CADMIUM: CHEMICAL TRACER OF DEEPWATER PALEOCEANOGRAPHY

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Abstract. The oceanic distribution of cadmium resembles that of phosphorus. Because the cadmium content of foraminiferal shells is governed by the cadmium content of seawater, planktonic and benthic fossil shells can be used to infer nutrient distributions within ancient oceans. Empirical studies demonstrate that cadmium in benthic foraminiferal shells is related to the bottom water composition through a proportionality constant $D \cong 2.9$. This constant is the same for each of the species studied: Cibicidoides wuellerstorfi, Cibicidoides kullenbergi, Nuttallides umbonifera, and Uvigerina.spp. Downcore cadmium data from high-quality Pacific and Atlantic sediment cores suggest that the cadmium inventory of the ocean did not change significantly between the most recent glacial maximum and the present. Hence changes in the cadmium content of fossils at a site directly reflect changes in nutrient distributions due to altered oceanic circulation patterns. Studies of cadmium in Pleistocene sediments show that deep ocean circulation patterns were significantly different during the most recent glacial maximum. In the western North Atlantic Ocean, the nutrient content of waters from 2500 to 3500 m was twice as high during glacials as during interglacial periods, signifying an increase in the proportion of waters of Antarctic origin in this depth interval and a decrease (but not a cessation) in the flux of North Atlantic Deep Waters through this depth range. Below 3500 m, the nutrient increase was greater, indicating a higher proportion of Antarctic Bottom Water. Above 2500 m, the nutrient content was lower during glacial periods than it has been during interglacial times. The Cd content of high-latitude North Atlantic and southern ocean surface waters does not show a significant glacial/interglacial change, which argues against theories for changes atmospheric carbon dioxide that require changes in high-latitude nutrient concentrations.

CHEMICAL TRACERS OF PRESENT AND PAST OCEAN CIRCULATION

Movements of water, salt, heat, and chemicals through the ocean significantly affect global climate. In the Atlantic, northward flow of warm upper water is balanced by southward flow of cold deep water [Bryden and Hall, 1980]; this circulation carries a significant flux of heat to high latitudes, both directly by the ocean and indirectly from moisture and heat transferred from the ocean to the atmosphere. This circulation pattern is influenced by internal salt and external water vapor transport [Reid, 1979; Warren, 1983]. The atmospheric carbon dioxide content (an important contributor to global "greenhouse" warming) is regulated by oceanic nutrient geochemical cycles [Broecker, 1982a; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984; Knox and McElroy, 1984]. If we are to understand

the geological record of climate change, we must first understand the variability of ocean chemistry and circulation.

The determination of circulation patterns from salinity and potential temperature has become standard practice in physical oceanography since its introduction by Wust [1978]. But Wust also appreciated that other chemical tracers (such as oxygen, phosphorus, and silicon) also provide independent useful information on the spreading of water types, despite the nonconservative behavior of these tracers. The initial signatures of these chemical tracers are often more important than chemical reactivity in determining large-scale oceanic chemical distributions. Paleoceanographers are newcomers to the use of chemical tracers of oceanic water masses. Initial efforts in this field concentrated on variations in the relative populations of different species of benthic foraminifera. It was hoped (by analogy with planktonic foraminifera) that benthic foraminiferal paleoecology would prove useful in reconstructing past deep ocean conditions. Other tracers have been proposed as well: the oxygen isotope composition of benthic foraminifera, the grain size and mineralogy of advected particles, and paleomagnetic properties of sediments. These efforts are discussed in articles in the June special issue on Quarternary deepwater circulation in Paleoceanography.

Two chemical tracers are now being employed in deepwater paleoceanography: the carbon isotope composition ($\delta^{13}C$) and the cadmium content (Cd/Ca) of the shells of benthic foraminifera. Both $\delta^{13}C$ and Cd have similar oceanographic distributions, being linked with processes controlling the nutrient and carbon dioxide content of deep ocean water. Since it appears that both tracers are recorded reliably by at least some species of benthic foraminifera, numerous studies employing these tracers have been published in recent years. Carbon 13 studies are discussed by Duplessy et al. [1988] and Curry et al. [1988]. This paper will review basic principles of the benthic Cd technique, provide new documentation of the technique's validity, and summarize the results of investigations employing Cd in benthic foraminifera as compared with results from $\delta^{13}C$ studies.

TRACE ELEMENTS AS TRACERS OF PRESENT AND PAST OCEANIC PROCESSES

The last decade has seen a revolution in the understanding of oceanic trace element distributions. Although marine chemists worked on this problem for many years, success was delayed until the role of contamination in oceanographic sampling and laboratory analysis was appreciated. Most older trace element literature must be discounted; only results obtained over about the last 10 years are considered useful (see the review by Bruland [1983] and references therein).

One of the earliest discoveries in the short history of trace element oceanography was that there is a global linear relationship between cadmium (Cd) and phosphorus (P) [Boyle et al., 1976; Bruland et al., 1978; Bruland, 1980]. Cd and P are removed efficiently from the surface ocean by organisms; these elements are incorporated into organic debris that sinks and decomposes in a nearly stoichiometric fashion in the upper ocean [Martin and Knauer, 1976; Collier and Edmond, 1984]. The general circulation of the ocean is then superimposed on this one-dimensional cycle to create signature variations in the chemical composition of oceanic water masses.

Phosphorus is an essential micronutrient, and the reasons for its incorporation into organisms are understood. The reason for Cd uptake is uncertain, since Cd has no documented biological utility, and it is known to be harmful at elevated concentrations. It is plausible that organisms inadvertently remove Cd from seawater in their quest for chemically similar essential micronutrients such as zinc and have evolved pathways for sequestering toxic or unnecessary elements into sites where they do not damage the organism. The similarity in the oceanic distributions of phosphorus and cadmium results from the similarity in the depth zones of uptake and remineralization. Both P and Cd are associated with organic debris that undergoes rapid and nearly quantitative degradation in the upper water column [Collier and Edmond, 1984; Knauer et al., 1979; Knauer and Martin, 1981].

The Cd-P relationship is remarkably uniform globally (Figure 1) This observation is remarkable in view of the wide variety of environments occurring in the modern ocean and the basic chemical dissimilarity of the two elements. It is likely that a global linear Cd-P relationship has prevailed throughout Phanerozoic ocean history. It would be possible for the oceanic Cd:P ratio to change over geologic time, although Delaney [1987] presented evidence that oceanic mean Cd was not much different from the present value in the Miocene. Analytically significant deviations from the modern global Cd-P correlation are known, particularly for surface waters, marginal basins, and continental shelf waters [Boyle et al., 1981, 1982, 1984, 1985; Bruland, 1983]. In deep waters of the open ocean, Cd at a given value of P appears consistent to within about $\pm7\%$. There is a significant slope change in the Cd-P relationship at about 1.3 μmol/kg P. Below P~1.3 μmol/kg (dominated by Atlantic and upper ocean data), the Cd-P
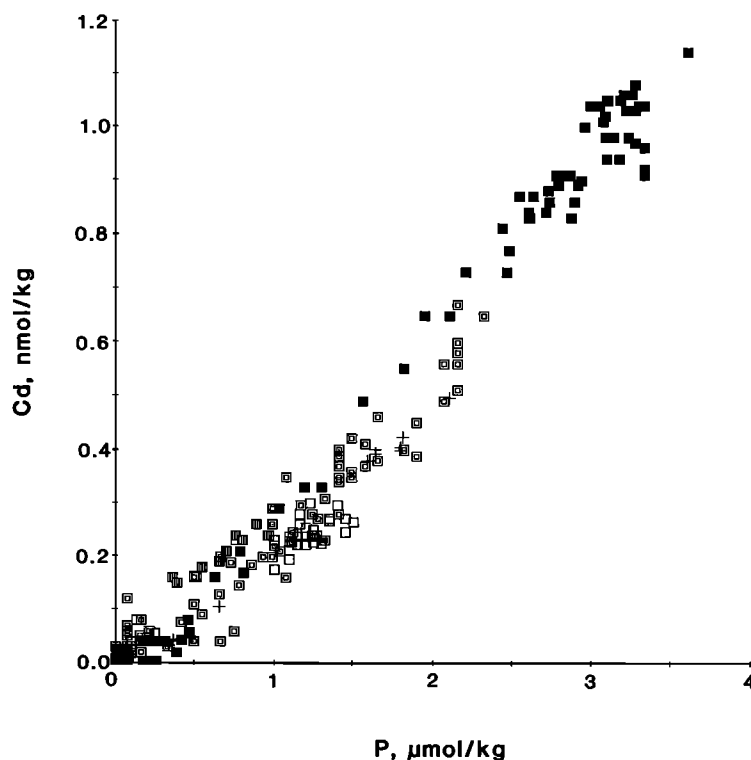
Fig. 1. Cd versus P for open ocean samples below the mixed layer. Solid squares represent the northeast Pacific [Bruland et al., 1978; Bruland, 1980]. Open squares represent samples from the northwest Atlantic [Bruland, 1983; Sakamoto-Arnold et al., 1987]. Concentric squares represent samples from the eastern North Atlantic [Boyle et al., 1984; P. Statham and J. D. Burton, unpublished data, 1986]. Hatched Squares represent samples from the Arctic Ocean [Danielsson and Westerlund, 1983]. Plus signs represent samples from the Gulf of Mexico [Boyle et al., 1983].

