

Sensitivity of the phosphate-cadmium-carbon isotope relation in the ocean to cadmium removal by suboxic sediments

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Abstract. Reconstructions of past deep ocean nutrient concentrations rely largely on the carbon isotopic composition and cadmium content of shells of benthic foraminifera. When comparing records of these two paleonutrient tracers, a relation similar to the phosphate-cadmium-carbon isotope relation in the water column today is generally assumed. We present new water column, sediment, and pore water data from the California continental margin which demonstrate that Cd accumulation is enhanced in suboxic sediments. These results suggest that the oceanic Cd inventory is sensitive to changes in the areal extent and redox intensity of suboxic sediments and thus that the phosphate-cadmium relation in the ocean could have been different in the past. The magnitude of this effect and its evolution through time is presently hard to quantify because the oceanic Cd budget is poorly constrained.

Introduction

Plankton growth in surface water followed by sinking and decay of this material at depth establish a vertical gradient in the water column of the nutrient phosphate (P), the trace element Cd, and the $^{13}\text{C}/^{12}\text{C}$ ratio of inorganic carbon [Bruland, 1980; Knauer and Martin, 1981; Broecker and Peng, 1982; Kroopnick, 1985; Boyle, 1988]. Near-linear relationships between P, Cd, and $^{13}\text{C}/^{12}\text{C}$ (expressed as $\delta^{13}\text{C}$) illustrate the intimate link between the uptake and regeneration cycles of P, Cd, and carbon. Recent studies have pointed out the potential impact of changes in sea surface temperature and air-sea gas exchange on $^{13}\text{C}/^{12}\text{C}$ in the ocean [Broecker, 1993; Charles *et al.*, 1993], but the current view is that the distributions of P and Cd probably remained closely linked throughout glacial-interglacial cycles because biological processes dominate the spatial patterns of both elements. However, while Cd and P are expected to generally covary in the water column, any glacial change in the inventory of either element would change the slope of the P-Cd relationship and therefore could change the predicted $^{13}\text{C}/^{12}\text{C}$ value for a given foraminiferal Cd/Ca ratio [Boyle, 1986; Delaney, 1990].

Bituminous shales can be enriched in Cd by several orders of magnitude relative to the average content of the Earth's crust of

$0.1 \mu\text{g g}^{-1}$ [Taylor and McLellan, 1985], suggesting an enrichment mechanism specific to low oxygen conditions [Holland, 1984]. Pronounced depletions of Cd in the water column have also been measured in a number of anoxic basins such as the Black Sea, Saanich Inlet, and Framvaren Fjord [Jacobs and Emerson, 1982; Jacobs *et al.*, 1985, 1987]. Sediments underlying these systems contain up to $19 \mu\text{g g}^{-1}$ Cd [Skei *et al.*, 1988] suggesting that water column depletions are due to the formation of a particulate Cd phase, possibly an insoluble Cd-sulfide. This is consistent with observations of low Cd concentrations in anoxic and suboxic pore waters [Elderfield *et al.*, 1981; Westerlund *et al.*, 1986; Gobeil *et al.*, 1987; McCorkle and Klinkhammer, 1991]. While it seems unlikely that oxygen in the deep ocean was ever totally consumed during the past several million years, the areal extent of suboxic sediments probably varied over time. The connection between such variations and the oceanic Cd budget was pointed out by Rosenthal *et al.* [1993] by looking at Cd enrichments in Southern Ocean sediments deposited during glacial time. We present here new evidence of enhanced Cd accumulation in suboxic sediments to suggest that the slope of today's P-Cd relation in the ocean may depend to a large extent on the areal extent of suboxic sediments and the intensity of reduction below the sediment-water interface. The data presented here include water column, pore water, and sediment Cd measurements from the California slope and margin. This region is well suited to study redox-sensitive diagenetic processes because of rapid pore water oxygen depletion in the sediment and wide a range of oxygen concentrations in overlying bottom water.

Methods

Water column samples from the Santa Barbara Basin (Figure 1) were collected from RV *Sprout* in August 1993 with Teflon-coated lever-action Niskin bottles. Dissolved Cd was measured by graphite-furnace atomic absorption spectroscopy (GFAAS) following pre-concentration with a device described by *van Geen and Boyle* [1990] and *van Geen and Luoma* [1993]. The blank from this method is 0.002 ± 0.001 nmol/kg based on repeated Cd determinations for North Pacific central gyre surface water [Bruland, 1980]. Reproducibility and recovery were ± 0.015 nmol kg⁻¹ and $101 \pm 4\%$ (n=15), respectively, based on North Pacific surface water spiked to 0.4 nmol kg⁻¹ and used as a consistency standard. Dissolved P and silicate (Si) concentrations were measured spectrophotometrically by flow injection (QuickChemAE, Lachat Instruments, Milwaukee, Wisconsin). Procedures for P and Si determinations prescribed by the manufacturer are adaptations of standard colorimetric methods described by *Strickland and Parsons* [1968]. P and Si blank corrections determined by analyzing Sargasso Sea surface water were 0.1 and 0.5 $\mu\text{mol/kg}$, respectively. Reproducibility of P and Si determinations by this method is typically on the order of $\pm 5\%$. Samples were also drawn from the Niskin bottles to determine the isotopic composition of dissolved inorganic carbon according to procedures detailed by *McCorkle and Klinkhammer* [1991].

California margin sediment samples (Figure 1) were obtained from a set of eight box cores in the 589-3728 depth range described by *Reimers et al.* [1992]. Nine piston and gravity cores collected and radiocarbon dated by the U.S. Geological Survey (610-3305 m) and samples from four box cores collected during

