to identify protoplasm [Corliss, 1985; Corliss and Emerson, 1990]. Those foraminifera having at least one chamber filled with protoplasm were identified as "live," or more precisely, recently living.

Benthic foraminiferal samples, each consisting of ~5-15 individuals (>250  $\mu\text{m}$ ), were cleaned following the methods of Boyle and Keigwin [1985/86] as modified by Rosenthal [1994], who reversed the order of the oxidative and reductive steps to remove authigenic sulfides [Boyle and Rosenthal, 1996]. Specimens stained with Rose Bengal were pretreated with bleach overnight (P. Martin, personal communication, 1999). Additional precautions were taken to minimize the risk of laboratory contamination, which has historically been a major obstacle to Zn work [Bruland et al., 1978]. Zn, Cd, and Mn were measured by graphite furnace atomic absorption

spectrophotometry (AAS), and Ca was measured by flame AAS, all on a Hitachi Z-8200. Analytical precision, based on frequent analyses of three consistency standards, is  $\pm 2$ -3% for Zn,  $\pm 3$ -6% for Cd,  $\pm 8$ -9% for Mn, and  $\pm 1$ % for Ca.

Modern dissolved Zn concentrations in bottom waters overlying each site in the core top calibration were estimated from nearest Geochemical Ocean Sections Study (GEOSECS) Si measurements [Bainbridge, 1981; Broecker et al., 1982; Weiss et al., 1983] and the global deep water Zn:Si relationship (Figure 1):

$$[\text{Zn}] = 0.052[\text{Si}] + 0.79 \quad (1)$$

with [Zn] in  $\text{nmol kg}^{-1}$  and [Si] in  $\mu\text{mol kg}^{-1}$ . For Brazil margin multicore sites, dissolved Si was measured in waters collected using a Niskin bottle mounted on the multicorer frame (D. McCorkle and Z. Mlodzinska, unpublished data, 1999). Dissolved Ca concentrations were taken to be constant at  $0.01 \text{ mol kg}^{-1}$  [Boyle, 1992].

Degree of calcite saturation, defined by

$$\Delta\text{CO}_3^{2-} = [\text{CO}_3^{2-}]_{\text{in situ}} - [\text{CO}_3^{2-}]_{\text{saturation}}, \quad (2)$$

was calculated at each calibration site from nearest GEOSECS measurements of alkalinity,  $\Sigma\text{CO}_2$ , temperature, and salinity (for Brazil margin multicore sites, alkalinity,  $\Sigma\text{CO}_2$ , and salinity were again measured directly (D. McCorkle and G. Eiseid, 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  $\Delta\text{CO}_3^{2-}$  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  $+6 \mu\text{mol kg}^{-1}$  at 1660 m to  $-8 \mu\text{mol kg}^{-1}$  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  $5.84 \mu\text{mol mol}^{-1}$  (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  $1.8 \pm 0.5 \mu\text{mol mol}^{-1}$ ), intermediate values are found in the tropical and South Atlantic ( $2.8 \pm 0.6 \mu\text{mol mol}^{-1}$ ), and highest values are found in the Indian and Pacific ( $4.4 \pm 0.7 \mu\text{mol mol}^{-1}$ ), following the expected pattern. All but three of the Mn/Ca ratios in these samples are below  $30 \mu\text{mol mol}^{-1}$ , and there is no evidence of Zn contamination related to  $\text{MnCO}_3$  overgrowths [Boyle, 1983].

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

$$D_{\text{Zn}} = (\text{Zn/Ca})_{\text{foram}} / (\text{Zn/Ca})_{\text{seawater}}, \quad (3)$$

