Pergamon

Preservation of particulate non-lithogenic uranium in marine sediments

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Abstract—Particulate non-lithogenic uranium (PNU), excess U above detrital background levels found in marine particulate matter, is formed in surface waters throughout the ocean. Previous studies have shown that PNU is regenerated completely prior to burial of particles in sediments within well-oxygenated open-ocean regions. However, the fate of PNU has never been examined in ocean margin regions or in anoxic basins. Here we evaluate the preservation of PNU in ocean margin sediments and within semi-enclosed basins using samples from sediment traps deployed at multiple depths and surface sediments. Organic carbon fluxes at the sediment trap locations ranged from 0.1 to 4.3 g/cm^2 kyr, while the dissolved oxygen concentration in the water column ranged from <3 μM to $\sim$ 270 μM. Preservation of PNU increases with decreasing dissolved oxygen concentration, approaching 100% preservation at oxygen concentration $<$ 25 μM. PNU contributes as much as 40 to 70% of the total authigenic U in sediments in the Santa Barbara Basin and seasonally anoxic Saanich Inlet, and some 10% to 50% of the total authigenic U in sediments off the central California Margin. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

Over the past twenty years, much progress has been made in our understanding of the marine geochemistry of U, particularly regarding its removal pathways in the ocean via precipitation in chemically-reducing sediments (Anderson, 1987; Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991). Diffusion of U(VI) from bottom water into sediments, followed by its reduction to U(IV), which is precipitated or adsorbed to sediment solids, is regarded as the primary source of authigenic U in these sediments.

Although not a biologically essential element, excess U ($\sim$ 0.8–8 μg/g) above detrital background levels (referred as particulate non-lithogenic U) is found in marine particulate matter (Miyake et al., 1970; Anderson, 1982; Knauss and Ku, 1983; Hirose and Sugimura, 1991). Anderson (1982) demonstrated that particulate non-lithogenic U (PNU) is completely regenerated at pelagic sites, contributing to a general view that the PNU is labile and that it is never preserved in sediments. However, the efficiency with which PNU is preserved and buried has never been evaluated in ocean margin and anoxic basin sediments. Delivery of PNU might contribute significantly to the burial of authigenic U in ocean-margin and anoxic-basin sediments if a significant amount of PNU survives the oxidation in the water column and at the sediment-water interface, especially when these sediments are bathed in waters with low dissolved oxygen.

In this study, we evaluate PNU preservation in the water column and at the sediment water interface, as well as the factors that control the PNU preservation efficiency. The preservation efficiency of PNU in the water column was evaluated using sediment traps deployed at different water depths from sites located in the midlatitudes of the northeast Pacific and the northwest Atlantic Oceans (Fig. 1). The preservation efficiency of PNU at the sediment-water interface was further evaluated by comparing the concentrations of the PNU of sediment trap samples with authigenic U concentrations in surface-most sediments from nearby box cores or multi-cores. Finally, we evaluate the contribution of PNU to total authigenic U accumulating in the sediment by comparing the PNU concentration in surface-most sediments with the authigenic U concentration at depths below the zone of in situ chemical reduction and precipitation of U.

2. STUDY SITES

Sediment trap results from Saanich Inlet, Santa Barbara Basin, from the California Margin at $\sim$ 42°N, and from two locations within the middle Atlantic Bight (designated SEEP-I and SYNOP) were utilized in this study (Table 1 and Fig. 1). Saanich Inlet is a seasonally anoxic basin. At depth of 200m, bottom water oxygen concentration varies from anoxic to $\sim$ 50 μM (Crusius et al., 1996). The organic carbon flux is highest among all sites, with an annual average of 4.3 g/cm^2 kyr (Table 1). A substantial bottom water oxygen gradient (<3 μM to 25 μM) exists along the slope of the Santa Barbara Basin, another semienclosed basin. Annual average organic carbon flux there amounts to 2.8 g/cm^2 kyr (Table 1). Sites along the continental slope of the California Margin have bottom water oxygen spanning from $\sim$ 12 μM to $\sim$ 140 μM. Organic carbon fluxes at the California Margin decreases offshore, from $\sim$ 0.5 g/cm^2 kyr to $\sim$ 0.1 g/cm^2 kyr (Table 1). The mid-Atlantic Bight region has the highest bottom water oxygen ($\sim$ 190 μM to $\sim$ 270 μM). The organic carbon flux at SEEP-I ($\sim$ 0.5 g/cm^2 kyr; Table 1) is lower than that at SYNOP sites ($\sim$ 2.2 g/cm^2 kyr at 2340 m; Table 1). The organic carbon flux at SEEP-II, the region where the sediment cores are located (see below), is $\sim$ 2.4 g/cm^2 kyr (Table 1).

