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Glacial enrichments of authigenic Cd and U in Subantarctic sediments: A climatic control on the elements' oceanic budget ?

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Abstract. We examine the possibility that glacial increase in the areal extent of reducing sediments might have changed the oceanic Cd inventory, thereby decoupling Cd from PO₄. We suggest that the precipitation of Cd-sulfide in suboxic sediments is the single largest sink in the oceanic Cd budget and that the accumulation of authigenic Cd and U is tightly coupled to the organic carbon flux into the seafloor. Sediments from the Subantarctic Ocean and the Cape Basin (South Atlantic), where oxic conditions currently prevail, show high accumulation rates of authigenic Cd and U during glacial intervals associated with increased accumulation of organic carbon. These elemental enrichments attest to more reducing conditions in glacial sediments in response to an increased flux of organic carbon. A third core, overlain by Circumpolar Deep Water (CPDW) as are the other two cores but located south of the Antarctic Polar Front, shows an approximately inverse pattern to the Subantarctic record. The contrasting patterns to the north and south of the Antarctic Polar Front suggest that higher accumulation rates of Cd and U in Subantarctic sediments were driven primarily by increased productivity. This proposal is consistent with the hypothesis of glacial stage northward migration of the Antarctic Polar Front and its associated belt of high siliceous productivity. However, the increase in authigenic Cd and U glacial accumulation rates is higher than expected simply from a northward shift of the polar fronts, suggesting greater partitioning of organic carbon into the sediments during glacial intervals. Lower oxygen content of CPDW and higher organic carbon to biogenic silica rain rate ratio during glacial stages are possible causes. Higher glacial productivity in the Cape Basin record very likely reflects enhanced coastal upwelling in response to increased wind speeds. We suggest that higher productivity might have doubled the areal extent of suboxic sediments during the last glacial maximum. However, our calculations suggest low sensitivity of seawater Cd concentrations to glacial doubling of the extent of reducing sediments. The model suggests that during the last 250 kyr seawater Cd concentrations fluctuated only slightly, between high levels (about 0.66 nmol kg⁻¹) on glacial initiations and reaching lowest values (about 0.57 nmol kg⁻¹) during glacial maxima. The estimated 5% lower Cd content at the last glacial maximum relative to modern levels (0.60 nmol kg⁻¹) cannot explain the discordance between Cd and δ¹³C, such as observed in the Southern Ocean. This low sensitivity is consistent with foraminiferal data, suggesting minimal change in the glacial Cd mean oceanic content.

Introduction

Acknowledging that changes in ocean circulation and nutrient distributions play key roles in the Earth climate, paleoceanographers have tried to reconstruct the deepwater circulation during the Quaternary ice ages. Such records

may provide a test for climate hypotheses and improve the sensitivity of climate models. At present, deep ocean circulation and nutrient distributions are inferred from the δ¹³C, and Cd composition of deep-sea benthic foraminifera. The strong relationships among the Cd, δ¹³C and PO₄ distributions in the modern deep ocean, which constitute the basis for paleochemical reconstructions, reflect the biological cycling of organic matter as modified by ocean circulation [*Kroopnick*, 1985; *Boyle*, 1988]. Consequently, these properties are expected to covary in the ocean in response to glacial-interglacial changes in circulation. However, any change in the oceanic inventory

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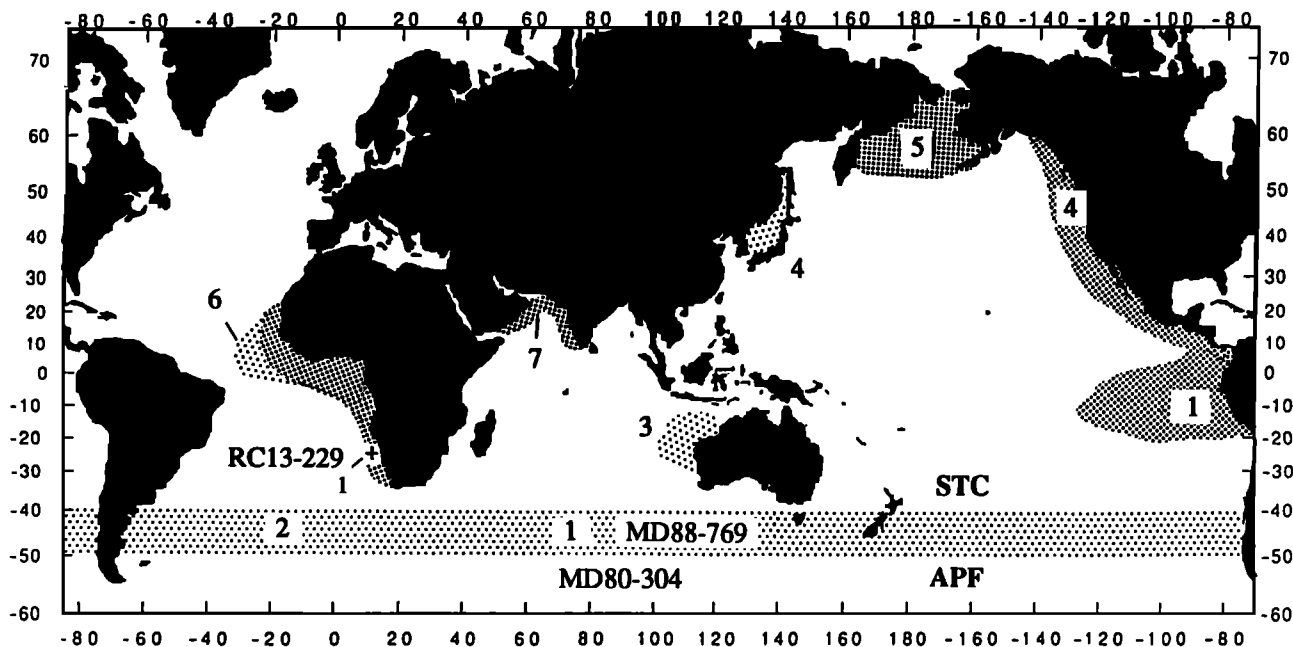


Figure 1. Location map of the three cores studied here. Also included is a comparison between the modern distribution of suboxic sediments (heavily shaded areas) and the proposed additional area during the last glacial maximum (lightly shaded areas). Data are from 1, this study; 2, *Anderson et al.*, 1993; 3, *McCorkle et al.*, 1994; 4, *Piper and Isaacs*, 1995; 5, *Yamada and Tsunogai*, 1984; 6, *Thomson et al.*, 1990; 7, *Sarkar et al.*, 1993. Abbreviations are STC, Subtropical Convergence; APF, Antarctic Polar Front.

of either element might have altered the modern ocean relationships among Cd, $\delta^{13}\text{C}$, and PO_4 , thereby influencing our interpretations of glacial ocean circulation [*Boyle*, 1986].

Emerson and Husted [1991] proposed that seawater concentrations of U, Mo, and V (which are highly enriched in anoxic sediments) may be sensitive to changes in the area of seafloor overlain by oxygen-depleted seawater. Similarly, studies of continental margin sediments suggest that suboxic sediments are the major oceanic sink for U and therefore the size of the suboxic sink may control the oceanic budget of U [*Klinkhammer and Palmer*, 1991]. Strong enrichments of authigenic Cd were observed in sulfide-bearing sediments underlying anoxic water [e.g., *Jacobs et al.*, 1987; *Skei et al.*, 1988]. *Rosenthal et al.* [1993] proposed that precipitation of cadmium-sulfide (CdS) in suboxic sediments, where reducing conditions occur close to the sediment-water interface, is the single most important sink in the Cd oceanic budget. In this paper we explore the possibility that temporal changes in the areal extent of suboxic sediments control the oceanic inventories of Cd and U. The removal of Cd in suboxic sediments and its postdepositional mobility are discussed in greater detail elsewhere [*Rosenthal et al.*, 1995].

Cores from the Subantarctic zone in the southeast Indian Ocean and from the Cape Basin western continental margin of southern Africa record significant enrichments in authigenic Cd and U during glacial intervals in association with increased accumulation of organic carbon.

Such changes reflect either increase in surface productivity, a decrease in the bottom water oxygen content, or a combination of them. By contrast, a core from the Southern Ocean, south of the Antarctic Polar Front (APF), shows an inverse pattern to that from the Subantarctic region. Since all three core sites are overlain by Circumpolar Deep Water (CPDW) we propose that the observed enrichments in authigenic Cd and U reflect primarily enhanced surface productivity. However, there are also some suggestions in the records for lower bottom water oxygen content at that time. The possibility that climatically driven increase in surface productivity may lead to significant decrease in seawater Cd concentration and the sensitivity of the oceanic Cd- PO_4 correlation to these changes are investigated with a simple sensitivity test.

Methods

Core Selection

Three cores around the Southern Ocean perimeter were studied (Figure 1): (1) MD88-769 ($46^\circ 04'S$ $90^\circ 07' E$, 3420 m), from the Indian sector of the Subantarctic zone; (2) MD80-304 ($51^\circ 04'S$ $67^\circ 26' E$, 1930 m), located on the northern Kerguelen Plateau; and (3) RC13-229 ($26^\circ 00'S$ $11^\circ 00' E$, 4194 m), a South Atlantic core from the deep Cape Basin. At present, all three sites are overlain Circumpolar Deep Water [*Bainbridge*, 1980; *Spencer et al.*, 1982]: MD88-769 and MD80-304 are located close to

the core of the Antarctic Circumpolar Current (ACC), whereas the deep Cape Basin is filled by lower CPDW flowing northward from the Drake Passage [Mantyla and Reid, 1983]. The decreasing depth of these cores from the Cape Basin to the Southern Ocean follows the southward shoaling of CPDW as it overrides the denser Antarctic Bottom Water. The three sites have similar bottomwater oxygen content (205-220 $\mu\text{mol kg}^{-1}$).

