

Ocean anoxia and the concentrations of molybdenum and vanadium in seawater

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ABSTRACT

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Molybdenum and vanadium are relatively unreactive in seawater and are preferentially concentrated in sediments overlain by anoxic or near-anoxic waters. We investigate the geochemistry of these metals by interpreting measurements from anoxic basins and sediment porewaters. The concentrations of Mo and V in the water column of anoxic basins are usually lower than in oxic seawater because of uptake into highly anoxic sediments. The mechanism of removal from solution appears to be diffusion across the sediment–water interface and immobilization within the sediments. Measurements from open ocean porewaters imply fluxes of vanadium from sediments that are greater than 10 times the dissolved and particulate river inflow, which is inconsistent with the distribution of vanadium in deep waters of the ocean and previous geochemical studies; this inconsistency shows that early diagenesis of this element is poorly understood. We estimate that the area of ocean sediment at present overlain by anoxic and near-anoxic water is accumulating $25 \pm 15\%$ and $8 \pm 5\%$ of the river influx of Mo and V, respectively. This fraction is $17 \pm 10\%$ for uranium, which has been shown to share some of the redox behavior of Mo and V. A case is made that changes in the concentrations of these elements in the ocean should be sensitive indicators of the portion of the ocean bottom overlain by anoxic seawater through geologic time.

INTRODUCTION

Of the elements most strongly enriched in anoxic, organic-rich sediments (Holland, 1984; Brumsack, 1986; Koide et al., 1986), molybdenum, vanadium and uranium are among the most well understood geochemically. As sediments overlain by oxygen-depleted waters are preferential sinks for these metals, their dissolved concentrations in the ocean should depend upon the areal extent of bottom water anoxia. We examine the geochemistries of molybdenum and vanadium by interpreting concentration distributions in regions where the metals behave nonconservatively—the water column of anoxic basins and sediment porewaters. The discussion begins with a review of the marine geochemistries of Mo and V and proceeds to a discussion of re-

sults from anoxic basins and sediment porewaters. We then present preliminary estimates of the sensitivity of the seawater concentrations of these elements and uranium to the area of sediments overlain by oxygen-depleted bottom waters. The goal is to assess the utility of temporal changes in the concentration of these elements in seawater as potential tracers for the areal extent of anoxia at the sediment–water interface in the ocean.

THE MARINE GEOCHEMISTRIES OF Mo AND V

Thermodynamic data suggest that molybdenum should have an oxidation state of six, Mo(VI), in oxic seawater. The metal is strongly hydrolyzed, and is present in the anionic form MoO_4^{2-} at neutral pH (Manheim, 1974; Baes and Mesmer, 1976). Under reducing conditions the stable oxidation state is Mo(IV), and molybdenum sulfide minerals are favored thermodynamically in the presence of H_2S . Vanadium in oxic seawater should be present as V(V) and be hydrolyzed to $\text{VO}_2(\text{OH})_3^-$ at neutral pH (Baes and Mesmer, 1976). Below pH of about three the dioxovanadium cation VO_2^+ is the stable species. Under moderately reducing conditions V(IV) is stable as the oxovanadium cation VO^{2+} , which should also hydrolyze at seawater pH to $\text{VO}(\text{OH})_3^-$. Both V(IV) and V(V) are surface reactive, but the reduced form should be far more strongly adsorbed in natural waters (Wehrli and Stumm, 1989). For this reason, one might expect removal from solution under reducing conditions. Vanadyl (VO^{2+}), however, has the additional characteristic of being associated with organic ligands and humic and fulvic acids in nature (Cheshire et al., 1977; Wehrli and Stumm, 1989) which leads to competition between dissolved organic matter and solid surfaces for the V(IV) species.

To within the accuracy of present measurements, molybdenum holds a constant ratio to salinity in the ocean (references in Bruland, 1983; Collier, 1985); this indicates that reactivity in the water column is relatively unimportant and results in a relatively high concentration (about 105 nM) in seawater. Hydrothermal processes should be unimportant as a source or sink for molybdenum because the concentrations in Reykjanes hydrothermal brines are roughly the same as in seawater (Bjornsson et al., 1972).