relationship has a slope of about 2.1×10^{-4}, passing only slightly below the origin at zero phosphorus (Figure 1). Above P~1.3 μmol/kg (dominated by South Atlantic and Pacific data), the Cd-P relationship has a slope of about 4.0×10^{-4} and passes through the zero-phosphorus axis at Cd = -0.25 nmol/kg. The cause of this kink is not known with certainty, but it is likely to reflect a slightly deeper regeneration cycle for Cd relative to P. Differences such as these have little bearing on the use of Cd as a circulation tracer, but they may limit the degree to which Cd can be interpreted as a P analogue.

Boyle [1981] proposed that cadmium was incorporated into foraminifera shells in proportion to the concentration of the surrounding water, and that Cd could serve as a paleoceanographic tracer of past phosphorus distributions. Because sedimentary foraminifera are contaminated by a variety of mechanically and chemically adhering phases (which

have Cd concentrations many orders of magnitude higher than foraminiferal calcite), it is not easy to ensure complete removal of contaminant phases before chemical analysis. A series of basic oxidative and reductive treatments and weak acid cleaning was developed to clean foraminifera [Boyle, 1981; Boyle and Keigwin, 1985]. Studies of core top planktonic foraminifera [Boyle, 1981] and core top benthic foraminifera [Hester and Boyle, 1982] showed that the Cd content of shells cleaned in this way was proportional to the Cd content of the water in which the shells formed. Delaney [1983] cultured live planktonic foraminifera with radiotracer Cd and showed that the proportionality was similar to that observed from core top studies of benthic foraminifera.

Although foraminifera incorporate Cd into their shells and are good recorders of the Cd content of seawater, they are not significant vectors of Cd in the

oceanic geochemical cycle. The only significant vector of Cd in the water column of the ocean is organic particulate matter. The insignificance of foraminifera as a Cd vector can be seen from the ratio of Cd:C in organic matter (3.3×10^{-6}) and Cd:C in carbonate materials (less than 0.2×10^{-6}). Since 4 times more carbon falls out of the mixed layer in organic form relative to inorganic calcium carbonate [Broecker and Peng, 1984], foraminifera and other calcareous phases are responsible for less than 2% of vertical cadmium transport. In this respect, foraminifera are similar to thermometers; they record the property without significantly altering the system. This property is important because it ensures that carbonate sedimentation does not influence the oceanic cadmium distribution.

A number of other trace elements show similarities to better-known chemical tracers in the ocean. It is possible that some of these elements may also be incorporated into shells and be useful in the study of past oceans. The example of foraminiferal cadmium shows that a great deal of work is necessary to overcome artifacts and to prove that there is a strict relationship between shell composition and water composition. It should be expected that progress in this area will not come easily.

MEASUREMENT

Because foraminifera contain as little as 0.01 ppm Cd and reasonable benthic foram sample sizes often are restricted to less than 1 mg, the analytical technique must have a detection limit better than 10^{-11} g for Cd. Of those methods with sufficient sensitivity, graphite furnace flameless atomic absorption (with a Cd detection limit of 10^{-13} g) has been preferred because it is relatively rapid. In the author's hands, average analysis time for a batch of 90 picked samples is now 20 min per sample, including sample preparation, cleaning, standardization, and blank runs. It is also reasonably precise; precision of replicates on a given day is better than 2%, while precision for more than 100 analyses of a consistency standard over a 3-year period is better than 3.5%. Since the reproducibility of analyses of replicate picks from a given sample is rarely better than 5% (as discussed later), it would not be worthwhile to use a more precise analytical technique unless the reproducibility of replicate samples can be improved. It is not certain why analyses of replicate samples are less reproducible than replicate analysis of the same solution, but it is likely that biological stirring of sediments produces a heterogeneous mix of individuals that lived under different bottom water conditions. This matter is considered further in a later section of this paper.

CADMIUM INCORPORATION INTO FOSSIL CARBONATE SHELLS

Thermodynamic and Kinetic Expectations

The following explanation of thermodynamic solid solution theory is common knowledge among chemists but may be unfamiliar to other readers. Further documentation can be found in fundamental thermodynamics texts.

Given thermodynamic equilibrium between a solution and calcium carbonate, the concentration of a trace divalent element such as cadmium (Cd) in the solid would be related to the solution composition. This relation can be expressed by the exchange reaction:

$$CaCO_3 + Cd^{2+} = CdCO_3 + Ca^{2+} \qquad (1)$$
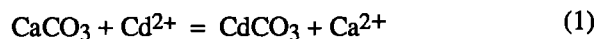
where it is expected that

$$(Cd/Ca)_{CaCO_3} = D_H \frac{\gamma_{Cd} \, f_{Cd} \, [Cd]}{\gamma_{Ca} \, f_{Ca} \, [Ca]} \qquad (2)$$

where D_H defines a "Henry's Law" distribution coefficient, γ is the thermodynamic activity coefficient in solution (which should be similar for divalent ions of the same radius, so these terms almost cancel), f is the fraction of the element occurring as the free (uncomplexed) ion in solution ($f_{Ca} \sim 0.9$, $f_{Cd} \sim 0.01$ for seawater), and [Cd] and [Ca] are the total concentrations in the solution. However, for empirical purposes it is often convenient to lump thermodynamic terms on the right hand side of the equation into a single "D" distribution coefficient which relates the concentrations in the shell material to concentrations in the water; there has been some confusion in the literature over these two types of distribution coefficients.

D_H is determined by the relative free energy difference between ions in solution and ions within the solid crystal lattice. For an ideal solid solution (where the electrical contributions to energy would be the same for $CdCO_3$ in $CaCO_3$ as for $CdCO_3$ in $CdCO_3$), the distribution coefficient of cadmium in a calcium carbonate lattice equals the ratio of the solubility product of $CaCO_3$ to that of $CdCO_3$:
calcium carbonate lattice equals the ratio of the solubility product of $CaCO_3$ to that of $CdCO_3$:

$$D_{ideal} = K_{sp}(CaCO_3) / K_{sp}(CdCO_3) \qquad (3)$$

$K_{sp}(CaCO_3) \sim 10^{-8.47}$ and $K_{sp}(CdCO_3) \sim 10^{-11.3}$ [Davis et al., 1987], so the concentration distribution coefficient for ideal solid solution Cd in calcite relative to seawater (D) would be $(0.01 \times 680) \approx 7$.

Most solids are not ideal, and additional contributions to the free energy are introduced by the mismatch between ionic radii of Cd and Ca, by differences between the crystal structures (e.g., the minerals calcite, $CaCO_3$, and otavite, $CdCO_3$, have the same crystal structure, which differs from that of aragonite), and by covalency, polarizability, and other nonhard ionic-sphere interactions. Davis et al. [1987] measured an equilibrium D_H of 1510, which would imply that the concentration distribution coefficient (D) of Cd in calcite solid solution crystallized from seawater would be ≃15.

For divalent elements existing in trace amounts (which therefore cannot interact with one another and do not influence the total free energy of the crystal), it is expected that these factors are only slight functions of temperature (T) and pressure (P). Similarly, γ and f are expected to be only slight functions of T and P. The fraction f is determined by the solution speciation of the metal. In seawater, where the major complexing ions are in constant proportions, f should only be a slight function of T, P and possibly also of pH. It will be a function of pH only for ions which interact most strongly with OH^-, HCO_3^-, and $CO_3^=$; furthermore, the limited range of pH found in the marine environment limits variations in D due to this factor. Over a limited temperature and pH range (which characterizes the environments of many marine organisms), it is expected that the equilibrium $CaCO_3$ trace metal composition is proportional to the trace metal content of the water.