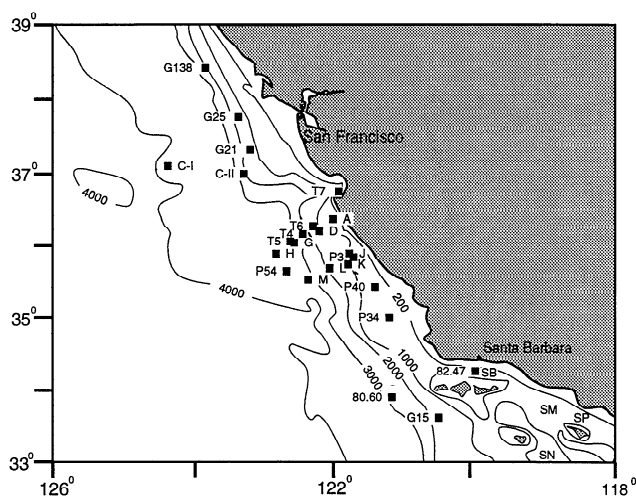


Figure 1. Location of cores used to determine authigenic Cd fluxes to California margin sediments. Sites of *Reimers et al.* [1992] labeled by capital letters A, D, H, J, K, L, and M. USGS cores indicated by last portion of core labels in Table 1. Teflon-2 sites labeled T4, T5, T6, and T7. Also indicated are water column profiles C-I and C-II of *Bruland* [1980] and CalCoFI stations 80.60 and 82.47 discussed in text. GEOSECS station 201 is located outside the boundary of this map ($34^{\circ} 10' \text{ N}$, $127^{\circ} 54' \text{ W}$). Locations of Santa Barbara (SB), Santa Monica (SM), San Pedro (SP), and San Nicolas (SN) are also indicated.

the Teflon program (100-3360 m) were also used in this study. For solid phase Cd determinations, approximately 100 mg of dried sediment was leached overnight in 1 mL of 2 N HCl at 60°C. Cd in the leachate solution was quantified by GFAAS with Zeeman background correction and calibration by standard additions. A reproducibility of $\pm 10\%$ is estimated. For a number of samples, sediment remaining after decanting the acid solutions was subsequently totally dissolved in HF/HClO₄ at $\sim 140^{\circ}\text{C}$. Following evaporation to dryness, these residues were redissolved in 8 N HNO₃ for analysis.

Pore waters were extracted from some of the same California margin box cores described in *Reimers et al.* [1992] and were sampled for Cd and $\delta^{13}\text{C}$ following procedures described by *McCorkle and Klinkhammer* [1991]. Following pre-concentration of 1.0 mL samples with 1-pyrrolidine-dithiocarbamate (APDC), Cd was determined at OSU by GFAAS with a precision of $\pm 5\%$ [Klinkhammer et al., 1982; *McCorkle and Klinkhammer*, 1991]. The $\delta^{13}\text{C}$ samples were extracted and analyzed at WHOI, with a precision of ± 0.1 ‰ [McCorkle and Klinkhammer, 1991].

Results

Santa Barbara Basin Water Column

A water column profile collected in the Santa Barbara Basin in August 1993 offers direct evidence that suboxic conditions can uncouple the distributions of P proxies Cd and $\delta^{13}\text{C}$ in the water column. The basin has a relatively shallow sill at 275 m to the east and a deeper sill at 475 m to the west [Emery, 1960]. Oxygen concentrations in the 100 m below the deep sill typically vary from 1 to 15 μM as the deep basin is flushed [Sholkovitz and Gieskes, 1971, Sholkovitz and Soutar, 1975; *Reimers et al.*, 1990]. To compare our results with data from nearby stations outside the borderland basins, we plot Cd and $\delta^{13}\text{C}$ as a function of P in Figure 2. The upper 400 m of the water column within the basin show P, Cd, and $\delta^{13}\text{C}$ variations consistent with the offshore profiles at stations C-I and C-II of *Bruland* [1980] for Cd, and GEOSECS station 201 for $\delta^{13}\text{C}$ [Broecker et al., 1982; *Ostlund et al.*, 1987]. Below about 400 m depth, there is a clear divergence between the P-Cd relations which can be expressed as a 0.2 nmol kg⁻¹ deficit in deep water Cd relative to seawater at equal P outside the basin. No deviation from the GEOSECS 201 P- $\delta^{13}\text{C}$ relationship is seen in deep water of the Santa Barbara Basin.

California Margin Sediments

Sediment samples from the California continental slope and rise were analyzed to estimate the importance of Cd trapping in suboxic sediments under a wide range of bottom water oxygen concentrations (Table 1). At a number of stations, both core top (0 - 0.5 cm) and slightly deeper (8 - 10 cm) sediment samples were analyzed for bulk Cd. The bathymetric profile of sediment Cd concentrations in California margin sediments shows a significant enrichment at the depth of the oxygen minimum zone, and downcore Cd concentrations higher than core-top values at all depths but one (Figure 3). The Cd content of sediment remaining after the HCl leach averaged 0.09 ± 0.04 $\mu\text{g g}^{-1}$ (n=13), a value indistinguishable from the mean crustal content of 0.1 $\mu\text{g g}^{-1}$ [Taylor and McLellan, 1985]. There was no discernable difference in residual Cd between samples from the oxygen minimum and other depths (Figure 3). This indicates that the hot