The concentration of vanadium in the ocean (35–45 nM) deviates slightly from conservative behavior by exhibiting a roughly 10% depletion in surface waters (Collier, 1984), where concentration changes correlate with phosphate. There is also some evidence that V concentrations in the Pacific Ocean deep water are 5–15% greater than those in the Atlantic (Jeandel et al., 1987), although this trend is not definitive because the two laboratories that determined these values do not agree that Pacific and Atlantic deep waters are significantly different in concentration. Shiller and Boyle (1987) showed that vanadium exhibited a nutrient-like behavior in estuaries, with a strong correlation with phosphate. High-temperature hydrothermal processes are prob-

ably unimportant in determining the concentration of vanadium in the ocean because preliminary measurements for hydrothermal seawater (Jeandel et al., 1987) indicate little concentration change, and laboratory experiments (Seyfried and Mottl, 1982) suggest that V is not leached from basalt during hydrothermal alteration. Trefry and Metz (1989) observed that vanadium was efficiently scavenged by iron oxides in mid-ocean ridge vent plumes, which indicates that hydrothermal processes may indirectly function as a sink for this metal; however, the magnitude of this process on a global scale is difficult to estimate.

Concentrations, river fluxes, and steady-state residence times are presented in Table 1. An important difference in the geochemistries of Mo and V is illustrated by the ratio of river particulate to dissolved flux (about 2.5 and about 100, respectively); vanadium is much more strongly concentrated in the solid phase. This affinity is reflected in its shorter dissolved residence time with respect to river inflow and makes identification of authigenic V in sediments much more difficult than for molybdenum because of the high detrital background.

Molybdenum and vanadium are preferentially concentrated in organic-rich sediments (Brumsack and Gieskes, 1983; Holland, 1984; Brumsack, 1986). Although most of the observed enrichments are in anoxic basins such as the Black Sea, Cariaco Trench, Saanich Inlet and Framvaren Fjord (Gross, 1967; Veeh, 1967; Dorta and Rona, 1971; Pilipchuk and Volkov, 1974; Skei, 1981; Francois, 1988), very high values have also been reported in sediments from the Peru and West African upwelling areas where bottom water oxygen con-

TABLE 1

Concentrations, river fluxes and steady-state residence times with respect to river input for molybdenum, vanadium and uranium

	Mo	V	U
Concentrations			
River, dissolved (nmol l^{-1})	5 ^a	15 ^b	1.2–2.5 ^c
River, particulate ($\mu\text{g g}^{-1}$)	3 ^a	170 ^a	2.0 ^d
Ocean (nmol l^{-1})	105 ^e	(34–45) ^{f,g}	14 ^h
River fluxes ($\text{mol year}^{-1} \times 10^6$) ⁱ			
River, dissolved	185	555	40–80
River, particulate	468	50 000	126
Steady-state residence times (10^3 years)			
	778	100	250–500

^aMartin and Meybeck (1979). ^bShiller and Boyle (1987). ^cBarnes and Cochran (1990). ^dKu (1965). ^eCollier (1985). ^fCollier (1984). ^gJeandel et al. (1987). ^hKu et al. (1977).

ⁱDissolved river flow = $3.7 \times 10^{13} \text{ m}^3 \text{ year}^{-1}$ (Martin and Meybeck, 1979). Particulate river flow = $15 \times 10^{15} \text{ g year}^{-1}$ (Martin and Meybeck, 1979). Ocean area = $3.6 \times 10^{14} \text{ m}^2$. Ocean volume = $1.37 \times 10^{18} \text{ m}^3$.

tent is low (Bertine and Turekian, 1973; Calvert, 1983; Seralathan and Hartmann, 1986). There is strong environmental evidence that very low or zero bottom water O_2 concentrations are necessary to promote formation of measurable authigenic solid phase molybdenum and vanadium. Shaw et al. (1990) showed in their study of metals in the Californian Borderland basin sediments that Mo and V were enriched most strongly in sediments of the Santa Monica Basin, which has the lowest bottom water O_2 concentration (less than $5 \mu M$). In addition, sedimentary molybdenum and vanadium concentrations from areas overlain by anoxic waters in both the Saanich Inlet and the Black Sea are much greater than in sediments from oxygenated locations in these basins (Pilipchuk and Volkov, 1974; Francois, 1988). Finally, Hallberg (1974) observed a correlation between anoxia in the Baltic Sea bottom waters and Mo content of the underlying sediments from 1953 to 1973. The oxygen content of Baltic deep water during this time was reduced by restricted circulation with the open ocean.

The mechanisms of incorporation of molybdenum and vanadium into anoxic sediments are different. Molybdenum is believed to be reduced to Mo(IV) and coprecipitated with iron sulfides (Bertine, 1972). Complexation by organic matter in the porewaters or sediments is also necessary to explain some of the data (Brumsack and Gieskes, 1983; Malcolm, 1985). The most insoluble vanadyl solid phase is the oxide VO_2 (Sadiq, 1988); however, the experimental results of Wehrli and Stumm (1989) suggested that adsorption of V(IV) to surface oxide phases in sediments should be more effective in binding the dissolved metal than either mineral formation or complexation with most dissolved organic ligands. Vanadium(IV) is known to be incorporated into organic-rich shales via substitution for Mg in porphyrins which are degradation products of chlorophyll (Lewan and Maynard, 1982). The quantitative importance of this mechanism of vanadium removal from solution in anoxic sediments has not been established.

