Evidence of a dissolution effect on benthic foraminiferal shell chemistry: $\delta^{13}C$, Cd/Ca, Ba/Ca, and Sr/Ca results from the Ontong Java Plateau

Daniel C. McCorkle

Department of Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

Pamela A. Martin and David W. Lea

Department of Geological Sciences and Marine Science Research Institute, University of California, Santa Barbara

Gary P. Klinkhammer

College of Oceanography, Oregon State University, Corvallis

Abstract. Core-top benthic foraminifera (*Cibicidoides wuellerstorfi*) from a depth transect of Soutar box cores from the Ontong-Java Plateau (1.6 - 4.4 km) were analyzed for cadmium, barium, and strontium (Cd/Ca, Ba/Ca, and Sr/Ca) and for their stable isotopic composition ($\delta^{13}C$ and $\delta^{18}O$). We also measured bottom water $\delta^{13}C$, Cd, and Ba at these sites. Foraminiferal $\delta^{13}C$ values remain roughly constant over the entire depth range while bottom water $\delta^{13}C$ values increase slightly, such that the $\delta^{13}C$ difference between *C. wuellerstorfi* and bottom water ranges from about +0.2 ‰ in cores above 2.5 km to about -0.2 ‰ in cores below 4 km. This apparent depth dependence has not been previously reported, but this range in $\Delta\delta^{13}C$ values is comparable to the uncertainty in published $\delta^{13}C$ calibration studies. We observe strong decreases in foraminiferal Cd/Ca, Ba/Ca, and Sr/Ca ratios (50, 25, and 15 percent, respectively) at water depths greater than about 2.5 km. These decreases are substantially larger than the corresponding changes in bottom water trace element concentrations, and they are not correlated with variations in pore water Cd and Ba concentrations at these sites. Together, the foraminiferal and bottom water Cd/Ca, Ba/Ca, and Sr/Ca data yield decreases in the apparent distribution coefficients for these metals into calcite with increasing water depth, again a pattern which has not been previously reported. These results when combined with the data from published core-top calibration studies suggest that a preferential loss of Cd, Ba, and Sr occurs during the dissolution of benthic foraminiferal calcite on the sea floor and raise the possibility of a dissolution-driven decrease in benthic foraminiferal $\delta^{13}C$ values.

Introduction

Isotopic and elemental studies of foraminiferal calcite are widely used to reconstruct changes in deep water circulation patterns and rates on glacial-interglacial time scales [e.g., *Shackleton*, 1977; *Boyle and Keigwin*, 1985/1986; *Duplessy et al.*, 1988; *Curry et al.*, 1988; *Boyle*, 1992; *Lea and Boyle*, 1990a; *Lea*, 1993]. Such reconstructions provide a quantitative picture of changes in ocean circulation and chemistry and are used to constrain and test models of the ocean's role in climate change. Three tracers have received particular attention in paleochemical studies: $\delta^{13}C$, cadmium, and barium. The carbon isotopic composition of deep water reflects both the initial ("preformed") $\delta^{13}C$ of newly formed deep water and the release of ^{13}C-depleted CO_2 during organic matter decomposition [*Kroopnick*, 1985; *Charles and Fairbanks*, 1990;

Broecker and Maier-Reimer, 1992; *Lohmann et al.*, Reassessment of the influence of temperature on the distribution of ^{13}C in the upper ocean, submitted to *Paleoceanography*, 1994]. Cadmium exhibits a water column distribution similar to the nutrient elements P and N, with near-zero concentrations in surface waters and a strong Atlantic - Pacific deep water increase [*Boyle et al.*, 1976; *Bender and Gagner*, 1976; *Bruland et al.*, 1978; *Boyle*, 1988]. Barium also has low concentrations in low-nutrient surface waters, but its depth profile typically shows a deeper maximum than do Cd, N, and P [*Chan et al.*, 1977; *Lea and Boyle*, 1989; *Lea*, 1993]. Although the barium flux to the sea floor is thought to be dominated by barite ($BaSO_4$) [*Bishop*, 1988; *Dymond et al.*, 1992] (see also *Bernstein et al.* [1992]), the dissolved Ba distribution pattern is similar to that of alkalinity.

Another elemental tracer recorded in foraminiferal shells is Sr. In the modern ocean, strontium is present in an essentially fixed ratio to calcium, although slight upper ocean Sr depletions have been observed [*Bernstein et al.*, 1992; *de Villiers et al.*, 1994]. As a result, planktonic foraminiferal Sr/Ca ratios

have been used to infer changes in the whole ocean mass balances of Sr and Ca [*Graham et al.*, 1982].

Calibration studies have been carried out for each proxy, generally based on comparison of the isotopic or elemental composition of core-top benthic foraminifera with measured or estimated bottom water composition. Carbon isotope calibration studies [e.g., *Graham et al.*, 1981; *Belanger et al.*, 1981; *Duplessy et al.*, 1984; *McCorkle and Keigwin*, 1994] have shown that the $\delta^{13}C$ values of the benthic foraminifera *C. wuellerstorfi* are approximately equal to the $\delta^{13}C$ of bottom water dissolved inorganic carbon (DIC), presumably as a result of a constant isotopic offset ("vital effect") between the test calcite of this species and calcite in equilibrium with bottom water DIC [*Woodruff et al.*, 1980; *Grossman*, 1984; *Mackensen and Douglas*, 1989; *McCorkle et al.*, 1990]. The most extensive core-top $\delta^{13}C$ calibration [*Duplessy et al.*, 1984] shows that *Cibicides* $\delta^{13}C$ values are on average 0.07 ± 0.15 ‰ higher than bottom water DIC. These studies also document substantial interspecies $\delta^{13}C$ differences (including a nearly 1 ‰ offset between *C. wuellerstorfi* and *U. peregrina*) which are thought to reflect a combination of microhabitat and vital effects. Just over half of the 87 cores in the *Duplessy et al.* [1984] data set are from the Atlantic, and about one quarter each are from the Indian and Pacific; about a quarter of the 87 are from shallower than 2 km.

The calibration data set for cadmium [*Boyle*, 1988; 1992] is about the same size as the $\delta^{13}C$ data set of *Duplessy et al.* [1984]. About a quarter of the 81 cores are from shallower than 2 km; half are from the Atlantic, and most of the rest from the Pacific. The original Cd/Ca calibration data set, based largely on deep water cores, suggested a constant relationship between foraminiferal Cd/Ca and the Cd concentration of bottom water, with an apparent distribution coefficient (D(Cd) = (Cd/Ca)foram / (Cd/Ca)bottom water) of about 2.9 [*Boyle*, 1988]. This value did not show any significant interspecies differences between the four taxa analyzed (*C. wuellerstorfi, C. kullenbergi, Uvigerina peregrina*, and *Nutallides umbonifer*). *Boyle* [1992] added a substantial number of

shallower core tops to the calibration data set and observed an apparent depth-dependence of D(Cd); cores from less than 1 km gave D(Cd) values of about 1.3, while the data from greater than 3 km indicated a D(Cd) of about 2.9.

The barium calibration data set is the smallest of the three [*Lea and Boyle*, 1989; *Lea*, 1993]. Four of the 50 cores are from shallower than 2 km; 36 are from the Atlantic, 12 from the Pacific, and two from the Indian Ocean. The initial Ba calibration study reported that the apparent distribution coefficient for barium (D(Ba)= (Ba/Ca)foram / (Ba/Ca)bottom water) is 0.37 for *C. wuellerstorfi*, with only minor (± 10%) differences for the other two taxa studied (*C. kullenbergi* and *Uvigerina* spp.) [*Lea and Boyle*, 1989].

The apparent distribution coefficient for strontium in calcitic planktonic foraminifera (D(Sr) = (Sr/Ca)foram / (Sr/Ca)bottom water) is about 0.16 [*Bender et al.*, 1975; *Delaney et al.*, 1985]. There has not yet been a global calibration using core top benthic foraminifera, but recent data suggest somewhat higher D(Sr) values and a temperature- or pressure-related effect which lowers D(Sr) with increasing water depth [*Rosenthal*, 1994; *Lloyd-Kindstrand et al.*, 1994]. The data also suggest that species-specific fractionation occurs. For instance, *U. peregrina* D(Sr) values are systematically lower than those of other species.

Study Area

Samples were collected in 1991 on cruise 91-9 of R/V *Moana Wave* to the Ontong-Java Plateau (OJP) in the western equatorial Pacific Ocean (Table 1 and Figure 1). A bathymetric transect of Soutar box cores and 4.5 inch (≈11.4 cm) diameter gravity cores was collected from water depths of 1615 m to 4440 m. The shallowest stations were at 1 to 2 °S, and the remainder were right on the equator. This cruise track closely followed previous coring work on the Ontong-Java Plateau, which was discussed by *Berger and Killingley* [1977] and more recently by *Herguera et al.* [1992]. The surface ocean productivity is low in this region [*Berger et al.*,