Quantitative determination of these thermodynamic constants is more difficult than it might appear. Sparingly soluble crystals can approach thermodynamic equilibrium very slowly at low Earth surface temperatures, so it is difficult to ensure that a laboratory determination of the distribution coefficient is truly at equilibrium; kinetic artifacts are possible. Lorens [1981] measured solid concentration ratios relative to a seawaterlike solution ranging from 70 (at low precipitation rates) to 10 (at higher precipitation rates). It is also difficult to measure the speciation of trace elements at natural concentrations (although extrapolation from higher concentrations is possible). Of course, slow kinetics are also an advantage in that the original trace metal content can be preserved for millions of years.

Thermodynamic equilibrium favors a simple relation between the trace element composition of $CaCO_3$ and that of the seawater from which it is precipitated. Biological and environmental artifacts might upset this expectation, so empirical studies are necessary to demonstrate that fossil shells are reliable indicators of the metal concentration of the water in which the organisms live.

Empirical Results: Core tops, species

Since shells are rapidly precipitated by organisms, biochemical and kinetic considerations may shift the trace metal composition of the shell away from that expected at equilibrium. The relation between shell and solution composition must be established empirically, either by comparing the composition of living or fossil shells with the known variations in the metal concentration of their environment or by experimental manipulation of the environment of the organism in the laboratory. It is possible that contaminant phases (either organic tissues from the organism or detrital or authigenic phases cemented onto fossil shells after deposition into sediments) can cause a significant bias in measured metal contents relative to the amount actually incorporated into solid solution within the carbonate crystal lattice. Thorough systematic studies are necessary to establish proper cleaning procedures for removing contaminant phases and documenting the magnitude of any residual contamination.

For Cd in foraminifera, the proportionality of response has been determined in three ways: (1) by comparison of fossil planktonic shells cleaned in a variety of ways with the composition of the upper water column [Boyle, 1981], (2) by comparison of fossil benthic foraminifera with the composition of the overlying deep water [Hester and Boyle, 1982], and (3) by experimentally growing planktonic foraminifera in solutions containing radioactive cadmium [Delaney, 1983]. These lines of evidence indicated that the distribution coefficient for Cd in foraminifera was approximately 2 over the temperature range 2°-30^oC.

A disadvantage of any empirical study is the possibility that a limited data set may produce a relationship that is not borne out by subsequent studies. In order to ensure that the above studies are not anomalous, continued scrutiny is necessary.

From a limited number (12) of core tops, Hester and Boyle [1982] showed that C. kullenbergi and Uvigerina spp. appear to incorporate cadmium into their shells in proportion to the concentration of the overlying bottom water and that both species show the same proportionality constant. Ongoing studies of deep-sea cores have resulted in a significant increase in core top documentation and interspecies comparisons. The results of this work generally support that of Hester and Boyle, but a larger number of core tops and further information on dissolved oceanic Cd would allow for improved estimates of the relationship between shell composition and bottom water composition. Continuing documentation of the response of foraminifera to
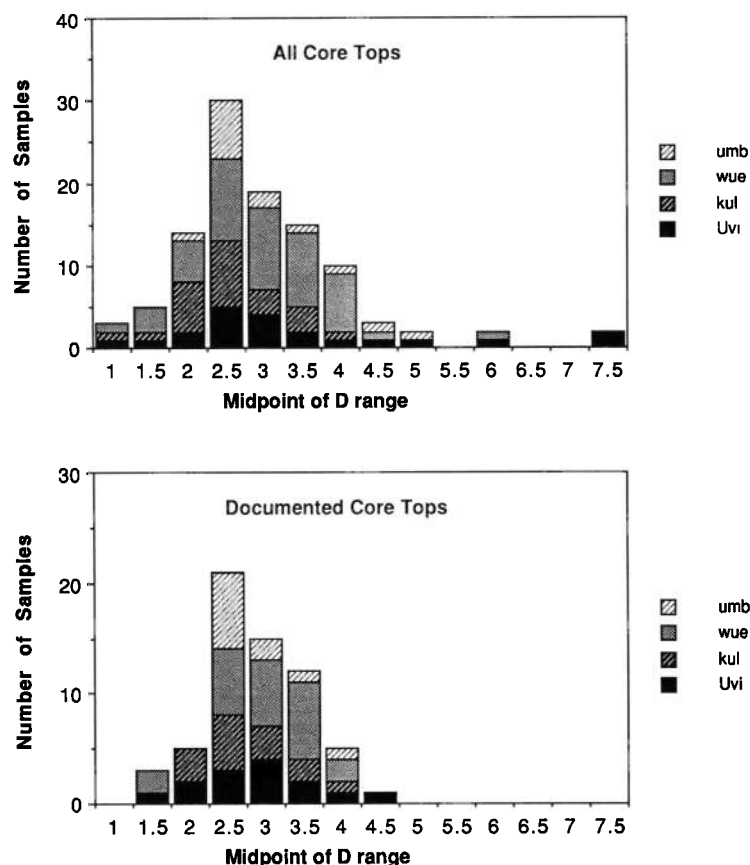
Fig. 2. Histograms of estimated distribution coefficients (top) from all core tops in Table 1 and (bottom) from documented core tops where the author knows that there is at least 15 cm of Holocene sediment (underlined in Table 1).

bottom water conditions is important in establishing the reliability of foraminiferal Cd as a tracer of past bottom water composition.

New data on near-core top foraminiferal Cd are given in Table 1. The distribution coefficients have been calculated assuming the Cd:P relationship noted previously; these are then plotted as histograms in Figure 2. While there is some dispersion in these data, it is to be expected as there is some uncertainty in the estimation of bottom water Cd and in the reliability of the near-core top samples. The dispersion is less for cores which are confirmed as having at least 15 cm of Holocene material by oxygen isotope analysis.

The core top data show that there is a relationship between foraminiferal Cd and bottom water P (which is related to bottom water Cd) (Figure 3). All of the species plot in the same field; there are no evident systematic differences between the four species studied. The lack of systematic differences between species is also documented by paired downcore

species data (Figure 4). The scatter in the relationships (about ±25% for all of the core top data and about ±15% for the paired downcore data) exceeds the standard deviation on standards (in our laboratory, better than 2% on a given day and 3.5% over a period of 3 years). Some of the scatter must be due to imperfections in the core top samples (i.e., they may not be true core tops). Selecting only those cores for which there are published oxygen isotope stratigraphies indicating sedimentation rates of at least 1.5 cm/kyr, the scatter is reduced considerably (Figure 2, bottom). Some of the scatter is likely due to bad analyses (there always is some chance of contamination during analysis) or an unrepresentative subsample from the population of individuals; this factor can be assessed by examining those samples for which duplicate or triplicate analyses are available (Tables 1 and 2).

The core top data allow for the estimation of Cd distribution coefficients in benthic foraminifera and assessment of their statistical reliability (Table 2).
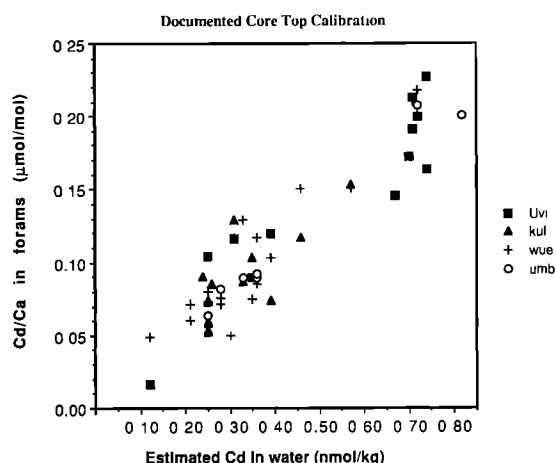
Documented Core Top Calibration

Fig. 3. Benthic foraminiferal Cd versus estimated bottom water Cd. Data are from cores with published isotopic records indicating continuous sedimentation at a rate of at least 1.5 cm/kyr.