are decreased in waters that are near or below saturation with

Table 1. Zn/Ca Ratios of Holocene Benthic Foraminifera

Core	Sample		Latitude	Longitude	Water Depth, m	GEOSECS <sup>a</sup> Estimates, $\mu\text{mol kg}^{-1}$		Zn/Ca, <sup>b</sup> $\mu\text{mol mol}^{-1}$		Stratigraphy Reference <sup>c</sup>
	Depth, cm					Si	$\text{ACO}_3^{2-}$	<i>C. wueller.</i>	<i>Uvigerina</i>	
AII15-765	3	32°01'S	49°56'E	3698	126	-6	3.91 ± 0.05			Graham et al. [1981]
AII54-9-5	0-2	9°31'S	94°13'W	3960	138	-4	3.85 ± 0.29	4.20 ± 0.30		Graham et al. [1981]
AII107-65GGC	1-3	32°02'S	36°11'W	2795	33	45	2.31 ± 0.12			Jones et al. [1984]
AII107-67GGC	3-9	31°55'S	36°12'W	2587	32	47	2.40 ± 0.12	2.51 ± 0.58		Jones et al. [1984]
AII107-69GGC	4	31°40'S	36°01'W	2158	39	47	1.90 ± 0.03	1.68 ± 0.01		Jones et al. [1984]
AII107-71GGC	5-7	31°31'S	35°56'W	1887	49	43	2.99 ± 0.09	3.27 ± 0.47		Jones et al. [1984]
AII107-73GGC	3-5	31°25'S	35°53'W	1660	56	38	3.28 ± 0.03	3.61 ± 0.16		Jones et al. [1984]
AII107-124GGC	3-5	30°55'S	38°39'W	3800	77	9	3.36 ± 0.06			Jones et al. [1984]
AII107-131GGC	4	30°53'S	38°03'W	2925	34	43	2.37 ± 0.24			Jones et al. [1984]
AII107-142GGC	3-6	30°57'S	39°00'W	4148	120	-10	3.08			Jones et al. [1984]
AII107-144GGC	0-1	31°01'S	38°52'W	3988	105	-2	3.65 ± 0.04			Jones et al. [1984]
AII107-147GGC	3-5	30°49'S	38°31'W	3658	68	18	3.39 ± 0.08			Jones et al. [1984]
CHN82-4PG	0-3	41°43'N	32°51'W	3427	21	23	1.65 ± 0.01			Boyle and Keigwin [1985/86] <sup>d</sup>
CHN82-11PG	6-8	42°23'N	31°48'W	3209	19	23	1.70			Boyle and Keigwin [1982] <sup>d</sup>
CHN82-15PC	0-6	43°22'N	28°14'W	2151	14	30	2.11 ± 0.21			Boyle and Keigwin [1987]
CHN82-20PG	3-9	43°30'N	29°52'W	3020	18	24	1.60 ± 0.06			Boyle and Keigwin [1985/86]
DSDP-552A-1-1	7-9	56°03'N	23°14'W	2311	14	29	2.78 ± 0.22			Shackleton and Hall [1984]
EN66-36GGC	3-4	4°18'N	20°13'W	4270	49	7	2.53			Curry and Lohmann [1983]
KNR73-3PC	13-15	0°22'N	106°11'W	3606	150	-1	4.76 ± 0.05	5.55		Boyle and Keigwin [1985/86]
KNR73-4PC	5-7	10°51'N	110°16'W	3681	154	-4	3.93 ± 0.03	3.49		Boyle [1992]
KNR110-50GGC	0-2	4°52'N	43°12'W	3995	42	15	3.62			Curry and Lohmann [1990]
KNR110-55GGC	0-2	4°57'N	42°53'W	4556	106	-6	3.06 ± 0.11			Curry and Lohmann [1990]
KNR110-58GGC	7	4°48'N	43°20'W	4341	81	2	2.72 ± 0.05			Curry and Lohmann [1990]
KNR110-66GGC	7	4°34'N	43°23'W	3547	32	27	2.24 ± 0.04			Curry and Lohmann [1990]
ODP-658A-1H-1	18-20	20°45'N	18°35'W	2263	30	46	2.04 ± 0.21	1.69 ± 0.40		Sarnthein and Tiedemann [1989]
ODP-714A-1H-1	3-5	5°04'N	73°47'E	2195	132	17	5.38			Droxler et al. [1990]
ODP-806B-1H-1	3-5	0°19'N	159°22'E	2520	149	8	5.84			Berger et al. [1993]
ODP-851B-1H-1	8-10	2°46'N	110°34'W	3761	153	-3	5.09			Ravelo and Shackleton [1995]
ODP-883D-1H-1	3-5	51°12'N	167°46'E	2384	175	-5		4.11 ± 0.33		Keigwin [1995]
RNDB-GGC1	9-11	51°09'N	167°39'E	2393	175	-5		3.85 ± 0.23		Keigwin [1998]
V29-204	15-20	61°11'N	23°01'W	1849	11	39	1.22			Curry et al. [1999]
VINO-BC26	3-11	52°59'N	164°39'E	2960	171	-5		3.85		Keigwin [1998]
VINO-GGC37	3-7	50°25'N	167°44'E	3300	168	-5	3.65	4.27		Keigwin [1998]