Table 1. Station Locations and Measured Bottom Water Concentrations

| Core	Depth, km	Latitude	Longitude	Oxygen, μmol/L	Nitrate, μmol/L	$\delta^{13}C$, ‰	Cadmium, nmol/L	Barium, nmol/L
BC 7	1.614	2° 10.75' S	157° 00.08' E	112.9	39.3	0.21	0.83	120
BC 3	1.616	2° 14.56' S	156° 59.87' E	112.9	39.1	0.63	0.84	119
BC 33	2.015	0° 59.86' S	157° 50.92' E	118.7	38.2	0.30	0.91	122
BC 13	2.301	0° 00.48' S	158° 54.77' E	124.5	40.8	0.29	0.92	135
BC 37	2.445	0° 00.28' N	159° 29.03' E	130.4	38.9	0.29		147
BC 16	2.959	0° 00.83' N	160° 27.10' E	136.2	39.3	0.30	0.82	139
BC-22	2.965	0° 01.45' N	160° 27.28' E	136.2	39.6	0.46		
BC 63	3.158	0° 00.83' N	160° 38.39' E	139.1	38.1	0.28	0.78	153
BC 59	3.393	0° 00.12' S	160° 00.04' E	144.0	36.3	0.47		144
BC 47	3.426	0° 01.01' S	161° 01.32' E	145.9	38.2	0.50	0.89	146
BC 53	3.711	0° 00.53' S	161° 23.32' E	145.9	37.4	0.56		136
BC 54	4.025	0° 00.80' S	161° 46.21' E	154.7	38.0	0.39		132
BC 56	4.041	0° 00.06' S	161° 47.39' E					
BC 58	4.341	0° 00.08' S	162° 13.41' E	167.3	35.0	0.51	0.88	124
BC 74	4.438	0° 00.04' N	162° 44.08' E	178.0	35.0	0.41	0.80	129
BC 66	4.440	0° 00.26' S	162° 42.28' E	180.0	35.9	0.49	0.84	124
BC 70	4.444	0° 00.90' S	162° 38.31' E	179.0	35.5	0.42		128
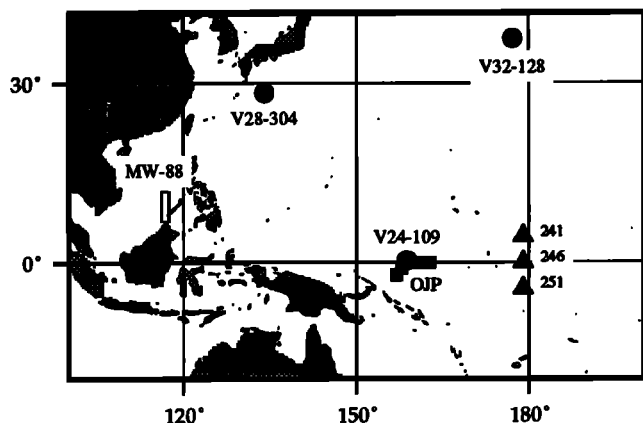
Figure 1. Location map of the Western Pacific Ocean, showing the Ontong-Java Plateau (OJP) cores (filled squares) and the Geochemical Ocean Sections Study (GEOSECS) stations used for comparison (numbered triangles). Locations of western Pacific cores from previous calibration studies are shown as solid circles [*Boyle*, 1988, 1992; *Duplessy et al.*, 1984; *Lea and Boyle*, 1989]; the large open box encompasses the locations of the South China Sea (MW-88) cores from *Boyle* [1992]. OJP core locations are listed in Table 1.

1987], as are benthic carbon fluxes [*Jahnke et al.*, 1994; W.R. Martin and D.C. McCorkle, unpublished pore water data, 1993]. Bulk sediment accumulation rates range from 0.6 to 2.2 cm/ky [*Berger et al.*, 1982]. The nearest Geochemical Ocean Sections Study (GEOSECS) stations with $\delta^{13}C$ data are stations 241, 246, and 251, and the nearest station with barium data is 241 (Figure 1). There are only modest changes in bottom water chemistry over the depth range of the OJP (Figure 2). The calcite saturation horizon lies near 3 km, and above this depth (from 1.6 to 3 km) the bottom water is within a few micromoles per kilogram of saturation [*Broecker et al.*,

1982]; strong carbonate dissolution is observed in deep cores from this region [*Berger et al.*, 1982].

Methods

At each core location, bottom water was collected using a small Niskin bottle mounted vertically on the box corer frame about 1.5 m above the bottom of the frame and rigged to close when the frame hit the bottom. Bottom water trace metal samples were collected directly from the Niskin spigot into acid-cleaned polypropylene vials. These samples were then acidified (5 µL quartz-distilled HCl per milliliter of sample) in a portable laminar flow bench in the ship's lab. Bottom water $\delta^{13}C$ samples were filtered into prepoisoned N_2-flushed borosilicate ampules and sealed for analysis on shore using methods developed for pore water $\delta^{13}C$ analysis [*McCorkle et al.*, 1985, 1990; *McCorkle and Keigwin*, 1994]. Bottom water nitrate (colorimetric) and oxygen (titration) concentrations were determined on board the ship with a precision of approximately ± 2 % and ± 1.5 % respectively [*Jahnke et al.*, 1994].

The dissolved inorganic carbon samples were extracted on a vacuum line and quantified manometrically with a precision of ± 0.25 %, based on 16 sets of replicates. The $\delta^{13}C$ values were then determined using the VG Micromass isotope ratio mass spectrometer in L. Keigwin's lab at Woods Hole Oceanographic Institution (WHOI). This instrument is equipped with triple collectors and a high-sensitivity source. Isotope ratios are reported relative to Pee Dee belemnite (PDB), based on National Bureau of Standards carbonate standards (NBS-19) run with each set of samples. Precision of these isotopic determinations (including sample collection and extraction) is ± 0.07 ‰, based on replicate samples. The bottom water and pore water Cd were determined by graphite furnace atomic absorption spectroscopy following preconcentration of a 1.0-mL sample by ammonium 1-pyrrolidine-
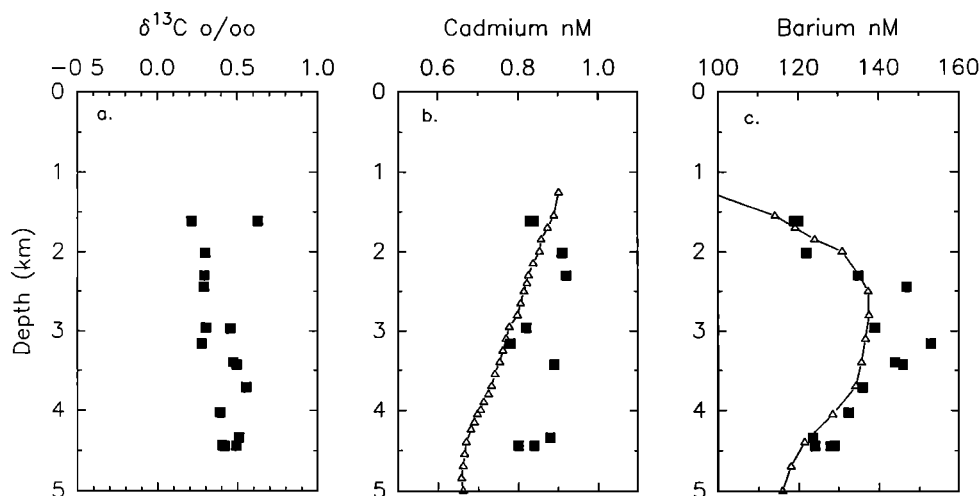

Figure 2. (a) Bottom water $\delta^{13}C$, (b) cadmium, and (c) barium concentrations on the Ontong Java Plateau (large solid squares). The Cd profile calculated from GEOSECS station 241 phosphate data and the Cd:P relationship of *Boyle* [1988] is shown by the connected open triangles in Figure 2b. The GEOSECS-derived Cd values are used for subsequent comparisons with the foraminiferal Cd/Ca data. The Ba profile from GEOSECS station 241 is shown by the connected triangles in Figure 2c. We use these GEOSECS Ba concentrations for comparison with foraminiferal Ba/Ca values.

dithiocarbamate coprecipitation [*McCorkle and Klinkhammer*, 1991]. Bottom water and pore water Ba concentrations were determined by isotope dilution on a Fisons VG PlasmaQuad inductively coupled plasma mass spectrometer (ICP-MS) at Oregon State University [*Klinkhammer and Chan*, 1990]. We estimate an overall precision of ±5% for Cd and ±2% for Ba.

Core-top benthic foraminifera (*C. wuellerstorfi*, >250 μm for isotopic analyses, >150 μm for trace metal analyses) were picked from large samples of the top 2-3 cm of Soutar box cores. The foraminiferal stable isotope samples (2 to 10 individuals per analysis) were sonicated in methanol, roasted in vacuo at 370 °C, reacted with 100% H_3PO_4 at 90°C, and run on L. Keigwin's VG Micromass mass spectrometer. Foraminiferal isotope ratios are also reported relative to PDB, based on analysis of NBS-19 carbonate standards which were reacted with each set of samples. The precision of these foraminiferal isotopic analyses is better than ± 0.1 ‰, based on replicate samples.

Foraminiferal Cd/Ca, Ba/Ca, and Sr/Ca ratios were determined at University of California Santa Barbara. Foraminifera samples of 0.3 to 0.7 mg (5-40 individual shells) were purified of contaminating phases by a series of steps modified from the procedure described by *Lea and Boyle* [1993] (D.W. Lea and P.A. Martin, manuscript in preparation, 1995). After cleaning, 0.1 to 0.4 mg of purified foraminiferal shells were dissolved in 0.5 mL of a 1% HNO_3 solution containing calibrated amounts of ^{45}Sc, ^{89}Y, ^{111}Cd, and ^{135}Ba. The solutions were aspirated into a Fisons/VG PlasmaQuad 2+ via a Cetac ultrasonic nebulizer, and the $^{44}Ca/^{45}Sc$, $^{88}Sr/^{89}Y$ (low-sensitivity analog mode), $^{111}Cd/^{114}Cd$, and $^{135}Ba/^{138}Ba$ (high-sensitivity pulse mode) ratios were determined by peak jumping. The concentrations of Sr and Ca were calculated via internal standardization and Cd and Ba via isotope dilution. Mn is determined by reference to ^{45}Sc. Analytical reproducibility, based on consistency standards matched in concentration and matrix to the foraminifera solutions, is better than 2.4% for Ba/Ca and 3.3% for Cd/Ca (1σ). Cd accuracy is based on a plasma grade Cd standard (Aldrich); UCSB Cd determinations have not been intercalibrated with other laboratories measuring foraminiferal Cd/Ca. Reproducibility of Sr/Ca ratios, based on replicate analyses of foraminiferal samples, is better than 2% (1σ). Accuracy of the Sr/Ca values is based on plasma grade Sr and Ca standards (SPEX Industries). From one to five replicates were run for each core top, depending on sample size.

Results

Bottom Water Data

Bottom water $\delta^{13}C$ values increase slightly with increasing water depth (Table 1 and Figure 2a) [*McCorkle and Keigwin*, 1994]. Without the relatively high $\delta^{13}C$ value from BC-33 the trend is more pronounced, but the range of $\delta^{13}C$ values is still less than 0.3 ‰; we have no independent reason to reject the high BC-3 value at 1.6 km. *McCorkle and Keigwin* [1994] discuss the offset between these bottom water $\delta^{13}C$ values and the corrected GEOSECS $\delta^{13}C$ values from stations 241, 246, and 251 [*Kroopnick*, 1985]. Because the corrected GEOSECS values appear to be too low in this paper we will use only the bottom water $\delta^{13}C$ data from the OJP.