Average distribution coefficients for the individual species and the aggregate of all species are calculated for three classes of reliability in the data: (1) all core tops, (2) documented Holocene core tops, and (3) documented Holocene core tops where replicate analyses could be undertaken. Although there is somewhat less scatter for the more reliable groups, average distribution coefficients do not change significantly. Furthermore, none of the selections (all core tops, well-documented core tops, and samples with replicated analyses) show any significant systematic differences between species. The better-documented samples show less variance in estimated distribution coefficient. It appears that the distribution coefficient of Cd in foraminiferal calcite is 2.9 ± 0.6 (i.e., about 21% scatter exists for Cd in better-documented samples). This estimate for D is higher than that of Hester and Boyle [1982]. The difference does not arise because of higher Cd contents in our foraminiferal data set (the new foraminiferal Cd values at a given P concentration are consistent with those of Hester and Boyle), but rather because this new estimate is based on a more accurate estimate for bottom water Cd (see the previous discussion). Hester and Boyle used a constant Cd:P ratio (3.5 x 10^{-4}) and hence did not take into account the kink in the Cd-P relationship mentioned previously. Since their data were dominated by Atlantic samples, they overestimated Cd and so underestimated the distribution coefficient.

Four factors may account for residual scatter in more reliable samples: (1) biology (e.g., foraminifera may not maintain a strict proportionality between

shell composition and bottom water composition, perhaps because of differences between genetic strains or a response of organisms to environmental stress), (2) environment (e.g., benthic foraminifera may live at some depth in the sediment where the pore waters do not correspond exactly to bottom water composition), (3) procedure (e.g., imperfections in the cleaning), or (4) artifacts (e.g., foraminiferal shell chemistry is faithful to bottom water composition, but core top benthic foraminifera may have grown at times during the last few thousand years when bottom water chemistry differed from that of the present).

It is important to establish the cause of the calibration scatter because it could represent a fundamental limit to the reliability of benthic Cd data. At present, it not possible to establish the reason for the scatter unequivocally, but doubt can be expressed concerning the significance of the first three factors. It is unlikely that biological artifacts are important within a species when there are no systematic offsets between the different species and genera of foraminifera. In general, it is to be expected that genotypic differences between species exceed phenotypic variability within a species. While it is possible that some species of foraminifera live within sedimentary pore waters (indeed, Corliss [1985] presents evidence that at least a few species do live within the sediments), the lack of correlated systematic differences between the carbon isotope and cadmium content of different species also argues against this possibility, since pore waters are known to be significantly depleted in ^{13}C and enriched in Cd due to the decomposition of organic matter in sediments (see Figure 5, data of Heggie et al. [1986] and McCorkle et al. [1985]).

The adequacy of cleaning treatments must be assessed by indirect evidence, given the limits of current analytical technology. Boyle [1981] showed that increasingly severe cleaning treatments led to a low Cd plateau, with no further Cd decrease upon prolonged or more severe cleaning. Further evidence that samples are adequately cleaned is provided by sequential ultrasonic dissolution of a large precleaned Uvigerina sample in strong nitric acid (Figure 6). The acid concentration was 1 N initially and greater than 0.1 N at termination of partial dissolution. There is very little difference between the cadmium contents of dissolution fractions. If anything, the Cd content of the later fractions increases slightly, which is the opposite of what would be expected from progressive removal of contaminated surfaces. This slight change may be due to selective early dissolution of thinner-walled specimens (which may have lived at different periods than thicker-walled specimens, or to some adsorption of Cd onto $CaCO_3$
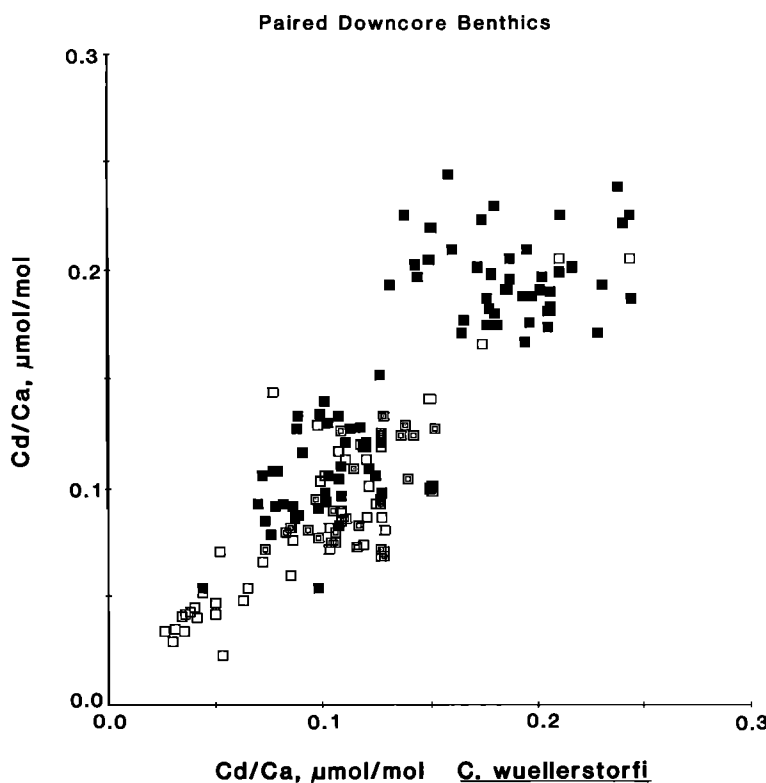
Paired Downcore Benthics

Cd/Ca, μmol/mol   C. wuellerstorfi

Fig. 4. Downcore paired-species analyses. C. wuellerstorfi Cd datum for each sample is plotted on the horizontal axis. Vertical axis is the Cd content of species other than C. wuellerstorfi. The symbols indicate the species: filled squares are Uvigerina spp., open squares are C. kullenbergi, crosses are C. wuellerstorfi and concentric squares are N. umbonifera. Most of the solid squares at high Cd are from Pacific core TR163-31B. Other cores included in this compilation are CHN82 Sta 50 20PG,PC; RC13-228; KNR64 5PG,PC; KNR73-3PC; EN120 GGC1; M12392; V32-161; V32-159; and several EN66 cores.

surfaces. In any event, more severe acid cleaning serves no purpose, since cadmium is uniformly distributed throughout portions dissolved at each stage. Also, if imperfect cleaning is the limiting factor, then the absolute scatter for Cd should be similar in low- and high-Cd environments; but it appears that low-Cd environments such as the Caribbean have lower absolute scatter. These data are consistent with a homogeneous lattice-bound site for cadmium.

The magnitude of irreproducibility due to bioturbation and sampling statistics can be calculated and shown to be comparable to scatter observed in core data. It is known that the bottom 3-15 cm of deep-sea sediments are homogenized by the stirring action of organisms. The ages of individual fossil organisms found in the tops of sediment cores range over several thousand years. Benthic foraminifera from the tops of cores may have grown at some time in the past when deepwater composition differed from that of recent years. In that case, comparison of

present bottom water composition with core top foraminiferal composition will not be the best guide to the relation between the composition of foraminifera and bottom waters. Furthermore, abundances of benthic foraminifera are often quite low, and the analyst is often limited to the analysis of only a few specimens (sometimes as few as three; more typically 5-20). Boyle [1984] developed a Monte-Carlo statistical model of this process which showed that sampling a small number of individuals from bioturbated sediments can lead to poor estimates of the average bottom water composition during the period represented by the mixed sediment. This factor almost certainly causes much of the scatter observed in Figures 2-4.