Surface water over the core sites represents very different conditions, in contrast with the similarity in bottom water chemistry. Subantarctic core MD88-769 is located on the southeast Indian Ridge. Surface water nutrient concentrations are intermediate between the nutrient enriched Southern Ocean and the nutrient-depleted subtropical surface water, thus reflecting the transition from divergent Ekman transport south of the Antarctic Polar Front (at 50°S) to a convergent regime north of the Subtropical Convergence (STC, at 40°S) [Taylor et al., 1978; Howard, 1992]. Among the nutrients, silica exhibits the most abrupt change from high concentrations (up to 60 $\mu\text{mol kg}^{-1}$) south of the APF, declining sharply (below 10 $\mu\text{mol kg}^{-1}$) in the northern Subantarctic zone. This latter change is associated with an ecological transition from high siliceous productivity in the belt south of the APF to a zone of lower, mostly carbonate productivity in the Subantarctic region. The sediment lithology at the site of MD88-769 shows large fluctuations between primarily carbonate composition during interglacials ($\text{CaCO}_3 > 80\%$) and mostly opaline sediment during glacial periods [Bareille, 1991; Bareille et al., 1991; Charles et al., 1991; Howard, 1992]. Antarctic core MD80-304, taken from the northwestern part of the Kerguelen Plateau, is located just south of the present APF beneath the zone of high siliceous productivity [DeMaster et al., 1991]. The high Holocene sedimentation rate and the mostly diatomaceous lithology reflect the overlying high productivity.

South Atlantic core RC13-229 is located in the Cape Basin where surface water is primarily dominated by the Benguela Current. Influenced by southeast trade winds and to a lesser extent by the westerlies, the Benguela Current forms the eastern boundary flow of the South Atlantic subtropical gyre. Cool surface water flows northward along the west coast of southern Africa between 35°S and 15°S before flowing westward. This water mass is modified not only by broad upwelling along the southwest African margin but also by inflow of Agulhas Water advected around the Cape of Good Hope [Darbyshire, 1966]. During the austral summer, southeasterly trade winds force the Benguela Current offshore, thereby causing upwelling of cold, fresh, and nutrient-rich thermocline water which supports high calcareous productivity. The lithology of core RC13-229 varies between mostly carbonate (approximately 80%) during interglacial stages to about 40% carbonate during glacial periods [Embley and Morley, 1980].

Analytical Procedure

Sediment samples were dried at 110°C for 2 hours. The dried sediment was leached with reducing solution

following the method of Chester and Hughes [1967]: about 10 mg of ground sample was leached with a solution of 0.02N hydroxyl-amine-hydrochloride in 25% vol/vol acetic acid for 3 hours at 80°C. The leachate was separated from the solid phase by centrifugation. Residual solids were rinsed thoroughly with distilled water and then digested in closed Teflon vials with a mixture of trace metal clean, concentrated HNO_3 and HF (500 μl and 100 μl respectively). After leaving samples for 4 hours at 80°C, 75 μl of 70% perchloric acid were added, and the solution was evaporated to near dryness and redissolved with distilled HNO_3 to the appropriate dilution. The concentrations of Cd and U in this latter fraction are much lower than in leachates obtained by the reductive dissolution, about 0.01-0.15 $\mu\text{g g}^{-1}$ for Cd and 0.1-1.5 $\mu\text{g g}^{-1}$ for U (for example, compare the two fractions in the upper section of MD88-769; Table 1). These values are typical of crustal minerals and are considered here as the detrital fraction of the sediment (note that the detrital fraction also includes biogenic opal, however, the Cd and U content in biogenic opal is negligible; Y. Rosenthal unpublished data, 1994). It follows that the initial extractions represent the authigenic/reactive fraction of the sediment. The contributions from partial dissolution of clay minerals to the extractable solutions are negligible because of the low detrital levels. In general, only a relatively negligible amount of clay minerals was dissolved by the reductive extraction. This contribution was estimated by measuring the Al content of the authigenic extracts (expressed as Al_2O_3). Bulk sediment Al measurements were obtained to provide an estimate for changes in the detrital content.

Studies of suboxic sediments suggest that Cd and U are insoluble under reducing conditions [Klinkhammer and

Table 1. Concentrations of Cd and U in the Detrital Fraction of Sediments From MD88-769

Depth, cm	Cd, $\mu\text{g g}^{-1}$	U, $\mu\text{g g}^{-1}$
15.0	0.01	0.12
18.5	0.02	0.11
24.0	0.01	0.12
39.0	0.01	0.17
43.5	0.07	0.24
54.0	0.03	0.37
59.0	0.02	0.39
63.5	0.04	0.60
69.0	0.03	0.65
75.5	0.04	0.82
83.5	0.09	0.94
88.0	0.16	1.25
97.0	0.10	1.50
118.0	0.08	1.63
138.0	0.07	1.48
142.5	0.06	1.17
157.0	0.05	1.29

Palmer, 1991; McCorkle and Klinkhammer, 1991; Rosenthal et al., 1995]. Therefore the extraction of authigenic Cd and U by reductive dissolution is not readily expected. However, it was suggested that sample storage and processing (e.g., oven drying) under ambient conditions may convert reduced species (e.g., CdS) into oxidic derivatives which may consequently be extracted by reductive dissolution [Kersten and Forstner, 1987]. These authors also proposed that despite possible phase alteration during sample storage, authigenic Cd is not spatially redistributed within the sediment during core storage. Extraction of replicate samples with strong acid (1N HNO₃) produced Cd and U results within $\pm 5\%$ from values obtained by reductive dissolution.

Solutions from the reductive leaching may also include elements which were originally associated with biogenic carbonates. However, because of the low concentrations of Cd and U in planktonic foraminifera, the dominant carbonate in these sediments, their contribution to the authigenic fraction is negligible: considering an extreme case of a 100% carbonate sediment composed primarily of planktonic foraminifera having a Cd/Ca ratio of 0.01-0.05 $\mu\text{mol mol}^{-1}$ (for subtropical and Subantarctic species, respectively), the carbonate component adds between 0.01 and 0.05 $\mu\text{g g}^{-1}$ to the extractable fraction. Likewise, assuming a U/Ca ratio of 0.01 $\mu\text{mol mol}^{-1}$ for planktonic foraminifera [Russell et al., 1994], a biogenic contribution of 0.02 $\mu\text{g g}^{-1}$ is obtained. Therefore the contribution of biogenic carbonates to the authigenic fractions is very small. Similarly, because of the low concentration of U and Cd in seawater, the direct contribution of sea salt to the authigenic fraction is negligible and therefore was ignored.

Cd, Mn, and Al were analyzed by a flameless atomic absorption spectroscopy (Hitachi model Z-8100 with Zeeman background correction). To avoid possible matrix effects, all samples were quantified by the method of standard additions. Uranium was determined by isotope dilution method using an inductively coupled plasma mass spectrometry (ICP-MS; VG Instruments PlasmaQuad I). Because the three major sedimentary components in our cores (calcium carbonate, opal, and detrital clays) exhibit significant temporal variability, the results are expressed on a total sediment basis. Organic carbon was determined on carbonate-free residues using a colorimetric method. Relative standard deviations of $\pm 6\%$ for Cd and U and of $\pm 10\%$ for organic carbon were estimated from replicate analyses. Isotope analyses were carried out in Gif sur Yvette (France) using a Finnigan MAT 251 with automated carbonate device (individual acid bath). Reproducibility of $\delta^{18}\text{O}$ analyses, which was determined from analysis of duplicate samples, is $\pm 0.1\text{‰}$ at 1σ .

Dry bulk densities (DBD) were estimated from calibrations between percent of CaCO₃ and bulk densities. For core MD88-769: DBD (gram dry weight per cubic centimeter of raw sediment) = $0.42 + (0.00018\% \text{CaCO}_3) + (0.000047\% \text{CaCO}_3)^2$ [Bareille, 1991]. This calibration agrees very well with a previous ones from the same region [Clemens et al., 1987]. The same equation was applied also for core MD80-304, whereas for RC13-229

the calibration of Curry and Lohmann [1986] was adopted, using the carbonate data from Embley and Morley [1980]. The average precision of estimates of dry bulk densities is about $\pm 10\%$.

Results

Stratigraphy

Stratigraphic correlations for this study are based on oxygen isotope records. The records of RC13-229 (Cibicides spp.) and MD80-304 (Neogloboquadrina pachyderma sinistral) were published previously [Labeyrie and Duplessy, 1985; Oppo et al., 1990]. The $\delta^{18}\text{O}$ record of MD88-769 was obtained from the planktonic foraminifera *N. pachyderma s.* (Table 2). Although planktonic $\delta^{18}\text{O}$ records from this region may be influenced by temperature and salinity variations, this record clearly shows all the isotopic stages with relatively large glacial-interglacial variations ($>2\text{‰}$). Age models were derived by correlating globally recognizable isotopic events in our records with the stacked planktonic foraminifera $\delta^{18}\text{O}$ record of Imbrie et al. [1984]. In addition, the upper part of the core (0-280 cm) was correlated with the nearby accelerator mass spectrometry (AMS) ¹⁴C dated MD88-770 (46°S 96°E, 3290 m) using records of benthic foraminifera $\delta^{18}\text{O}$ [Labeyrie, manuscript in preparation, 1995] and other sediment properties (%CaCO₃, %C. davisiana, foraminiferal abundance and magnetic susceptibility). Age models and linear sedimentation rates are given in Table 3. A calendar rather than radiocarbon chronology was adopted in order to avoid biasing sedimentation rates by ¹⁴C secular variations (uncorrected radiocarbon ages would lead to about 15% overestimation of sedimentation rate during the last glacial maximum (LGM)). Radiocarbon ages were converted to calendar ages using a calibration based on the tree ring and coral records [Bard et al., 1990; Edwards et al., 1993]. The published chronologies of RC13-229 and MD80-304 were modified accordingly (Table 3).

Variations in Organic Carbon and Authigenic Cd and U Concentrations

The temporal variability in concentrations of organic carbon and authigenic Cd and U is presented in Figures 2, 3, and 4. Sediments from the Subantarctic core MD88-769 reveal large temporal variability in present of organic carbon and concentrations of authigenic Cd and U (Figure 2, Table 4). There are strong visual correlations among $\delta^{18}\text{O}$, organic carbon content, authigenic Cd, and authigenic U: the highest concentrations occur during glacial maxima (stages 2 and 6), whereas low levels characterize the Holocene and last interglacial (stage 5.5). Organic carbon decreases from about 0.6% in LGM sediments to about 0.1% at the core top. Cadmium and uranium show a similar decrease from 2.2 and 6 $\mu\text{g g}^{-1}$, respectively, during the LGM to negligible levels during the Holocene. Comparable peaks were obtained in stage 6, while moderate enrichments are observed at stage 4 and substages 5.2 and 5.4.