The bottom water cadmium data show no clear trend with depth (Table 1 and Figure 2b, squares). The ± 10% scatter in these data is about twice our analytical precision; it most likely reflects low-level contamination from some step in the sample collection procedure. Most of the bottom water Cd values are higher than we would predict from the GEOSECS station 241 phosphate concentrations and the global deep water Cd:P relationship of *Boyle* [1988] (Figure 2b, small triangles). This offset increases from 5-10 % above 3 km to 20-30 % at our deepest stations. In the remainder of this paper we will use the (lower) Cd concentrations estimated from interpolated GEOSECS phosphate values in order to yield conservative (minimum) estimates of the decrease in D(Cd) with water depth on the OJP.

Several of the OJP bottom water barium values (Figure 2c, squares) are 10 to 15 nmol/L higher than the GEOSECS station 241 barium profile (Figure 2c, triangles) [*Ostlund et al.*, 1987]. The elevated Ba concentrations do not correlate with high-Cd samples, so we think it unlikely that there is a common explanation (i.e., sediment resuspension) for both Cd and Ba flyers. We suspect that contaminant Ba was introduced into some samples during sample processing. For the calculations and discussion below we will use barium concentrations interpolated from the GEOSECS station 241 barium data, which will again provide conservative (minimum) estimates of the decrease in D(Ba).

Foraminiferal Stable Isotopes and Elemental Ratios

The *C. wuellerstorfi* $\delta^{18}O$ values show generally good agreement with the oxygen isotopic composition predicted from deep water temperature and $\delta^{18}O$ data (Table 2 and Figure 3). The predicted $\delta^{18}O$ values (lines in Figure 3) were estimated from GEOSECS temperature profiles using the *O'Neil et al.* [1969] expression for the $\delta^{18}O$ of calcite (as corrected by *Friedman and O'Neil* [1977]) and the *Shackleton and Opdyke* [1973] estimate of the $\delta^{18}O$ offset between *C. wuellerstorfi* and equilibrium calcite (−0.64 ‰). This agreement suggests that our core-top samples are not contaminated with high-$\delta^{18}O$ (glacial) individuals [*McCorkle and Keigwin*, 1994]. However, these $\delta^{18}O$ results do not demonstrate that our core-top OJP foraminiferal samples are Recent; they indicate only that the specimens lived after continental ice volume had returned to nearly its current value, 8 or 9 kyr B.P. We note that *Herguera et al.* [1992] observed elevated $\delta^{18}O$ values in OJP core-top *C. wuellerstorfi* samples from deeper than 3.5 km, which they attributed to the incorporation of early Holocene individuals.

The *C. wuellerstorfi* $\delta^{13}C$ values show a slight decrease with depth (Table 2, Figure 4a, large squares). These values are consistent with the results of previous studies on the OJP (small squares) [*Herguera et al.*, 1992] and with the western equatorial Pacific data from the *Duplessy et al.* [1984] calibration study (small triangles). The total range in core top $\delta^{13}C$ values on the OJP is comparable to the uncertainty in foraminiferal $\delta^{13}C$ values [e.g., *Duplessy et al.*, 1984; *McCorkle and Keigwin*, 1994].

In contrast to the $\delta^{13}C$ results, the Cd/Ca, Ba/Ca, and Sr/Ca data show strong decreases with increasing water depth (Table 2, Figures 4b, 4c, and 4d). Cd/Ca values drop by 50%, from about 0.19 μmol/mol at 2 km to just 0.09 μmol/mol at 4

Table 2. Foraminiferal Isotope and Elemental Data and Bottom Water Values Used for Comparisons

Core	Depth, km	Bottom water data			Foraminiferal data				
		$\delta^{13}C$, ‰	Barium,[a] nmol/L	Cadmium,[b] nmol/L	$\delta^{13}C$, ‰ $(\pm, n)^c$	$\delta^{18}O$, ‰ $(\pm, n)^c$	Cd/Ca, μmol/mol $(\pm, n)^c$	Ba/Ca, μmol/mol $(\pm, n)^d$	Sr/Ca, mmol/mol $(\pm, n)^d$
BC 7	1.614	0.21	115.3	0.883	0.39 (.11, 2)	2.75 (.31, 2)	0.174 (.016, 4)	3.50 (.15, 4)	1.36 (.03, 4)
BC 33	2.015	0.30	128.9	0.852	0.51 (.03, 2)	2.60 (.05, 2)	0.195 (.014, 5)	3.87 (.12, 5)	1.35 (.02, 5)
BC 13	2.301	0.29	135.0	0.826	0.53 (.02, 2)	2.59 (.03, 2)	0.176 (.011, 5)	3.70 (.20, 5)	1.31 (.02, 4)
BC 37	2.445	0.29	136.5	0.818	0.26 (.10, 2)	2.92 (.40, 2)	0.202 (.032, 5)	3.82 (.12, 5)	1.28 (.01, 5)
BC 16	2.959	0.30	136.9	0.778	0.43 (.06, 2)	2.58 (.04, 2)	0.183 (.022, 5)	3.63 (.27, 5)	1.24 (.02, 5)
BC 63	3.158	0.28	136.5	0.767	0.46	2.64	0.161 (.003, 2)	3.35 (.11, 2)	1.17 (.02, 2)
BC 59	3.393	0.47	135.6	0.754	0.41	2.49	0.160	3.42	1.23
BC 53	3.711	0.56	132.9	0.733	0.43	2.61	0.113 (.015, 2)	3.20 (.05, 2)	1.19 (.02, 2)
BC 56	4.041	0.39[e]	128.6	0.701	0.19	2.64	0.088 (.000, 2)	2.76 (.01, 2)	1.12 (.01, 2)
BC 58	4.341	0.51	124.6	0.674	0.35	2.76	0.091 (.003, 2)	2.76 (.12, 2)	1.16 (.07, 2)
BC 66	4.440	0.49	123.3	0.669	0.39	2.65	0.101 (.004, 3)	2.96 (.09, 3)	1.16 (.04, 3)

[a] Interpolated from GEOSECS Station 241 barium [*Ostlund et al.*, 1987].

[b] Estimated from interpolated GEOSECS Station 241 phosphate [*Broecker et al.*, 1982] assuming
Cd (nM) = {(0.4)×(P(μM))} - 0.25 [*Boyle*, 1988].

[c] Mean and standard deviation for analysis of "n" independent foraminiferal samples.

[d] Mean and standard deviation for "n" replicate analyses of 2 or 3 independent foraminiferal samples.

[e] Bottom water value from BC-54.

km. The Ba/Ca ratios drop by 25%, from roughly 3.7 μmol/mol at 2 km to 2.8 μmol/mol at 4 km. The Sr/Ca ratios drop by 15%, from about 1.35 mmol/mol at 2 km to about 1.15 mmol/mol at 4 km.

The bathymetric drop in metal:calcium ratios is striking, but careful inspection of the published core-top Cd/Ca and Ba/Ca data shows that these decreases are consistent with the existing calibration data sets. *C. wuellerstorfi* and *C. kullenbergi* Cd/Ca data from cores in the western tropical and subtropical Pacific [*Boyle*, 1988, 1992] are shown by the small symbols in Figure 4b. Though the deepest samples from these two studies are from about 3.5 km, they show the same decrease with depth (below about 2.5 km) which we observe. Low core-top Cd/Ca values are observed in many Pacific cores, including previous (unpublished) analyses of box cores from the Ontong-Java Plateau [*Boyle*, 1992; E. Boyle, personal communication, 1993]. There is little published Ba/Ca data from this region, and none from deeper than 3 km, but the two existing points (Figure 4c, small squares) [*Lea and Boyle*, 1989] match our new OJP data. The low Cd/Ca and Sr/Ca values we observe on the OJP are also confirmed by the results of C. Bertram and H. Elderfield, who independently picked and analyzed Cd and Sr on *C. wuellerstorfi* from separate sediment samples from the same OJP cores, as part of a

study of foraminiferal Sr/Ca and Mg/Ca ratios (C. Bertram and H. Elderfield, personal communication, 1994).

Distribution Coefficients and $\delta^{13}C$ Differences

These variations in foraminiferal shell composition are best considered in terms of $\delta^{13}C$ differences from bottom water and trace element apparent partition coefficients. There is reasonable agreement between the core-top foraminiferal $\delta^{13}C$ values and measured bottom water $\delta^{13}C$ values ($\Delta\delta^{13}C$ values ($\delta^{13}C$ foram - $\delta^{13}C$ bottom water) are within 0.2 ‰ of 0, Table 3, Figure 5a), but the $\Delta\delta^{13}C$ values clearly decrease with increasing water depth [*McCorkle and Keigwin*, 1994]. The foraminiferal values are slightly higher than bottom water (+0.15 ‰) at depths shallower than 2.5 km and slightly lower than bottom water (-0.15 to -0.2 ‰) at greater depths. While changes in foraminiferal $\delta^{13}C$ at the ± 0.1 or 0.2 ‰ level are small relative to the range of $\delta^{13}C$ values observed in the deep sea today, they are not negligible when compared to the average glacial-interglacial whole-ocean $\delta^{13}C$ shift of approximately 0.3 - 0.4 ‰. A similar $\Delta\delta^{13}C$ range but no depth dependence was observed in the NW Pacific (Emperor Seamounts) core tops studied by *McCorkle and Keigwin* [1994], but these samples spanned a smaller depth range (2.4
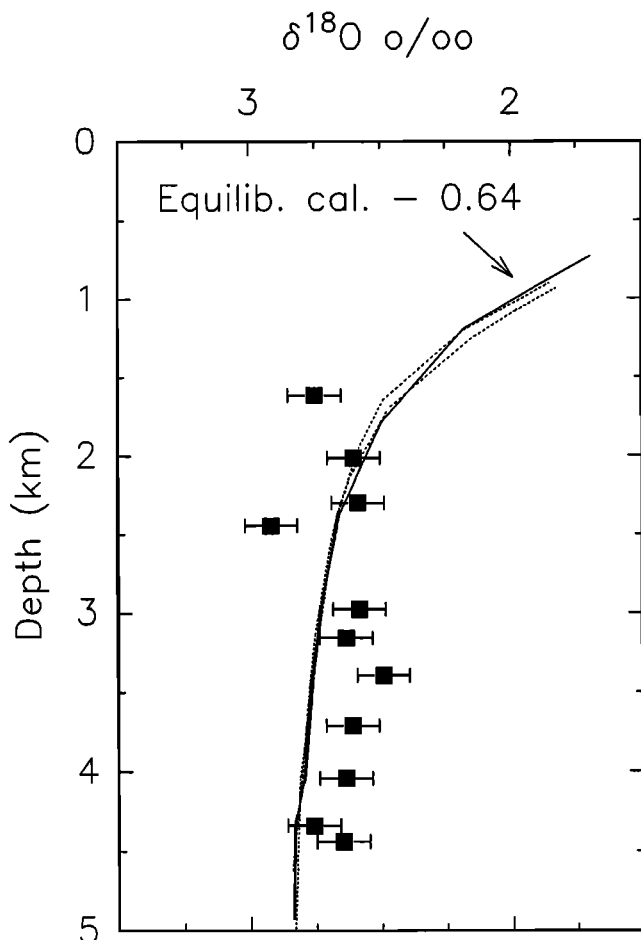
$\delta^{18}O$ o/oo