Shackleton et al. [1983] point out that analyses from adjacent core sections in high sedimentation rate cores provide a measure of the reproducibility of foraminiferal response to bottom water conditions (at least within a limited sedimentary environment). High sedimentation rate cores should show less

Table 1. Near- Core Top Foraminiferal Cd

Core	Sample Depth, cm	Latitude	Longitude	Water Depth, m	Estimated P, μmol/kg	Cd/Ca, μmol/mol			
						Uvi	kul	wue	umb
CHN82 1PC +	0-4	36°06'	-07°10'	830	0.60	0.016	0.049		
CHN82 4PC +	1-4	41°43'	-32°51'	3427	1.19		*0.074		
CHN82 11PC+	4-8	42°23'	-31°48'	3209	1.19		*0.052		
CHN82 15PC		43°14'	-28°08'	2155	1.18		0.050	0.051	
CHN82 20PG+	4-10	43°30'	-29°52'	3070	1.18		*0.073	0.073	
CHN82 21PG	7	43°17'	-29°50'	2103	1.18		0.053	0.056	0.064
EN66 10GGC	1	06°39'	-21°54'	3527	1.45	0.157	*0.079	*0.146	
EN66 16GGC	1	05°28'	-21°08'	3152	1.44	0.117	*0.086	*0.116	0.124
EN66 21GGC+	4	04°14'	-20°38'	3995	1.48		*0.087	*0.129	0.089
EN66 26GGC	1-5	03°05'	-20°01'	4745	1.48			*0.123	0.082
EN66 29GGC+	6	02°28'	-19°46'	5104	1.54			*0.085	*0.089
EN66 30GGC								0.100	0.093
EN66 32GGC+	5	02°28'	-19°44'	5003	1.54			0.117	*0.092
EN66 36GGC	3	04°19'	-20°13'	4270	1.48			*0.114	0.090
EN66 38GGC	4	04°55'	-20°30'	2931	1.43	0.231	0.064	0.113	0.163
EN66 44GGC	1	05°16'	-21°43'	3428	1.45	*0.237	0.088	*0.114	*0.141
EN120 1GGC+	0-10	33°40'	-05° 3'	4479	1.34			*0.071	*0.082
EN120 2GGC+	8-15	33°40'	-57°37'					*0.076	
IOS82PCS01+	0-2	42°23'	-23°31'	3540	1.25		*0.085		
KNR64 3PC +	1-3	17°01'	-74°26'	2681	1.40			0.050	
KNR64 5PG	4-7	16°32'	-74°48'	3047	1.40			0.095	
KNR73 3PC +	12	-00°22'	-106°11'	3606	2.39	*0.172			
KNR73 4PC +	7-12	04°02'	-114°01'	3775	2.42	0.191			
OCE86 2BC	0-4	38°13'	-71°30'	3000	1.21			*0.068	
RC10-65 +	5-8	-00°41'	-108°37'	3588	2.46	*0.199		*0.202	*0.207
RC10-65TW +	8-10	-00°41'	-108°37'	3588	2.46			0.217	
RC10-288	3-7	35°32'	-73°25'	3678	1.19		0.059	0.099	
RC11-120 +	5-7	43°31'	79°52'	3135	2.07		0.153	0.150	
RC12-267	8-1	-38°41'	-25°47'	4144	2.26			0.152	
RC12-294 +	5-8	-37°16'	-10°06'	3308	1.79		*0.117	0.150	
RC12-339	4-7	-09°08'	90°02'	3070	2.48			0.182	
RC13-205	5-8	-02°17'	05°11'	3731	1.47	*0.145	*0.096	*0.124	
RC13-228 +	6-7	-22°20'	-11°12'	3204	1.61	0.119	0.074	0.103	
RC15-52	5-9	-29°14'	-85°54'	3780	2.31	0.152	0.123	0.125	*0.161
RC15-65	5-8	-53°04'	-78°57'	3200	2.41	0.179			
TR163-31TW+	6-18	-03°37'	-83°58'	3210	2.42	*0.212		*0.210	
V17-42 +	5-7	03°32'	-81°11'	1814	2.71				0.200
V18-68 +	0-12	-54°33'	-77°51'	3972	2.31	*0.145			
V19-29 +	5-18	-03°35'	-83°56'	2673	2.51	0.227			
V19-30 +	5-7	-03°23'	-82°21'	3071	2.42	*0.151			
V22-174 +	9-11	-10°04'	-12°49'	2630	1.52	*0.089	0.103	0.075	
V22-182	7-10	-00°33'	-17°16'	3937	1.45			0.123	
V22-193	5-7			4956	1.53			0.105	0.123
V22-195	5-7	13°17'	-19°40'	4770	1.54			0.135	
V22-196	5-7	13°50'	-18°58'	3728	1.48			0.139	
V22-197 +	4-17	14°10'	-18°35'	3167	1.43	0.116	*0.111	*0.113	
V22-198	4-6	14°35'	-19°40'	1082	2.11	*0.069	*0.074	0.064	
V23-6	5-8	42°29'	-61°48'	2246	1.16	*0.133			
V24-109	5-8	00°26'	158°48'	2367	2.55			*0.209	
V25-59 +	6-9	01°22'	-39°29'	3824	1.26	0.104	*0.059	0.080	
V27-60	5-8	72°11'	08°34'	2525	1.03			*0.058	
V27-86 +	5-8	66°36'	01°07'	2900	1.03			*0.071	
V28-56 +	3-4	68°02'	-06°07'	2941	1.02			*0.060	
V28-304	6-9	28°32'	134°08'	2942	2.60			*0.140	

Table 1. (continued)

Core	Sample Depth, cm	Latitude	Longitude	Water Depth, m	Estimated P μmol/kg	Cd/Ca, μmol/mol			
						Uvi	kul	wue	umb
V28-345	3-6	-17°40'	117°57'	1004	2.40			0.151	0.147
V29-29	5-8	05°07'	77°35'	2673	2.47		0.086	*0.124	
V29-179	+ 5-8	44°00'	-24°32'	3371	1.17		*0.090		
V32-128	4-7	36°28'	177°10'	3623	2.54			*0.162	
V34-52	1-4	-06°10'	89°48'	3984	2.33			0.109	
V34-54	1-3	-06°05'	85°10'	3254	2.37				
V34-55	5-6	-06°02'	88°57'	2992	2.36			0.171	

CHN and EN cores curated at Woods Hole Oceanographic Institution (WHOI), RC and V cores curated at Lamont-Doherty Geological Observatory (LDGO), and TR core curated at the University of Rhode Island (URI). Sample depth is given from "top" of core. Sample depths in WHOI cores are determined by markings on core liner (in which samples are stored); shrinkage may result in the actual physical top of the core being several centimeters from the top of the core liner. Sample depths in LDGO cores are given relative to marker pins inserted into cores upon extrusion and splitting. Latitude and longitude are degrees, with south and west negative. Cd/Ca is given for Uvigerina spp. (Uvi), C. kullenbergi (kul), C. wuellerstorfi (wue), and N. umbonifera (umb). This table includes all data collected up to July 21, 1988.

+: Cores for which the author is aware of published isotopic stratigraphies indicating more than 15 cm of Holocene sediment.

*: Duplicate or triplicate analyses of these foraminifera samples.

downcore scatter due to mixing than low sedimentation rate cores, and core tops from high sedimentation rate cores should have a closer relationship with bottom water chemistry. The reproducibility of multiple analyses of foraminifera from short sections of cores of various sedimentation rates is shown in Table 3. It appears that high sedimentation rate cores do show better reproducibility. This evidence argues for sediment mixing and foraminiferal inhomogeneity as the cause for scatter rather than analytical errors or cleaning problems.

Despite these lines of evidence in favor of a reasonably good correspondence between bottom water and foraminiferal composition, the problem is worth pursuit in more detail; the most promising line of study at present appears to be (1) replicated analyses of core top foraminifera from high sedimentation rate cores and (2) analyses of live benthic foraminifera collected from the seafloor.

THE OCEANIC CADMIUM AND CARBON ISOTOPE INVENTORY

As organisms remove carbon from the surface ocean, they preferentially take up the lighter isotope

^{12}C relative to ^{13}C. When this light organic carbon degrades in the deep ocean, it makes the carbon isotope composition of the deep water depleted in ^{13}C relative to ^{12}C. The magnitude of the change in the isotope ratio between surface waters and deep waters depends on the mean oceanic C:P ratio. Similarly, organisms are highly efficient at the uptake of cadmium from surface waters, driving it to very low concentrations. When the organic debris decomposes at depth, cadmium is released, enriching the deep waters. This one-dimensional vertical cycle is complicated by the advection of water masses throughout the deep ocean.