<sup>a</sup>  $\text{ACO}_3^{2-}$  was recalculated from GEOSECS measurements of alkalinity,  $\Sigma\text{CO}_2$ , temperature, and salinity (see text).

<sup>b</sup> Reported Zn/Ca errors are  $\pm 1\sigma$  on means 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.

<sup>c</sup> Stratigraphy references indicate sources of data verifying that each core top is Holocene in age.

<sup>d</sup> Supplemented by our own unpublished stable isotope data.

respect to calcite, as *C. wuellerstorfi* Cd and Ba apparent partition coefficients are [McCorkle et al., 1995]. Figure 2b shows apparent  $D_{\text{Zn}}$  versus  $\Delta\text{CO}_3^{2-}$ ; in waters with  $\Delta\text{CO}_3^{2-}$  below  $\sim 25 \mu\text{mol kg}^{-1}$ ,  $D_{\text{Zn}}$  decreases with decreasing saturation. These data can be fitted with a simple two-part linear relationship, allowing us to predict  $D_{\text{Zn}}$  from  $\Delta\text{CO}_3^{2-}$ :

$$D_{\text{Zn}} = 0.15\Delta\text{CO}_3^{2-} + 5.25 \quad \Delta\text{CO}_3^{2-} < 25 \mu\text{mol kg}^{-1} \quad (4)$$

$$D_{\text{Zn}} = 9 \quad \Delta\text{CO}_3^{2-} > 25 \mu\text{mol kg}^{-1}. \quad (5)$$

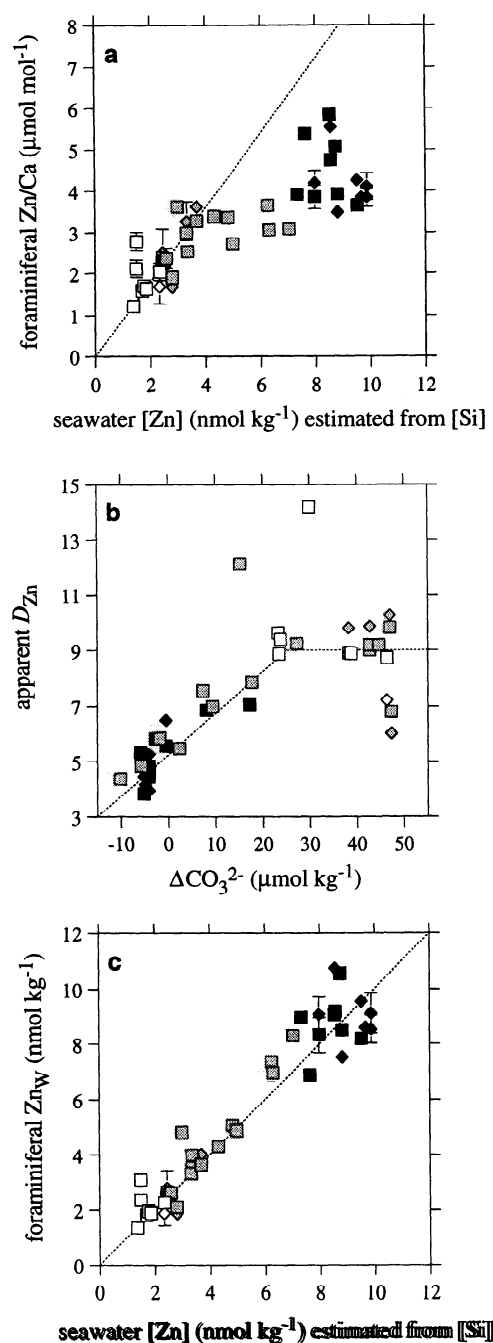
The true relationship is likely to be nonlinear, but the present data do not warrant anything more complex than two line segments. Such a simple relationship, which describes the data reasonably well, is preferable to a best fit, which would necessarily change with each new datum added to the calibration. The  $\Delta\text{CO}_3^{2-}$  effect on  $D_{\text{Zn}}$  appears to extend farther into supersaturated waters than for  $D_{\text{Cd}}$ ; combined Cd/Ca data from Boyle [1988, 1992], McCorkle et al. [1995], and our own