Figure 3. A comparison of $\delta^{18}O$ values from core-top *C. wuellerstorfi* (squares) with the *C. wuellerstorfi* $\delta^{18}O$ values predicted from bottom water temperature and $\delta^{18}O$(water) values from GEOSECS stations 241, 246, and 251 (lines). The predicted values are calculated using the corrected *O'Neil et al.* [1969] expression for the temperature dependence of the $\delta^{18}O$ of calcite [*Friedman and O'Neil*, 1977] and the *Shackleton and Opdyke* [1973] estimate (= −0.64 ‰) of the offset between *C. wuellerstorfi* and equilibrium calcite. The agreement suggests that the core-top foraminifera do not contain significant reworked glacial material [*McCorkle and Keigwin*, 1994].

to 3.8 km). The OJP $\delta^{13}C$ differences are barely larger than the scatter in the *Duplessy et al.* [1984] calibration data set (dotted lines in Figure 5a), but they show a trend which is qualitatively similar to the OJP trace element patterns.

The Cd/Ca, Ba/Ca, and Sr/Ca values in our core-top samples yield patterns of D(Cd), D(Ba), and D(Sr) which are quite different from previously published D values for these elements (Table 3, Figures 5b, 5c, and 5d). D values are calculated from measured foraminiferal elemental ratios and bottom water concentrations which were estimated as follows: Cd(nM) = 0.4 × P(μM)) - 0.25 (*Boyle* [1988] high-phosphate Cd:P relationship), with P values interpolated from the GEOSECS station 241 phosphate data; Ba was interpolated from the GEOSECS station 241 data; Sr was assumed to be 90 μM; and Ca was assumed to be 10.3 mM.

All three apparent distribution coefficients decrease with increasing water depth on the OJP, reflecting the decreases in foraminiferal Me/Ca ratios. D(Cd) (and perhaps $\Delta\delta^{13}C$) values show sharp decreases below about 3 km, while the D(Ba) and D(Sr) values exhibit a smoother decrease over the entire depth range of the OJP cores. The uncertainty in each $\Delta\delta^{13}C$ value is large (about ± 0.15 ‰), and only one or two points would have to shift to give a fairly linear $\Delta\delta^{13}C$ versus depth trend. The D(Cd) profile is complicated by the D(Cd) decrease above 3 km documented by *Boyle* [1992]. If the shallowest D(Cd) points have been affected by this effect they may make the deep D(Cd) decrease appear particularly steep. Because of these uncertainties, we will not try to account for the qualitative differences between the D versus depth profiles.

Previous studies have reported high and relatively constant values for benthic foraminiferal D(Cd) below about 3 km, with lower values above this depth [*Boyle*, 1992] (dashed lines in Figure 5b). Our OJP data from above 3 km are consistent with the 2-3 km D values reported by *Boyle* [1992], but we calculate deep water D(Cd) values which are roughly a factor of two (1.46/2.9) lower than the deep water average of the published data set.

The reported D(Ba) for *C. wuellerstorfi* is approximately 0.37 [*Lea and Boyle*, 1989] (dashed line in Figure 5c). We calculate D(Ba) values for *C. wuellerstorfi* which are lower than 0.37 at all depths; the difference is only about 15% above 2 km but increases to about 40% in the deepest cores.

The D(Sr) for foraminiferal calcite is approximately 0.16 (dashed arrow in Figure 5d), although this estimate is largely based on planktonic foraminifera [*Bender et al.*, 1975; *Graham et al.*, 1982; *Delaney et al.*, 1985]. These studies suggest that there is not a direct link between calcification temperature and D(Sr). However, calcification rate may be correlated with temperature and is known to influence D(Sr) in inorganic precipitation studies [*Lorens*, 1981]. Recently, Rosenthal [*Rosenthal*, 1994; *Lloyd-Kindstrand et al.*, 1994] showed that D(Sr) values from several *Cibicidoides* species decrease with increasing water depth. These studies point out that the decrease in D(Sr) is correlated with both decreasing temperature and increasing pressure and note that other factors (i.e., calcification rate) may also show similar correlations.

Discussion

In order to read the benthic foraminiferal record of changing bottom water composition with confidence, we need to understand the observed decreases in *C. wuellerstorfi* $\Delta\delta^{13}C$ and D values. The $\Delta\delta^{13}C$ variations on the OJP are of the same magnitude as the whole-ocean glacial-interglacial $\delta^{13}C$ shift, and the trace element variations are substantially larger than the glacial-interglacial changes in whole-ocean Cd, Ba, and Sr. We will discuss several possible explanations for the observed $\delta^{13}C$ and Me/Ca patterns, including pore water effects, mixing up of glacial foraminifera or temporal variations in bottom water chemistry during the Holocene, fractionation during biomineralization, and the preferential loss of ^{13}C and noncalcium cations from calcite during partial dissolution of the foraminiferal tests. Only the last two explanations, fractionation during calcification or preferential disso-
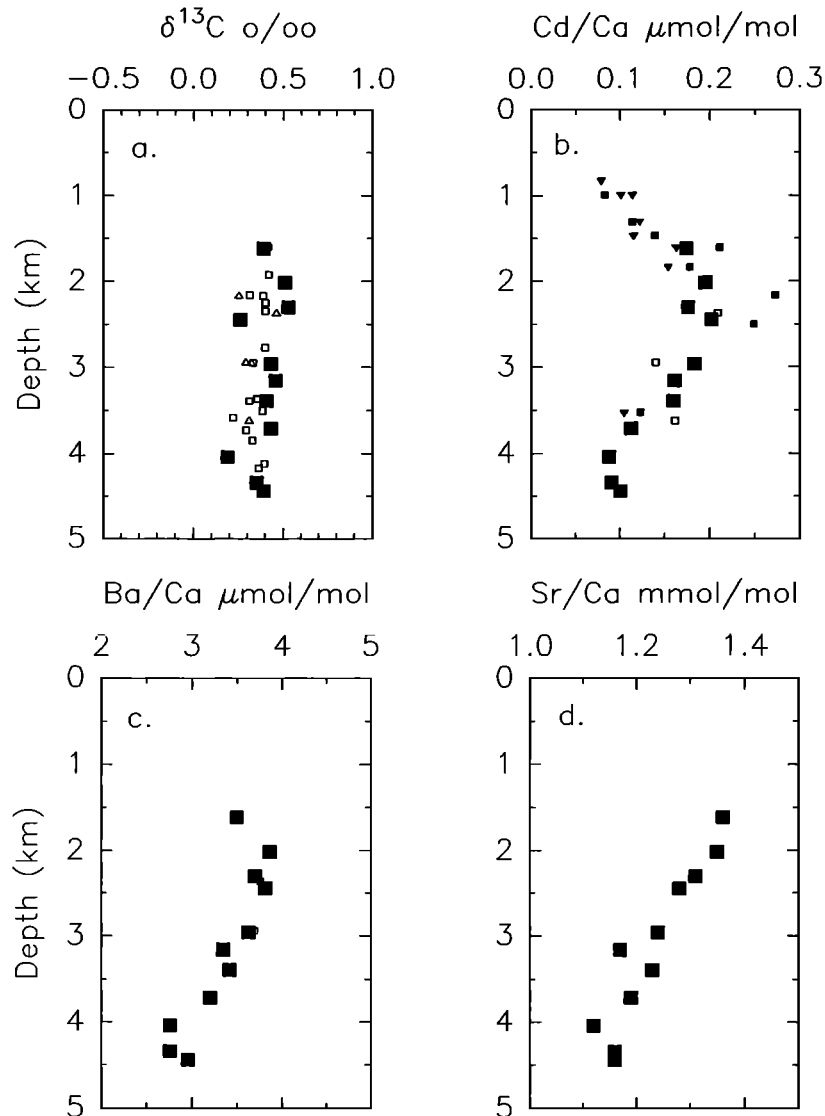
Figure 4. (a) The $\delta^{13}C$, (b) Cd/Ca, (c) Ba/Ca, and (d) Sr/Ca of core-top *C. wuellerstorfi* on the Ontong Java Plateau (large solid squares). Each of the three metal:calcium ratios shows a significant drop with increasing water depth, though the percent changes are different for each metal. The $\delta^{13}C$ data from this study show good agreement with the OJP core top *C. wuellerstorfi* data of *Herguera et al.* [1992] (small squares) and the western equatorial Pacific core-top *Cibicidoides* data of *Duplessy et al.*[1984] (small triangles) (Figure 4a). Our OJP core-top *C. wuellerstorfi* Cd/Ca data are consistent with the western Pacific *C. wuellerstorfi* (small squares) and *C. kullenbergi* (small triangles) data from the calibration studies of *Boyle* [1988, 1992] (Figure 4b). The solid small symbols in Figure 4b indicate the "documented Holocene" core-tops from *Boyle* [1988, 1992]. Our OJP Ba/Ca results are consistent with the two western Pacific core top Ba/Ca values from *Lea and Boyle* [1989] (small squares) (Figure 4c). We know of no other benthic foraminiferal Sr/Ca data from this region (Figure 4d).

lution, seem consistent with all of the available OJP benthic foraminifera data. The existence of similar depth-linked decreases in planktonic foraminiferal elemental ratios and a clear correlation between benthic foraminiferal D values and calcite saturation state lead us to favor the dissolution-based mechanism.