Although the oceanic distribution of nutrient-like tracers is determined by the general circulation of the ocean, absolute nutrient concentrations at a site in the ocean are also a function of the global oceanic inventory of those nutrients. Since both circulation and global inventory may vary independently, paleochemical data are a complex of both factors. The general circulation determines dispersion from the mean:

$$1 - \psi = \frac{\overline{P - P}}{\overline{P}} \quad \frac{\overline{Cd - Cd}}{\overline{Cd}} \quad \frac{\overline{\delta^{13}C - \delta^{13}C}}{R \overline{P}} \quad (4)$$

Table 2.   Estimated distribution coefficients (D) for Cd in Benthic
Foraminifera, Excluding Samples With D>4.75

Selection	Species	D	Standard Deviation	n
All core tops	Uvigerina	3.43	1.73	20
	C. kullenbergi	2.49	0.63	23
	C. wuellerstorfi	2.89	0.78	46
	N. umbonifera	3.05	0.87	14
	All species	2.93	1.05	103
Well-documented core tops	Uvigerina	2.75	0.80	11
	C. kullenbergi	2.75	0.55	13
	C. wuellerstorfi	2.90	0.58	19
	N. umbonifera	2.65	0.19	7
	All species	2.79	0.58	50
Well-documented core top replicates	Uvigerina	2.49	0.35	6
	C. kullenbergi	2.90	0.54	9
	C. wuellerstorfi	3.00	0.49	9
	N. umbonifera	2.71	0.22	4
	All species	2.82	0.47	28

n is the number of core tops included in the estimated mean.

where ψ is a circulation parameter that describes how tracer concentrations at any point in the ocean relate to the oceanic mean value; P, Cd, and $\delta^{13}C$ are the values of the tracers at that point in the ocean; the overlying bar signifies the oceanic mean of each tracer; and R is the $\Delta\delta^{13}C:\Delta P$ ratio in the ocean (determined by the organic C:P ratio and oceanic

mean total dissolved carbon dioxide) [Boyle, 1986]. In order to interpret ocean circulation from the tracer concentration history at a site over time, it is necessary to know how the oceanic mean value of the tracer changes over time.

It has been shown that the glacial average oceanic $\delta^{13}C$ was 0.5 o/oo more negative relative to interglacial times [Shackleton, 1977; Shackleton et
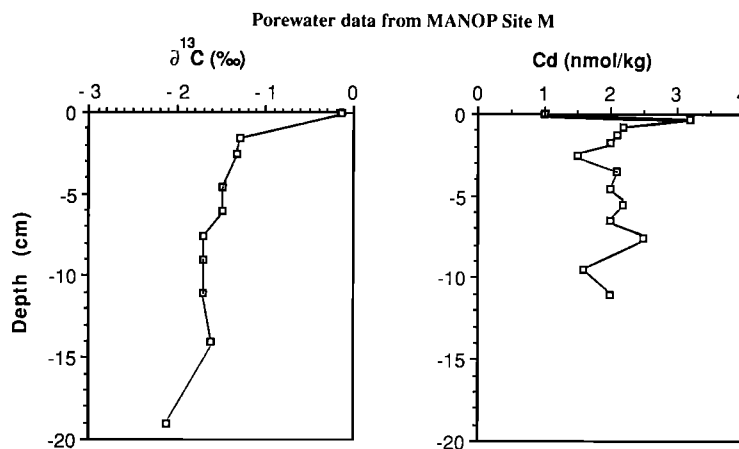
Porewater data from MANOP Site M

Fig. 5. Porewater data from Manganese Nodule Program site M. Cd data are from Heggie et al. [1986]; $\delta^{13}C$ data are from McCorkle et al. [1985]. Note the rapid decrease in $\delta^{13}C$ and rapid increase in Cd in the upper centimeters.

Table 3. Reproducibility of Replicate Analyses in Cores
of Varying Sedimentation Rates

Core	Depth Range, cm	Approx. sedimentation rate, cm/kyr	Species	mean Cd, μmol/mol	Standard Deviation, μmol/mol	Relative Standard Deviation, %	n	r
AII107 65GGC	37-60	1.5	wue	.129	.024	19	14	0
CHN82 4PC	148-172	3	Uvi	.086	.011	13	31	0
TR163 31B	63-83	7	Uvi	.184	.022	12	20	2
EN120 GGC1	79-91	10	umb	.073	.007	10	18	1

n, number of analyses included in mean; r, number of analyses rejected from mean; see table 1 for species definitions.

al., 1983; Boyle and Keigwin, 1985]. Downcore $\delta^{13}C$ records contain a large component due to oceanic inventory changes. The oceanic inventory of Cd appears less variable. Boyle and Keigwin [1982] made measurements of Cd in a North Atlantic core and assumed that global Cd was constant. This assumption enabled them to interpret downcore Atlantic benthic Cd as a record of changing North Atlantic Deep Water hydrography. Broecker and Peng [1984] suggested instead that the Cd inventory during glacial times was about 42% higher than during interglacial times (due to the dissolution of Cd-rich organic shelf sediments). Partial resolution of the validity of these assumptions was made possible when Boyle and Keigwin [1985] obtained Cd data from a Pacific sediment core. They estimated that global oceanic Cd was probably not much more than 17% higher during glacial periods than during interglacial times. However, in the sediment core that was available to them, the sedimentation rate was low (2 cm/kyr) and benthic foraminifera were scarce in the interglacial sections, so that very few measurements were included in the mean interglacial Cd estimates.

Cd measurements have now been made on a more suitable Pacific core (Kasten core TR163-31B) located near the site of well-known cores V19-29 and V19-30. This region has high sedimentation rates (about 3 cm/kyr in interglacials and up to 7 cm/kyr in glacial periods). The large-sized core and higher absolute abundances of benthic foraminifera have allowed for the generation of a good benthic Cd record for the last 25,000 years (Table 4; Figure 7). From this record it appears that Pacific Cd was about 12% lower during the last glacial maximum relative to the Holocene. This is about the amount needed to balance the Atlantic Cd increase documented by Boyle and Keigwin [1982], Boyle [1984], and Boyle and Keigwin [1985] (Figure 8). From this evidence it appears that the most reasonable assumption is that the cadmium inventory of the ocean remains constant

(probably for the last few hundred thousand years) and that downcore benthic Cd changes are due only to changes in the general circulation patterns of the ocean.

Table 4. Benthic Cd data from core TR163-31B

Depth Range, cm	Species	Cd/Ca, μmol/mol	sigma	n	r
7-10tw	Uvi	0.203		1	
	wue	0.164		1	
10-13tw	Uvi	0.219		1	
16-19tw	Uvi	0.239		1	
	wue	0.259		1	
1-2	Uvi	0.244	0.010	3	
	wue	0.159		1	
3-4	Uvi	0.229	0.017	3	
	wue	0.181		1	
6-7	Uvi	0.199	0.012	3	
	wue	0.211	0.019	2	
9-10	Uvi	0.223	0.005	3	
	wue	0.175		1	
13-14	Uvi	0.225	0.002	3	1
	wue	0.244		1	
16-17	Uvi	0.216	0.017	3	2
19-20	Uvi	0.212	0.021	3	1
23-24	Uvi	0.221	0.077	3	1
	wue	0.241		1	
25-26	Uvi	0.251	0.007	2	
26-27	Uvi	0.238	0.001	3	2
	wue	0.239		1	
29-30	Uvi	0.219	0.021	2	1
	wue	0.151		1	
33-34	Uvi	0.202	0.015	3	
	wue	0.144		1	
36-37	Uvi	0.220	0.028	3	
37-38	Uvi	0.225	0.041	2	
	wue	0.212		1	
39-40	Uvi	0.224	0.012	3	1

Table 4. (continued)

Depth Range, cm	Species	Cd/Ca, μmol/mol	sigma	n	r
43-44	Uvi	0.214	0.017	4	
46-47	Uvi	0.205	0.022	4	1
	wue	0.188		1	
49-50	Uvi	0.191	0.005	3	1
	wue	0.186		1	
53-54	Uvi	0.188	0.013	3	1
	wue	0.198		1	
56-57	Uvi	0.197	0.012	3	
	wue	0.145	0.001	2	
59-60	Uvi	0.198	0.031	4	
	wue	0.179		1	
61-62	Uvi	0.197	0.050	3	
63-64	Uvi	0.191	0.005	4	
	wue	0.187		1	
66-67	Uvi	0.173	0.023	4	
	wue	0.206		1	
69-70	Uvi	0.187	0.020	4	1
	wue	0.245		1	
73-74	Uvi	0.181	0.026	3	
	wue	0.206		1	
76-77	Uvi	0.176	0.031	3	1
	wue	0.197		1	
79-80	Uvi	0.201	0.013	3	
	wue	0.173		1	
83-84	Uvi	0.187	0.025	3	
	wue	0.177		1	
85-86	Uvi	0.191	0.042	3	1
	wue	0.202		1	
86-87	Uvi	0.196	0.016	2	1
	wue	0.188		1	
89-90	Uvi	0.206	0.006	2	
93-94	Uvi	0.180	0.001	2	
	wue	0.181		1	
96-97	Uvi	0.209	0.038	5	
	wue	0.196		1	
99-100	Uvi	0.193	0.007	3	
	wue	0.231		1	
103-104	Uvi	0.181	0.031	3	
	wue	0.207		1	
106-107	Uvi	0.167	0.010	3	
	wue	0.195		1	
109-110	Uvi	0.177	0.020	5	
	wue	0.166	0.070	3	
113-114	Uvi	0.175	0.025	3	1
	wue	0.177		1	
116-117	Uvi	0.160	0.023	3	
119-120	Uvi	0.190	0.025	4	
	wue	0.207		1	
123-124	wue	0.203		1	
	Uvi	0.197	0.009	3	1
123-124	wue	0.203	0.000	2	
126-127	Uvi	0.183	0.004	4	
	wue	0.207		1	
129-130	Uvi	0.204	0.028	4	
	wue	0.150		1	
133-134	Uvi	0.201	0.043	5	2
	wue	0.217		1	1