Table 2. Oxygen Isotope Measurements of *N. pachyderma* s. From MD88-769

Depth, cm	$\delta^{18}\text{O}$, ‰
21	1.63
26	2.08
31	2.05
36	1.97
41	2.13
46	2.05
51	2.19
56	1.90
61	...
66	1.95
71	2.64
76	3.24
81	3.58
86	3.37
91	3.70
96	3.07
101	3.49
111	3.41
116	2.99
121	3.34
126	2.96
131	3.20
136	2.39
141	2.77
146	3.34
151	3.69
156	2.80
161	3.38
166	3.12
171	3.04
176	2.90
181	3.13
186	3.01
191	3.13
196	3.13
201	2.86
211	2.75
221	3.13
236	3.04
241	2.64
296	2.88
301	2.73
311	2.91
316	3.30
321	...
326	2.91
331	2.72
341	2.73
351	2.72
361	2.68
371	2.75
381	2.89

Table 2. (continued)

Depth, cm	$\delta^{18}\text{O}$, ‰
391	3.36
401	3.38
421	3.05
441	2.54
461	2.72
481	2.64
511	2.27
521	2.73
531	2.12
541	2.27
551	2.59
561	2.51
571	2.76
581	2.42
591	2.53
601	2.30
611	2.14
621	2.15
641	2.36
651	2.62
661	2.35
681	2.58
691	2.75
701	1.47
711	2.07
721	1.92
731	0.88
811	3.56
821	3.42
831	3.43
851	3.15
861	3.09

A very small glacial-interglacial change is observed in the organic carbon record of the Antarctic core (MD80-304, Figure 3; Table 5). The sharp decrease in %organic carbon below the core top may be due to early diagenetic loss of labile organic carbon, a common phenomenon in deep-sea sediments [Emerson and Hedges, 1988]. Authigenic Cd and U in glacial Antarctic sediments from MD80-304 exhibit relatively small and rather erratic enrichments. No correlation with either %organic carbon or $\delta^{18}\text{O}$ is observed.

The Cape Basin record (RC13-229) is similar to the Subantarctic record (MD88-769): large enrichments in %organic carbon and authigenic Cd and U occur during glacial stages 2 and 6, whereas low concentrations characterize the Holocene and the last interglacial (Figure 4, Table 6). Note that although glacial organic carbon levels in RC13-229 (1.2%) are twice as large as the levels observed in MD88-769 (0.6%), the glacial Cd enrichments in RC13-229 ($1.2 \mu\text{g g}^{-1}$) are significantly lower than in MD88-769 ($2.2 \mu\text{g g}^{-1}$) suggesting that there is no simple relationship between the two properties.

Table 3. Age-Depth Relationships Used in This Study

Depth, cm	Age, kyr	Event	Sedimentation Rate, cm kyr ⁻¹
<i>MD88-769</i>			
0	4.0	...*	
16	7.9	...*	4.2
51	14.1	2.0*	5.6
76	18.5	2.2*	5.7
151	27.8	3.0*	8.1
241	41.0	...*	6.8
341	53.0	3.3	8.3
381	59.0	4.0	6.7
400	65.0	4.2	3.2
451	71.0	5.0	8.5
531	80.0	5.1	8.9
566	87.0	5.2	5.0
616	99.0	5.3	4.2
671	107.0	5.4	6.9
731	123.0	5.5	3.8
761	128.0	6.0	6.0
801	134.0	6.2	6.7
861	142.0	6.3	7.5
<i>MD80-304</i>			
0	0	top	
170	10	...	17.0
227	13.5	2.0	16.3
300	28	3.0	5.0
371	61.9	4.0	2.1
383	67.1	...	2.3
400	74.7	5.0	2.2
450	82	5.1	6.8
490	85.3	...	12.1
520	93.9	...	3.5
560	98.1	5.3	9.5
640	117.9	...	4.0
725	124.2	5.5	13.5
750	127	6.0	8.9
800	135	6.2	6.3
<i>RC13-229</i>			
0	2.8	top+	
12	6	1.1	3.8
42	14	2.0	3.8
57.5	18.8	2.2	3.2
110	28	3.1	5.7
155	53	3.3	1.8
180	65	4.2	2.1
212.5	80	5.1	2.2
252.5	99	5.3	2.1
270	107	5.4	2.2
290	122	5.5	1.3
339	135	6.2	3.8
365	151	6.4	1.6
415	183	6.6	1.6
430	194	7.1	1.4
450	224	7.?	0.7

Table 3. (continued)

Depth, cm	Age, kyr	Event	Sedimentation Rate, cm kyr ⁻¹
455	228	7.4	1.3
465.5	238	7.5	1.1
490	260	8.?	1.1

* Ages are based on correlation with the AMS dated MD88-770.

+ core-top age were determined by assuming constant Holocene sedimentation rate.

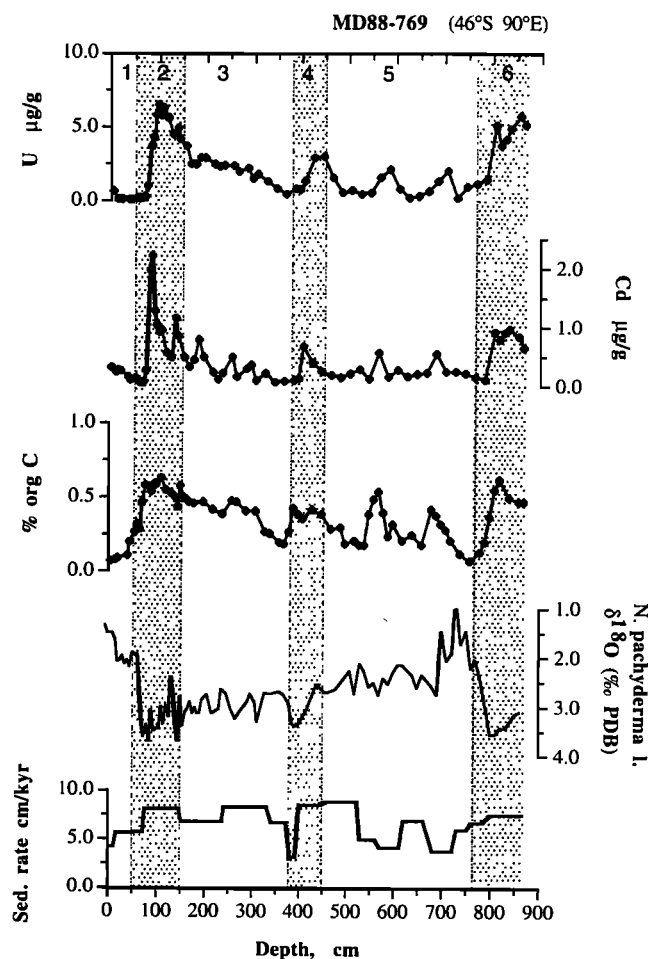


Figure 2. Down-core variations of %organic carbon and authigenic Cd and U in Subantarctic core MD88-769. Also shown are the $\delta^{18}\text{O}$ record of *N. pachyderma l.* and the sedimentation rate. Isotope stage boundaries are indicated by the Shaded lines. The depth-age relationship is given in Table 3. All concentrations are expressed on a total sediment basis.

Table 4. Concentrations of Organic Carbon and Authigenic Cd and U in Subantarctic Sediments From MD88-769

Depth, cm	%Organic Carbon	Cd, $\mu\text{g g}^{-1}$	U, $\mu\text{g g}^{-1}$	MnO, $\mu\text{g g}^{-1}$	%Detrital Al_2O_3
4.5	0.07	0.31	0.65	267	0.96
14.5	0.08	0.23	0.11	250	0.98
18.5	0.09	0.26	0.12	272	1.16
23.5		0.25	0.12	261	1.18
39.0	0.11	0.15	0.09	454	1.87
43.5	0.20	0.10	0.10	568	2.99
54.0	0.27	0.13	0.20	662	3.92
59.0	0.32	0.09	0.18	311	4.16
63.5	0.29	0.05	0.20	529	7.31
69.0	0.47	0.05	0.29	395	7.04
75.5	0.58	0.26	1.03	32	6.63
83.5	0.57	1.96	3.70	46	5.98
88.0	0.54	2.20	4.31	48	6.43
93.5	0.59	1.27	5.84		
98.0	0.59	1.03	6.50	42	6.92
103.5		0.91	5.82		
108.0	0.63	0.94	6.29		
118.0	0.55	0.56	5.62	55	6.93
128.0	0.53	0.48	4.51	58	
138.0	0.50	1.14	4.93	48	6.97
142.5	0.44	0.84	4.18	49	6.73
148.0	0.58				
156.0	0.50	0.48	3.72	51	5.80
166.0	0.47	0.32	2.51		
176.0	0.46	0.44	2.48		
186.0		0.78	2.94		5.00
196.0	0.47	0.49	2.92	49	1.99
216.0	0.42	0.23	2.49		3.51
226.0		0.11	2.35		2.37
236.0	0.39	0.22	2.42		2.96
256.0	0.48	0.49	2.41		
266.0	0.47	0.16	2.01	61	3.92
286.0	0.41	0.29	2.24	96	1.23
296.0		0.36	1.54		1.38
306.0	0.41	0.10	1.84	78	4.17
326.0	0.27	0.22	1.36		2.28
336.0	0.26				
346.0		0.07	0.89		
356.0	0.20				
366.0	0.19	0.09	0.50	60	4.04
376.0	0.27				
386.0	0.43	0.10	0.88	75	2.74
396.0	0.39	0.14	0.82		
406.0	0.36	0.67	1.40	25	4.13
426.0	0.42	0.40	2.96	34	
446.0	0.39	0.25	3.05		3.98
466.0	0.29	0.19	1.61	53	1.52
486.0	0.30	0.15	0.61		0.38
496.0	0.19				
506.0		0.22	0.77	92	0.64
516.0	0.21				
526.0	0.18	0.29	0.50	84	0.95
536.0	0.18				

Table 4. (continued)

Depth, cm	%Organic Carbon	Cd, $\mu\text{g g}^{-1}$	U, $\mu\text{g g}^{-1}$	MnO, $\mu\text{g g}^{-1}$	%Detrital Al_2O_3
546.0	0.39	0.13	0.60	56	1.87
556.0	0.49				
566.0	0.54	0.57	1.65	49	1.95
576.0	0.40				
586.0	0.24	0.16	2.18	76	1.32
596.0	0.32				
606.0		0.28	0.86	82	1.18
616.0	0.21				
626.0		0.17	0.27	79	1.72
636.0	0.25				
646.0		0.21	0.38	65	1.79
656.0	0.18				
666.0		0.23	0.70	41	2.53
676.0	0.42				
686.0	0.38	0.55	1.39	36	2.05
696.0	0.32				
706.0	0.28	0.25	2.08	51	2.58
716.0	0.21				
726.0		0.25	0.25	108	0.71
736.0	0.12				
746.0		0.22	1.01	85	1.57
756.0	0.07				
766.0		0.15	1.19		1.08
776.0	0.13				
786.0	0.20	0.11	1.51	38	3.77
796.0	0.37				
806.0	0.55	0.92	5.19	37	4.76
816.0	0.62	1.06	3.80		4.79
826.0		0.91	4.23		
836.0	0.50	0.97	4.97	39	6.20
856.0	0.47	0.84	5.81	43	4.80
866.0	0.47	0.65	5.22		4.59

All concentrations are expressed on a whole sediment basis.