As the authigenic component of solid phase molybdenum is much more readily recognized in sediments than vanadium because of the differences in background detrital concentration, the global importance of sediments overlain by anoxic water as a sink for Mo has been developed in detailed mass balances. Bertine and Turekian (1973) concluded that $80 \times 10^6 \text{ mol Mo year}^{-1}$ (about 40% of the present river influx) must be deposited in anoxic regions because they assumed an ocean at steady state, and could account for only about half of the sink in marine sediments overlain by oxic waters. The accumulation rate of Mo in anoxic systems was determined by Manheim (1974) to be about $20 \times 10^6 \text{ mol year}^{-1}$ for the Black Sea, Baltic Sea and continental margin of SW Africa. This value is roughly a third of the oxic sediment Mo accumulation rate, but the sediment area for this sink is only 0.3% of the oceanic total, illustrating the efficiency of accumulation in these areas.

MOLYBDENUM AND VANADIUM CONCENTRATIONS IN ANOXIC BASINS AND SEDIMENT POREWATERS

Methods

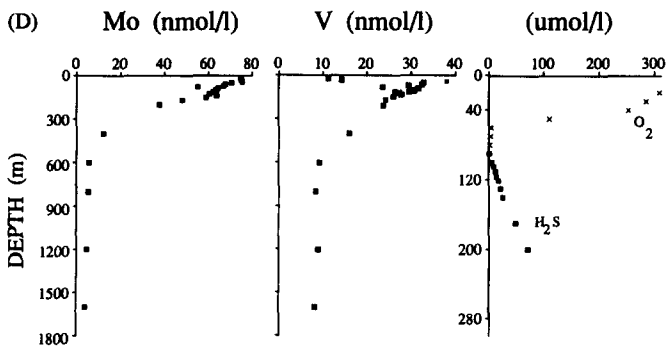
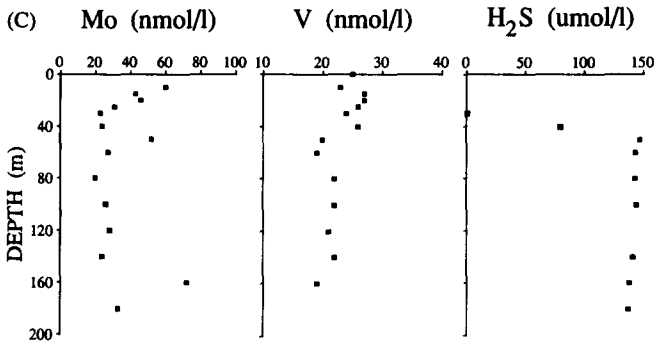
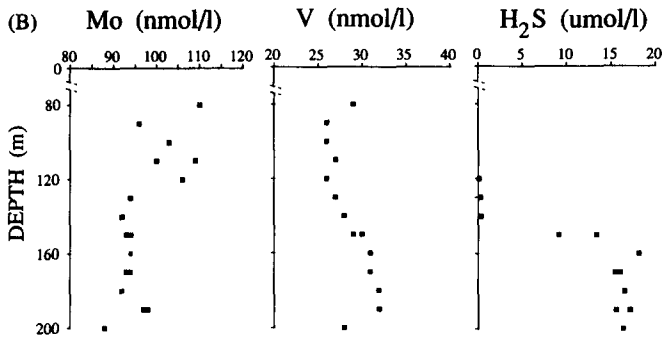
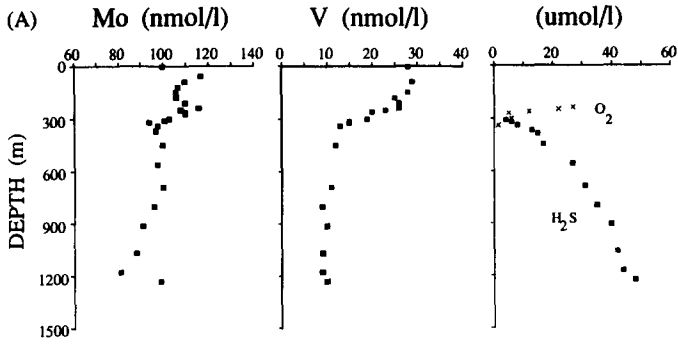
To assess the processes responsible for authigenic accumulation in anoxic systems, we determined concentrations in profiles from the water column of anoxic basins and in sediment porewater. Descriptions of the anoxic basins, sampling procedures and other trace metal data for Saanich Inlet, Lake Nitinat, Framvaren Fjord and the Cariaco Trench have been presented by Jacobs et al. (1985, 1987). Samples from the Black Sea were collected during the 1988 expedition of the R/V "Knorr". Porewaters were sampled from sediments with a wide range of oxidation state; from oxic central equatorial Pacific and Atlantic locations (see Emerson et al. (1985) and Jahnke et al. (1989) for site descriptions), to suboxic sediments of the eastern equatorial Pacific and Atlantic (McCorkle and Emerson, 1988; Jahnke et al., 1989), and to strongly reducing sediments of the continental margins. The samples were retrieved by shipboard centrifugation of sediments that were extracted in N₂-filled glove bags when the sediments were anoxic. We have compared both Mo and V results extracted by this method with samples retrieved using an in situ 'harpoon' sampler and found no consistent differences. All samples were filtered through cleaned 0.45 μm Nuclepore filters and acidified to pH < 2 for storage in precleaned polyethylene bottles.