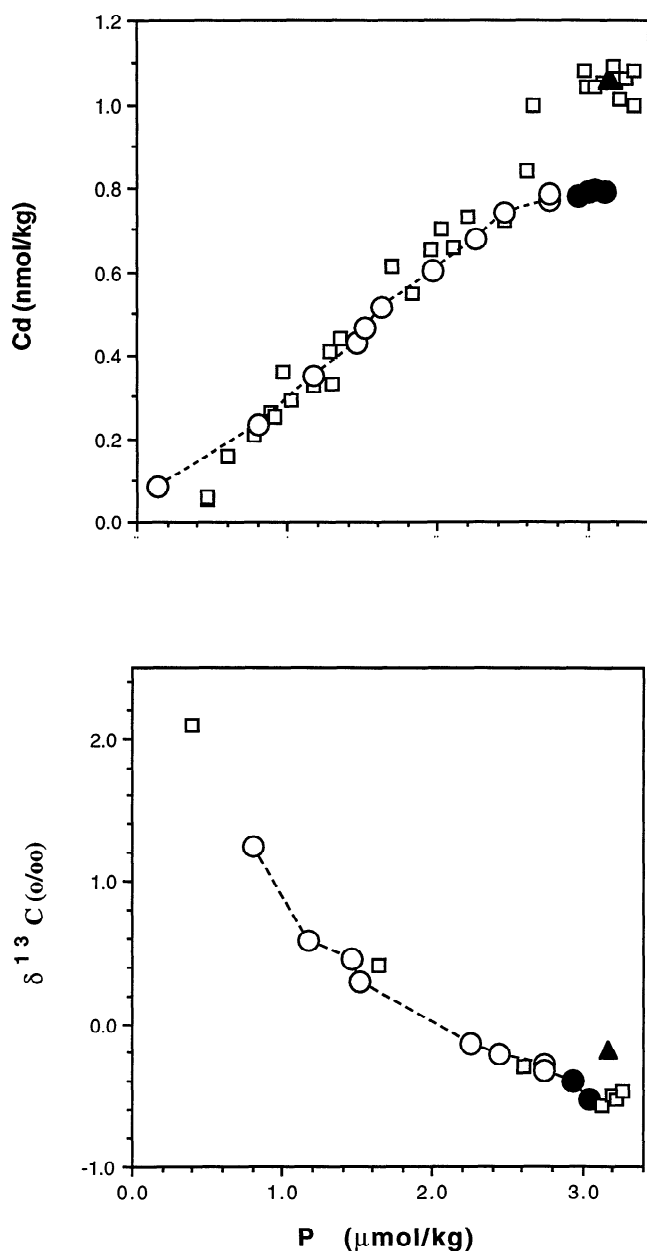


Figure 2. P-Cd and P- $\delta^{13}\text{C}$ relations in the Santa Barbara Basin water column. Open circles connected by dotted line indicate samples collected between 19 and 396 m depth. Surface water was analyzed for Cd and P only. Samples indicated by filled circles were taken between 423-537 m depth. Cd and P data to 1000 m depth from stations C-I and C-II of *Bruland* [1980], and nearby stations of *Bruland et al.* [1978], and *Knauer and Martin* [1981] shown by open squares in upper panel. Squares in lower panel show P- $\delta^{13}\text{C}$ relation to 1000 m depth at GEOSECS station 201 [*Broecker et al.*, 1982; *Ostlund et al.*, 1987]. A correction of +0.1 ‰ was applied to the deepest GEOSECS 201 sample plotted here (943 m) [*Kroopnick*, 1985]. Triangle shows bottom water composition at box core site J of *McCorkle and Klinkhammer* [1991]. P concentration at site J was estimated from the measured O_2 concentration and the O_2 -P relation at station C-I of *Bruland* [1980].

HCl-leach procedure effectively releases the authigenic Cd fraction, without significantly affecting the crustal component.

California Margin Pore Waters

Pore water Cd and $\delta^{13}\text{C}$ profiles for two of the box cores of *Reimers et al.* [1992] were presented by *McCorkle and Klinkhammer* [1991]. Pore water Cd and $\delta^{13}\text{C}$ data for three additional cores are listed in Table 2. Cd concentrations typically increase sharply just below the sediment-water interface and by 3-5 cm depth display a strong decrease to values $\leq 0.3 \text{ nmol kg}^{-1}$. This pattern reflects the release of Cd from decomposing organic matter at the sediment-water interface, and subsequent redox-controlled removal near the top of the anaerobic zone of the sediments [*McCorkle and Klinkhammer*, 1991].

Flux Estimates

The three sets of data (water column, sediment, and pore water) provide independent estimates of the rate of Cd removal by suboxic sediments, and enable us to evaluate the sensitivity of the oceanic Cd cycle to plausible changes in this removal.

Santa Barbara Basin

An estimate of the Cd removal flux can be made by using the Santa Barbara Basin water column data and assuming that salinity and temperature are conservative during mixing in the deep basin. In order to make this estimate, we assume that the composition of the bottom 100 m of the Santa Barbara Basin water column is at steady state even though the short time scale of flushing has been emphasized in a number of studies [*Emery*, 1960; *Sholkovitz and Gieskes*, 1971; *Sholkovitz and Soutar*, 1975; *Reimers et al.*, 1990]. Steady state is dictated by the availability of a single Cd profile for this study, but this assumption is supported by recent work suggesting that flushing of California borderland basins is a continuous process [*Berelson*, 1991; *Hammond et al.*, 1990].

Starting in 1986, bottom waters of the basin were sampled by quarter-annual cruises of the California Cooperative Fisheries Investigation program (CalCoFI). On the basis of the CalCoFI data, a representative estimate of the mean composition of three end-members contributing to the basin can be calculated (Table 3). These end-members (EM) are water of (1) subarctic and (2) equatorial origin at the sill depth outside the basin, and (3) water at the sill depth within the basin. Over the long-term, these end-members must mix in proportions of 12%, 31%, and 57%, respectively, to match the mean salinity and temperature of the deep basin in the 500-570 m depth range (Table 3). The composition of these end-members in terms of oxygen, P, Si, and Cd concentrations is also listed in Table 3. EM 1 and EM 2 contribute $1.05 \text{ nmol kg}^{-1}$ Cd based on their mean P content of $3.05 \mu\text{mol kg}^{-1}$. On the basis of the mixing model, deviations from conservative behavior are calculated for these constituents. Oxygen depletion and nutrient enrichment in the deep basin relative to the product of conservative mixing reflect decomposition of planktonic debris produced in surface waters [*Sholkovitz and Gieskes*, 1971; *Sholkovitz and Soutar*, 1975]. The calculations show a P excess relative to conservative mixing of $0.44 \mu\text{mol kg}^{-1}$. The same mixing model applied to Cd predicts a concentration of $0.90 \text{ nmol kg}^{-1}$ for the deep basin, $0.11 \text{ nmol kg}^{-1}$ higher than the measured value.

Table 1. Cd Concentrations in California Margin Sediments

Station	Depth m	Oxygen μM	HCl leach Cd $\mu\text{g g}^{-1}$ Surf. - Deep	Residual Cd $\mu\text{g g}^{-1}$ Surf. - Deep	Sedimentation Rate cm kyr^{-1}	Authigenic Cd Accumulation $\text{ng cm}^{-2} \text{yr}^{-1}$	
						Sediment	Pore water
Teflon 2-7	100		0.17-0.28	0.05-0.06			
Reimers A	589	18	0.38-0.37				
F2-92-P34	610	18	1.84	0.16	13	10.5	
F2-92-P40	760	12	1.43	0.14	12	7.6	
Reimers J	786	12	1.30-1.60		13	9.2	4.7-14
F2-92-P3	799	12	1.56	0.14	12	8.2	
Reimers K	998	20	0.61-0.75		8	2.6	5.3-43
Teflon 2-6	1395		0.36-0.39	0.05-0.09			
VI-81-G15	1430	38	0.65	0.06	8	2.3	
Reimers D	1443	38	0.27-0.50		1	0.2	
F8-90-G21	1605	55	0.43	0.05	17	3.2	
F8-90-G25	1720	60	0.48	0.05	20	4.2	
Reimers L	1894	72	0.10-0.76		2	0.7	
Teflon 2-4	2145		0.22-0.86	0.05-0.11			
L13-81-G138	2531	95	0.57	0.06	9	2.3	
F2-92-P54	3305	115	0.42	0.08	11	2.0	
Reimers G	3344	120	0.15-0.40		23	4.0	1.2-6.0
Teflon 2-5	3360		0.29-0.43	0.05-0.06			
Reimers H	3571	125	0.18-0.24		5	0.5	
Reimers M	3705	126					5.3-12
	3728		0.23-0.52	0.05-0.06	19	4.4	5.1-13