Pore Water Effects

C. wuellerstorfi are thought to be generally free from possible pore water influences on test composition [e.g., *Mack-*

ensen and Douglas, 1989; *McCorkle et al.*, 1990], although *Mackensen et al.* [1993, 1994] present evidence of a productivity-linked artifact in *Fontbotia wuellerstorfi* ($\approx$ *C. wuellerstorfi*) $\delta^{13}C$ values, which may be a consequence of low $\delta^{13}C$ values in the pore water of phytodetritus at the sediment-water interface. We see no evidence of pore water influences on the shell chemistry of *C. wuellerstorfi* on the OJP. Pore water $\delta^{13}C$ values are lower than bottom water at all sites, and none of the OJP cores exhibit pore water Cd or Ba concentrations lower than bottom water values (D.C.

Table 3. $\delta^{13}C$ Differences, Apparent Distribution Coefficients, and Calcite Saturation States

Core	Depth, km	$\Delta\delta^{13}C$ [a] cib-bw	D(Cd) [b]	D(Ba) [b]	D(Sr) [b]	ΔCO_3^{-2}, $\mu mol/kg$ [c]
BC 7	1.614	0.18	2.03	0.313	0.156	8.8
BC 33	2.015	0.21	2.36	0.309	0.154	10.3
BC 13	2.301	0.23	2.20	0.282	0.150	7.8
BC 37	2.445	-0.03	2.54	0.288	0.146	6.9
BC 16	2.959	0.13	2.42	0.273	0.142	2.9
BC 63	3.158	0.18	2.16	0.253	0.134	1
BC 59	3.393	-0.07	2.19	0.260	0.141	-3.3
BC 53	3.711	-0.12	1.59	0.248	0.136	-4.8
BC 56	4.041	-0.20	1.30	0.221	0.128	-7.1
BC 58	4.341	-0.16	1.39	0.228	0.133	-11.1
BC 66	4.440	-0.10	1.56	0.247	0.133	-9.8

[a] $\Delta\delta^{13}C$ cib-bw is the $\delta^{13}C$ difference between *C. wuellerstorfi* and bottom water.

[b] Calculated using GEOSECS Station 241 cadmium and barium (Table 2) and assuming bottom water [Sr] = 90 μM.

[c] CO_3^{-2} (in situ) - CO_3^{-2} (calcite saturation) for GEOSECS Station 241 from *Broecker et al.* [1982].

McCorkle and G.P. Klinkhammer, unpublished results, 1994). Pore water Sr concentrations increase over long depth scales on the OJP (through the top 100-200 meters) as a consequence of carbonate recrystallization [*Delaney and Linn*, 1993], and there is no reason to suspect low pore water Sr concentrations over the millimeter to centimeter depth scales relevant to *C. wuellerstorfi* calcification. In addition to these absolute concentrations, there is no trend of steeper $\delta^{13}C$ gradients or lower $\delta^{13}C$ values in the deeper cores, and the observed increases in pore water trace metal concentrations do not decrease with increasing water depth. We conclude that the observed decreases in foraminiferal Cd/Ca, Ba/Ca, and Sr/Ca ratios (and $\Delta\delta^{13}C$ and D values) are unlikely to be explained by pore water effects.

Mixing up of Glacial or Early Holocene Foraminifera

As noted above (Figure 3) there is no $\delta^{18}O$ evidence for contamination with glacial individuals, yet we observe core-top Cd/Ca and Ba/Ca values which are as low as or lower than previous estimates of glacial Cd/Ca and Ba/Ca in the Pacific Ocean [*Boyle*, 1992; *Lea and Boyle*, 1990a]. We cannot rule out the possibility that the low $\delta^{13}C$ values in the deep cores may reflect the presence of ^{13}C-depleted early Holocene specimens. To be consistent with such a "mixing up" explanation, the lowest core-top Cd/Ca and Ba/Ca values would require that essentially all of the core-top specimens were reworked and that early Holocene Cd and Ba concentrations

were as low as glacial values. This explanation would also require an uncoupling of bottom water $\delta^{13}C$ from Cd and Ba, since we observe slightly lower deep $\delta^{13}C$ values, rather than the higher $\delta^{13}C$ values which we would predict to be associated with substantially lower bottom water Cd and Ba. The core top Cd/Ca and Ba/Ca values which are below previous glacial estimates cannot be explained simply by bioturbation, unless the glacial Cd/Ca and Ba/Ca values on the OJP were lower than those elsewhere in the Pacific. Analysis of downcore (glacial) samples from our OJP cores will enable us to test this possibility, but we consider it an unlikely explanation. Strong Holocene Cd/Ca and Ba/Ca variations have not been reported in other Pacific Cd/Ca and Ba/Ca records [*Boyle*, 1992; *Lea and Boyle*, 1990a].

Sr and Ca both have long residence times in the ocean (millions of years), and the modern seawater Sr/Ca ratio is essentially constant from basin to basin and with depth in the water column. These long residence times make it unlikely that the deep water Sr/Ca ratio has varied on glacial - interglacial timescales, so we cannot attribute the observed *C. wuellerstorfi* Sr/Ca variations to mixing up of early Holocene specimens which recorded bottom water of a different Sr/Ca. Mixing up of early Holocene individuals could be invoked to explain the OJP foraminiferal Sr/Ca data if there are factors other than bottom water Sr/Ca which influence benthic foraminiferal Sr/Ca and which have changed through time.

Recrystallization or Addition of Low-Cd/Ba/Sr Calcite

Studies of long timescale diagenetic processes demonstrate that calcite recrystallization substantially lowers the carbonate Sr/Ca ratio [e.g., *Baker et al.*, 1981; *Elderfield et al.*, 1982; *Richter and Liang*, 1993]; the concentrations of minor trace elements (e.g. Cd and Ba) may also be altered by this process [*Pingitore and Eastman*, 1984]. However, the recrystallization rates which have been estimated from these studies of Deep Sea Drilling Project (DSDP) cores are many orders of magnitude too low (i.e., less than a few percent per million years) to explain the observed drop in core-top Me/Ca ratios on the OJP.

In principle the low Me/Ca values we observe could reflect the addition of calcite with low trace element concentrations. However, previous studies on the OJP demonstrate that dissolution intensity increases substantially with increasing water depth [e.g., *Berger et al.*, 1982], and it is hard to envision a way to accommodate both strong dissolution and substantial diagenetic $CaCO_3$ precipitation. At present, we have no data (e.g., scanning electron microscope studies of benthic foraminiferal wall thickness or shell mass/shell volume measurements) with which to evaluate this possibility directly.

Fractionation During Precipitation

The $\Delta\delta^{13}C$ and D patterns could be explained if *C. wuellerstorfi* fractionate against Cd, Ba, Sr, and ^{13}C in the deeper cores. We know of no previous report of depth-dependent $\delta^{13}C$ fractionation by benthic foraminifera. *Boyle* [1992] has reported a depth-linked increase in D(Cd) for *C. wuellerstorfi*, *C. kullenbergi*, *U. peregrina*, and *N. umbonifer* between 1 and 3 km. *Rosenthal* [1994] reported a depth-linked decrease in D(Sr) for *Cibicidoides* species between 0.3 and 1.5 km in

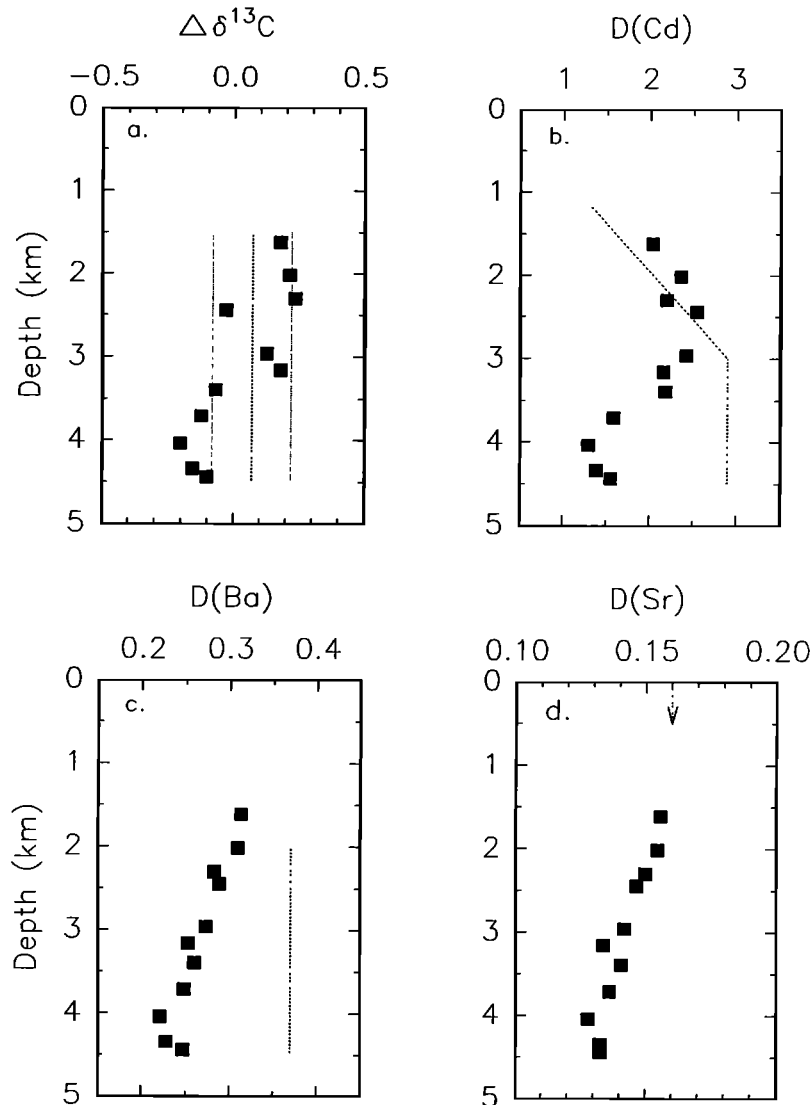**Figure 5.** (a) The $\delta^{13}C$ difference between *C. wuellerstorfi* and bottom water dissolved inorganic carbon (DIC) at each site ($\Delta\delta^{13}C$) decreases with depth (solid squares), but all points lie within 0.2 °/oo of the +0.07 (± 0.15 °/oo) global average $\Delta\delta^{13}C$ value reported by *Duplessy et al.* [1984] (dashed lines). (b) The calculated cadmium distribution coefficients at each site (D(Cd) = (Cd/Ca)foram /(Cd/Ca)b.w.) (solid squares) are consistent with the D(Cd) versus depth relationship from *Boyle* [1992] (dashed line) at sites shallower than 2.5 km, but the deeper OJP cores yield substantially lower D(Cd) values. (c) The calculated barium distribution coefficients (D(Ba) = (Ba/Ca)foram /(Ba/Ca)b.w.) (solid squares) are lower than the *C. wuellerstorfi* D(Ba) value from *Lea and Boyle* [1989] (0.37, dashed line) at all depths, though the shallowest OJP cores have D(Ba) values which are similar to the all-species average D(Ba) of 0.32 reported by *Lea and Boyle* [1989]. Like D(Cd), D(Ba) values decrease with increasing water depth. (d) The calculated strontium distribution coefficients (D(Sr) = (Sr/Ca)foram / (Sr/Ca)b.w.) (solid squares) decrease with increasing water depth. A typical planktonic D(Sr) value of 0.16 [*Bender et al.*, 1975] is shown by the dashed arrow.