Molybdenum and vanadium concentrations were determined by Co-APDC coprecipitation at pH about 4.5 (Collier, 1984, 1985) and graphite furnace atomic absorption spectrophotometry using a Perkin-Elmer 5000 spectrophotometer. Precision on the water column samples, as assessed by duplicates, is $\pm 5\%$; for porewaters, precision is somewhat less, presumably because of smaller sample size. Day-to-day accuracy was monitored by determining the concentration on the same deep seawater sample during each sample run.

Mo and V in anoxic basins

Profiles of dissolved water-column concentrations in five anoxic basins with over a 100-fold range in total hydrogen sulfide concentration are presented in Fig. 1. The molybdenum concentration decreases across the O₂-H₂S interface in every case. This trend follows that observed previously in Saanich Inlet (Berrang and Grill, 1974; Collier, 1985) and in the Black Sea (Pilipchuk and Volkov, 1974). Our values for the anoxic waters of the Black Sea are, however, much lower than reported in the previous study.

Trends in the vanadium data are less consistent. Whereas the concentrations decrease in the anoxic waters of the Black Sea, Cariaco Trench and Lake Nitinat, they increase in the anoxic waters of Saanich Inlet and Framvaren



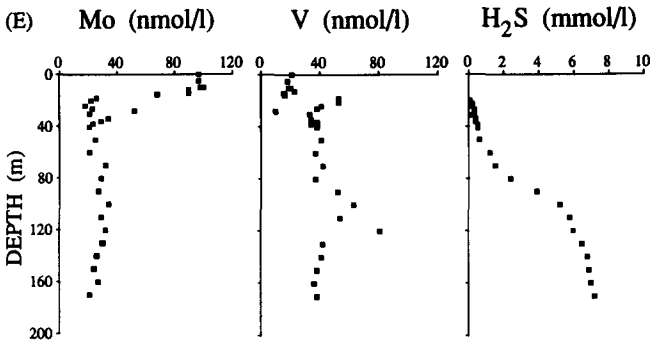


Fig. 1. Molybdenum, vanadium, O_2 and H_2S concentrations in waters of (A) Cariaco Trench, (B) Saanich Inlet, (C) Lake Nitinat, (D) the Black Sea and (E) Framvaren Fjord. Data are normalized to a salinity of 35‰ except for (C).

Fjord. Saanich Inlet is only seasonally anoxic, and it is likely that elevated vanadium concentrations result from a slower removal after the onset of anoxia than for other trace metals (Jacobs et al., 1985) and Mo. The lack of removal in anoxic waters of Framvaren Fjord requires a different explanation, as the deep waters have been anoxic for thousands of years (Skei, 1981). The extremely high levels of dissolved organic carbon in the deeper portions of Framvaren Fjord ($5\text{--}10\text{ mg}^{-1}$; Skei, 1981), may have formed complexes with the reduced form of vanadium, VO^{2+} , which cause the relatively high levels observed in solution in this environment.

The lack of a systematic relationship between the deep-water molybdenum or vanadium concentrations and H_2S content indicates that mineral solubility equilibrium is not the controlling factor, as was suggested for iron and manganese sulfides in these anoxic systems (Jacobs et al., 1985). On the other hand, the concentration of these metals in the anoxic waters is not uniformly near detection limit, as found for Cu, Zn and Cd (Jacobs et al., 1985). The alternative explanation is that concentrations of Mo and V are controlled by the flux to sediments and water renewal from outside the basins.