In some cases, sediment cores used in this study were collected at sites in close proximity to the sediment traps (e.g., Saanich Inlet, Santa Barbara Basin). In other cases, cores are from sites which bear first-order similarities, but which are sometimes as much as several hundred km from the sites at which sediment traps were deployed. For example, in the middle Atlantic Bight, sediment trap data from $\sim$ 39.5°N (SEEP-I) and $\sim$ 35.5°N (SYNOP), are compared with results from core sites at $\sim$ 37°N (SEEP-II; Table 2). In the northeast Pacific, off northern California, sediment trap data from 42°N (MULTITRACER)
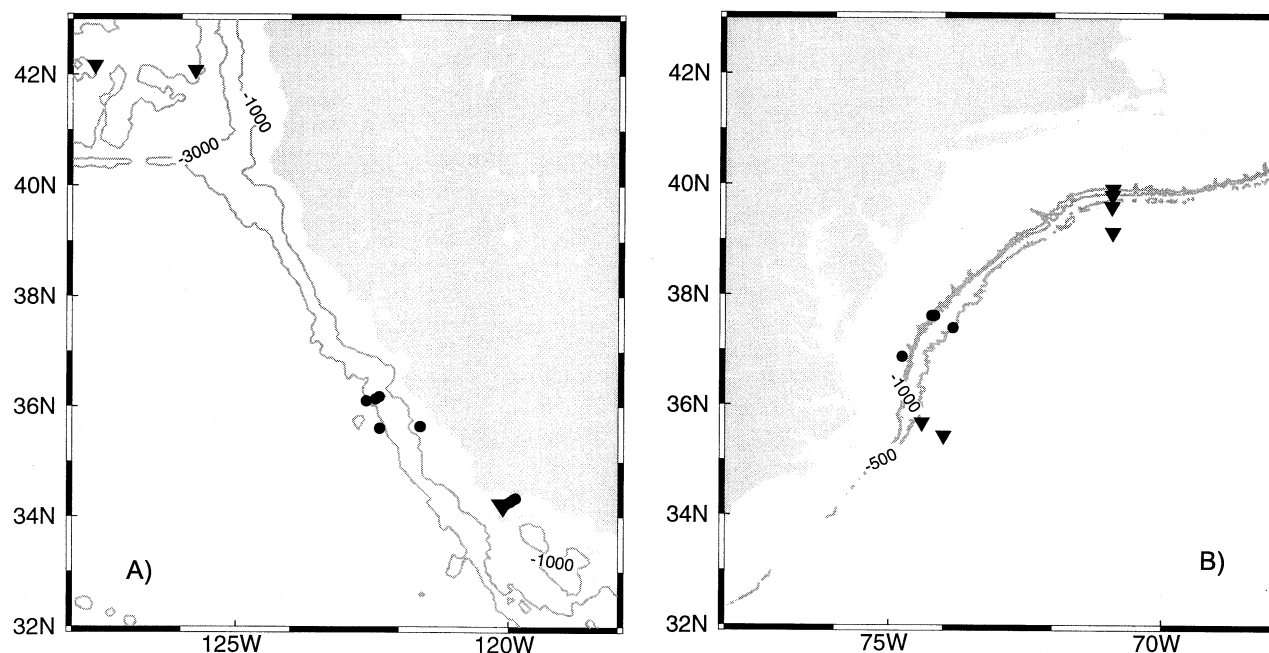
Fig. 1. a) Locations of cores in the Santa Barbara Basin and along the California Margin. Solid circles are locations of sediment cores. Locations of sediment traps deployed during the MULTITRACER program (Lyle et al., 1992) at $\sim 42°N$ (excluding the Gyre site) are indicated by inverse triangles. The inverse triangle indicating the location of the sediment trap deployed in the Santa Barbara Basin ($\sim 34°N$) by Thunell et al. (1995) lies above the sediment core that is most westward, hence not visible. The bathymetry contours are 1000 m and 3000 m, respectively. b) Locations of cores in the Middle Atlantic Bight SEEP-II region (solid circles), as well as the locations of sediment traps deployed at the SEEP-I region ($\sim 39.5°N$) and the SYNOP region ($\sim 35.5°N$) (inverse triangles). The bathymetry contours are 500 m, 1000 m and 2000 m, respectively. The source of bathymetry data is HYDNOS data set from NOAA, which is a compilation of high-resolution U.S. coastal bathymetry.

are used with results from cores taken along a transect down the continental slope at $\sim 35°N$. While combining results from geochemically similar but geographically separated sites is less than ideal, this is the best that can be done in many cases with existing data.

3. SAMPLING AND EXPERIMENTAL METHODS

All sediment traps were poisoned at deployment. The Santa Barbara Basin sediment traps were poisoned with sodium azide (~ 11 g/L) and sodium borate (~ 0.25 g/L) was added for buffering (R. Thunell, personal communication). The sediment traps deployed at 42°N off California were poisoned with sodium azide as well. The SEEP-I and SYNOP traps were poisoned with 10% sodium azide (Biscaye and Anderson, 1994). Supernant brines from Santa Barbara Basin trap samples were stored frozen in 50 mL centrifuge tubes and thawed after 3 yr of storage before ~ 7 mL subsamples were filtered through a 0.45 μm syringe filter and acidified using Seastar HCl to pH ~ 2 before their analysis for dissolved U.

3.1. Chemical Analyses of Dissolved Constituents

The concentration of dissolved U in sediment trap brine samples (Santa Barbara Basin) was measured by isotope dilution inductively coupled plasma-mass spectrometry (ID ICP-MS), by a method similar to that described by Toole et al. (1991) and by Colodner (1991). One hundred μL of water and an appropriate amount of isotope spike (^{236}U) were diluted to 10 mL in a matrix of 0.1% HNO_3 (Seastar) and equilibrated for over 24 h before measurement. The reproducibility is ~ 2% for U.

3.2. Analyses of Solid Phase Samples for U and Th

Isotope dilution ICP-MS methods for U and Th in Santa Barbara Basin trap solids and surface sediments are described by Zheng (1999). The long term (over one year) precision is about 3% for U and 4% for Th based on 15 repeated analysis of a Santa Barbara Basin sediment sample. Trap results from Saanich Inlet (Anderson et al., 1989), 42°N in the Pacific (Lao, 1991) and from the middle Atlantic Bight (Anderson et al., 1994a) are taken from literature. These results were obtained by alpha spectrometry for which the precision is about 5%.