Discussion

Variations in Organic Carbon Accumulation Rates

Organic carbon mass accumulation rates (MAR) were computed by assuming linear sedimentation rates between age control points: $\text{MAR (mg cm}^{-2} \text{ kyr}^{-1}) = \text{weight fraction of organic carbon} \times \text{dry bulk density (g cm}^{-3}) \times \text{linear sedimentation rate (cm kyr}^{-1})$. The strong similarity between the temporal variations in organic carbon accumulation rates and %organic carbon observed in cores MD88-769 (Subantarctic) and RC13-229 (Cape Basin) indicates that changes in sedimentation rate or dilution by detrital material had only a minor effect on the records of organic carbon accumulation rates in these two cores (Figure 5). The pattern of the variations in organic carbon MARs in the Subantarctic core (MD88-769) is similar to that observed in other records from equatorial divergence and continental margin regions; these records are characterized by high accumulation rates during isotopic

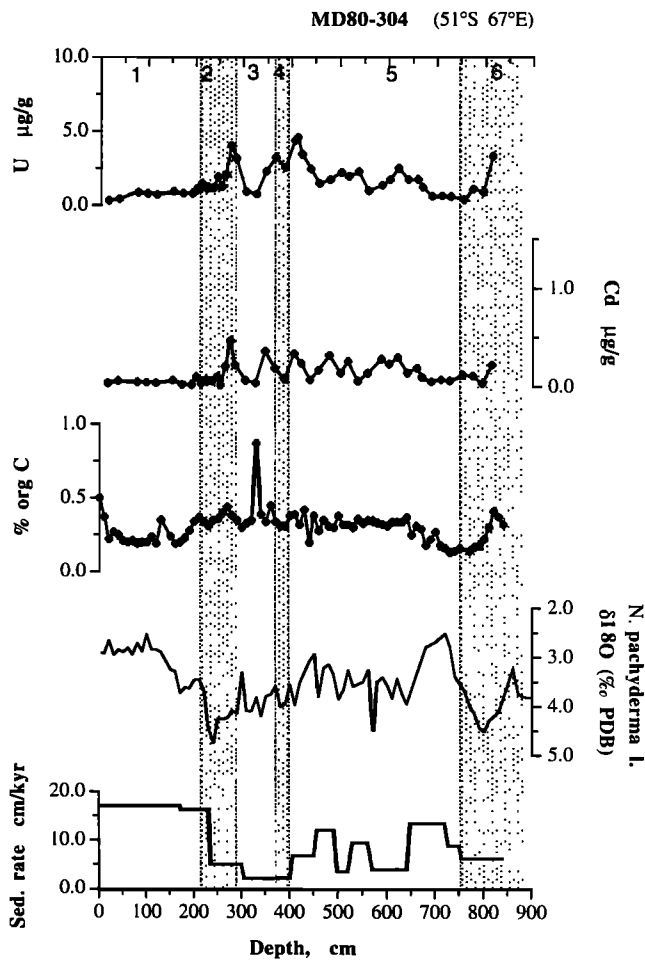


Figure 3. Down-core variations of %organic carbon and authigenic Cd and U in Antarctic core MD80-304. Also shown are the $\delta^{18}\text{O}$ record of *N. pachyderma s.* [Labeyrie and Duplessy, 1985] and the sedimentation rate. Isotope stage boundaries are indicated by the shaded lines. The depth-age relationship is given in Table 3. All concentrations are expressed on a total sediment basis.

stages 6, 3, and 2 [Muller and Suess, 1979; Pedersen et al., 1988; Shimmield, 1992; Sarkar et al., 1993]. Organic carbon accumulation rates in core MD80-304, located south of the Antarctic Polar Front, exhibit an inverse pattern to the Subantarctic record, with a relatively high accumulation rate of organic carbon during the Holocene and the last interglacial ($20\text{--}30 \text{ mg C cm}^{-2} \text{ kyr}^{-1}$), and significantly lower during the glacial stages. Note that there are only small glacial-interglacial changes in the %organic carbon record of MD80-304, and therefore estimates of the organic carbon MAR in this core reflect primarily changes in sedimentation rates. Sedimentation rates in MD80-304 are high during interglacials ($15 \pm 2 \text{ cm kyr}^{-1}$) and low during glacial intervals ($3.2 \pm 1.6 \text{ cm kyr}^{-1}$, Table 3). The Al_2O_3 data indicate that minimum contributions of detrital material are associated with interglacial periods when sedimentation rates are relatively high. In addition, hydrographic studies suggest that in this

Table 5. Concentrations of Organic Carbon and Authigenic Cd and U in Subantarctic Sediments From MD80-304

Depth, cm	%Organic Carbon	Cd, $\mu\text{g g}^{-1}$	U, $\mu\text{g g}^{-1}$	MnO, $\mu\text{g g}^{-1}$	%Detrital Al_2O_3
0	0.5		38		
10	0.37			49	
16	0.03	0.33	162		0.25
19	0.22		53		
29	0.27		21		
38	0.06	0.44	10		0.31
40	0.25				
49	0.21		21		
58	0.2	0.07	1.12	14	0.31
69	0.21				
78	0.19	0.05	0.88	11	0.42
89	0.2				
98	0.2	0.04	0.81	10	0.39
109	0.24				
118		0.04	0.73	19	0.45
120	0.19				
130	0.35				
150	0.24				
153		0.07	0.96	10	0.69
159	0.19				
169	0.2				
173		0.02	0.83	17	0.99
181	0.23				
189	0.28				
193		0.13	0.92	20	1.30
199	0.34				
203		0.10	1.14	14	1.19
211	0.37				
213		0.03	1.52	23	1.76
219	0.34				
223		0.07	1.16	16	1.09
227		0.06	1.25	24	1.56
230	0.31				
237		0.06	1.21	20	1.99
239	0.35				
247		0.10	1.94	35	3.43
250	0.36				
254		0.02	1.30	27	4.33
260	0.4				
264		0.21	2.09	31	3.91
270	0.44				
275		0.46	4.06		5.53
281	0.38				
285		0.22	3.19	22	6.93
289	0.35				
300	0.3				
306		0.06	0.95	13	3.62
310	0.33				
319	0.35				
327		0.04	0.78	17	2.08
330	0.87				
340	0.39				
347		0.36	2.33	18	1.92

Table 5. (continued)

Depth, cm	%Organic Carbon	Cd, $\mu\text{g g}^{-1}$	U, $\mu\text{g g}^{-1}$	MnO, $\mu\text{g g}^{-1}$	%Detrital Al_2O_3
350	0.34				
360	0.45				
367		0.19	3.26	15	2.20
370	0.34				
380	0.31				
387		0.08	2.59	16	2.20
390	0.31				
400	0.38				
407		0.34	4.40	16	4.60
410	0.39				
413		0.03	4.61		4.01
420	0.32				
422		0.24	3.47		1.26
431	0.42				
439	0.2				
440		0.07	2.48		0.60
450	0.38				
458	0.28	0.17	1.51		0.47
469	0.35				
479	0.31				
481		0.32	1.78		5.25
490	0.3				
499	0.38				
503		0.13	2.25		0.95
509	0.32				
518		0.26	1.99		1.49
520	0.32				
530	0.3				
538		0.06	1.31		1.30
540	0.36				
548	0.33				
558		0.14	1.02		
560	0.35				
568	0.35				
580	0.33				
586		0.28	1.40		0.31
589	0.32				
600	0.31				
602		0.23	1.76	22	0.68
610	0.34				
620	0.34	0.30	2.53	8	0.89
630	0.34				
641	0.37	0.14	1.77	8	0.86
650	0.25				
661	0.31	0.19	1.77	10	1.30
671	0.29	0.10	1.25	7	0.49
680	0.18				
691	0.22	0.05	0.63	6	0.43
700	0.27				
710	0.18	0.06	0.65	20	0.44
728		0.06	0.60	28	0.78
730	0.16				
740	0.13				
750	0.14				
755		0.12	0.38	51	0.99

Table 5. (continued)

Depth, cm	%Organic Carbon	Cd, $\mu\text{g g}^{-1}$	U, $\mu\text{g g}^{-1}$	MnO, $\mu\text{g g}^{-1}$	%Detrital Al_2O_3
760	0.16				
771	0.14				
775		0.11	1.12	40	1.07
780	0.17				
792	0.18				
795		0.03	0.89		3.03
800	0.22				
811	0.3				
815		0.22	3.32	6.23	
820	0.41				
831	0.37				
840	0.32				
850	0.31				

All concentrations are expressed on a whole sediment basis. Organic carbon data is from M. Fontugne (unpublished data, 1994).

region the flow of Antarctic Circumpolar Current is mostly concentrated in a narrow frontal zone between the Subantarctic and subtropical Fronts (43°-46°S) and that the polar front is not associated with any strong current [Park *et al.*, 1991] with the corollary of weak bottom currents in this region. Therefore it is most likely that sedimentation rates in this core are tightly linked to surface productivity rather than to inputs of detrital material. The high Holocene sedimentation rates are typical of rapidly accumulating siliceous sediments beneath the Antarctic Polar Front [DeMaster *et al.*, 1991] while, as suggested below, the lower glacial accumulation rate is consistent with a northward migration of the diatomaceous belt during glacial periods [Hays *et al.*, 1976; Howard and Prell, 1992].