As the authigenic component of molybdenum in these systems is readily distinguishable, we constructed a sediment–water column Mo mass balance to test the above hypothesis. The accumulation rate of Mo in sediments (F_{Au}) of these basins is calculated from sediment concentrations $[Mo]_s$ and sedimentation rate in Table 2. Reported values vary within basins and between workers, so there is a considerable uncertainty; none the less, accumulation rate differences between the basins appear to be mainly due to the range in sedimentation rates rather than sediment concentration. A steady-state mass balance equates the flux of Mo into the basin via water renewal and authi-

TABLE 2

Authigenic Mo accumulation rate F_{Au} in four anoxic basins and the SW African shelf

Location	[H ₂ S] (μ M)	[Mo] _{sed} (ppm)	[Al] _{sed} (%)	S (cm year ⁻¹)	F_{Au} (nmol Mo cm ⁻² year ⁻¹)
Black Sea	300	33–66 ^a	6	~0.03 ^a	3–6
Cariaco Trench	40	40 ^{b,c}	7	0.05 ^b	5
Saanich Inlet	30	26 ^{d,c}	4	0.50 ^d	32
Framvaren Fjord	6000	132 ^e	1.5	0.30 ^e	103
SW African Shelf	0	53 ^f	1.5	0.027 ^f	3.7

^aPilipchuk and Volkov (1974). ^bDorta and Rona (1971). ^cEmerson (unpublished data, 1991). ^dGross (1967). ^eSkei (1981). ^fCalvert (1983).

Conversion from sediment concentration (in ppm) assumes a porosity of 0.9 (cm³_{p.w.} cm⁻³_{bulk}) and a sediment density of 2.5 (g cm⁻³). $F_{Au} = S[\text{Mo}]_{\text{sed}}\{1 - (\text{Mo}/\text{Al})_{\text{shale}}[\text{Al}]_{\text{sed}}\}$, where S is the sedimentation rate and $(\text{Mo}/\text{Al})_{\text{shale}} = 0.09 \times 10^{-4}$ mol Mo \times mol⁻¹ Al (Manheim, 1974). The average H₂S concentration is given for comparison.

TABLE 3

The predicted and measured gradient of molybdenum concentration between oxic and anoxic waters, $\Delta[\text{Mo}]$

Location	h (m)	τ_w (years)	$\Delta[\text{Mo}]$	
			Calculated (nmol l ⁻¹)	Observed (nmol l ⁻¹)
Black Sea	2000	1×10^3 ^a	15–30	33
Cariaco Trench	1100	100 ^a	5	7
Saanich Inlet	30	0.5 ^b	5	10
Framvaren Fjord	90	–	–	30

^aRichards (1965). ^bEmerson et al. (1979).

Predicted values are calculated from the equation $\Delta[\text{Mo}] = F_{Au}/(h/\tau_w)$ where F_{Au} is the authigenic accumulation rate (Table 2), h is depth of the anoxic zone and τ_w is the water renewal time.

genic removal to the sediments:

$$\Delta\text{Mo}(h/\tau_w) = F_{Au} \quad (1)$$

where ΔMo is the change in concentration between oxic and anoxic waters, h is the mean depth of the anoxic water column and τ_w is the water renewal residence time. For three of the basins, where water renewal times are known (the Black Sea, Cariaco Trench and Saanich Inlet), calculated depletions agree