the western North Atlantic, *Lloyd-Kindstrand et al.* [1994] reported a depth-linked decrease in D(Sr) for *C. wuellerstorfi* between 0 and 5 km in both the Atlantic and Pacific Oceans, and *Martin et al.* [1994] reported a depth-linked decrease in D(Sr) (relative to bottom water Sr/Ca) for several species of infaunal benthic foraminifera between 0.3 and 3.7 km. The *Martin et al.* [1994] results are noteworthy because live (Rose Bengal-stained) benthic foraminifera were analyzed, which

should rule out the possibility that the observed changes reflect postmortem dissolution. In addition to these published studies, several laboratories have observed consistent decreases in *C. wuellerstorfi* Sr/Ca values with increasing water depth in both the Atlantic and the Pacific Oceans (Y. Rosenthal, personal communication, 1994; H. Elderfield, personal communication, 1994; H. Elderfield and C.J. Bertram, A kinetic model for the incorporation of trace elements into
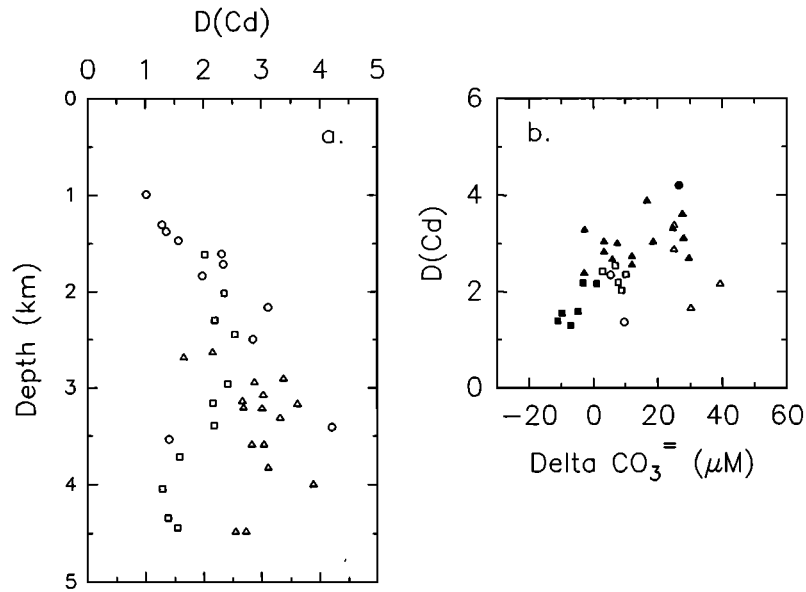
Figure 6. (a) D(Cd) is plotted as a function of water depth. Data are from this study (squares) and the "documented Holocene" core tops of *Boyle* [1988] (triangles) and *Boyle* [1992] (circles). The OJP values are significantly lower than most deep water values derived from the calibration data sets. (b) D(Cd) is plotted as a function of ΔCO_3^{-2}, the difference between the in situ bottom water carbonate ion concentration and the saturation carbonate ion concentration with respect to calcite. As discussed in the text, the GEOSECS ΔCO_3^{-2} values give an objective relative measure of the tendency for bottom water-driven calcite dissolution at each site. Symbols are as in Figure 6a; solid symbols indicate samples from > 3 km water depth. The D(Cd) values for deep water samples (solid symbols) show a strong positive correlation with the bottom water saturation state at low ΔCO_3^{-2} values and a less steep correlation at ΔCO_3^{-2} values above about 0; samples which are more likely to have experienced calcite dissolution have lower D(Cd) values.

foraminiferal calcium carbonate, submitted to Earth and Planetary Sciences Letters, 1995; D. Lea and P. Martin, unpublished results, 1994).

However, there is not a simple depth-dependence in the deep water (≥ 3 km) *C. wuellerstorfi* calibration data sets for Cd/Ca, Ba/Ca, or $\Delta\delta^{13}C$ (Figures 6a, 7a, and 8a). The OJP D(Cd) and D(Ba) values for water depths greater than 3 km are substantially lower than most of the calibration data, but the $\Delta\delta^{13}C$ results do not show an analogous offset. We note that even without the OJP data, there is a significant range in deep water D values for both Cd and Ba, suggesting that some factor other than water depth influences foraminiferal Cd/Ca and Ba/Ca.

The foraminiferal Sr/Ca data help constrain the possible effects of temperature or calcification rate on trace element incorporation. Inorganic precipitation studies and studies of foraminiferal calcite suggest that the Sr/Ca of calcite may vary with both precipitation temperature and precipitation rate [*Delaney et al.*, 1985; *Elderfield et al.*, 1982; *Katz et al.*, 1972; *Bender et al.*, 1975; *Lorens*, 1981; *Morse and Bender*, 1990]. The temperature dependence for inorganic precipitation is very small; D(Sr) increases by 0.001 per 20°C [*Katz et al.*, 1972]. The temperature dependence for biogenic calcite may be larger, but bottom water temperatures on the OJP decrease by less than 2° over the depth of our core transect, which would seem to rule out temperature variations as a direct explanation for the observed Sr/Ca decrease.

The inorganic precipitation study of *Lorens* [1981] suggests that D(Sr) increases as precipitation rate increases, while D(Cd) decreases as a function of precipitation rate. To the extent that these results are applicable to benthic foraminiferal calcite, they would argue against a common precipitation rate-based explanation for the observed Cd/Ca and Sr/Ca decreases. However, the link between calcification rate and D(Me) for biogenic calcite is not well known [*Morse and Bender*, 1990]. Controlled studies of Ba incorporation into the tests of planktonic foraminifera suggest little growth rate effect on D(Ba) [*Lea and Spero*, 1992, 1994]. In any event, it is not clear that we should expect substantially different foraminiferal growth rates over the depth range of the OJP since the pore water data do not suggest a strong, depth-related trend in benthic organic matter decomposition rates (D.C. McCorkle and W.R. Martin, unpublished pore water data, 1993).

We also note that OJP core-top Sr/Ca values from planktonic foraminifera decrease with increasing water depth (C. Bertram and H. Elderfield, personal communication, 1994), as do the OJP core-top planktonic U/Ca values reported by *Russell et al.* [1994]. These decreasing planktonic metal/calcium (Me/Ca) ratios cannot be explained by any mechanism which relies on fractionation during precipitation at the seafloor. This does not rule out such fractionation during benthic foraminiferal calcification, but a dissolution-based explanation is consistent with all the available data.
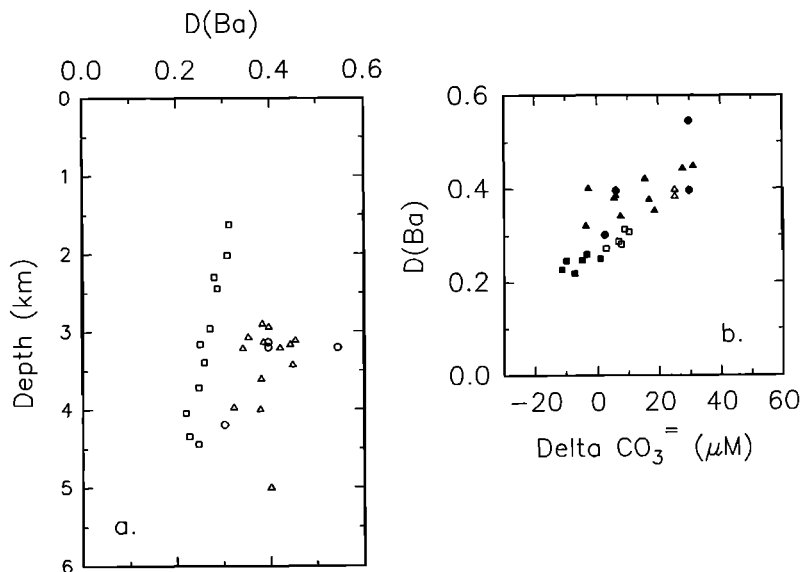
Figure 7. (a) D(Ba) is plotted as a function of water depth. Data are from this study (squares) and the "documented Holocene" core tops of *Lea and Boyle* [1989] (triangles) and *Lea* [1993] (circles). The OJP D(Ba) values are significantly lower than most of the calibration data set values. (b) D(Ba) is plotted as a function of ΔCO_3^{-2}. Symbols are as in Figure 7a; solid symbols indicate samples from > 3 km water depth. The D(Ba) values for deep water samples show a strong positive correlation with the bottom water saturation state, though the slope appears to decrease at higher ΔCO_3^{-2} values. Samples which are more likely to have experienced calcite dissolution have lower D(Ba) values.