In the absence of any information about the nature of the organic matter in these cores, it is difficult to assess the contributions from terrestrial sources to these cores. However, because of the relatively large distance of the Subantarctic site (MD88-769) from the continents, substantial variations in the input from continental sources seem quite unlikely. Likewise, sedimentological studies suggest that there were no substantial glacial-interglacial changes in riverine fluxes into the Cape Basin [Embley and Morley, 1980], thus precluding a significant contribution from terrestrial sources to the high glacial organic carbon accumulation rates at this site. Therefore we suggest that changes in organic carbon accumulation rates in these sites reflect surface productivity. Increased burial flux of marine organic matter is also consistent with enhanced accumulation of authigenic Cd and U, because of its higher reactivity compared with the more refractory terrigenous organic matter.

Accumulation of Authigenic Uranium and Cadmium

In the modern ocean, authigenic U and Cd precipitate primarily in organic-rich continental margin sediments

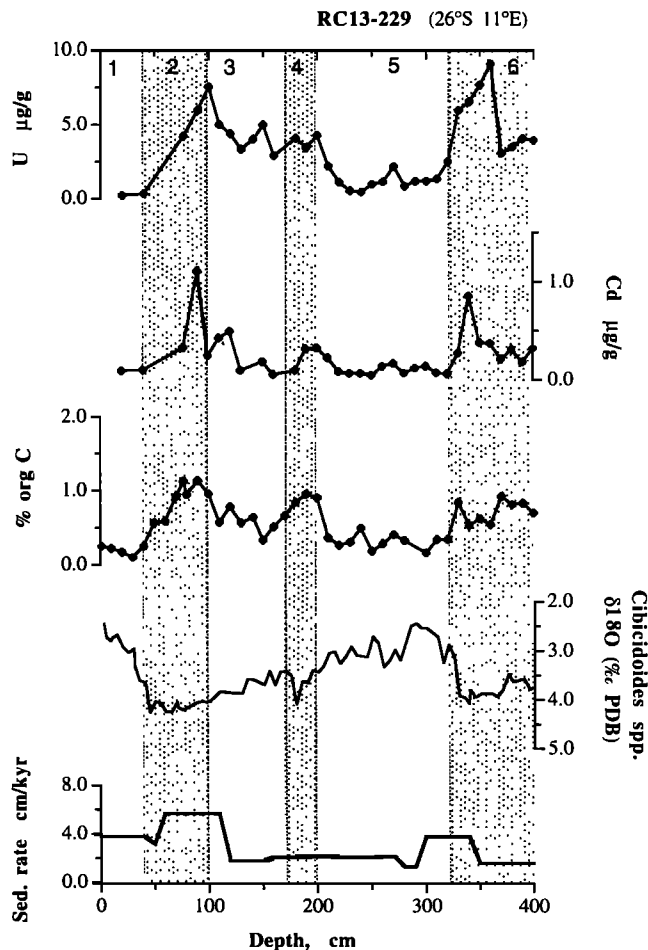


Figure 4. Down-core variations of %organic carbon and authigenic Cd and U in Cape Basin core RC13-229. Also shown are the $\delta^{18}\text{O}$ record of *Cibicides* spp. [Oppo *et al.* 1990] and changes in sedimentation rate. Isotope stage boundaries are indicated by the shaded lines. The depth-age relationship is given in Table 3. All concentrations are expressed on a total sediment basis.

where reducing conditions occur close to the sediment-water interface [Cochran *et al.*, 1986; Gobeil *et al.*, 1987; Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991; McCorkle and Klinkhammer, 1991; Lapp and Balzer, 1993]. Such conditions may be caused by bottom water oxygen depletion or by a relatively high flux of labile organic matter into the sediment, resulting in complete consumption of oxygen near the sediment-water interface. Porewater profiles from suboxic sediments indicate that Cd diffuses downward along a concentration gradient established by its removal near the redox boundary [Gobeil *et al.*, 1987; McCorkle and Klinkhammer, 1991; Lapp and Balzer, 1993]. Due to the strong tendency of Cd to form insoluble sulfides in the presence of H_2S , it is very likely that the removal of Cd in suboxic sediments is related to the precipitation of CdS. This process is discussed in greater detail elsewhere [Rosenthal *et al.*, 1995]. The recurrent subsurface maximum in dissolved Cd suggests that release of Cd

during early diagenetic oxidation of organic matter rather than diffusion from bottom water is the primary source of dissolved Cd into the porewater. The data also suggest that Cd removal occurs in shallower depth than U [Klinkhammer and Palmer, 1991].

Table 6. Concentrations of Organic Carbon and Authigenic Cd and U in Subantarctic Sediments From RC13-229

Depth, cm	%Organic Carbon	Cd, $\mu\text{g g}^{-1}$	U, $\mu\text{g g}^{-1}$	MnO, $\mu\text{g g}^{-1}$	%Detrital Al_2O_3
0	0.25				
9					
10	0.22				
20	0.17	0.09	0.22		1.66
30	0.10				
40	0.25	0.10	0.34	277	1.51
50	0.57				
60	0.59				
70	0.92				
77	1.13	0.33	4.26	61	5.55
80	0.95				
90	1.14	1.11	6.00	145	6.36
100	0.96		7.57		5.06
110	0.58	0.43	5.04		4.37
120	0.79	0.50	4.44	235	4.15
130	0.57	0.10	3.38		4.52
140					
141	0.65		4.07		3.54
150	0.34	0.19	5.04		4.38
160	0.52	0.06	2.95	100	
170	0.67				
180	0.85	0.10	4.13		1.95
190	0.96	0.32	3.50		9.12
200	0.91	0.33	4.32		7.47
210	0.37	0.23	2.25		7.27
220	0.27	0.09	1.15		5.15
230	0.31	0.07	0.57		2.43
240	0.50	0.07	0.48		
250	0.19	0.05	1.01		4.07
260	0.29	0.14	1.17		4.68
270	0.41	0.17	2.20		
280	0.33	0.07	0.86		3.19
290		0.12	1.19		1.66
300	0.16	0.14	1.19		1.98
310	0.34	0.07	1.35		2.29
320	0.34	0.06	2.50		
330	0.84	0.27	5.95		4.28
340	0.53	0.85	6.55		
350	0.62	0.38	7.66		3.01
360	0.54	0.37	9.06		4.06
370	0.92	0.21	3.07		3.07
380	0.81	0.31	3.48		3.80
390	0.83	0.18	4.07		7.03
400	0.70	0.32	3.94		4.88

All concentrations are expressed on a whole sediment basis.

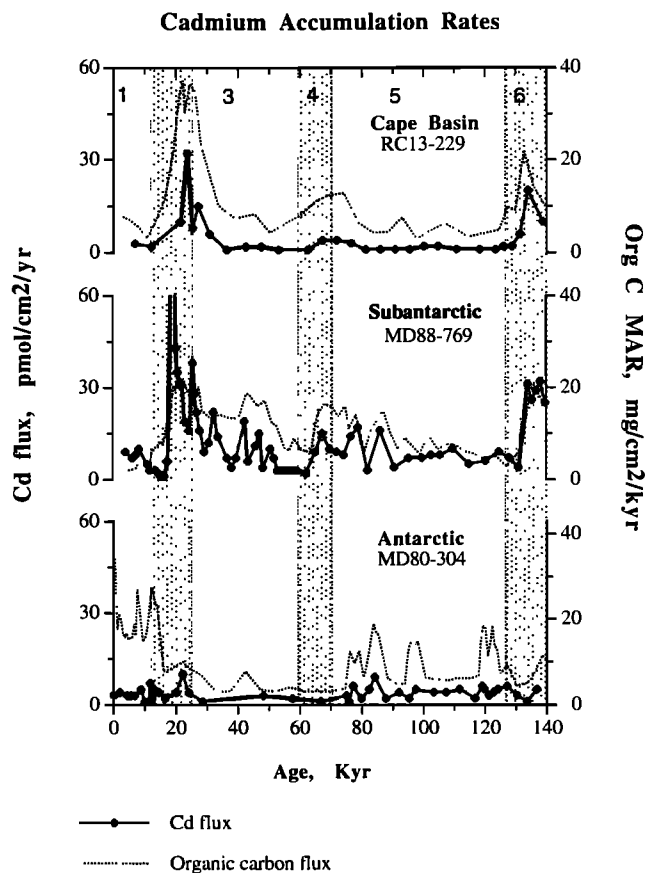


Figure 5. A comparison between records of organic carbon (dotted lines) and authigenic Cd (solid lines with solid circles) accumulation rates during the last 150 kyr. The Cd record was shifted by -5 cm before converting to age scale in order to account for the difference between the age of the authigenic enrichments and of the host sediment. Because these records were most likely modified by postdepositional remobilization, only the broad, glacial-interglacial changes in the integrated flux of Cd are considered. MAR is mass accumulation rate.

In absence of porewater data from the core sites we deduce the redox conditions of the sediments from the solid phase data. On the basis of the distribution of Mn-oxides, surface sediments in all three sites are oxidized to a considerable depth, reflecting a low organic carbon input to the sediment. The sharp downward decrease in Mn-oxide concentration (Tables 4, 5, and 6, note that Mn oxide concentrations are expressed as MnO) marks the approximate depth of the O_2 -Mn²⁺ redox front. In the Subantarctic site, oxic conditions occur to a great depth, about 70-75 cm below the water-sediment interface. In the Antarctic site, Mn-oxide levels of surface sediments are relatively low throughout, but the significant decrease between 15 and 25 cm suggests that oxic conditions probably prevail down to 15-20 cm. This inference is consistent with recent porewater oxygen measurements from Southern Ocean sediments underlying the APF (Indian sector) showing a shallow oxic layer [Jean-

Francois Gaillard, personal communication, 1995]. The deep redox boundaries explain the low concentrations of Cd and U in surface sediments from these sites. Considering that sedimentation rates in MD88-769 were higher during the glacial stage than during the Holocene, the enrichments of authigenic Cd and U most likely reflect more reducing conditions during that time (i.e., shoaling of the redox front). More reducing conditions during glacial intervals are also evident in the Cape Basin site (RC13-229). In contrast, a fivefold lower glacial sedimentation rate in the Antarctic site (MD80-304) is enough to explain the small, nevertheless significant, enrichments observed in glacial sediments from this site. Fluctuations in sedimentation rate during this period might have led to postdepositional redistribution of Cd and U, resulting in a spiky record which shows no coherence with the $\delta^{18}O$ record.