Table 4.(continued)

Depth Range, cm	Species	Cd/Ca, μmol/mol	sigma	n	r
136-137	Uvi	0.188	0.021	4	
139-140	Uvi	0.175	0.018	3	
	wue	0.182		1	
143-144	Uvi	0.188	0.013	3	1
	wue	0.194		1	
145-146	Uvi	0.171	0.021	3	
	wue	0.229		1	
149-150	Uvi	0.182	0.028	2	
	wue	0.178		1	
153-154	Uvi	0.193	0.024	3	
	wue	0.132		1	
156-157	Uvi	0.171	0.004	2	
	wue	0.165		1	
159-160	Uvi	0.225	0.012	2	
	wue	0.139		1	

Note that $CaCO_3$ curves for the trigger core (tw) and Kasten core indicate that the top 15 cm of the Kasten core was lost (M. Leinen, personal communication, 1987). Sigma, standard deviation of replicates includes in mean; n, number of replicates included in mean; r, nuymber of analyses rejected from mean. See table 1 for definition of species' abbreviations.

APPLICATION OF PALEO-Cd DATA TO PALEOCEANOGRAPHIC PROBLEMS

Cd in Benthic Foraminifera and Changes in Deep Ocean Circulation Patterns: Comparison to C-13 Studies

Although ^{13}C and Cd provide similar information about deep ocean circulation, they are not redundant. The advantages of ^{13}C are (1) it is measured by more laboratories and has a larger data base, (2) it does not suffer from contamination problems, and (3) paleoceanographers are familiar with this tracer and understand its qualitative and quantitative significance. Disadvantages of ^{13}C are (1) there are significant (and variable) offsets between species, whose cause is not understood, and (2) changes in the global average are comparable to those due to ocean circulation changes, making it more difficult to isolate the circulation component. This last factor is a serious problem for older sediments where it is more difficult to define isochronous horizons. The advantages of Cd are (1) there are no significant interspecies offsets, leading to less difficulty in comparing records where different species must be analyzed, and (2) there is no significant inventory change for Cd, so downcore records are simply
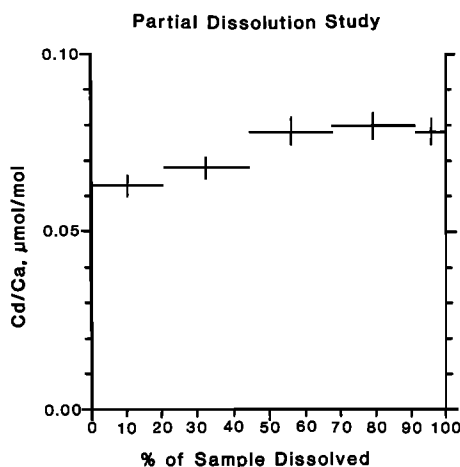
Partial Dissolution Study

Fig. 6. Partial dissolution study. A sample of Uvigerina from core CHN 82 Sta 50 Core 20PC (179-189 cm; the glacial maximum in this core is at 80 cm [Boyle and Keigwin, 1985], and this sample is in oxygen isotope stage 3 and is roughly 40,000 years old. After cleaning the crushed fragments according to the procedure described by Boyle and Keigwin [1986], 13.1 mg of cleaned sample remained. This sample was placed in a 500-μl microcentrifuge tube. A 150-μl aliquot of 1 N HNO3 was added to the sample, followed by several minutes of ultrasonic agitation, until visible bubbling began to slow. The overlying acid was then drawn off and saved; this procedure was then repeated for four more aliquots of acid. The goal of this experiment was to selectively dissolve and clean the surfaces of the foraminifera, leaving behind only the clean inner portions of the crystal. Since there is no decrease in the Cd content of the fractions, it is clear that further acid cleaning serves no useful purpose for foraminiferal Cd analysis.

interpretable as historical records of ocean circulation patterns. The disadvantages of Cd are (1) susceptibility to contamination, difficulty in analysis, and uncertain faith in any single analysis, and (2) only one laboratory has published results on this tracer, so the data base is smaller and less understood by the paleoceanographic community.

Use of the established ^{13}C technique was hampered initially by a problem alluded to earlier. Benthic foraminifera (e.g., Uvigerina) are not always reliable recorders of bottom water ^{13}C. This variable reliability has been documented by Zahn et al. [1986], who showed that the $\delta^{13}C$ value of Uvigerina seems to be influenced by the organic carbon content (or flux) of the sedimentary environment. Unfortunately, this species is the dominant source for much published ^{13}C data,

leading to conclusions of uncertain reliability, particularly when species used are not reported (as in the work of Duplessy and Shackleton [1984]). It appears that C. wuellerstorfi is more reliable as a tracer of deepwater carbon isotope values. This result is now generally accepted by carbon isotope paleoceanographers, and the job of redoing the glacial/interglacial ^{13}C history is underway (as indicated by the articles by Duplessy et al. [1988] and Curry et al. [1988].

Both Cd and ^{13}C data from C. wuellerstorfi were used in the first artifact-free assessment of the scale of chemical changes in North Atlantic Deep Water (NADW). Boyle and Keigwin [1982] determined that the nutrient content of the deep North Atlantic Ocean at 3200 m depth doubled during glacial periods. This result implied a significant reduction in the relative production of NADW relative to Antarctic water sources and confounded the notion that NADW production ceased (an idea based on benthic foraminiferal populations [Streeter and Shackleton, 1979] and Uvigerina carbon isotope records [Shackleton et al., 1983]). Further evidence for diminished but continuous NADW flow was provided by other North Atlantic records and a
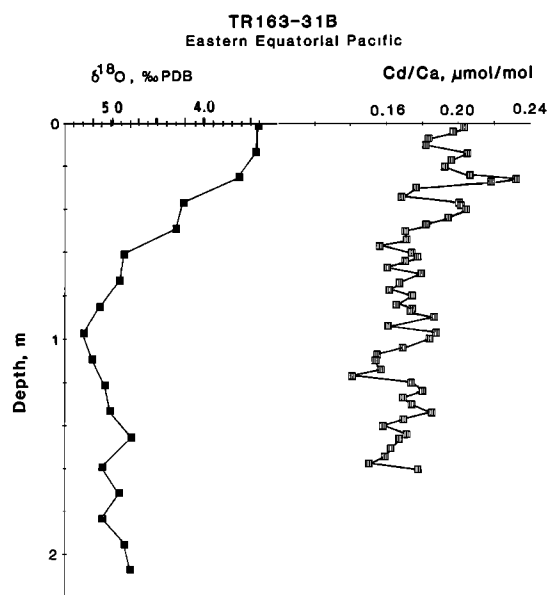
TR163-31B
Eastern Equatorial Pacific

Fig. 7. Cd and $\delta^{18}O$ data from benthic foraminifera in core TR163-31B. The Cd record is dominated by Uvigerina replicates (at least three for most samples; see Table 4) but also includes C. wuellerstorfi analyses (usually one for each sample); there was no systematic difference between the species (see figure 3). Data for $\delta^{18}O$ are from N. J. Shackleton (unpublished data, 1988).

MID-WATER ATLANTIC-PACIFIC CHEMISTRY
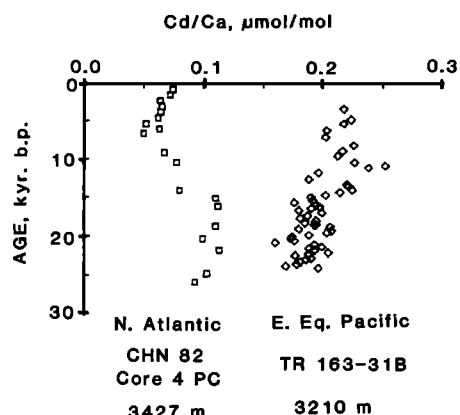FOR THE LAST 18,000 YEARS

Cd/Ca, µmol/mol

Fig. 8. Benthic Cd records from middepth cores in the Atlantic and Pacific oceans (CHN 82 Sta 24 Core 4PC and TR163-31B), showing the volumetrically compensating Atlantic increase (about a factor of 2) and Pacific decrease (about 12%).