A Dissolution Control on Metal:Calcium Ratios?

Our most direct evidence of a dissolution effect is based on an observed correlation between the distribution coefficients for Cd and Ba and the calcite saturation state of bottom water (Figures 6b and 7b). Sites with high ΔCO_3^{-2} values, which are in general less prone to calcite dissolution, yield high D values for both Cd and Ba; undersaturated (low-ΔCO_3^{-2}) sites have low D values. The *C. wuellerstorfi* - bottom water $\delta^{13}C$ difference ($\Delta\delta^{13}C$) shows little trend with ΔCO_3^{-2} (Figure 8b). The OJP D(Sr) values show a correlation similar to the other trace metals, but we do not present a plot because there is no independent benthic foraminiferal calibration study for Sr/Ca.

In Figures 6-8, our OJP data are plotted as squares and data from published calibration studies are plotted as triangles and circles [*Duplessy et al.*, 1984; *Boyle*, 1988, 1992; *Lea and Boyle*, 1989; Lea, 1993; *McCorkle and Keigwin*, 1994]. We have plotted only *C. wuellerstorfi* data from "documented" core tops from the Cd/Ca and Ba/Ca calibration studies, while the *Duplessy et al.* [1984] $\delta^{13}C$ calibration includes analyses of other species from the genus *Cibicides*, and the $\delta^{18}O$ documentation criteria for these cores are not explicitly described.

The ΔCO_3^{-2} values plotted on the abscissa show the difference between the in situ carbonate ion concentration and the saturation carbonate ion concentration (with respect to calcite), as reported in the GEOSECS hydrographic data atlases [*Broecker and Takahashi*, 1978; *Bainbridge*, 1981; *Broecker et al.*, 1982; *Weiss et al.*, 1983]. For each core-top sample, ΔCO_3^{-2} values from the nearest GEOSECS station were interpolated to the appropriate water depth. These

ΔCO_3^{-2} values are lower than the values which would be calculated using *Sayles'* [1985] estimate of the depth dependence of the saturation carbonate ion concentration or recent experimental determinations of the pressure dependence of calcite solubility [e.g., *Millero*, 1982]. However, the ranking of sites is relatively insensitive to the method used to estimate the saturation carbonate ion concentration. We have used the GEOSECS ΔCO_3^{-2} values as a readily available, objective measure of the tendency for dissolution at each core location.

Data from water depths deeper than 3 km are plotted as solid symbols to identify cores where we might expect bottom water chemistry to have the greatest influence on calcite dissolution. If a couple of high D(Cd) values are discounted, the deep water D(Cd) values increase only slightly above a ΔCO_3^{-2} (GEOSECS) of about 0 to 10 μmol/kg (Figure 6b). The D(Cd) points from shallower than 3 km fall off the trend defined by the deep (solid) points [*Boyle*, 1992]. The OJP data set does not help us determine whether the low D(Cd) values above 3 km result from the same processes which generate the low D values for Cd, Ba, and Sr in the deep OJP cores. For barium, there is relatively little data from above 3 km, and the entire "documented" *C. wuellerstorfi* data set displays a positive correlation with ΔCO_3^{-2} (Figure 7b). Again, the slope appears to decrease for ΔCO_3^{-2} values above 0 to 10 μM. A plot of $\Delta\delta^{13}C$ versus ΔCO_3^{-2} shows only a hint of a similar positive correlation (Figure 8b). The $\Delta\delta^{13}C$ range is large (0.3 to 0.4 ‰) at all ΔCO_3^{-2} values, but the OJP and northwest Pacific [*McCorkle and Keigwin*, 1994] data have an average $\Delta\delta^{13}C$ value about 0.2 ‰ lower than the deep water data set as a whole. The preponderance of Atlantic cores in each of the three calibration data sets ($\delta^{13}C$, Cd, and Ba) may have pre-
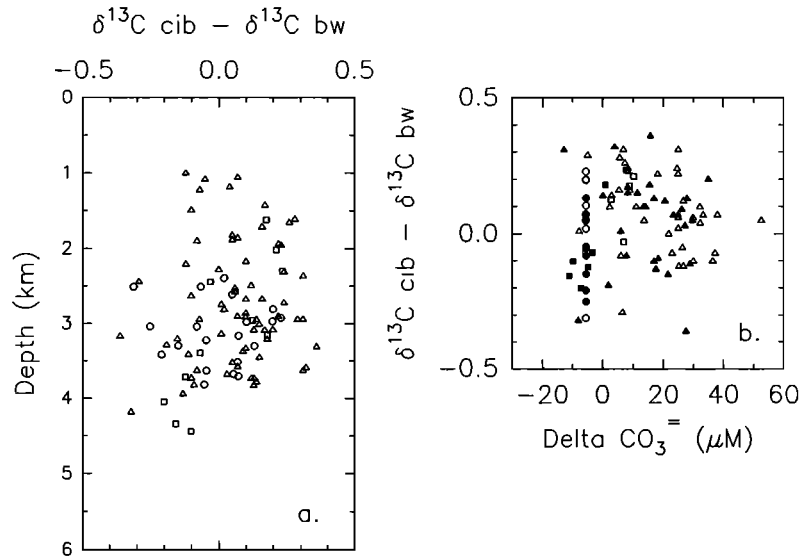
Figure 8. (a) The observed $\delta^{13}C$ difference between *C. wuellerstorfi* and bottom water ($\Delta\delta^{13}C$) is plotted as a function of water depth. Data are from this study (squares), *McCorkle and Keigwin* [1994] northwest Pacific (circles), and *Duplessy et al.* [1984] (triangles). There is little trend to the data, though the few samples from ≥ 4 km (3 from the OJP, 1 from the South Atlantic) all have low $\Delta\delta^{13}C$ values. (b) The observed $\delta^{13}C$ difference between *C. wuellerstorfi* and bottom water ($\Delta\delta^{13}C$) is plotted as a function of ΔCO_3^{-2}. Symbols are as in Figure 8a; solid symbols indicate samples from > 3 km water depth. There is no overall correlation between $\Delta\delta^{13}C$ and bottom water saturation state, though the deep samples with low ΔCO_3^{-2} values have a lower average $\Delta\delta^{13}C$ than the entire deep water data set.

vented the earlier recognition of the pattern seen in the D(Cd) and D(Ba) versus ΔCO_3^{-2} plots.

Bottom water chemistry is not the only control on seafloor carbonate dissolution. In particular, there is considerable evidence that organic matter decomposition in surficial sediments can drive carbonate dissolution at sites where the bottom waters are supersaturated with respect to calcite [*Emerson and Bender*, 1981; *Archer et al.*, 1989; *Hales et al.*, 1994]. Respiration-driven dissolution is a function of bottom water chemistry, sediment mixing rates, and the rain rates and reaction rates of organic matter and $CaCO_3$. This potentially significant component of dissolution cannot be easily assessed, but respiration-driven undersaturation should only tend to increase the dissolution intensity at a site. However a high sinking flux of $CaCO_3$ may deepen the lysocline at a site (i.e., minimize the effect of dissolution), so in principle the GEOSECS ΔCO_3^{-2} values may either underestimate or overestimate the true dissolution intensity.

Many studies have explored the role of selective dissolution on the elemental composition of biogenic calcite. In particular, there are well-documented, dissolution-driven decreases in planktonic foraminiferal Mg/Ca, F/Ca, and U/Ca [e.g., *Savin and Douglas*, 1973; *Hecht et al.*, 1975; *Lorens et al.*, 1977; *Rosenthal and Boyle*, 1993; *Russell et al.*, 1994]. *Russell et al.* [1994] also observed depth-linked decreases in *C. wuellerstorfi* Mg/Ca and U/Ca in a set of Atlantic core tops but could not determine whether these changes reflected partial dissolution or variable fractionation during calcification. Although *Lorens et al.* [1977] report that seafloor dissolution does not alter the Sr/Ca of planktonic foraminifera, the scatter in their data would obscure changes at the 10% level,

such as we observe on the OJP. Laboratory dissolution experiments do not show evidence of selective dissolution of Sr, Cd, or Ba and have been used to conclude that Cd and Ba are homogeneously distributed in lattice sites in foraminiferal calcite [*Lorens et al.*, 1977; *Boyle*, 1988; *Lea and Boyle*, 1993]. However, as discussed by *Lorens et al.* [1977] the homogeneity implied by these experiments may be a consequence of a much more aggressive dissolution than is likely to occur on the seafloor.

If carbonate dissolution is the cause of the observed trace element depletions, the pattern of dissolution should be consistent with our understanding of the different solubilities of the various metal carbonates. In practice, it is hard to evaluate this consistency. We are interested in the relative solubilities (in sea water at low temperature and high pressure) of trace amounts of Sr, Ba, and Cd substituted for Ca into calcite. The available mineral solubility data is largely from studies in low ionic strength solutions at 25°C and 1 atm pressure [e.g., *Plummer et al.*, 1992; *Stipp et al.*, 1993]. In addition, the pure $SrCO_3$ (strontianite) and $BaCO_3$ (witherite) phases which yield data that can be used to estimate low-mole-fraction solid solution solubilities have the crystal structure of aragonite rather than calcite; otavite ($CdCO_3$) has the calcite lattice structure. All of these differences between laboratory solubility studies and the seafloor dissolution of benthic foraminifera are likely to impact key aspects of the dissolution process. Bearing these large uncertainties in mind, we note that the pattern of (25°C, 1 atm) mineral solubilities is broadly consistent with the observed foraminiferal Me/Ca patterns (Table 4). For a given bottom water carbonate ion concentration and typical bottom water concentrations of Ca,

Table 4. Relative Solubility Estimates for Pure Metal Carbonates

Mineral	log K(so) (25°C, 1 atm, I=0)	Bottom Water Cation Concentration	Relative Saturation State [a]
CaCO₃ (calcite)	-8.4 [b]	10.3 mmol/kg	2.4
SrCO₃ (strontianite)	-9.3 [c]	90 μmol/kg	1
BaCO₃ (witherite)	-8.3 [b]	100 nmol/kg	-2.7
CdCO₃ (ovatite)	-12.1 [d]	1 nmol/kg	-1

[a] log (IAP / K(so)), assuming CO_3^{-2} = 100 μmol/kg
[b] Stumm and Morgan [1981]
[c] Busenberg et al. [1984]
[d] Stipp et al. [1993]

Sr, Ba, and Cd (and neglecting pressure and complexation effects on cation activities), $BaCO_3$ and $CdCO_3$ are more strongly undersaturated than is $SrCO_3$, which is more undersaturated than $CaCO_3$ (calcite).