The accumulation of Cd in suboxic sediments is tightly coupled to the early diagenetic degradation of organic matter. In principal, the redox state of the sediment reflects the balance between the flux of organic matter into, and consumption of oxygen in, the sediment. A schematic depiction of the precipitation and postdepositional redistribution of authigenic Cd is given in Figure 6. At a steady state (i.e., constant organic carbon flux) the redox front will move upward in pace with the accumulating sediment, resulting in relatively elevated concentration of authigenic Cd. In regions of high organic carbon flux the redox front will be relatively shallow: the higher the organic carbon flux is, the shallower the redox boundary will be. In turn, changes in the depth of the redox front will determine, to a large extent, the porewater concentration gradient and consequently the accumulation rate of authigenic Cd. The subsurface maximum in dissolved Cd enhances the porewater gradient, thereby enhancing the accumulation of authigenic Cd. This situation, which at present characterizes continental margin sediments, is the best modern analog for regions of enhanced glacial productivity such as proposed for the Subantarctic and Cape Basin regions. However, authigenic Cd and U may be redistributed in the sediment due to postdepositional remobilization. It has been suggested that a significant decrease in the organic carbon flux or bulk sedimentation rate may increase the oxygen availability in the sediment, thus leading to fixation or even deepening of the redox front [Thomson *et al.*, 1990; Francois *et al.*, 1993; McCorkle *et al.*, 1994]. A deepening of the oxidation front into organic-rich sediments will lead to a "burn down" (i.e., oxidation) of organic carbon and remobilization of authigenic Cd and U. This process will result in formation of a sharp peak below the oxidation front as suggested from studies of North Atlantic turbidites [Thomson *et al.*, 1990; Rosenthal *et al.*, 1995]. The sharp peaks in authigenic Cd and U in our records, particularly below glacial terminations, are probably a result of such postdepositional remobilization.

In order to compare records from different cores, we computed the accumulation rates of authigenic Cd and U using the following relationship: J (pmol cm⁻² yr⁻¹) = sedimentation rate (cm yr⁻¹) * dry bulk density (g cm⁻³)

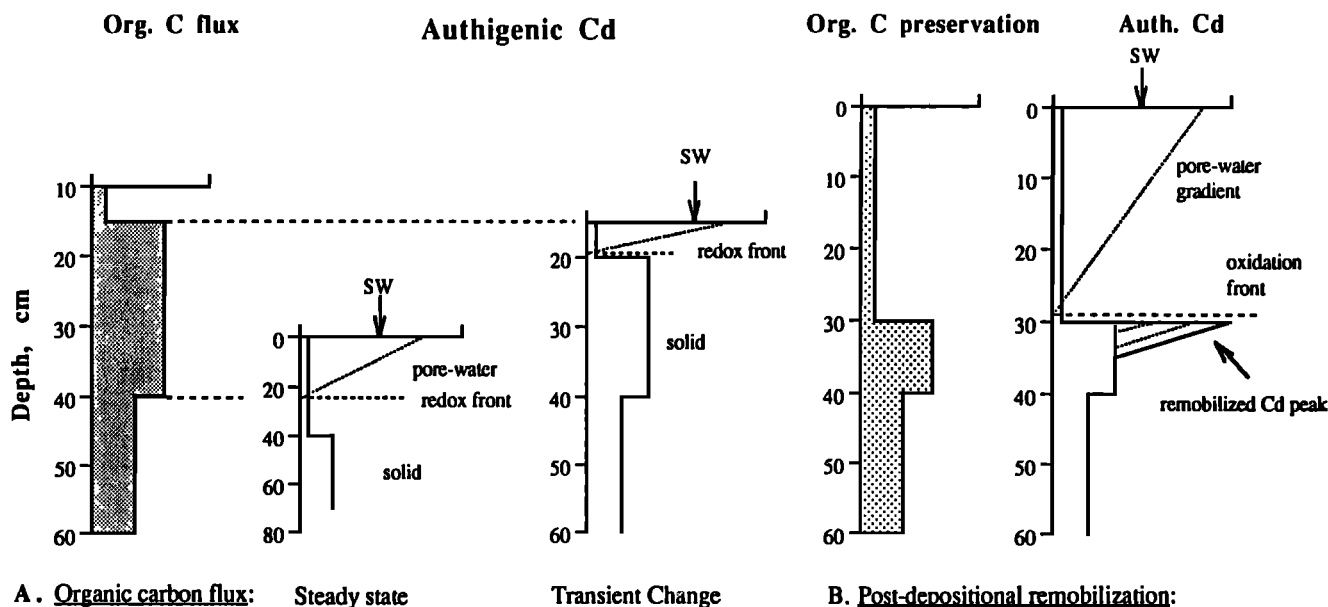


Figure 6. Schematic depiction of the diagenetic processes controlling the accumulation of Cd in sediments underlying productive surface water. (a) At steady state the redox front moves upward, in pace with the sediment-water interface resulting in relatively high and constant concentration of authigenic Cd. Increased organic flux into the sediment leads to shoaling of the redox front thus resulting in greater porewater gradient and consequently a new steady state where Cd concentrations are higher than before. (b) A decrease in the flux of organic carbon leads to deeper penetration of O_2 , resulting in deepening of the oxidation front, "burn down" of organic carbon and remobilization of Cd into the suboxic zone. The deepening of the oxidation front will continue until a new steady state between the downward diffusion of O_2 and the oxidation of organic carbon is achieved. The arrow (SW) marks the bottom water Cd concentration.

*concentration (mol g^{-1}), where J is the downward diffusive flux. We have used the sedimentation rate at the time of precipitation of the authigenic Cd and U phases. This sedimentation rate may be different than that of the host sediment, where the authigenic peak is found. Because the offset between the sediment surface and the precipitation zone below it is variable, it is difficult to assign an accurate chronology to the authigenic enrichments. Therefore we calculated Cd and U accumulation rates simply by using constant precipitation depths (ΔZ) of 5 and 10 cm below the sediment-water interface for Cd and U, respectively. The records of Cd and U accumulation rates were shifted by the corresponding time differences ($\Delta t = \Delta Z/S$) to account for the offsets between the age of the host sediment and the estimated age of formation of the authigenic enrichments (S is the sedimentation rate). Cadmium and uranium accumulation rates are presented in Figures 6 and 7.

In the interpretation of the Cd and U oceanic budgets we consider only the broad glacial-interglacial variations in the integrated flux rather than the point-by-point removal flux. In the Subantarctic core (MD88-769), we obtain average glacial downward diffusive fluxes of about $15 \text{ pmol cm}^{-2} \text{ yr}^{-1}$ for Cd and $30 \text{ pmol cm}^{-2} \text{ yr}^{-1}$ for U (stages 6, late 3, and 2) which are comparable to, although tending to be on the lower side of, estimates from continental margin sediments [Klinkhammer and Palmer, 1991;

McCorkle and Klinkhammer, 1991]. These glacial fluxes are significantly higher than average interglacial removal fluxes of about 1 and $5 \text{ pmol cm}^{-2} \text{ yr}^{-1}$ for Cd and U, respectively. The lower fluxes are typical of deep ocean pelagic sediments [Rosenthal *et al.*, 1995]. Mass accumulation rate records from core MD80-304 are dominated by substantial glacial-interglacial changes in sedimentation rates. While there are only minor variations in concentrations of the authigenic phases throughout the record, we compute significantly higher interglacial, relative to glacial accumulation rates of authigenic Cd and U, in accord with organic carbon MAR. This pattern is approximately the inverse of the one seen in the Subantarctic site.

Productivity Changes in the Antarctic Ocean

In principal, enrichments in organic carbon and authigenic Cd and U may result from a decrease in bottom water oxygen content, an increase in the flux of labile organic carbon into the sediment, or any combination of them. The three cores in this study are well positioned to distinguish between these hypotheses. At present all three sites are overlain by Circumpolar Deep Water [Bainbridge, 1980; Spencer *et al.*, 1982; Broecker *et al.*, 1991]. Therefore oxygen depletion in glacial CPDW should have resulted in greater preservation and consequently higher

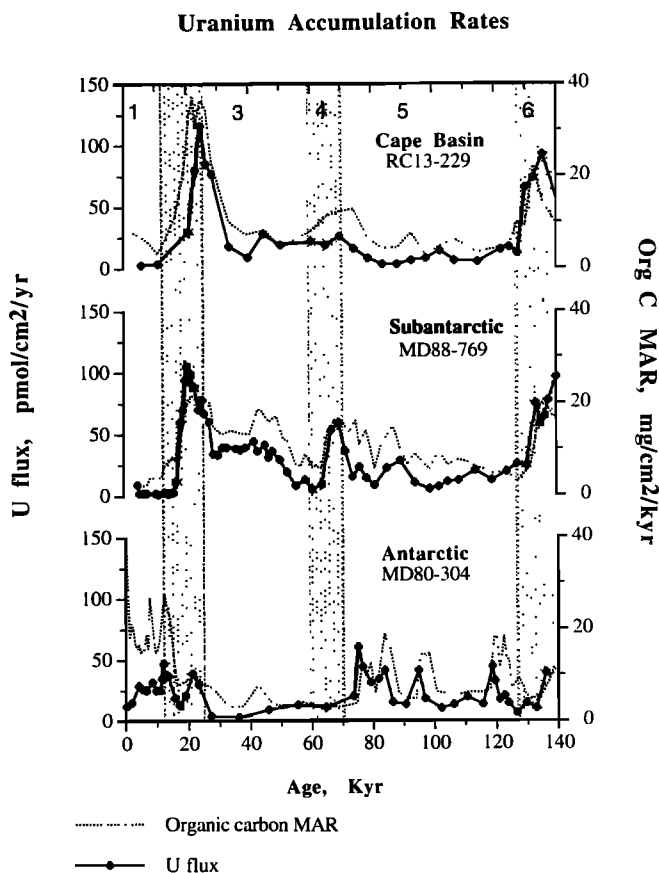


Figure 7. A comparison between records of organic carbon (dotted lines) and authigenic U (solid lines with solid circles) accumulation rates during the last 150 kyr. The U record was shifted by -10 cm before converting to age scale in order to account for the difference between the age of the authigenic enrichments and of the host sediment. Because these records were most likely modified by postdepositional remobilization, only the broad, glacial-interglacial changes in the integrated flux of U are considered.

accumulation rates of organic carbon and authigenic Cd and U at all three sites. The elevated concentrations and accumulation rates of organic carbon and authigenic Cd and U in the Subantarctic record (MD88-769) suggest a shoaling of the redox front during glacial periods. The enrichments are positively correlated with changes in biogenic silica accumulation rates in this core [Bareille *et al.*, 1993]. In contrast, the Southern Ocean record (MD80-304) shows lower glacial than interglacial accumulation rates of organic carbon and authigenic Cd and U. The small enrichments in authigenic Cd and U concentrations observed in this record are not significantly different than those simply expected from variations in sedimentation rate (assuming a constant depth of the redox boundary). This contrasting behavior in cores located to the north and south of the Antarctic Polar Front suggests that increased surface productivity is the dominant cause of the enrichments of organic carbon and authigenic Cd and U in

glacial Subantarctic and Cape Basin sediments. The Southern Ocean record of MD80-304 suggests no such increase in glacial surface productivity, and perhaps there are even indications for lower glacial productivity, south of the Antarctic Polar Front. These conclusions are consistent with results from other paleoproductivity tracers (biogenic silica; $^{231}\text{Pa}/^{230}\text{Th}$) [Charles *et al.*, 1991; Mortlock *et al.*, 1991; Kumar *et al.*, 1993].