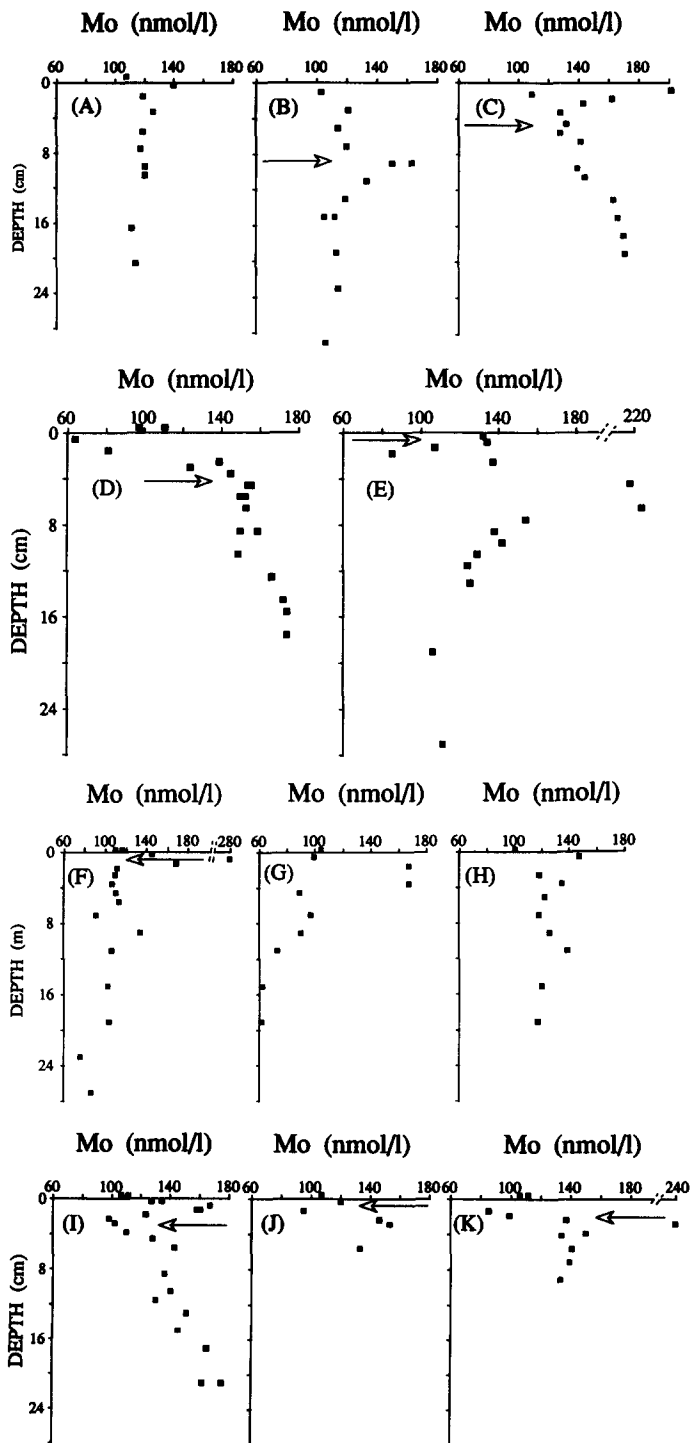
remarkably well with measured values (Table 3), given the crude nature of the model. This result supports the flux balance as the mechanism controlling molybdenum concentrations in the anoxic basins.

Francois (1988) observed that material retrieved in sediment traps in anoxic waters of Saanich Inlet had lower concentrations of Mo and V than the bottom sediments; this observation indicates that the mechanism of enrichment in anoxic basins is uptake at the sediment-water interface rather than attachment to particles raining through the water column. The reason for the observed correlation between Mo burial flux and sedimentation rate (Table 2) probably has to do with the chemical nature of the sediment porewaters, as it has been shown that the sulfate reduction rate is correlated with sedimentation rate in anoxic sediments (Berner, 1980). The decrease in Mo and V concentration in the anoxic basins apparently has little to do with water column anoxia, beyond the fact that it contributes to the extremely reducing character of the sediments.

The geochemical behavior of Mo and V in anoxic basins follows that of uranium to a great extent. Anderson et al. (1989a,b) showed that diffusion of uranium into sediment porewaters, where it was reduced, controlled uranium enrichment in sediments of the Black Sea and Saanich Inlet. The removal of all three of these metals from the water column of anoxic basins is, thus, brought about by processes that remove them from solution within the sediments.

Mo and V concentrations in marine porewaters

Previous studies of molybdenum and vanadium in marine porewaters indicated that the concentration is strongly influenced by manganese cycles (Seralathan and Hartmann, 1986; Shaw et al., 1990) and that molybdenum is associated with dissolved organic matter (Brumsack and Gieskes, 1983; Malcolm, 1985). Most of the measurements to date have been from near-shore regions characterized by anoxia within the upper few centimeters (see also Contreras et al., 1978). Our measurements (Fig. 2) span the range of oxic central ocean basin sediments to shallow organic-rich borderland locations. Samples from siliceous sediments of the central Pacific and carbonate sediments of the Atlantic (Figs. 2A, G and H), where porewaters contain oxygen throughout, indicate a slight Mo enrichment as compared with bottom water (about 10% in the top 10 cm and about 25% in the top centimeter). As the porewaters become more highly reducing, at other locations, the influence of manganese redox cycling is apparent. Arrows on the figures indicate the depth of first detectable porewater manganese (about 1 μM), and we assume this marks the level of nearly complete oxygen depletion. Mo concentrations increase dramatically in the oxic region of the porewaters and then are removed, probably by Mn precipitation, above the depth of manganese



mobilization. This cycle was also observed by Seralathan and Hartmann (1986) and Shaw et al. (1990), and was inferred from sediment chemistry in a series of cores studied by Shimmiel and Price (1986). As the manganese remobilization depth in the porewaters becomes shallower, there is a point in some of the profiles at which the molybdenum concentration immediately below the interface is depleted with respect to bottom water values (Figs. 2D, G and K).