Cd concentration in sediment following HCl leach procedure from ~0.5 cm (Surf.) and ~10 cm depth (Deep), respectively. Residual Cd following the HCl leach determined by total dissolution of the remaining sediment. The authigenic Cd component was determined from the HCl data because the average composition of the residual ($0.09 \pm 0.04 \mu\text{g g}^{-1}$) was indistinguishable from the mean crustal Cd content ($0.1 \mu\text{g g}^{-1}$). The rate of authigenic Cd accumulation was determined assuming a mean porosity of 0.80 and a sediment density of 2.2 g cm^{-3} . Published sedimentation rates were used as listed by *Reimers et al.* [1992] except for site G. At this location, the mean sedimentation rate was calculated from the radiocarbon data for two cores, excluding an outlier at 9-11 cm depth. Radiocarbon ages of foraminifera from the U.S. Geological Survey cores were provided by J. V. Gardner and P. Dartnell (Menlo Park, CA). The cumulative uncertainty in authigenic Cd accumulation at a single site due to errors in porosity and sedimentation rate is estimated at $\pm 50\%$. Pore water Cd gradients measured at *Reimers et al.* [1992] sites J, K, G, and M were used to estimate the Cd flux into the sediments as: $\text{Flux} = \phi \times D_{\text{sed}} \times (d\text{Cd}/dz)$ where ϕ is the porosity in the top few centimeters ($= 0.85$), the sediment diffusivity of Cd is given by $D_{\text{sed}} = D_{\text{molec}} / (\phi \times F)$, $F = \phi^{2.75}$, and $D_{\text{molec}} = 3.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [Li and Gregory, 1974]. For each core, we calculate maximum and minimum flux estimates, using the steepest and second-steepest observed two-point Cd gradients (Cd data from *McCorkle and Klinkhammer* [1991] and Table 2).

The actual Cd deficit may be considerably larger if most of the P excess in the water column is due to decomposition of plankton matter that is also enriched in Cd. Comparison with other water column properties provides some indication of the origin of the P excess. CalCoFI profiles show that P is typically enriched by $0.1\text{-}0.5 \mu\text{mol kg}^{-1}$ in deep water of the Santa Barbara Basin relative to the value obtained by extrapolating the linear P-O₂ relation in the upper water column to zero oxygen. This suggests that a significant fraction of the organic matter flux is regenerated by nitrate reduction, in agreement with sediment studies of similar environments such as the Santa Monica Basin [Jahnke, 1990] and the California margin [Reimers et al., 1992].

CalCoFI data also show decreasing nitrate concentrations when flushing of the Santa Barbara Basin is reduced [Reimers et al., 1990]. Assuming the P excess of $0.44 \mu\text{mol kg}^{-1}$ is solely due to plankton matter regeneration, a corresponding Cd contribution to the water column of $0.15 \text{ nmol kg}^{-1}$ is calculated from the mean composition of oceanic plankton (Cd/P ratio of $0.3 \times 10^{-3} \text{ mol mol}^{-1}$) [Knauer and Martin, 1981]. The total Cd deficit in the deep Santa Barbara Basin could therefore be as high as $0.11 + 0.15 = 0.26 \text{ nmol kg}^{-1}$. We cannot exclude the possibility that some of the P excess in the deep basin is due to dissolution of P-enriched Fe-oxides under reducing conditions [Shiller et al., 1985; Ingall and Jahnke, 1994]. It is important to note, however,

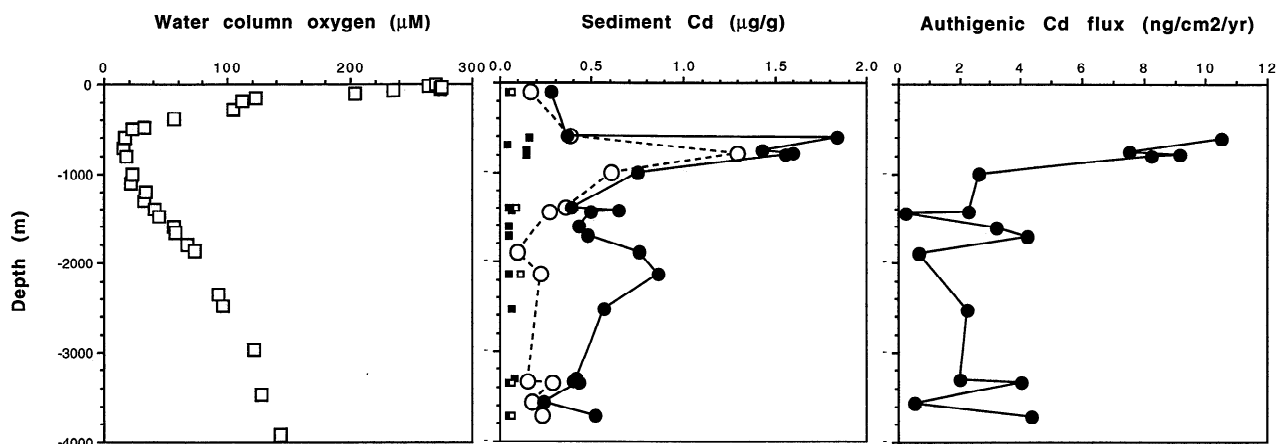


Figure 3. Comparison of water column oxygen concentration and Cd accumulation in California margin sediments (not including the borderland basins). (left) Dissolved O_2 profile at station C-I of *Bruland* [1980]. (middle) Cd concentrations in the sediment at 0-0.5 cm and ~10 cm depth in the cores are indicated by open and solid circles, respectively. Small squares indicate the Cd content of the sediment residue after the HCl leach for surface (open symbols) and deeper sediment (solid symbols). (right) Authigenic Cd accumulation as a function of depth calculated from Cd concentrations at ~10 cm depth (Table 1).

that both the CalCoFI and the RV *Sprout* profiles collected in August 1993 show a P excess in the deep Santa Barbara Basin of at most $0.1 \mu\text{mol kg}^{-1}$ relative to the linear P- O_2 relation above the sill. Therefore the deviation from a linear P-Cd relation within the basin visible in Figure 2 cannot be attributed to a P source other than plankton matter regeneration. The few $\delta^{13}\text{C}$ data points below the sill are also consistent with a primarily plankton-derived source of P to the water column.