4. RESULTS

4.1. Santa Barbara Basin Sediment Trap Results

Bi-weekly samples were collected by a sediment trap deployed between August 1993 and August 1994 (Thunell et al., 1995). Solid phase U concentrations in trapped particles range from 2.7 to 3.5 μg/g, with a flux weighted average of 2.9 μg/g (Fig. 2a). There is an excess, on average, of 1.3 μg/g of U in the sediment trap solid phase when compared to the detrital background U value (Fig. 2a) derived from the Th concentration in the solid sample and an assumed detrital U/Th ratio of 0.2123 (g/g) that is characteristic of post-Archean average shale (Taylor and McLennan, 1985). This excess U is referred to as particulate non-lithogenic U (PNU). Uranium concentrations in the supernant brines deviate from the bottom-water U concentration (12.2 nM) by ~ 3 nM in both directions, more often enriched than depleted (Fig. 2a). The portion of particulate U

Table 1. Location of sediment traps and annual fluxes of organic carbon and of particulate non-lithogenic U.

Locale	Latitude	Longitude	Trap Depth (m)	Dissl. O_2 (μM)	Annual Mean Corg Flux (g/cm^2 kyr)	Annual Mean Auth U Flux (μg/cm^2 kyr)	Ref
Saanich Inlet							
	48.5500	−123.5450	180	0–50	4.3	183	Anderson, 89
Santa Barbara Basin							C flux: Thunell, 95
	34.2333	−120.0333	540	5	2.79	91	U flux: this study
California Margin-Multitracer							
Nearshore	42.0833	−125.7500	500	40	0.47	12.4	C flux: Lyle, 92
			1000	20	0.48	17.8	U flux: Lao, 91
			2329	90	0.49	21.9	
Midway	42.1667	−127.5833	500	40	0.20	6.0	
			1750	60	0.24	5.9	
			2330	90	0.18	5.6	
Gyre	41.5000	−132.0000	1000	20	0.13	2.3	
Mid-Atlantic Bight							
SEEP-I							
Mooring 4	39.9172	−70.9057	150	220	0.56	3.9	C flux: Biscaye, 88
			450	200	1.12	7.6	U flux: Anderson, 94a
Mooring 5	39.8050	−70.9220	150	220	0.76	6.5	
			455	200	1.10	11.2	
			855	150	0.65	6.3	
			1200	250	0.60	5.4	
Mooring 6	39.6015	−70.9225	163	220	0.61	3.4	
			486	190	0.45	5.3	
			862	150	0.39	5.0	
			1762	270	0.29	1.7	
			2257	270	0.22	1.7	
Mooring 7	39.1327	−70.9070	152	220	0.55	3.2	
			452	200	0.22	1.8	
			857	150	0.25	3.0	
			1757	270	0.15	1.1	
			2257	270	0.19	2.1	
			2702	270	0.22	1.6	
SEEP-II							
Mooring 7	37.3196	−74.1643	990	160	2.37		C flux: Biscaye, 94
Mooring 10	36.8692	−74.5750	990	160	2.37		
SYNOP							
Mooring 2	35.6783	−74.3917	2340	270	2.19	12.9	C flux: Biscaye, 94
Mooring 1	35.4417	−73.9917	3110	270	0.69	4.9	U flux: Anderson, 94a

remobilized into the supernant brine is a negligible fraction of the total particulate U (Fig. 2a).

The annual mean PNU flux to the sediment is 91 μg/cm^2 kyr (Table 1) after correcting for the small amount of U released to the brine (Fig. 2b). The PNU flux peaks when the organic carbon flux peaks in the summer months (Fig. 2b).

4.2. California Margin Sediment Trap Results

With one exception, the flux-weighted annual mean PNU concentrations of sediment trap samples collected along a transect normal to the coast at ∼ 42°N are ∼ 1 μg/g (Fig. 3a). The seasonal range of PNU concentration is 1.1 to 2.0 μg/g at the Nearshore site, and 1.0 to 3.4 μg/g at the Midway site. Traps at all depths (500, 1000 and 2300 m) from the Nearshore site have flux-weighted annual mean PNU concentrations of ∼ 1.3 μg/g. Flux-weighted annual mean PNU concentrations from 1750m and 2300m at the Midway site (1.1 and 1.3 μg/g, respectively) are similar to those measured at the Nearshore site. Only in the 500-m trap from the Midway site was the annual mean PNU concentration (3.4 μg/g) significantly greater than for the other traps. The PNU fluxes are much

smaller at all sites off the California Margin (5–22 μg/cm^2 kyr) than in the Santa Barbara Basin (91 μg/cm^2 kyr), and decrease with the distance offshore (Fig. 3b).

4.3. Middle Atlantic Bight Sediment Trap Results

Flux weighted mean PNU concentrations decrease with water depth from 0.6 to 1.0 μg/g among the shallowest traps to ∼ 0.3 μg/g in the deepest traps in the middle Atlantic Bight (Fig. 3c). The decrease with depth results from a combination of midwater regeneration together with dilution of the vertical flux by sediment supplied by lateral transport processes (Biscaye and Anderson, 1994). The seasonal range of PNU is 0 to 1.1 μg/g for four moorings deployed in the SEEP-I region, and is 0 to 0.7 μg/g for two moorings deployed in SYNOP region, where traps deployed at 2340 m and 3110 m display flux-weighted annual mean PNU concentrations of 0.22 and 0.25 μg/g, respectively (Fig. 3c).