The data presented here are consistent with suggestions of a northward migration of the polar front along with the "silica belt" [Charles *et al.*, 1991; Mortlock *et al.*, 1991; Bareille *et al.*, 1993]. According to the paleoproductivity equation of Sarnthein *et al.* [1988] the organic carbon record from MD88-769 suggests that new production decreased from about $30 \text{ g C m}^{-2} \text{ yr}^{-1}$ at the LGM to about $10 \text{ g C m}^{-2} \text{ yr}^{-1}$ during the Holocene; estimates for MD80-304 show an opposite change of similar magnitude (or perhaps slightly smaller). At present, a new production level of about $20\text{-}30 \text{ g C m}^{-2} \text{ yr}^{-1}$ is typical of high-latitude surface waters between 50° and 60°S [Wefer and Fischer, 1991; Berger and Herguera, 1992]. Therefore a threefold increase in surface productivity during the LGM, estimated in the Subantarctic core, is consistent with about $4\text{-}5^\circ$ northward migration of the polar front [Howard and Prell, 1992] and its associated zone of siliceous productivity. Our estimates are in good agreement with reconstructions of glacial opal fluxes from the Atlantic and Indian sectors of the Southern Ocean, suggesting a threefold to fivefold increase in diatom productivity in the Subantarctic region and a synchronous decrease of similar magnitude in the zone south of the modern APF. However, the accumulation rates of authigenic Cd and U in glacial Subantarctic sediments are significantly higher than might be expected simply from northward displacement of the polar front. This is evident when comparing the glacial accumulation rates in MD88-769 and Holocene accumulation rates in MD80-304. Currently, Cd and U accumulation rates under the APF are relatively low (Figures 5 and 7) reflecting the oxic conditions in the underlying sediments. In other words, our records suggest that Subantarctic glacial sediments were characterized by more reducing conditions than presently observed in sediments under the Antarctic Polar Front. Further, the Antarctic record suggests that despite the lower accumulation rate of organic carbon during the glacial interval, the depth of the glacial redox front might not have been significantly different than in the modern ocean. If these observations are representative of the whole Southern Ocean, then the data suggest that along with significant changes in surface productivity, there might have also been a decrease in the bottom water oxygen content. Alternatively, it is possible that the organic carbon to biogenic silica ratio in particulate matter reaching the seafloor in both the Antarctic and the Subantarctic regions was greater during glacial than interglacial periods. Whatever mechanism was responsible for these enrichments, the implications are that glacial periods were associated with greater partitioning of organic carbon into the sediment than occurs in the modern Southern Ocean. Clearly, more records on both sides of the

Antarctic Polar Front are needed in order to estimate the integrated increase in organic carbon burial during glacial intervals and the causes for this changes.

Records from the Cape Basin (RC13-229) suggest that surface productivity along this continental margin was significantly higher during the LGM than the Holocene (Figures 5 and 7). Higher glacial productivity in the Cape Basin is consistent with paleo-sea surface temperature reconstructions for the LGM which suggest about 2°C cooling of sea surface temperatures in this region, associated with stronger zonal gradients off the coast of southwest Africa [CLIMAP, 1976; Embley and Morley, 1980]. The distribution of LGM sea surface temperatures is consistent with stronger wind-driven coastal upwelling, which would have supported higher productivity. The multiple peaks in the Subantarctic and Cape Basin Cd records suggest that there might have been significant fluctuations in biological productivity in this region, even during glacial periods when productivity was generally high.

Implications for the Global Oceanic Budget

The importance of suboxic sediments as a Cd sink in the modern ocean can be assessed by comparing the removal fluxes of Cd into reducing sediments with Cd inputs into the ocean. Estimates of effective riverine Cd concentrations vary between 100 pmol kg⁻¹ (Amazon River) [Boyle et al., 1982] and 400 pmol kg⁻¹ (Yangtze and Mississippi Rivers) [Edmond et al., 1985; Shiller and Boyle, 1991]. On the basis of these data, we calculate a global Cd riverine input of about 0.4-1.4x10⁷ mol yr⁻¹. Estimates of the natural atmospheric Cd input are poorly constrained and may also be biased toward high values, because of the strong impact of anthropogenic pollution during this century. Measurements of aerosols over the Atlantic Ocean suggest Cd/Al enrichment factors (EF) between 30 and 300 above crustal abundance [Prospero, 1981]. The lower estimate was obtained in regions under strong influence of the trade winds originating from the Saharan desert and therefore is more representative of the natural background. The higher EF value was measured in regions under the influence of the prevailing westerlies, carrying material from the North Atlantic continent which is probably highly contaminated by anthropogenic sources. If the estimated tenfold increase in atmospheric Cd emissions since preindustrial times [Nriagu, 1979] is translated into atmospheric deposition, then a preindustrial enrichment factor of about 30 may also be assumed for the North Atlantic aerosols, consistent with measurements of Saharan dust. Assuming aerosol deposition of 500-850x10¹² g yr⁻¹ [Prospero, 1981], a 5-10% aluminum content in aerosols [Prospero, 1981], a Cd/Al crustal ratio of 2.4x10⁻⁶ g g⁻¹ [Wedepohl, 1978] and EF=30, we obtain Cd atmospheric deposition of about 1.6-5.5x10⁷ mol Cd yr⁻¹. At present, there are no data on how much Cd dissolves when dust falls into seawater. However, assuming about 10-20% dissolution, we estimate the natural atmospheric Cd input to the world ocean to about 0.2-1.1x10⁷ mol yr⁻¹ which is of the magnitude of the

riverine input. This brings the global Cd input into the ocean to about 0.6-2.5x10⁷ mol yr⁻¹.

Using available porewater profiles from continental margin sediments underlying oxic water [McCorkle et al., 1994], we estimate a removal flux of about 20-50 pmol Cd cm⁻² yr⁻¹. Applying similar flux over the entire area of modern suboxic sediments (estimates vary between 8% [Klinkhammer and Palmer, 1991] and 13% [Reimers et al., 1992] of the seafloor), we obtain an areally integrated Cd removal of 0.6-2.3x10⁷ mol yr⁻¹ which is in balance with the estimated inputs. Although higher fluxes of about 70-100 pmol Cd cm⁻²yr⁻¹ are observed in sediments underlying oxygen minimum water [Gobeil et al., 1987; Lapp and Balzer, 1993; McCorkle et al., 1994], their contribution to the areally integrated removal is relatively small (≈0.1x10⁷ mol yr⁻¹). On the basis of mean oceanic Cd concentration of 600 pmol kg⁻¹ [Boyle, 1992] we estimate the Cd oceanic residence time to be between 33,000 and 150,000 years. Estimates of the global uranium riverine range between 2.5 and 5x10⁷ mol yr⁻¹ [Palmer and Edmond, 1993]. Removal fluxes of 2.5x10⁷ mol yr⁻¹ into reducing sediments (primarily suboxic) and about 1.3x10⁷ mol yr⁻¹ into hydrothermal systems balance the riverine inputs [Klinkhammer and Palmer, 1991]. The oceanic residence time of uranium is about 250,000-500,000 years [Palmer and Edmond, 1993].

In view of the significance of the suboxic sink, it is possible that climatically induced variations in the areal extent of suboxic sediments might have changed the oceanic inventories of Cd and U. Enhanced accumulation of authigenic Cd and U in glacial sediments suggests that such changes might have occurred in the past. A comparison between the modern and LGM distribution of reducing sediments is shown in Figure 1. In the modern ocean, hemipelagic and organic-rich sediments are the primary sink for U and Cd. These sediments, which are found under the highly productive waters of the western continental margins and the equatorial divergence, occupy about 8-13% of the ocean seafloor [Klinkhammer and Palmer, 1991; Reimers et al., 1992]. Results reported here indicate more reducing conditions in Subantarctic and Cape Basin sediments, where oxic conditions presently prevail, thus suggesting an increase in the size of the suboxic sink. Evidence from multitracer studies of equatorial Pacific and Northwest African coastal sediments also suggest more reducing conditions in response to increased productivity during glacial intervals [Muller and Suess, 1979; Pedersen et al., 1988; Sarnthein et al., 1988; Finney et al., 1988; Lyle et al., 1988; Shimmield, 1992; Sarkar et al., 1993]. These suggestions are supported by preliminary data from the east equatorial Pacific showing an increase in glacial accumulation rates of authigenic Cd and U in accord with higher organic carbon accumulation rates [Y. Rosenthal-unpublished data, 1994]. Enhanced levels of authigenic U were also observed in the Atlantic sector of the Subantarctic Ocean [Anderson et al., 1993], the southeast Arabian Sea [Sarkar et al., 1993], the southeastern Indian Ocean [McCorkle et al., 1994] and the Equatorial Atlantic [Thomson et al., 1990]. Similarly, strong enrichments of authigenic Cd and U, which were

observed in early Quaternary sediments from the Sea of Japan, occur predominantly during cold periods [Piper and Isaacs, 1995]. All these records indicate more reducing conditions in glacial sediments with the corollary of larger suboxic sink. However, there are also suggestions of lower glacial productivity along the North American continental margins and the Arabian Sea [Lyle *et al.*, 1992; Altabet *et al.*, 1994; Ganeshram *et al.*, 1994] suggesting that Cd removal into hemipelagic sediments might have been reduced during glacial intervals. Cadmium accumulation rates in Southern Ocean sediments were continuously low throughout the last 150 kyr, whereas uranium accumulation rates show the inverse pattern to that observed in the Subantarctic zone, i.e., relatively high rates during interglacial and lower during glacial periods (Figures 5 and 7). The available data suggest that the integrated accumulation of U in glacial Subantarctic sediments exceeds the accumulation of U in the Southern Ocean during interglaciations. In conclusion, we propose that the areal extent of reducing sediments doubled to about 16% of the seafloor at the LGM (Figure 1).