The timescale of deep water flushing is needed to calculate fluxes corresponding to nonconservative behavior of oxygen, P, Si, and Cd. A lower limit to the residence time of the water in the deep basin is provided by the vertical eddy mixing rate, $0.5 \text{ cm}^2 \text{ s}^{-1}$, measured directly in the nearby Santa Monica Basin by injecting conservative tracers at 800 m depth [Lewell *et al.*, 1986]. At this rate, the mean mixing time for a 100 m layer of water is 6 years. A simple steady state diffusion model of the distribution of ^{222}Rn in deep water of the Santa Barbara Basin, however, yields a vertical eddy coefficient of $3.9 \text{ cm}^2 \text{ s}^{-1}$ corresponding to a mean mixing time of 0.8 years [Chung, 1973]. The difference between the two approaches can be reconciled by considering that mixing of basin deep water is the sum of vertical eddy diffusion and boundary mixing, which is likely to be stronger [Berelson, 1991]. Comparable mixing rates have been estimated by various approaches for adjacent deeper California borderland basins [Berelson *et al.*, 1987; Hammond *et al.*, 1990]. O_2 , P, and Si fluxes corresponding to mean water residence times of 0.8-6 years in the bottom 100 m are comparable to fluxes of these constituents measured directly by benthic chamber deployments in the adjacent Santa Monica Basin [Jahnke, 1990].

The Cd deficit of 0.26 nmol/kg integrated over the bottom 100 m of the water column corresponds to a flux of 0.4 to $3.2 \text{ nmol cm}^{-2} \text{ yr}^{-1}$ (45 - $360 \text{ ng cm}^{-2} \text{ yr}^{-1}$) depending on the actual mixing rate of the deep basin. This flux is predicted to increase the Cd content of Santa Barbara sediment from a crustal concentration of $0.1 \mu\text{g g}^{-1}$ [Taylor and McLellan, 1985] to 0.6 - $4.1 \mu\text{g g}^{-1}$, based on the sediment accumulation rate of 0.09 ng

$\text{cm}^{-2} \text{ yr}^{-1}$ determined by *Bruland et al.* [1981]. Sediment Cd concentrations ranging between 1 - $2 \mu\text{g g}^{-1}$ in the Santa Barbara Basin are well within this range [Bruland *et al.*, 1981; Schmidt and Reimers, 1991]. The comparison demonstrates that Cd missing from deep water of the Santa Barbara Basin could be accommodated in the underlying sediment.

California Margin

We can determine a more direct estimate of Cd trapping by calculating actual Cd accumulation rates in excess of the crustal content of $0.1 \mu\text{g g}^{-1}$ for the California margin sediments (Table 1). These burial fluxes are plotted as a function of depth in Figure 3 and as function of bottom water oxygen in Figure 4. Authigenic Cd accumulation rates are high at all sites, and are about four times higher within the oxygen minimum zone at 800 m depth than in the 1000-4000 m depth range. While Cd accumulation appears to be sensitive to bottom water oxygen, anoxic bottom waters are clearly not required.

These burial fluxes on the California margin can be compared to direct estimates of Cd removal based on pore water Cd profiles. Pore water flux estimates based on data by *McCorkle and Klinkhammer* [1991] and data from Table 2 are included in Table 1. In general, there is good agreement between solid phase and pore water flux estimates at similar bottom water oxygen concentrations suggesting that diffusion down pore water gradients provides the link between Cd removal from the water column (as observed in the Santa Barbara Basin) and Cd accumulation in the sediments. At three of these sites, the pore water flux estimates are higher than authigenic Cd accumulation in the sediment (Figure 4). The discrepancy may be due to the different timescales averaged by the two methods, which is on the order of months for pore water profiles and centuries for the solid phase. We also note that there are differences in solid phase Cd accumulation rates at similar oxygen concentrations. This may reflect spatial or temporal variability related to downslope transport of sediment in the region [Reimers *et al.*, 1992].

Table 2. New Pore Water Data from the California Margin

Site K BC-213			Site G BC-255			Site M BC-231	
Depth cm	Cd nM	$\delta^{13}\text{C} \text{‰}$	Depth cm	Cd nM	$\delta^{13}\text{C} \text{‰}$	Depth cm	Cd nM
0	0.96	-0.40	0	0.96	0.20	0	0.87
0	0.94	-0.32	0.25	1.43		0	0.88
0	0.86		0.75	1.77	-1.19	0	0.85
0.25	3.93	-0.73	1.25		-1.47	0.25	2.64
0.75	1.35	-1.27	1.75		-1.56	0.75	2.47
1.25		-1.22	2.5	0.51	-1.35	1.25	2.96
1.75	0.71	-1.48	3.5	0.37		2.5	0.96
2.5	0.87	-1.61	4.5	0.21	-1.55	3.5	0.35
3.5		-1.84	5.5	0.37	-1.73	4.5	0.25
4.5	0.57	-1.84	6.5	0.33		7.0	0.48
5.5	0.18	-1.91	7.5	0.58	-2.61	(no $\delta^{13}\text{C}$	data)
6.5		-2.04	8.5	0.65	-3.00		
7.5	0.34	-2.31	9.5	0.36	-3.55		
8.5	0.27	-2.46	11.0	0.20	-4.21		
9.5	0.16	-2.54	13.0	0.30	-5.28		
11.0	0.19	-2.69	15.0	0.24	-6.17		
13.0	0.16	-2.83	17.0		-7.08		
15.0	0.14	-2.98	19.0	0.27	-8.10		
17.0	0.36	-2.85					
19.0	0.51	-2.92					

The pore water profiles and the downcore solid phase Cd gradients suggest that Cd is removed just below the depth where pore water oxygen becomes undetectable [McCorkle and Klinkhammer, 1991; Reimers *et al.*, 1992]. The pore water profiles also indicate that Cd enrichments in suboxic sediments are not driven solely by diffusion from overlying bottom water. The dissolved Cd maximum at the sediment-water interface recurrent in both oxic and suboxic settings indicates an additional contribution from the decomposition of Cd-enriched organic matter reaching the sediment [McCorkle and Klinkhammer, 1991, Table 2]. The California margin results from sites deeper than the oxygen minimum suggest that the trapping efficiency of this flux is not strongly dependent on bottom water oxygen in the 50-150 μM range (Figure 4). Authigenic Cd enrichments are therefore probably formed on other continental margins such as the western North Atlantic where pore waters are anoxic near the sediment-water interface, despite relatively high bottom water oxygen concentrations [Hales *et al.*, 1994].