Pacific Cd record [Boyle, 1984; Boyle and Keigwin, 1985], (also see Figure 8). Subsequent work by other investigators using ^{13}C in C. wuellerstorfi has confirmed these conclusions concerning the persistence of Atlantic/Pacific chemical fractionation [see Curry et al.,1988].

Curry and Lohmann [1983] used ^{13}C evidence from C. wuellerstorfi to discover a significant change

in the depth gradient of carbon isotopes in the tropical eastern basin of the Atlantic Ocean. Shackleton [1985] found that intermediate depth sediment cores in the northwestern Pacific revealed significant nutrient depletion in this depth zone during glacial periods; this discovery has been amplified by more recent work by Duplessy et al. [1988] is confirmed by Cd data from a core in the Sea of Okhotsk [Boyle, 1988].

Boyle and Keigwin [1986, 1987] used Cd and ^{13}C data from a high sedimentation rate core from the deep (4400 m) western North Atlantic to show that there was a strong reduction in relative NADW flow during the cold "Younger Dryas" climate event which occurred 10,000-11,000 years ago. This result implies that the relative flow of NADW through the deep North Atlantic is quite strongly coupled to surface climate (e.g., glacial ^{18}O in ice cores [Dansgaard et al., 1984], European pollen records, and movements of the North Atlantic polar front documented by Ruddiman and McIntyre [1977]).

Boyle and Keigwin [1986] provided Cd/Ca and C. wuellerstorfi data showing that glacial North Atlantic intermediate waters were significantly more nutrient-depleted than at present. In the depth range 2000-2500 m, the Cd and $\delta^{13}C$ values from mid-Atlantic ridge cores at 40°N are similar in glacial and interglacial times. In a Caribbean core, Cd and $\delta^{13}C$ values indicate more nutrient-depleted waters. Since the Caribbean is ventilated by Atlantic waters originating at about 1800 m depth, this result applies to the North Atlantic intermediate waters as well. Cofer-Shabica and Peterson [1986] presented a long
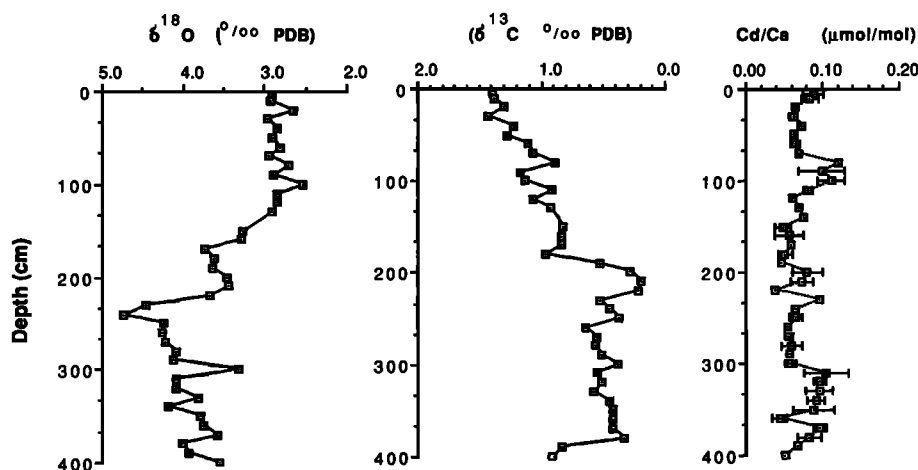

Fig. 9. High latitude planktonic Cd (N. pachyderma) for core from the southern ocean, Indian sector (MD 80-304). The picked foraminiferal samples were provided by Laurent Labeyrie; the oxygen and carbon isotope data are provided by Labeyrie and Duplessy [1985]. Data are reported by Boyle [1988].

downcore Caribbean $\delta^{13}C$ record which indicates that ^{13}C enrichments during glacial periods have occurred repeatedly during the late Quaternary. Zahn et al. [1986] found that intermediate depth cores near Gibraltar showed a significantly heavier ^{13}C during glacial periods. Although they interpreted this data as indicating enhanced outflow of nutrient-depleted Mediterranean water, the carbon isotope values they found near Gibraltar are similar to those found by Boyle and Keigwin [1986, 1987] and Cofer-Shabica and Peterson [1986] in the Caribbean. It could be argued that the absence of a gradient from east to west comprises evidence against a Mediterranean source for these low-nutrient waters. Boyle and Keigwin [1987] suggested that this source was near the North Atlantic polar front, where it should be expected that cold low-salinity waters would exist analogous to those presently found in the North Pacific.

Paleoceanographers are trying to do with a few dozen cores what contemporary physical oceanographers do with a network of thousands of hydrographic stations. While we cannot expect to match the precision and detail of the knowledge of modern oceans, it should be possible to outline the major characteristics of ancient deep ocean hydrography. From the evidence outlined here, it appears that the ocean has undergone complex three-dimensional changes in its nutrient distribution.

Cadmium in High-Latitude Planktonic Foraminifera and Changes in the Preformed Nutrient Content of the Ocean

The nutrient content of oceanic water masses when first cut off from gas equilibration with the atmosphere and sinking into the deep ocean is called the "preformed nutrient content". The preformed nutrient content in polar ocean waters is important for two reasons: (1) it serves as a boundary condition on the chemical composition of deepwater masses, and (2) it is linked to the biological uptake of deep ocean carbon dioxide after it upwells into high-latitude surface oceans. As a number of recent papers have suggested [Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984; Knox and McElroy, 1984], the preformed nutrient content of polar waters is a measure of the effectiveness of the ocean in isolating deep ocean CO_2 from the atmosphere: when preformed nutrients are lower, the isolation is more effective and atmospheric carbon dioxide concentrations are lower. The preformed nutrient content of polar ocean waters has a significant role in control of atmospheric CO_2 and in particular may be a cause of the reduction of atmospheric carbon dioxide observed during glacial periods.

The only direct measure we have of changes in the preformed nutrient content of ocean waters is the Cd record contained in the high-latitude plantonic foraminifera N. pachyderma (left coiling). Carbon 13 provides an indirect indicator. Both types of evidence are imperfect tracers of preformed phosphate because there can be no guarantee that foraminifera actually lived in the late winter surface waters that sank into the deep ocean. The problem is twofold:

1. Deep water has very restricted sites of formation [Warren, 1981]; the typical southern ocean core containing N. pachyderma is not within this area. Even if one can locate cores that are in the modern region of bottom water formation, there is no guarantee that glacial bottom waters formed in the same area.

2. N. pachyderma grows over a range of depths at variable rates over the course of 1 year (not to mention the possibility of interannual variability). The sedimentary record represents a flux-weighted average over that depth zone and many annual cycles of production. Unless maximum foraminiferal flux coincides with bottom water formation, the sedimentary record may not be an accurate indication of preformed nutrients.

Despite these problems, something can be learned from the record contained in planktonic foraminifera. A Cd/Ca record has been obtained for the southern ocean, in collaboration with Laurent Labeyrie of Centre de Faibles Radioactivites (Figure 9; also see Boyle, [1988]). While analytically significant changes in preformed nutrients appear to occur, these changes are not systematic between glacial and interglacial times, nor are they quantitatively sufficient to satisfy hypotheses attributing changes in atmospheric carbon dioxide to changes in the preformed nutrient content of high-latitude oceans. While this evidence is not yet sufficiently documented to demand the rejection of the preformed nutrient scenarios used to explain the glacial decrease in carbon dioxide, it does not provide much encouragement for those theories either.

CONCLUDING REMARKS

The Cd content of foraminifera is a useful tracer of past ocean circulation changes. While it has some unique advantages relative to other techniques which are being employed (such as ^{13}C), the combination of all available techniques is likely to prove more powerful than the use of any individual tracer. Continued documentation of the reliability of these tracers is needed, but large interocean fractionations and major circulation changes can be documented reliably by these techniques. The perspective

provided by modern physical oceanography suggests that many discoveries await explorers of the circulation of past oceans and that this area of research will be scientifically fruitful for many years.

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