unpublished results suggest that  $D_{\text{Cd}}$  is related to  $\Delta\text{CO}_3^{2-}$  below roughly  $5 \mu\text{mol kg}^{-1}$ . Although we have not examined Ba/Ca in detail, the data compiled by McCorkle et al. [1995] imply that  $D_{\text{Ba}}$  may be affected over a range of  $\Delta\text{CO}_3^{2-}$  similar to that observed for  $D_{\text{Zn}}$ . There is no additional relationship between  $D_{\text{Zn}}$  and water depth or temperature within the range of these data.

Once  $D_{\text{Zn}}$  is predicted from  $\Delta\text{CO}_3^{2-}$ , it can be applied to foraminiferal Zn/Ca to yield an inferred seawater Zn concentration:

$$\text{Zn}_{\text{w}} = [(\text{Zn/Ca})_{\text{foram}} / D_{\text{Zn}}] [\text{Ca}]_{\text{seawater}}. \quad (6)$$

Applying this conversion to the core top data (in a somewhat circular fashion) increases the correlation between foraminiferal and seawater data significantly ( $r^2=0.92$ ; Figure 2c). The remaining scatter in this relationship may be due to uncertainties in estimating bottom water Si and  $\Delta\text{CO}_3^{2-}$  from GEOSECS data,

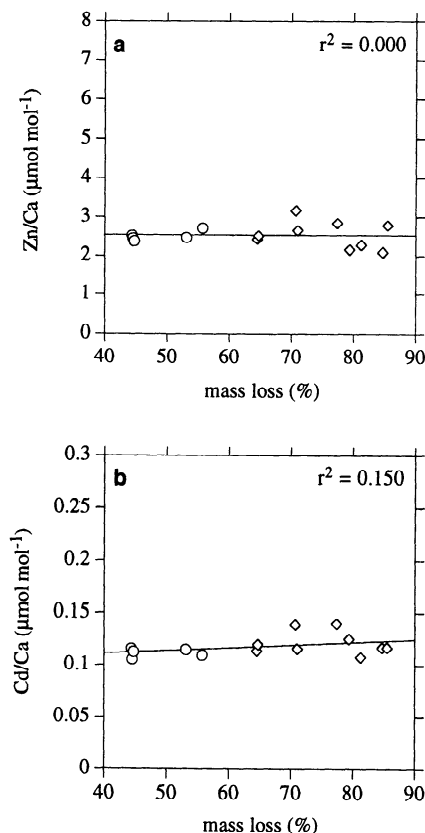


**Figure 2.** (opposite) (a) Zn/Ca ratios in Holocene benthic foraminifera *C. wuellerstorfi* (squares) and *Uvigerina* spp. (diamonds), versus bottom water dissolved Zn concentrations estimated from nearby GEOSECS dissolved Si measurements and the global deep water Zn:Si linear relationship shown in 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  $\pm 1\sigma$  of replicates. Dotted line represents the relationship for waters in which the apparent partition coefficient for Zn into benthic foraminiferal calcite ( $D_{\text{Zn}}$ ) appears to be unaffected by  $\Delta\text{CO}_3^{2-}$ , i.e.,  $D_{\text{Zn}} = 9$  (estimated from Figure 2b). (b) Apparent  $D_{\text{Zn}}$  of the samples in Figure 2a versus  $\Delta\text{CO}_3^{2-}$  calculated from GEOSECS 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 ( $D_{\text{Zn}} = 18.6$ ,  $\Delta\text{CO}_3^{2-} = 28$ ). (c) Foraminiferal  $\text{Zn}_w$ , calculated using  $D_{\text{Zn}}$  derived from the linear relationship in Figure 2b, versus seawater dissolved Zn estimated from GEOSECS Si. Symbols are as in Figure 2a. Dotted line is the 1:1 line, not the best fit.