Porewater vanadium concentrations were determined less frequently than those of molybdenum; however, the stations span the range from completely oxic to oxygen depletion in the top few centimeters. Vanadium concentrations are high relative to bottom water (Fig. 3) in all cases. Recycling with manganese is also observed, but the gradient across the sediment–water interface always indicates a strong flux to bottom waters. This observation is consistent with the studies of Seralathan and Hartmann (1986) and Shaw et al. (1990).

One of the critical unknowns in the geochemistry of vanadium and molybdenum is the exchange across the sediment–water interface. A traditional method of calculating this flux is by assuming molecular diffusion down the linear gradient between the bottom water and the first concentration measured within the porewaters. This exercise applied to the porewater data (Table 4) implies fluxes both into and out of the porewaters for molybdenum, and a large flux out of the porewaters for vanadium. The average vanadium flux is more than 10 times the flow to the ocean of particulate V from rivers, which is unrealistic. We suspect that V (and maybe Mo) are not as mobile as presumed using free ion molecular diffusion coefficients. Malcolm (1985) illustrated that most of the porewater molybdenum above the sulfide zone in Lock Fyne sediments was not extractable on Chelex-100 at neutral pH but became extractable after UV oxidation; this result implies that Mo was complexed by dissolved organic carbon (DOC). As thermodynamic calculations suggest that vanadyl, VO^{2+} , has a strong affinity for complexation with dissolved organic ligands (Wehrli and Stumm, 1989), it is probable that this

Fig. 2. Molybdenum concentrations in marine porewaters. Box core bottom water values are indicated above the line. The horizontal arrow indicates the depth of Mn remobilization ($[\text{Mn}] \geq 1 \mu\text{M}$). No arrow means Mn^{2+} is below $1 \mu\text{m}$ throughout the porewater. Locations and depths are as follows. The Equatorial Pacific: (A) MANOP Site S (11°N , 140°W , 4450 m), (B) MANOP Site H (6.55°N , 92.8°W , 3530 m) and (C) Guatemala Basin ($2^\circ 31'\text{S}$, 84°W , 2350 m); the California Borderlands: (D) Patton Escarpment (32.5°N , 120°W , 3800 m) and (E) San Clemente Basin (32.5°N , 118°W , 1800 m); the Equatorial Atlantic: (F) ($14^\circ 41'\text{N}$, $19^\circ 56'\text{W}$, 3804 m), (G) ($2^\circ 08'\text{N}$, $19^\circ 40'\text{W}$, 5036 m) and (H) ($0^\circ 00'\text{N}$, 23°W , 3558 m); the NW Atlantic continental margin: (I) (42°N , 65°W , 1575 m); (J) (42°N , 65°W , 1075 m) and (K) (42.6°N , 69.6°W , 228 m).

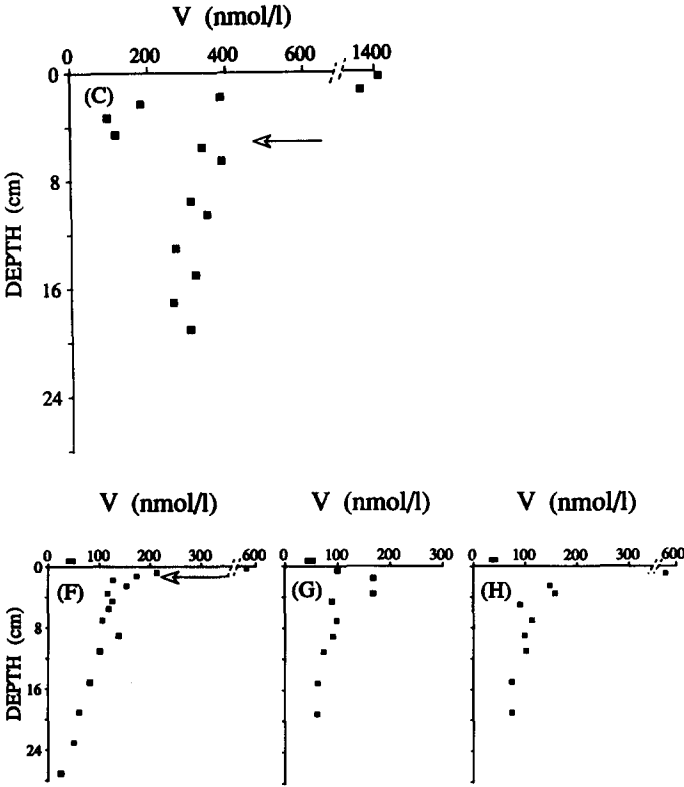


Fig. 3. Vanadium concentration in marine porewaters. Guatemala Basin (C) and equatorial Atlantic (F-H) locations are presented in the caption for Fig. 2.

metal is also bound by DOC in porewaters; this will reduce its mobility by an unknown amount.