A range of mechanisms could account for preferential loss of non-Ca cations from benthic foraminiferal tests. It is possible that the trace elements are enriched in a distinct, more soluble carbonate phase within the tests. While planktonic foraminfera are known to deposit gametogenic calcite which is compositionally distinct from primary (chamber) calcite, these chemical differences are thought to reflect secondary calcification at greater water depths by the sinking foraminifera [Orr, 1967; Duplessy et al., 1981; G.P. Lohmann, personal communication, 1994], and we know of no analogous environmental gradient for benthic foraminifera. (As noted above, precipitation from pore water does not seem consistent with the observed patterns in shell chemistry). It is also possible that the trace elements are enriched at dissolution-prone sites (e.g., crystal edges or lattice dislocations) within a monomineralic test. Finally, it may be that on a site-by-site basis, lattice positions containing non-Ca cations dissolve before $CaCO_3$ sites, reflecting the range of mineral solubilities illustrated in Table 4.

A saturation state-linked process can explain much of the variation in deep water D(Cd) and D(Ba), but these correlations do not prove that dissolution causes the observed trace element depletions. For instance, there could be a link between bottom water saturation state and trace element fractionation during calcification. The observed variations in bottom water saturation state are small relative to the active intracellular concentration of carbonate ion (and perhaps calcium (T. McConnaughey, personal communication, 1995) which occurs during biomineralization, but perhaps cation uptake ratios are particularly sensitive to external CO_3^{-2} or pH. If dissolution is the controlling mechanism, our results suggest that Cd, Ba, and perhaps Sr are more prone to dissolution from benthic foraminferal calcite than is Ca and that the same mechanism may also result in the preferential loss of ^{13}C.

Sr/Ca Normalization of Cd/Ca and Ba/Ca Values

All three metals (Cd, Ba, and Sr) display a similar first-order pattern (a depth-linked decrease), though they each have different fractional depletions, and Sr and Ba seem to display a more monotonic decrease with depth than does Cd. If the observed trace element patterns all reflect a common process it may be possible to improve our estimates of the original Cd/Ca and Ba/Ca values in benthic foraminifera samples by using Sr/Ca data to estimate the loss of Cd and Ba (or, alternatively, the extent of fractionation during precipitation). Before this approach can be evaluated, it will be necessary to determine whether there is a single controlling process for all three Me/Ca ratios and to demonstrate that all three Me/Ca ratios respond to this process in fixed proportions.

Paleoceanographic Implications

The published calibration studies show that foraminiferal Cd/Ca, Ba/Ca, and $\delta^{13}C$ values reflect the variation of Cd, Ba, and $\delta^{13}C$ in much of the modern ocean, and these proxies yield consistent patterns in downcore studies. This implies that the dissolution effect suggested by our data is in a sense a second-order process. However, if dissolution (or saturation state-linked fractionation during precipitation) can change foraminiferal trace element ratios by tens of percent or $\delta^{13}C$ values by tenths of a per mil, this effect must be addressed in paleochemical reconstructions of ocean chemistry and circulation.

It is difficult to make a quantitative prediction of the net impact of a dissolution effect on glacial-interglacial records of deep water Cd, Ba, and $\delta^{13}C$. Circulation shifts which lower $\delta^{13}C$ values and increase Cd and Ba at a site will also tend to decrease the carbonate ion concentration, making the dissolution effect more likely. This enhanced dissolution would lower foraminiferal Cd/Ca, Ba/Ca, and $\delta^{13}C$ values; in this way circulation changes and dissolution will tend to offset each other for Me/Ca ratios but work in the same direction for $\delta^{13}C$. In addition, productivity changes in the surface ocean may drive seafloor carbonate dissolution independent of changes in bottom water chemistry. Finally, it is important to note that at present we have no knowledge of whether or not dissolution will affect all benthic foraminiferal species in the same way; the data presented here are from C. wuellerstorfi which have been used for most deep water $\delta^{13}C$ reconstructions, while most glacial Cd and Ba reconstructions are based on analysis of U. peregrina. Despite these uncertainties, two examples will illustrate the possible paleoceanographic implications of a selective dissolution influence on foraminiferal shell chemistry.

The suggestion of low glacial Cd in the deep northwest Pacific (which is not mirrored by high foraminiferal $\delta^{13}C$ values) is based on comparison of foraminiferal Cd/Ca from LGM specimens with the modern Cd profile predicted from water-column phosphate [Boyle, 1992]. As noted by Boyle [1992] Holocene foraminifera in this region also have low Cd/Ca values; if these reduced ratios are a consequence of selective dissolution, the last glacial maximum (LGM) reconstruction may overestimate the glacial-interglacial change and thus underestimate the Cd content of the glacial North Pacific.

In the Southern Ocean, benthic foraminiferal Cd/Ca values show no glacial increase, despite the strong glacial decrease in benthic foraminiferal $\delta^{13}C$ values [*Boyle*, 1992]; the benthic Ba/Ca shift lies in between, with glacial values about 20% higher than Holocene [*Lea*, 1993]. At least a part of this discrepancy may result from other influences on the benthic foraminiferal carbon isotope values, such as changes in the actual glacial $\delta^{13}C$ distributions [*Charles et al.*, 1993] or in productivity-linked variations in benthic foraminiferal $\delta^{13}C$ in the Southern Ocean [*Mackensen et al.*, 1993, 1994]. However, if dissolution intensity increased in Southern Ocean sediments during the LGM [*Howard and Prell*, 1994], the measured benthic foraminiferal Cd/Ca and Ba/Ca values for glacial samples will underestimate the Cd and (to a lesser extent) Ba concentration of glacial Southern Ocean deep water and also will underestimate the $\delta^{13}C$ of bottom water, exactly the observed patterns. An increase in Southern Ocean dissolution intensity could reflect either deep water circulation changes (i.e., a reduction in North Atlantic Deep Water (NADW) production [*Boyle and Keigwin*, 1982, 1985/1986; *Oppo and Fairbanks*, 1987]) or an increase in respiration-driven carbonate dissolution at the sea floor [*Archer and Maier-Reimer*, 1994].

Our main hypothesis (a dissolution effect on foraminiferal Cd/Ca, Ba/Ca, and Sr/Ca (and perhaps $\delta^{13}C$) values) can be tested by studies of the shell chemistry of living benthic foraminfera (which are presumably free from dissolution effects) and by an improved understanding of benthic foraminiferal Sr/Ca. In particular, a global core-top Sr/Ca calibration data set, and regional bathymetric Sr/Ca transects analogous to the OJP data set, will show whether the dissolution effect implied by the OJP data is a general phenomenon. Similarly, Sr/Ca analysis of core top and LGM samples from the regions discussed above (northwestern Pacific and southern ocean) will enable us to evaluate the influence of this effect on the observed foraminiferal Cd/Ca and Ba/Ca records.

Conclusions

Core-top *C. wuellerstorfi* from the Ontong-Java Plateau display striking decreases in foraminiferal Cd/Ca, Ba/Ca, and Sr/Ca values at water depths greater than about 2.5 km. These concentration changes yield apparent distribution coefficients for Cd, Ba, and Sr into calcite which are substantially lower than the generally accepted values for D(Cd), D(Ba), and D(Sr). We also observe a depth-linked increase in *C. wuellerstorfi* - bottom water $\delta^{13}C$ differences, though this increase is not much larger than the precision of our $\Delta\delta^{13}C$ estimates. The OJP foraminiferal Me/Ca and $\delta^{13}C$ data are consistent with the western Pacific data in the published core-top calibration data sets for Cd, Ba, and $\delta^{13}C$. These results together with the published calibration data sets for each proxy show a clear correlation between foraminiferal D(Cd) and D(Ba) values and bottom water saturation state (with respect to calcite), a pattern which is only weakly expressed in the full $\Delta\delta^{13}C$ calibration data set. With the available data we cannot rule out the possibility of saturation state-linked fractionations during calcification or the possibility of a simple pressure dependence of benthic foraminiferal Sr/Ca values. However, consideration of various possible mechanisms for the observed patterns leads us to suggest that incongruent dissolution results in a

preferential loss of Cd, Ba, and Sr (and perhaps ^{13}C) from foraminiferal calcite.

It is clear that we need a firm understanding of the mechanism which is responsible for these decreases in foraminiferal Me/Ca and $\delta^{13}C$ values. The first task is to see if the Me/Ca patterns observed on the Ontong Java Plateau can be reproduced in other sample sets and to determine whether similar patterns are observed for other benthic foraminiferal species. If it can be demonstrated that there is a consistent relationship between the loss of Sr, Cd, and Ba from dissolving tests and if we can adequately constrain estimates of the initial Sr/Ca for benthic foraminifera, it may be possible to use measured Sr/Ca values to remove the dissolution overprint from downcore cadmium and barium data. Sr/Ca analysis of available material from the benthic foraminiferal Cd/Ca and Ba/Ca calibration data sets should help define these elemental relationships. It seems advisable that Sr/Ca analyses be routinely carried out in paleoceanographic studies of foraminiferal Cd/Ca and Ba/Ca.

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G.P. Klinkhammer, College of Oceanography, Oregon State University, Corvallis, OR, 97331 (email: gklinkhammer@oce.orst.edu)

D.W. Lea and P.A. Martin, Department of Geological Sciences and Marine Science Research Institute, University of California, Santa Barbara, CA, 93106 (email: lea@magic.ucsb.edu; martin@magic.ucsb.edu)

D.C. McCorkle, Department of Marine Geology and Geophysics, Woods Hole Oceanographic Institution, Woods Hole, MA, 02543. (email: dmccorkle@cliff.whoi.edu)