The PNU fluxes to the sediment in the middle Atlantic Bight are comparable to those measured at Midway site off the California Margin (Figs. 3b and 3d), but are substantially less than those measured at the Nearshore site. The annual PNU flux

Table 2. Preservation efficiency of particulate non-lithogenic uranium.

Core	Latitude	Longitude	Water Depth (m)	Oxygen (μM)	Sed Trap PNU[a] (μg/g)	Surf. Sed U_auth[b] (μg/g)	Deep Sed U_auth[c] (μg/g)	PE at SWI[d] (%)	Percentage of deep U_auth from PNU[e]
Saanich Inlet									
	48.5500	−123.5450	200	0–50	1.8	–	5	100*	36
Santa Babara Basin									
M340-2	34.3343	−119.8708	340	23	1.3	1.3	1.8	100	72
M430-2	34.3095	−119.9030	430	15	1.3	1.3	1.9	100	68
M430-3	34.3107	−119.9037	440	11	1.3	1.3	2.3	100	57
M550-3	34.2678	−119.9673	550	5	1.3	1.9	4.2	100	31
M580-2	34.2308	−120.0482	580	3	1.3	1.9	2.7	100	48
M590-3	34.2308	−120.0490	590	3	1.3	–	2.8		46
California Margin									
BC208	35.6348	−121.6068	781	12	1.3	1.1	2.0	85	54
BC151	35.6333	−121.6167	787	12	1.3	1.1	2.9	85	37
BC150	36.1797	−122.3613	1585	50	1.3	0.7	2.8	54	25
BC106	36.1392	−122.4320	2055	80	1.3	0.7	3.4	54	20
BC116	36.1005	−122.5998	3340	130	1.3	0.3	3.1	23	10
BC231	35.5990	−122.3550	3728	140	1.3	0.3	3.3	23	9
Middle Atlantic Bight									
EN187-BC4	37.6222	−74.2217	512	200	0.7	0.0	0.6	0	0
EN187-BC5	37.6175	−74.1672	1045	190	0.5	0.0	0.9	0	0
EN187-BC9	36.8700	−74.5640	1165	220	0.3	0.8	1.6	267	51
EN187-BC6	37.4002	−73.8282	2000	270	0.3	0.0	0.7	0	0

[a] Annual mean particulate non-lithogenic U (PNU) concentrations in sediment traps at depths closest to those of the cores Refs for each location in sequence are: Anderson (1989), this study, Lao (1991), and Anderson (1994a).

[b] Authgenic U concentration in surface sediments. Refs for each location in sequence are: Kolodny and Kaplan (1973), this study, Klinkhammer and Palmer (1991), & Anderson (1994b) Except Saanich Inlet and the 550 m, 580 m and 590 m sites of SBB, the authigenic U is of PNU origin.

[c] Average authigenic U concentration for sediment samples below the depths of U diagenesis.

[d] Preservation efficiency (PE) of PNU at sediment water interface (SWI). For Saanich Inlet, 100% was assumed.

[e] Contributaion of PNU to total sediment authigenic U below the depth of U reduction and precipitation.

in the SEEP-I region ranges from 1 to 8 μg/cm^2 kyr, and seems to have a midwater (500–1000 m) maximum, below which the flux decreases with increasing water depth (Fig. 3d). The annual PNU flux at the SYNOP region (south of SEEP-II) is 13 μg/cm^2 kyr at 2340 m and is 5 μg/cm^2 kyr at 3110 m (Fig. 3d) at a site further offshore. Particulate non-lithogenic U fluxes are not available for the SEEP-II sites, where the organic carbon flux is the highest among SEEP-I, SEEP-II and SYNOP (Table 1).

5. DISCUSSION

5.1. Preservation of Particulate Non-Lithogenic U in the Water Column

Preservation of PNU as particles sink through the water column varies with the water column oxygen content, as evident both in our results and in data published previously. The flux of PNU decreases with water depth where the water column is well oxygenated. For example, in the middle Atlantic Bight, the PNU flux displays a midwater ($\sim$ 500 m) maximum, and then decreases to $\sim$ 2 μg/cm^2 kyr at water depths > 2000 m (Table 1 and Fig. 3d). At Site E (13.5°N, 54.0°W, O$_2$ > 200 μM) in the subtropical Atlantic, the PNU flux decreases from 1.4 μg/cm^2 kyr at a water depth of 390 m, to 0.4 μg/cm^2 kyr at 5086 m (Anderson, 1982). In contrast, the flux of PNU remains unchanged with water depth when the water column oxygen content is low. At 42°N off the California Margin, the

Nearshore site displays a PNU flux ranging from 12 to 22 μg/cm^2 kyr, increasing with water depth. The Midway site has a PNU flux of $\sim$ 6 μg/cm^2 kyr which does not vary with depth over a range of 500 m to 2330 m (Table 1 and Fig. 3B). At the STIE site (5°21′N, 81°53′W) in the Panama Basin, the PNU flux is 3.4 μg/cm^2 kyr at 667 m water depth, and increases to $\sim$ 5.2 μg/cm^2 kyr at greater depths (2265 m −3791 m; Anderson, 1982). Nearly constant PNU flux with water depth is observed in low-oxygen marine basins, such as Saanich Inlet (Anderson et al., 1989) and the Santa Barbara Basin (Moore et al., 1981) as well. These results present a consistent picture of rapid regeneration of PNU from sinking particles at sites with high dissolved O$_2$ concentrations throughout the water column (middle Atlantic Bight and Site E), but little or no regeneration of PNU in the water column at sites where at least part of the water column is strongly depleted in dissolved O$_2$ (California Margin, Panama Basin, Santa Barbara Basin, and Saanich Inlet).