We evaluate the sensitivity of seawater Cd and U concentrations to changes in the areally integrated removal flux using simplified mass balance calculations. The time-dependent concentration of stable element in seawater is

$$\frac{d}{dt} \int_V C dv = R_i - R_o \quad (1)$$

where C is the concentration per unit volume and R_i and R_o are the global input and removal fluxes, respectively. We assumed that R_i was constant during the last 250 kyr. In contrast, R_o depends on the areal extent of reducing sediments:

$$R_o = k \int_A J dA \cdot f(t) \quad (2)$$

where J is the diffusive flux into the sediment per unit area (based on our estimates of MARs we chose average fluxes of 30 and 50 pmol cm⁻² yr⁻¹ for Cd and U, respectively), and k is a first-order reaction coefficient relating the diffusive flux of an element to its bottom water concentration. We define k as $k=C_t/C_0$ where C_t and C_0 are the mean oceanic concentrations at time t and at present. The seafloor area A is 3.6x10¹⁴ m². The function $f(t)$ represents the changes in the areal extent of reducing sediments which increases from 8% during interglacial periods to 16% during glacial maxima. Because of the similarity among the records of authigenic Cd and U accumulation rates and the oxygen isotope record, changes in the magnitude of the sink were scaled linearly to the stacked planktonic foraminifera oxygen isotope record of Imbrie *et al.*, [1984]. The removal of Cd and U into oxic sediments was ignored, but a constant hydrothermal U sink of 10 pmol cm⁻² yr⁻¹ was included [Klinkhammer and Palmer, 1991]. Cadmium input was constant at 1.5x10⁷ mol yr⁻¹. The solution shows that under these conditions seawater Cd did not change by more than ±5% during the last 250 kyr (Figure 8). Changes in uranium concentrations are negligible. Note that seawater Cd concentrations are controlled by excess removal during periods of expanded suboxic sink (i.e., glacial intervals) and excess input during

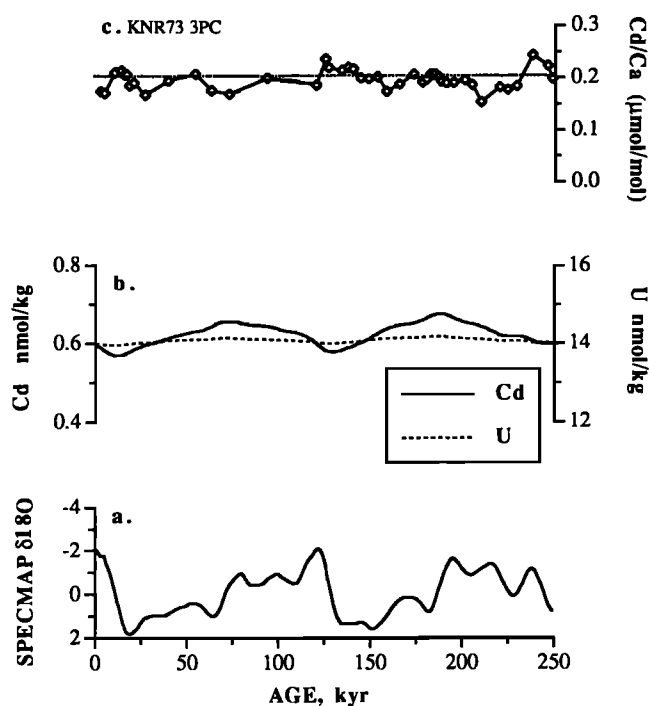


Figure 8. Sensitivity analysis of the response of seawater Cd and U concentrations to changes in the size of the suboxic sink during the last 250 kyr. (a) Changes in the areal extent of suboxic sediments were scaled to the stacked planktonic foraminifera oxygen isotope record of Imbrie *et al.*, [1984], (b) Results of the sensitivity test are shown. (c) Foraminiferal Cd/Ca record from the eastern tropical Pacific (core KNR73 3PC) [Boyle and Keigwin, 1985/6] shows low temporal variability in agreement with our predictions. The dotted line marks the modern ocean bottom water Cd concentrations at this site.

interglacial intervals. As a result, Cd concentrations fluctuate between generally high levels during interglacials (when input > output) and lower levels during glacial intervals (when input < output). Maximum concentrations are reached at glacial initiations and minimum concentrations characterize glacial terminations.

One might wonder if variations in the extent of reducing sediments may decouple Cd from PO₄ and δ¹³C, thereby explaining the apparent discrepancies between Cd and δ¹³C in some of the paleoceanographic record [Boyle, 1992]. Such a decoupling has been previously demonstrated in anoxic basins [Jacobs *et al.*, 1987]. The model shows that during the last 250 kyr seawater Cd concentrations fluctuated only slightly, between reaching high levels (≈0.66 nmol kg⁻¹) during glacial initiations and reaching lowest values (≈0.57 nmol kg⁻¹) during glacial maxima (assuming constant riverine inputs). The low sensitivity of the Cd oceanic budget to glacial increase in the extent of suboxic sediments, implied by this model, is consistent with the absence of discernible glacial Cd drop in the Pacific foraminiferal Cd/Ca record (KNR73 3PC) [Boyle and Keigwin, 1985/6]. It is also in agreement with the compilation of LGM foraminiferal Cd data, suggesting

at most a small decrease in the Cd mean oceanic content (formally calculated as 13% but with an uncertainty comparable to the calculated change) [Boyle, 1992]. The estimated <5% lower 18 Ka glacial Cd content than modern levels cannot explain the discordance between Cd and $\delta^{13}\text{C}$, such as observed in the Southern Ocean. The model results suggest that fluctuations in the oceanic U inventory were less than 1%, consistent with its much longer residence time.

Although the uncertainty associated with the distribution of authigenic Cd and U in the glacial ocean is relatively large, larger glacial-interglacial fluctuations in seawater concentrations of Cd and U are unlikely because of their relatively long residence time. For example, even if one assumes larger removal fluxes of Cd than assumed here, because of the relatively low input flux, it will take a long time for the system to return to its steady state following an increase in glacial removal rates. This response time is much larger than the time difference between glacial and interglacial maxima (20 kyr). Acknowledging this limitation, *Emerson and Huested* [1991] suggested that U might have been released from glacial anoxic sediments back into seawater, following oxidation of the sediment during postglacial times. However, it is more likely that downward diffusion of remobilized U and Cd into the reducing zone is the dominant process during the postdepositional oxidation of organic-rich sediments [Thomson *et al.*, 1993; Rosenthal *et al.*, 1995]. Therefore, with the current estimates of riverine fluxes, larger fluctuations in seawater Cd and U concentrations than those suggested here are unlikely.

Conclusions

Precipitation of authigenic cadmium and uranium is enhanced in suboxic sediments where reducing conditions occur close to the sediment-water interface. Such conditions may occur either because of oxygen depletion of bottom water or due to relatively high flux of labile organic matter into the sediment, resulting in a complete consumption of oxygen near the sediment surface. Precipitation of authigenic Cd-sulfide under such conditions likely explains the uptake of Cd into suboxic sediments. We estimate here that the areally integrated removal of Cd into organic-rich and continental margin sediments represents the largest sink in the oceanic Cd budget. This study assesses the possibility that seawater Cd concentrations may depend on the long-term average of the areal extent of reducing sediments.

Because the removal of Cd and U from seawater is tightly coupled to the early diagenesis of organic matter, the accumulation of authigenic Cd and U should be coupled to variations in the organic carbon cycle. Down-core records of Subantarctic and Cape Basin sediments, where oxic conditions currently prevail, show significantly higher glacial than interglacial accumulation rates of authigenic Cd and U associated with increased accumulation of organic carbon. In contrast, a record south of the Antarctic Polar Front exhibits an approximately inverse pattern: that is, the high

accumulation rates are associated with interglaciations. The contrasting patterns on both sides of the APF suggest that increased biological productivity is the most likely cause of enhanced accumulation of organic carbon and authigenic Cd and U in Subantarctic sediments. Increased glacial productivity in the Subantarctic site is consistent with a 4-5° northward displacement of the APF and its associated zone of high siliceous productivity as suggested from studies of other paleoceanographic proxies. However, the increase in authigenic Cd and U glacial accumulation rates is higher than expected simply from a northward shift of the polar fronts, suggesting greater partitioning of organic carbon into the sediment during glacial intervals. Lower oxygen content of CPDW and higher organic carbon:biogenic silica rain rate ratio during glacial stages are possible causes. Higher glacial productivity is also evident in the Cape Basin record, off the southwest coast of Africa, most likely reflecting enhanced coastal upwelling. These changes in productivity are consistent with increased zonal wind speeds during glacial periods in the mid and high latitudes of the southern hemisphere.

Our studies of Late Quaternary paleoproductivity suggest that in certain ocean regions increased productivity during glacial intervals resulted in more reducing conditions in sediments which are currently fully oxidized. Therefore we propose that the areal extent of glacial suboxic sediments might have been significantly larger than in the modern ocean. A doubling of the suboxic sink from 8% of the seafloor at present to 16% at the LGM is consistent with the available data. Our calculations suggest a low sensitivity of seawater Cd concentrations in response to this increase, implying that in the open ocean there is no significant decoupling between Cd and PO_4 by this mechanism. The model-estimated 5% lower glacial Cd content than modern levels cannot explain the discordance between Cd and $\delta^{13}\text{C}$, such as observed in the Southern Ocean. This result is consistent with foraminiferal data showing no discernible decrease in glacial Cd levels. All the available evidence suggests that the Cd oceanic residence time is longer relative to the timescale of glacial-interglacial transitions.

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