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  $\Delta\text{CO}_3^{2-}$  levels.

### 3.2. $\Delta\text{CO}_3^{2-}$ Effect in Live *C. wuellerstorfi*

The observed drops in apparent  $D_{\text{Zn}}$ ,  $D_{\text{Cd}}$ , and  $D_{\text{Ba}}$  in low- $\Delta\text{CO}_3^{2-}$  waters may be due to decreased incorporation of these trace metals during growth or to post mortem preferential dissolution of trace metals over Ca [McCorkle *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



**Figure 3.** Results of a progressive dissolution experiment using *Uvigerina* spp. from core AII107-67GGC (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.

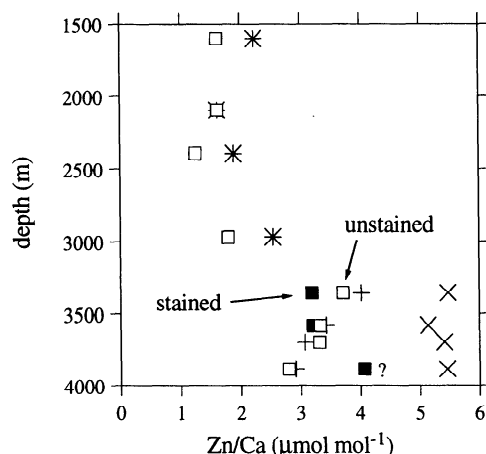
dissolution-prone phase. It is conceivable, however, that dissolution at the seafloor is more effective at selecting for trace metals than the rapid dissolution that occurs in the laboratory. Therefore a better test to distinguish between decreased incorporation and post mortem dissolution is to look for the  $\Delta\text{CO}_3^{2-}$  effect in living benthic foraminifera. This strategy has been used to infer that  $\Delta\text{CO}_3^{2-}$  influences the fractionation of  $^{13}\text{C}$  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  $\Delta\text{CO}_3^{2-}$  values of the waters overlying these sites range from -3 to 47  $\mu\text{mol kg}^{-1}$ . Figure 4 shows the Zn/Ca values predicted from bottom water Si, using a constant  $D_{\text{Zn}}$  of 9 (crosses) and  $D_{\text{Zn}}$  that varies with  $\Delta\text{CO}_3^{2-}$  according to equations (4) and (5) (pluses). Unstained *C. wuellerstorfi* clearly show the  $\Delta\text{CO}_3^{2-}$  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 ( $<2\sigma$  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  $\Delta\text{CO}_3^{2-}$  and the various apparent 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:

$$D_{\text{ideal}} = K_{\text{sp(calcite)}}/K_{\text{sp(metal carbonate)}}, \quad (7)$$

where  $D_{\text{ideal}}$  is a true thermodynamic distribution coefficient and



**Figure 4.** Zn/Ca in Rose 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  $D_{\text{Zn}}$  of 9, while pluses use  $D_{\text{Zn}}$  that varies with  $\Delta\text{CO}_3^{2-}$  (equations (4) and (5)). The predicted values coincide in waters with  $\Delta\text{CO}_3^{2-} > 25 \mu\text{mol kg}^{-1}$ . Sample marked with a question mark was by far the smallest ( $[\text{Ca}] = 3.8 \text{ mM}$ , compared to mean of 17.5 mM) and may be elevated by a slight laboratory Zn contamination.

$K_{\text{sp}}$  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 exchanging cations in solution and in the solid phase. For example, Crockett 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  $\text{Ca}^{2+}$  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  $\Delta\text{CO}_3^{2-}$ ) 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  $\alpha$  is  $>1$  and  $D_{\text{Zn}}$  and  $D_{\text{Cd}}$  decrease with decreasing  $\Delta\text{CO}_3^{2-}$ . It may also be consistent with McCorkle et al.'s [1995] Ba/Ca data if the biomineralization reservoir contains significantly less Ba than seawater, resulting in an  $\alpha > 1$  despite measured  $D_{\text{Ba}}$  values  $<1$  [Lea and Boyle, 1989].