The origin of the particulate non-lithogenic U remains enigmatic, even though it has been found in diverse environments, ranging from anoxic marine basins, to marginal seas and the open ocean. Anderson (1982) proposed that the origin of particulate non-lithogenic U was "bioauthigenic," a term suggesting that it could be of biogenic and/or authigenic origin. Particulate non-lithogenic U from the surface Pacific Ocean was inferred to be in the form of "labile" organic complexes (Hirose and Sugimura, 1991). Surface complexation and biologic up-
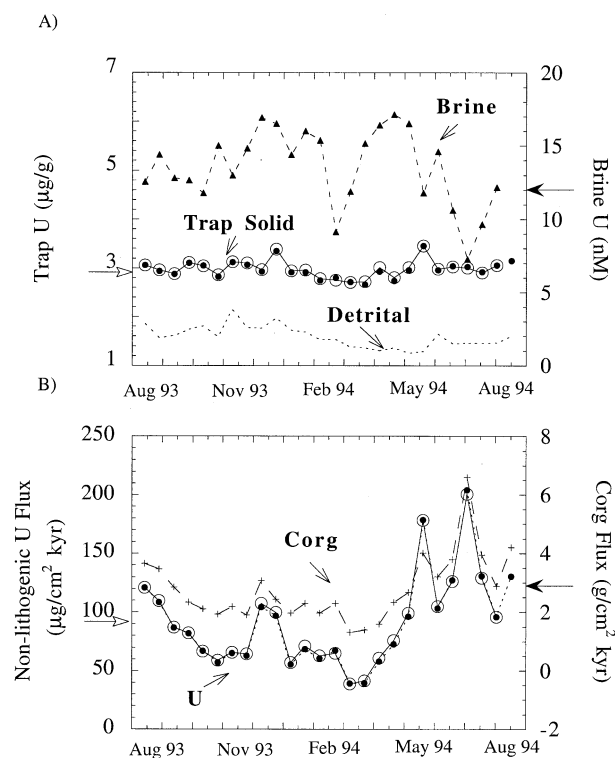
A)

B)

Fig. 2. a) Concentrations of U measured in two-week duration sediment trap solid (solid circles and lines) and brine (triangles and dashed lines) samples from the Santa Barbara Basin collected between August 1993 and August 1994. The open circles indicate the solid phase U concentration after correcting for the mobilized U in the brine. The thin dotted line indicates the detrital background level of U estimated from the Th concentration of the solids, assuming a detrital end member U/Th ratio of 0.2123 (g/g) (Taylor and McLennan, 1985). Hollow point arrow indicates the flux weighted mean concentrations of corrected U at 2.9 μg/g. Solid point arrow indicates the ambient seawater U concentration in the Santa Barbara Basin. b) Time series of fluxes of particulate non-lithogenic U, both un-corrected (solid symbols) and corrected for U remobilized in supernant brine (open symbols), and time series fluxes of Corg (crosses and dashed line). Hollow point arrow indicates annual average flux of particulate non-lithogenic U, at 91 μg/cm² kyr. Solid point arrow indicates annual average flux of Corg, at 2.8 g/cm² kyr (Thunell et al., 1995).

take (Knauss and Ku, 1983) are two plausible mechanisms responsible for particulate non-lithogenic U formation, although existing data are still insufficient to distinguish between these two possibilities.

5.2. Preservation of Particulate Non-Lithogenic U at the Sediment-Water Interface

The fraction of PNU that survives regeneration in the water column, and that is further preserved after it arrives at the sediment water interface, is again a function of dissolved oxygen. To demonstrate this point, we calculate the preservation of PNU assuming that the source of authigenic U in the surface-most sediment sample at each site is from sinking PNU. The concentration of total authigenic U, which consists of preserved PNU together with any U precipitated in situ, is calculated by subtracting from the total U concentration the detrital background U value derived from the Th concentration in the

sediment sample using an assumed detrital U/Th ratio of 0.2123 (g/g) (Taylor and McLennan, 1985). Thus, when the concentration of authigenic U in surface sediments (U_{auth}^{surf}) is compared to the PNU concentration in corresponding sediment trap samples (U_{PNU}^{trap}), a preservation efficiency (PE) of PNU at the sediment-water interface can be estimated:

$$PE = \frac{U_{auth}^{surf}}{U_{PNU}^{trap}} \times 100\% \qquad (1)$$
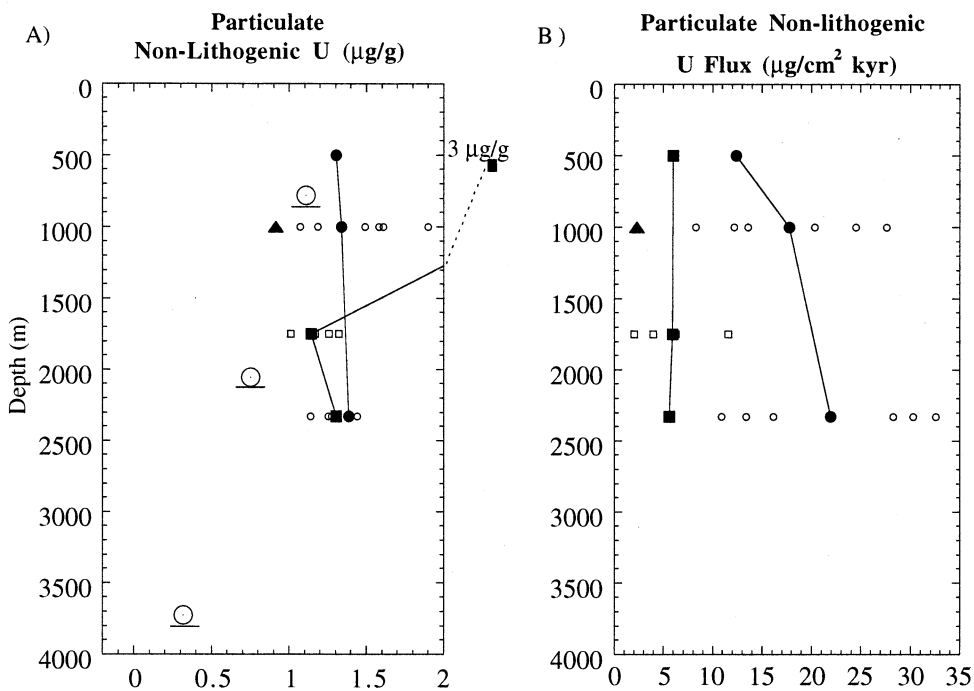
The comparison provides an upper limit for the PE of PNU because, in some cases, the authigenic U in surface-most sediments may include some U precipitated in situ.