The California margin data also show that the flux of authigenic Cd accumulation increases rapidly as bottom water oxygen concentrations decrease below 50 μM (Figure 4). This is seen not only in the oxygen minimum zone ($\sim 9 \text{ ng cm}^{-2} \text{ yr}^{-1}$) but also in the Santa Barbara Basin (90-180 $\text{ng cm}^{-2} \text{ yr}^{-1}$) [Bruland *et al.*, 1981; Schmidt and Reimers, 1991] where bottom water oxygen concentrations are further reduced. Accumulation of authigenic Cd is very high not only in the Santa Barbara Basin but also in the nearby Santa Monica and San Pedro basins (Figure 4), as calculated from the data of Bruland *et al.* [1981]. The inverse relation between authigenic Cd accumulation and bottom

water oxygen at levels $< 50 \mu\text{M}$ must be primarily due to higher trapping efficiency because organic matter (and therefore Cd) fluxes reaching the sediment in the oxygen minimum zone offshore and in the inner borderland basins are comparable [Jahnke, 1990; Reimers *et al.*, 1992]. Interestingly, Bruland *et al.* [1981] measured Cd fluxes through the water column of the inner California borderland basins very similar to authigenic Cd accumulation in the underlying sediment during 2-month sediment trap deployments. This result suggests that nearly all Cd supplied to the sediment-water interface by settling plankton matter is trapped in regions with bottom water oxygen concentrations below 20 μM . Because continental shelf sediments appear to contain relatively little Cd in excess of the crustal component (Figure 3), this argument is not affected by sediment focussing in the borderland basins. Boundary scavenging probably enhances the Cd flux reaching the basin sediments [Moore *et al.*, 1981]; we might expect a similar enhancement in the non-basin margin sites because organic carbon fluxes to basin and margin sediments are comparable [Jahnke, 1990; Reimers *et al.*, 1992]. We conclude that lower authigenic Cd accumulation on the margin relative to the inner borderland basins is due mainly to a reduced trapping efficiency.

The existing data do not allow us to determine the actual mechanism causing pore water depletions and formation of authigenic Cd in the sediment. One candidate is adsorption of Cd onto freshly precipitated iron oxides [McCorkle and Klinkhammer, 1991]. Another possibility is formation of Cd-sulfide phases. While the relevant thermodynamic data remain uncertain [Jacobs *et al.*, 1985], an attempt at coprecipitating Fe

Table 3. Composition of End-Members Contributing to the Deep Santa Barbara Basin

	EM1	EM2	EM3	Deep Basin Predicted	Deep Basin Measured	Deep Basin Difference
	Station 80.60 475 m	Station 80.60 475 m	Station 82.47 475 m	0.12 EM1 + 0.31 EM2 + 0.57 EM3	Station 82.47 >500 m	
T, °C	5.50	6.50	6.58	6.42	6.42	
Salinity	34.15	34.30	34.223	34.243	34.243	
O ₂	33	16	9	14	4	-10
P	3.05	3.05	3.32	3.20	3.64	+0.44
Si	80	72	89	83	104	+21
Cd	1.05 10 ⁻³	1.05 10 ⁻³	0.79 10 ⁻³	0.90 10 ⁻³	0.79 10 ⁻³	-0.26 10 ⁻³ *

* Includes 0.15 10⁻³ μmol/kg contribution scaled to P increase. Concentrations in μmol kg⁻¹. CalCoFI data (Station 82.47, Figure 1) show that temperature and salinity of the basin below 500 m depth fluctuated between 6.3°-6.5°C and 34.23-34.26, respectively, during 1986-1993. Dissolved O₂ (1 to 15 μmol kg⁻¹), P (3.3 to 4.2 μmol kg⁻¹), and Si (85 to 120 μmol kg⁻¹) varied over a wider range in the deep basin. The mean composition of deep basin water is listed under "Deep Basin Measured" heading. At a distance of 110 km west of the basin (Station 80.60), temperature (5.5°-6.5 °C) and salinity (34.15-34.30) fluctuations interpolated to a constant depth of 475 m were more pronounced. Property-property plots of the time series data suggest that these fluctuations reflect varying contributions of two end-members. A subarctic origin can be attributed to colder, fresher, high O₂ EM1 slightly enriched in Si [Lynn and Simpson, 1987]. The composition of the other warmer, saltier, low O₂ EM2 reflects an equatorial origin. EM3, average basin water at 475 m depth, accounts for entrainment of basin water at the sill depth during spillover events. Assuming conservative mixing, the mean temperature and salinity of the Santa Barbara Basin below the sill depth uniquely determine the long-term mixing proportions of EM1, EM2, and EM3.

and Cd sulfides in the laboratory suggests formation of insoluble Cd-sulfides could take place in anoxic pore waters at sub-μM hydrogen sulfide concentrations [Framson and Leckie, 1978].

Paleoceanographic Implications

We use the authigenic Cd accumulation rates measured on the California margin (not the borderland basin data) to evaluate the role of continental slopes and rises in the oceanic Cd budget. For this discussion, the bathymetric profile of authigenic Cd accumulation (Figure 3) is subdivided in a region of high Cd accumulation between 700-900 m depth (~9 ng cm⁻² yr⁻¹), and regions of intermediate Cd accumulation from 200 to 700 m and 900-4000 m depth (~2 ng cm⁻² yr⁻¹). On the basis of their depth ranges, these regions cover roughly 5 % and 95% of the surface area of the California margin, respectively. The aggregate Cd sink over the margin and slope region is therefore 2.4 ng cm⁻² yr⁻¹. Reimers *et al.* [1992] calculated that continental slopes and rises cover about 13% of the world ocean area. Assuming that the California margin is representative, the flux of authigenic Cd accumulating in continental slope and rise sediments normalized to the whole area of the ocean is 0.31 ng cm⁻² yr⁻¹.