### 3.3. Application to Paleooceanography

On glacial-interglacial timescales a given core location may fall into one of three  $\Delta\text{CO}_3^{2-}$  categories: (1)  $\Delta\text{CO}_3^{2-}$  always remains above ~25  $\mu\text{mol kg}^{-1}$ , so neither Zn/Ca nor Cd/Ca are affected by saturation state; (2)  $\Delta\text{CO}_3^{2-}$  falls below ~25  $\mu\text{mol kg}^{-1}$  but remains above roughly 5  $\mu\text{mol kg}^{-1}$ , so only Zn/Ca is affected; or (3)  $\Delta\text{CO}_3^{2-}$  falls below ~5  $\mu\text{mol kg}^{-1}$ , and both Zn/Ca and Cd/Ca are affected. Calcite lysocline reconstructions suggest that LGM [ $\text{CO}_3^{2-}$ ] was on the order of 5-10  $\mu\text{mol kg}^{-1}$  higher than today in the deep Pacific and ~10  $\mu\text{mol kg}^{-1}$  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  $\text{Zn}_w$  and  $\text{Cd}_w$ . 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,  $\text{Cd}_w$  (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  $[\text{Zn}]$  is predicted, it could be combined with observed foraminiferal Zn/Ca to yield estimates of  $\Delta\text{CO}_3^{2-}$ . Paleo- $\Delta\text{CO}_3^{2-}$  values are easily converted to  $[\text{CO}_3^{2-}]_{\text{in situ}}$  by calculating  $[\text{CO}_3^{2-}]_{\text{saturation}}$ ,

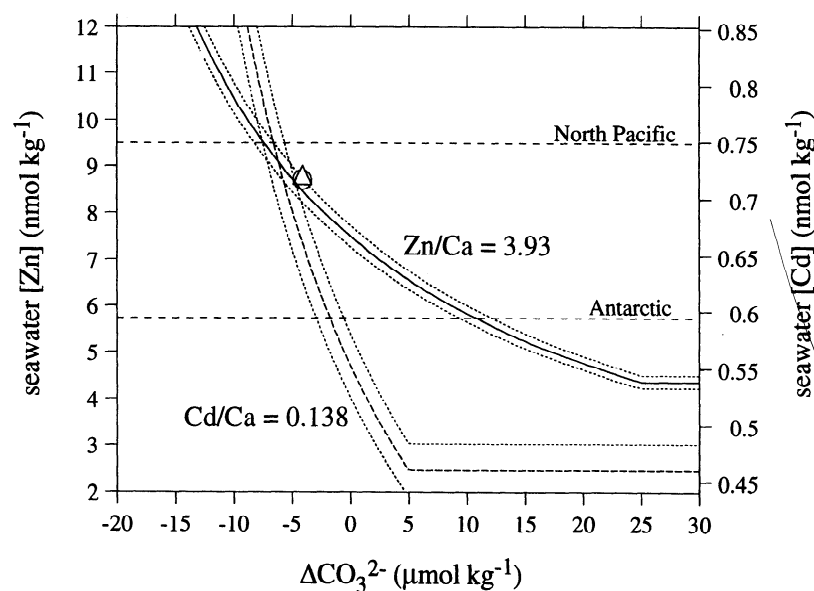
which is a function of pressure, temperature, and salinity, and predicted to change little with time in the deep ocean.

New constraints on paleo- $\text{CO}_3^{2-}$  are important for understanding the cycling of  $\text{CO}_2$  between the atmosphere and ocean and also the preservation of  $\text{CaCO}_3$  in marine sediments. Lysocline-based estimates could be inaccurate if significant glacial  $\text{CaCO}_3$  dissolution occurred within  $\text{CO}_2$ -rich pore waters [e.g., Emerson and Bender, 1981; Archer and Maier-Reimer, 1994]. Paleo-pH estimates based on benthic foraminiferal boron isotopes ( $\delta^{11}\text{B}$ ) imply that deep Pacific  $[\text{CO}_3^{2-}]$  was actually  $\sim 100 \mu\text{mol kg}^{-1}$  higher than today [Sanyal et al., 1995]. This estimate is large enough to explain the entire LGM atmospheric  $\text{CO}_2$  drop via an increase in ocean alkalinity [Broecker and Peng, 1987; Archer and Maier-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  $\text{CaCO}_3 > 63 \mu\text{m}$  can be used as a proxy for paleo- $\Delta\text{CO}_3^{2-}$ , but this index is also subject to the complications of pore water dissolution.