At the 340 m and 430 m (M430-2 and M440-3) sites of the Santa Barbara Basin, the surface-most sediment samples have authigenic U concentrations the same as in the sediment trap samples (Table 2), suggesting close to 100% preservation of PNU at these sites, with bottom water oxygen ranging from 15 to 25 μM. The fact that the authigenic U concentrations in surface-most sediment samples from 340 m and 430 m are identical despite sediment focusing factors that differ among the sites by a factor of 3 (Zheng et al., 2000) is consistent with our conclusion that the source of this U is from sinking particles rather than from precipitation in situ. At the 550 m and 590 m (M550-3 and M580-2) sites of the Santa Barbara Basin, the surface-most sediment samples of multi-cores have concentrations of authigenic U $\sim$ 1.5 times greater than the sediment trap samples, reflecting an additional source of U via precipitation in situ, an observation supported by sediment pore water data showing depletion of U in pore water within the first sample (depth 0.2 cm) below the sediment water interface (Zheng et al., 2001). Therefore, at 550 m and 590 m sites, the preservation efficiency should also be 100% (Table 2). Similarly, preservation of PNU in Saanich Inlet is expected to be $\sim$ 100%. Although surface sediment data from Saanich Inlet are unavailable, an average authigenic U concentration in the upper 15 cm of sediment is $\sim$ 5 μg/g (Kolodny and Kaplan, 1973), consistent with quantitative preservation of PNU.

In the California Margin, the preservation of PNU, evaluated as described above, ranges between $\sim$ 20% and $\sim$ 80% among the sites studied (Table 2). The highest preservation efficiency ($\sim$ 80%) is observed in sediments of the oxygen minimum zone (with bottom water oxygen $\sim$ 12 μM). At midslope depths ($\sim$ 2000 m), where with bottom water oxygen is $\sim$ 50 to $\sim$ 80 μM, preservation efficiency is $\sim$ 50%. At the deepest sites studied, where with bottom water oxygen rises to 130 to 150 μM, preservation efficiency drops to $\sim$ 20%.

Under highly oxygenated waters at the middle Atlantic Bight, PNU is completely regenerated at the sediment-water interface with the possible exception of a site at 1165 m (Fig. 3c). The reason that the box core at 1165 m has 0.8 μg/g authigenic U at the very top of the sediment may be that the sediment deposition rate at the site is too rapid to allow complete regeneration of PNU. Rapid deposition of laterally-transported sediment containing PNU would be consistent with the large unsupported ^{210}Pb inventory at this site (Anderson et al., 1994b). Another indication of complete regeneration of PNU in the middle Atlantic Bight is that a "fluff" layer on box core EN187-BC5 (1045 m) contained 1.8 μg/g non-lithogenic U,

Northern California Margin

A) **Particulate Non-Lithogenic U (µg/g)**

B) **Particulate Non-lithogenic U Flux (µg/cm² kyr)**

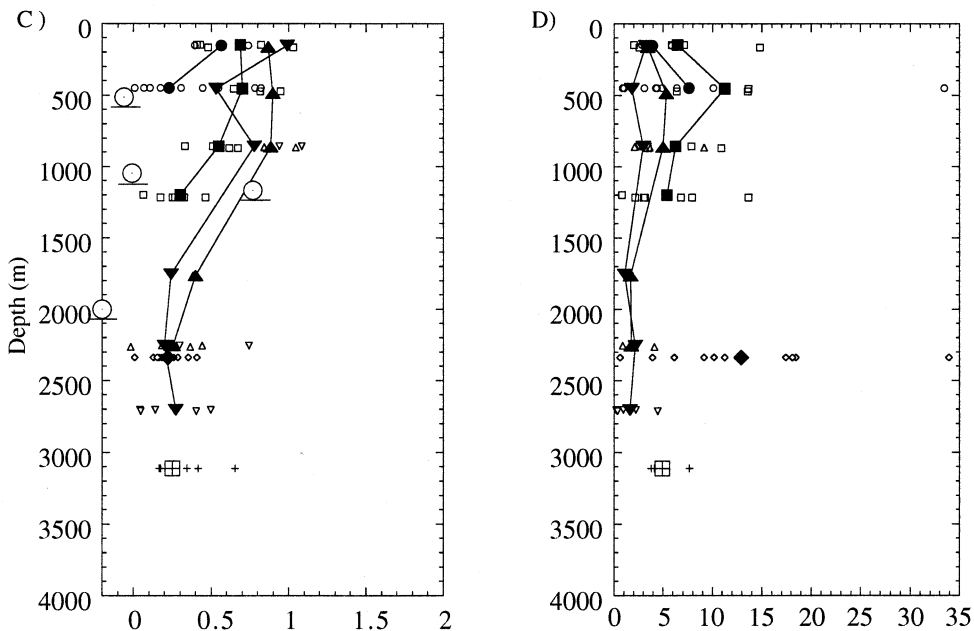## Middle Atlantic Bight

C)