The borderland basin data of Bruland *et al.* [1981] are used to make a separate estimate of the role of highly organic-rich sediments. While such sediments account for only 0.3% of the area of the seafloor today [Emerson and Husted, 1991; Colodner *et al.*, 1993], their contribution is included because of particularly high rates of authigenic Cd accumulation (90 ng cm⁻² yr⁻¹ on average for the inner basins, Figure 4). Normalized over the area

of the ocean, the Cd flux from the water column to highly organic rich sediments is 0.27 ng cm⁻² yr⁻¹, comparable to the authigenic Cd flux in slope and margin sediments. These rough estimates sum up to a total sink of Cd in the ocean of 0.58 ng cm⁻² yr⁻¹ due to formation of authigenic, sedimentary Cd.

Rivers, atmospheric deposition, and hydrothermal vents are the main sources of dissolved Cd to the ocean. Also, a significant fraction of particulate Cd typically desorbs during mixing with seawater in estuaries. This is taken into account by linearly extrapolating Cd-salinity relations at the mouth of an estuary to zero salinity [Boyle *et al.*, 1974]. A reasonable upper limit of 0.42 ng cm⁻² yr⁻¹ to riverine dissolved Cd input is calculated from a particulate input of 15x10¹⁵ g yr⁻¹ [Martin and Meybeck, 1979], assuming complete desorption and erosion of average crustal material containing 0.1 μg g⁻¹ Cd [Taylor and McLennan, 1985]. For a rate of continental runoff of 3.7x10¹⁶ L yr⁻¹ [Martin and Meybeck, 1979], a corresponding effective dissolved Cd concentration of 0.4 nmol kg⁻¹ is calculated, a value comparable to observations in the Orinoco, Changjiang, Huanghe, and Mississippi estuaries [Edmond *et al.*, 1985; Elbaz-Poulichet and Martin, 1987; Shiller and Boyle, 1991]. Effective dissolved Cd concentrations for unperturbed large rivers such as the Amazon and the Lena, on the other hand, are closer to 0.1 nmol kg⁻¹ [Boyle *et al.*, 1982; Martin *et al.*, 1993]. The corresponding flux of 0.12 ng cm⁻² yr⁻¹ is used as a lower bound for riverine input. The atmospheric input of Cd to the ocean is poorly constrained because aerosols are highly enriched by anthropogenic emissions, even over the remote North Pacific [Patterson and Duce, 1991]. A reasonable range for the

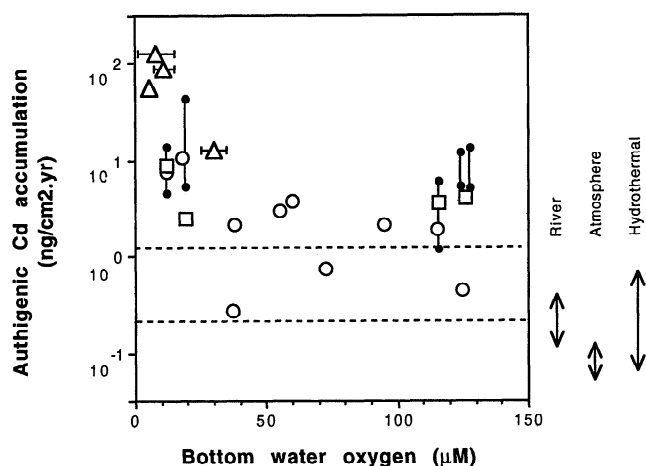


Figure 4. Authigenic Cd accumulation off California as a function of bottom water oxygen. Open circles and squares show same data as in right panel of Figure 3 on a log₁₀ scale. Square symbols identify five box cores where pore water Cd concentrations were also measured. Range of diffusive flux estimates (Table 1) associated with square symbols are indicated by vertical bars. Oxygen concentrations corresponding to replicate diffusive Cd flux measurements at location M slightly offset for clarity. Triangles indicate authigenic Cd accumulation fluxes in Santa Barbara, Santa Monica, San Pedro, and San Nicolas basins calculated from total Cd concentration in sediment (reduced by the $0.1 \mu\text{g g}^{-1}$ crustal contribution) and sedimentation rates determined by *Bruland et al.* [1981]. Note that the accumulation rates from these four basins were considered separately in our estimate of global Cd removal. Horizontal bars indicate range in bottom water conditions for the California borderland basins [*Reimers et al.*, 1990; *Jahnke*, 1990; *Berelson*, 1991]. Arrows at right margin indicate estimated ranges of dissolved Cd input from rivers, atmospheric deposition, and hydrothermal vents normalized to the surface area of the ocean ($3.6 \times 10^{18} \text{ cm}^2$). Dashed lines across figure show corresponding range in estimates of total Cd input.

preindustrial Cd input is calculated by reducing the present deposition flux of $0.6\text{--}1.2 \text{ ng cm}^{-2} \text{ yr}^{-1}$ 10-fold [*Duce et al.*, 1991], in proportion to the increase in anthropogenic Cd emissions following the industrial revolution [*Nriagu*, 1980]. The inferred composition of preindustrial aerosols ($2.5\text{--}5.0 \mu\text{g g}^{-1}$ based on the Al flux of *Duce et al.* [1991]) indicates significant enrichment relative to crustal material even after this correction, possibly due to volcanic emissions [*Nriagu*, 1980]. Nearly all Cd transported to the ocean by aerosols is soluble in seawater [*Patterson and Duce*, 1991]. A range of $0.07\text{--}0.81 \text{ ng cm}^{-2} \text{ yr}^{-1}$ was estimated by *Von Damm et al.* [1985] for Cd input by hydrothermal vents.

Based on these estimates, the total input of Cd to the oceanic water column ranges between 0.25 and $1.35 \text{ ng cm}^{-2} \text{ yr}^{-1}$. Despite the considerable uncertainties, comparison with the magnitude of the Cd sink to margin sediments and anoxic basins indicates formation of authigenic Cd could well be the dominant sink in the oceanic Cd budget. The role of suboxic sediments

was recently similarly reevaluated for the oceanic budget of the redox-sensitive element uranium [*Klinkhammer and Palmer*, 1991].