$\Delta\text{CO}_3^{2-}$  case (3), which probably holds for much of the Pacific deeper than  $\sim 3000 \text{ m}$ , is the most complex situation because both  $D_{\text{Zn}}$  and  $D_{\text{Cd}}$  are affected. In theory, however, seawater  $[\text{Zn}]$ ,  $[\text{Cd}]$ , and  $\Delta\text{CO}_3^{2-}$  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  $\Delta\text{CO}_3^{2-}$  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  $\Delta\text{CO}_3^{2-}$  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 tielines: Antarctic deep water entering the South Pacific with estimated  $[\text{Zn}] = 5.7 \text{ nmol kg}^{-1}$  and  $[\text{Cd}] = 0.59 \text{ nmol kg}^{-1}$  and northeast Pacific deep water with estimated  $[\text{Zn}] = 9.5 \text{ nmol kg}^{-1}$  and  $[\text{Cd}] = 0.75 \text{ nmol kg}^{-1}$  [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  $\Delta\text{CO}_3^{2-}$  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.  $\Delta\text{CO}_3^{2-}$  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  $\Delta\text{CO}_3^{2-}$ ; 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.** Plot showing the combinations of seawater dissolved Zn, Cd, and  $\Delta\text{CO}_3^{2-}$  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  $D_{\text{Zn}}/\Delta\text{CO}_3^{2-}$  relationship is given by equations (4) and (5). The preliminary  $D_{\text{Cd}}/\Delta\text{CO}_3^{2-}$  relationship for sites deeper than 3000 m ( $D_{\text{Cd}} = 0.1\Delta\text{CO}_3^{2-} + 2.5$  (below  $\Delta\text{CO}_3^{2-} = 5 \mu\text{mol kg}^{-1}$ ) and  $D_{\text{Cd}} = 3$  (above  $\Delta\text{CO}_3^{2-} = 5 \mu\text{mol kg}^{-1}$ )) is mainly based upon previously published data [Boyle, 1988, 1992; McCorkle et al., 1995] and subject to change as more high-quality core top data are analyzed. The ordinates are scaled to each other using tielines (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 ( $\pm 0.12 \mu\text{mol mol}^{-1}$  for Zn/Ca and  $\pm 0.007 \mu\text{mol mol}^{-1}$  for Cd/Ca). Uncertainties in the equations relating partition coefficients to  $\Delta\text{CO}_3^{2-}$  may introduce additional error. Also plotted for comparison are estimated values of dissolved Zn (triangle), Cd (circle), and  $\Delta\text{CO}_3^{2-}$  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 would be distinguishable from  $\Delta\text{CO}_3^{2-}$  changes because their spatial influences on benthic foraminifera would be very different. Eventually whole-ocean corrections might be applied, such as that used for  $\delta^{13}\text{C}$  during the LGM [Duplessy et al., 1988]. Only then could reliable paleo- $\Delta\text{CO}_3^{2-}$  and paleo- $[\text{CO}_3^{2-}]$  estimates be made. Even without a detailed assessment of the LGM oceanic Zn inventory, a  $\text{CO}_3^{2-}$  increase of the magnitude proposed by Sanyal et al. [1995] ( $\sim 100 \mu\text{mol kg}^{-1}$ ) 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, 1986; Lea and Boyle, 1989, 1990; McCorkle

et al., 1995], while  $\delta^{13}\text{C}$  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  $\text{CO}_2$  levels.

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W. B. Curry and D. W. Oppo, Woods Hole Oceanographic Institution, Woods Hole, MA 02543.

T. M. Marchitto Jr., Lamont-Doherty Earth Observatory, New Core Lab 204a, Route 9W, Palisades, NY 10964. (tmarchit@ldeo.columbia.edu)

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