D)

Fig. 3. Concentration (panel A) and flux (panel B) of non-lithogenic U in particulate matter collected by sediment traps deployed along a transect off the California Margin at 42°N. Circles, squares and triangles indicate sediment trap results from Nearshore, Midway and Gyre sites (Lao, 1991; see also Table 1). In panel A, underlined circles are the core top (<1 cm) sediment authigenic U concentration in cores collected at 35°N along the California Margin at water depths of 781 m, 1585 m, and 3728 m (Table 2); results at 781 m and 3728 m are from Klinkhammer and Palmer (1991). Concentration (panel C) and flux (panel D) of non-lithogenic U in particulate matter collected by sediment traps deployed in the Middle Atlantic Bight. Circles, squares, triangles and inverse triangles indicate sediment trap results from SEEP-I Moorings 4, 5, 6, and 7, respectively (see Table 1). Solid diamonds and crosses are for SYNOP Moorings 1 and 2, respectively (Anderson et al., 1994a). In panel C, underlined circles are the core top (<1 cm) sediment authigenic U concentrations measured in cores collected in the SEEP-II region (Table 2). The solid symbols in the authigenic U concentration plots (panels A and C) indicate flux weighted mean concentrations of U at trap water depths. The small open symbols are results for individual time-series samples, showing a seasonal range of particulate non-lithogenic U concentrations. The solid symbols in the PNU flux plot (panels B and D) are the average flux and, again, individual values are indicated by small open symbols.

whereas PNU had been completely regenerated in the surface-most sample of consolidated sediment (Zheng, 1999).

Results from all sites are consistent in showing quantitative, or near quantitative preservation of PNU delivered to the surface sediments where bottom water oxygen concentrations fall below 10 to 20 μM. Regeneration of PNU is quantitative when bottom water oxygen is $> \sim 200$ μM. Sites with intermediate bottom water oxygen concentrations exhibit intermediate fractions of PNU preserved.

5.3. Contribution of Particulate Non-Lithogenic U to Marine Sediment Authigenic U

Reduction and precipitation within suboxic continental margin sediments of uranium that has been supplied by diffusion across the sediment-water interface is recognized to be the most important sink (~ 1.2–2.8×10^7 moles/yr) in the global budget of this element (Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991). This diffusive pathway is the dominant process contributing to authigenic U burial in the northwest Atlantic margin sediments (Barnes and Cochran, 1990) because preservation of PNU in this region is generally negligible. However, PNU may contribute significantly to the burial of authigenic U when it is produced in large quantity and preserved in the sediments.

The contribution by PNU to the accumulation of total authigenic U can be estimated by comparing the concentration of preserved PNU (assumed to be equivalent to the concentration of total authigenic U in surface sediments, or to the concentration of PNU in deep sediment trap samples near the core site, whichever is smaller) with the average concentration of authigenic U accumulating in sediments below the zone of in situ reduction and precipitation. Following this approach, we find that PNU contributes 10 to 50% of the authigenic U accumulating in California Margin sediments, $\sim 36\%$ of the authigenic U in Saanich Inlet sediments, and as much as 70% of the authigenic U accumulating in the sediments of Santa Barbara Basin (Table 2). While we lack information from enough sites to evaluate the contribution of PNU to the global flux of authigenic U preserved and buried in marine sediments, it is clear from these examples that PNU may constitute a removal mechanism contributing tens of percent of the global U sink.

6. GEOCHEMICAL SIGNIFICANCE

Several studies have based their interpretations on the assumption that authigenic U in marine sediments is formed by molecular diffusion of U downward from the bottom water into a zone of reduction and precipitation. Reconstruction of the area of anoxic and suboxic sediments in the ocean under past climate regimes based on the change in whole ocean U concentrations (Russell et al., 1994) as well as diagenesis models developed to simulate the behavior of redox-sensitive trace elements (e.g., Van Cappellen and Wang, 1995) are such examples. Because PNU formed in surface waters may, under certain circumstances, contribute significantly to the total burial of authigenic U, this assumption needs to be reconsidered. Similarly, when climate-related changes in organic carbon flux (e.g., Kumar et al., 1995; Rosenthal et al., 1995) or bottom water oxygen (e.g., Francois et al., 1997) have been inferred

from the presence of authigneic U in marine sediments, these interpretations were made based on the assumption that all of the authigenic U in the sediments was supplied by diffusion from bottom waters. These interpretations may need to be re-examined as well. The reliability of paleoceanographic reconstruction will be improved by a more complete understanding of the processes contributing to the burial of authigenic U in marine sediments.

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REFERENCES

Anderson R. F. (1982) Concentrations, vertical flux, and remineralization of particulate uranium in seawater. *Geochim. Cosmochim. Acta* **46,** 1293–1299.

Anderson R. F. (1987) Redox behavior of uranium in an anoxic marine basin. *Uranium* **3,** 145–164.

Anderson R. F., LeHuray A. P., Fleisher M. Q., and Murray J. W. (1989) Uranium deposition in Saanich Inlet sediments, Vancouver Island. *Geochim. Cosmochim. Acta* **53,** 2205–2213.