The estimated range of Cd input fluxes corresponds to a residence of Cd in the ocean between 100,000 and 20,000 years, calculated for a mean depth of 3800 m and a concentration of 0.6 nmol kg^{-1} in the water column [*Boyle*, 1992]. Changes in Cd removal fluxes to margin sediments could therefore potentially affect the whole-ocean Cd inventory on glacial-interglacial time scales. This possibility warrants further study because there is strong evidence for large-scale changes in ocean sediment redox conditions. Sediment cores from the Southern Ocean [*Anderson et al.*, 1993], the southeastern Indian Ocean [*McCorkle et al.*, 1994], and the Arabian Sea [*Sarkar et al.*, 1993] show elevated levels of authigenic uranium consistent with more reducing sedimentary conditions during the last glacial maximum. Analogous Cd enrichments in sediments deposited during the last glacial maximum have also been observed in the Southern Ocean [*Rosenthal et al.*, 1993].

We explore the possibility of glacial-interglacial changes in the oceanic Cd inventory with a simple box model that is time-stepped through the past 120,000 years. The model removal rate of Cd is initially set to balance high and low estimates of preindustrial Cd input to the water column, 0.25 and $1.35 \text{ ng cm}^{-2} \text{ yr}^{-1}$. Removal is assumed to be proportional to the mean Cd concentration of the ocean. The sedimentary removal rate is increased by 50% in the model for the period between 70,000 and 20,000 years before present (BP) (Figure 5a). Because continental margin sediments account for about half the total Cd sink, this increase could reflect a doubling in the magnitude of authigenic Cd fluxes to such regions, while keeping the proportion of highly organic rich sediments constant. The higher flux of authigenic Cd could be caused by either a doubling in the areal extent of suboxic sediments or a doubling of the intensity of authigenic Cd accumulation over a constant area. Not surprisingly, the calculation shows that the response of the ocean inventory is very sensitive to the magnitude of the estimated Cd input to the system. The larger the flux, the more rapidly the water column responds to an increase in the removal rate and approaches a new steady state concentration of 0.4 nmol kg^{-1} , two thirds the present value of 0.6 nmol kg^{-1} (Figure 5b, 5c). The model also shows that the response of the Cd ocean inventory to a return to non-glacial conditions 20,000 years ago depends on the fraction of additional Cd removed from the water column between 70,000 and 20,000 years BP that is permanently trapped. Based on the limited change in the glacial oceanic Cd inventory relative to today documented by *Boyle* [1992], a scenario combining the upper limit to the Cd input with instantaneous release of excess Cd accumulation at the onset of deglaciation seems unlikely (thin line in Figure 5b). We cannot rule out the possibility that an increase in authigenic Cd accumulation during glacial times could have been offset by the increase in atmospheric deposition recorded in Antarctic ice [*Boutron et al.*, 1994].

Conclusion

California margin water column, sediment, and pore water data document links between anomalous Cd depletions in the water column of the Santa Barbara Basin, Cd removal from pore waters, and the accumulation of Cd in suboxic sediments. Our

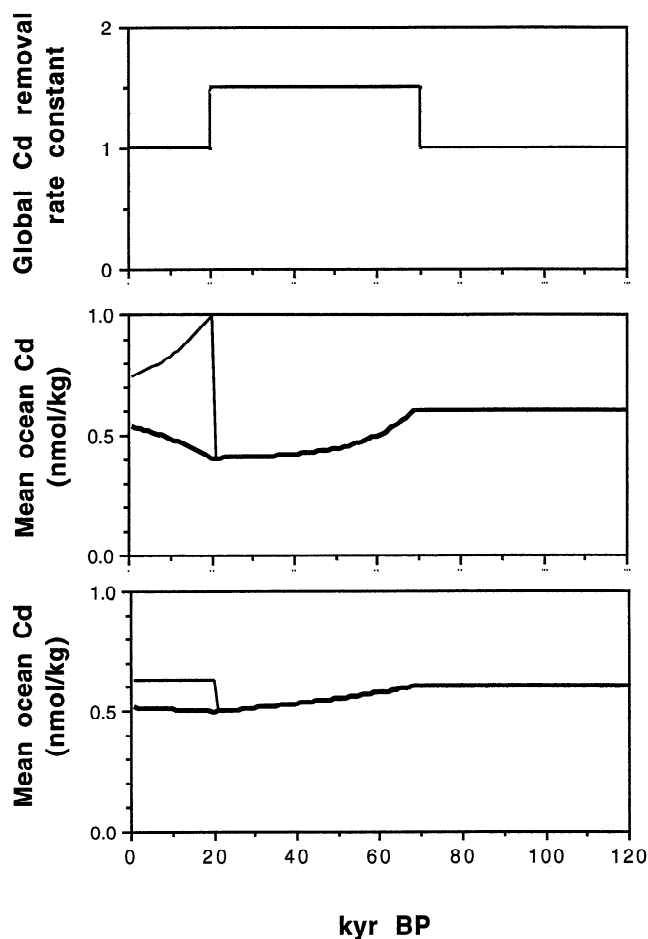


Figure 5. Time-stepped box model of mean Cd concentration in the ocean. (top) The global removal rate constant of Cd is increased by 50% between 70,000 and 20,000 years BP. This represents either doubling the proportion of suboxic sediments in the ocean or doubling the intensity of authigenic Cd formation over a constant area. Changes in mean concentration of Cd in the ocean using upper and lower limits for Cd input to the ocean of 1.35 (middle) and 0.25 (bottom) $\text{ng cm}^{-2} \text{yr}^{-1}$, respectively. Bold/thin lines show the oceanic response assuming none/all excess authigenic Cd accumulated between 70,000 and 20,000 years B.P. is released back to the water column.

results suggest that enhanced Cd accumulation is likely in sediment underlying other productive continental margins. Further investigation is needed to better understand the relative importance of bottom water oxygen and the organic matter flux to the seafloor for authigenic Cd accumulation. Suboxic sediments appear to be the major sink of Cd in the ocean, which implies that the inventory of Cd in the ocean is sensitive to the areal extent and intensity of reduction in suboxic sediments. Our data suggest that enhanced Cd accumulation in continental margin sediments may affect water column P-Cd relations, particularly in regions where the continental margin area to basin volume ratio is high.

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