Anderson R. F., Fleisher M. Q., Biscaye P. E., Kumar N., Dittrich B., Kubik P., and Suter M. (1994a) Anomalous boundary scavenging in the Middle Atlantic Bight: evidence from [230]Th, [231]Pa, [10]Be and [210]Pb. *Deep-Sea Res.* **41(2/3),** 537–561.

Anderson R. F., Rowe G. T., Kemp P. F., Trumbore S., and Biscaye P. E. (1994b) Carbon budget for the mid-slope depocenter of the Middle Atlantic Bight. *Deep-Sea Res.* **41(2/3),** 669–703.

Barnes C. E. and Cochran J. K. (1990) Uranium removal in oceanic sediments and the oceanic U balance. *Earth Planet. Sci. Lett.* **97,** 94–101.

Biscaye P. E. and Anderson R. F. (1994) Fluxes of particulate matter on the slope of the southern Middle Atlantic Bight: SEEP-II. *Deep-Sea Res.* **41(2/3),** 459–509.

Colodner D. (1991) The Marine Geochemistry of Rhenium, Iridium and Platinum. Ph.D., Woods Hole Oceanographic Institution Massachusetts Institute of Technology.

Crusius J., Calvert S., Pedersen T., and Sage D. (1996) Rhenium and molybdenum enrichments in sediments as indicators of oxic, suboxic and sulfidic conditions of deposition. *Earth Planet. Sci. Lett.* **145,** 65–78.

Francois R., Altabet M. A., Yu E.-F., Sigman D., Bacon M. P., Frank M., Bohrmann G., Bareille G., and Labeyrie L. D. (1997) Contribution of southern ocean surface water stratification to low atmospheric CO_2 concentrations during the last glacial period. *Nature.* **389,** 929–935.

Hirose K. and Sugimura Y. (1991) Chemical speciation of particulate uranium in sea water. *J. Radioanal. Nucl. Chem.* **149(1),** 83–96.

Klinkhammer G. P. and Palmer M. R. (1991) uranium in the oceans: where it goes and why. *Geochim. Cosmochim. Acta* **55,** 1799–1806.

Knauss K. and Ku T.-L. (1983) The elemental composition and decay-series radio-nuclide content of plankton from the east Pacific. *Chem. Geol.* **39,** 125–145.

Kolodny Y. and Kaplan I. R. (1973) Deposition of uranium in the sediment and interstitial water of an anoxic fjord. In *Proc. Symp. Hydrogeochemistry and Biogeochemistry* (ed. E. Ingerson) Vol. 1, pp. 418–442. The Clarke Co.

Kumar N., Anderson R. F., Mortlock R. A., Froelich P. N., Kubib P., Dittrich-Hannen B., and Suter M. (1995) Increased biological productivity and export production in the glacial Southern Ocean. *Nature.* **378,** 675–680.

Lao Y. (1991) Transport and burial rates of [10]Be and [231]Pa in the Pacific Ocean. Ph.D, Columbia University.

Lyle M., Zahn R., Prahl F., Dymond J., Collier R., Pisias N., and Suess E. (1992) Paleoproductivity and carbon burial across the California Current: The multitracers transect, 42°N. *Paleoceanog* **7(3),** 251–272.

Miyake Y., Sugimura Y., and Mayeda M. (1970) The uranium content and the activity ratio $^{234}U/^{238}U$ in marine organisms and sea water in the western north Pacific. *J. Oceanogr. Soc. Jap* **26(3),** 123–129.

Moore W. S., Bruland K. W., and Michel J. (1981) Fluxes of uranium and thorium series isotopes in the Santa Barbara Basin. *Earth Planet. Sci. Lett.* **53,** 391–399.

Rosenthal Y., Boyle E. A., Labeyrie L., and Oppo D. (1995) Glacial enrichments of authigenic Cd and U in Subantarctic sediments: A climatic control on the elements' oceanic budget? *Paleoceanog.* **10,** 395–413.

Russell A. D., Emerson S., Nelson B. K., Erez J., and Lea D. W. (1994) Uranium in foraminifera calcite as a recorder of seawater uranium concentration. *Geochim. Cosmochim. Acta* **58,** 671–681.

Taylor S. R. and McLennan S. M. (1985) The continental crust: its composition and evolution. Blackwells.

Thunell R. C., Tappa E., and Anderson D. M. (1995) Sediment fluxes and varve formation in Santa Barbara Basin. *Geol.* **23(12),** 1083–1086.

Toole J., McKay K., and Baxter M. (1991) Determination of uranium in marine sediment pore waters by isotope dilution inductively coupled plasma mass spectrometry. *Anal. Chim. Acta* **245,** 83–88.

Van Cappellen P. and Wang Y. (1995) Metal cycling in surface sediments: modeling the interplay of transport and reaction. In *Metal Contaminated Aquatic Sediments* (ed. H. E. Allen), pp. 21–63. Ann Arbor Press.

Zheng Y. (1999) The Marine Geochemistry of Germanium, Molybdenum and Uranium: the Sinks. Ph.D., Columbia University.

Zheng Y., Anderson R. F., Geen A. v., and Fleisher M. Q. (2002) Remobilization of authigenic uranium in marine sediments by bioturbation. *Geochim. Cosmochim. Acta* **66,** 1759–1772.

Zheng Y., Anderson R. F., van Geen A., and Kuwabara J. (2000). Authigenic molybdenum formation in marine sediments: A link to pore water sulfide in the Santa Barbara Basin. *Geochim. Cosmochim Acta* **64,** 4165–4178.