The maximum flux to the ocean interior that can be accommodated by either particles originating from above or porewaters fluxes from below is reflected in the difference between Atlantic and Pacific deep-water concentrations, ΔC :

$$F = \Delta C (V_0) \tau$$

where V_0 is the ocean volume and τ is the residence time of water in the Pacific and Indian Oceans. If we assume a maximum Atlantic to Pacific enrichment of 10% for vanadium (4 nmol kg^{-1}) and a deep-water residence time of 500 years, the flux is about 2 nmol cm^{-2} . This flux is about 10 times the river inflow rate, but still only a few per cent of the calculated porewater flux, illustrating the problem in calculating fluxes from the porewater data.

Studies of the deep-sea accumulation rate of molybdenum (Bertine and Turekian, 1973) and vanadium (Thompson et al., 1984) indicated that deep-sea sediments are enriched in these elements relative to the detrital back-

TABLE 4

Molybdenum and vanadium fluxes calculated from surface porewater gradients

Location	Porewater		Bottom water		Flux		
	Δz (cm)	[Mo] (nmol l ⁻¹)	[V] (nmol l ⁻¹)	[Mo] (nmol l ⁻¹)	[V] (nmol l ⁻¹)	[Mo] (nmol cm ⁻² year ⁻¹)	[V] (nmol cm ⁻² year ⁻¹)
Site S (A) ^a	0.25	140		108		18	
Site H (B)	1.0	103		(110)		-1	
Guatemala Basin (C)	0.75	206	1410	(110)	(40)	18	258
Patton Escarpment (D)	0.50	64		106		-12	
San Clemente Basin (E)	0.25	132		(110)		12	
Equatorial Atlantic (F)	0.25	145	564	110	32	20	300
Equatorial Atlantic (G)	0.50	99	161	110	31	-3	37
Equatorial Atlantic (H)	0.50	124	533	110	31	4	142
NW Atlantic (I)	0.25	130		111		11	
NW Atlantic (J)	0.25	120		105		8	
NW Atlantic (K)	0.25	100		80		-11	
Mean							184 ± 119
Dissolved river flux						0.05	0.15
Particulate river flux							13.9

$F = \phi D (dc/dz)_{z=0}$ ($\phi = 0.9$; $D_s = 5 \times 10^{-6}$ cm² s⁻¹). Concentrations in parentheses are assumed bottom water levels. River fluxes are given for comparison.

^aLetters relate to descriptions of locations given in caption of Fig. 2.

ground. Li (1981) suggested that molybdenum, like manganese, is remobilized from continental margin sediments and precipitated in the deep sea. The porewater data suggested that this is also an important cycle for vanadium, but clearly the definitive studies to establish the importance of internal ocean cycles of these elements and the role of sediment-seawater exchange remain to be done by benthic flux measurements.

CHANGES IN SEAWATER CONCENTRATION OF Mo, V AND U IN THE PAST?

We estimate the sensitivity of seawater concentrations of Mo, V and U to changes in the areal extent of sediments overlain by oxygen-depleted bottom water by evaluating the fraction of the river inflow that accumulates in these sediments today, and then speculate on the time response to change. Our analysis refers only to the anoxic sink and does not include the recently discussed uranium uptake in continental margin suboxic porewaters (Barnes and Cochran, 1990; Klinkhammer and Palmer, 1991).

Independent mass balances for molybdenum suggest that 10–40% of the present dissolved river inflow is accumulating in sediments overlain by anoxic waters (Manheim (1974) and Bertine and Turekian (1973) respectively; see Introduction). Anoxic and organic-rich sinks for uranium and vanadium are not as well known as that for Mo because they have been studied in less detail. We estimate the authigenically produced solid component of uranium and vanadium in these sediments using relative changes of U and V with respect to Mo determined in the Black Sea, US Devonian black shales and near-shore marine sediments. Values for $\Delta\text{Mo}/\Delta\text{U}$ are about 3 (wt.) in Devonian black shales (Holland, 1984) and 1–2 in continental margin marine sediments (Bertine and Turekian, 1973); we adopt a weight ratio of two as representative. The $\Delta\text{Mo}/\Delta\text{V}$ ratio is 1.0–3.0 (wt.) in Black Sea sediments (Holland, 1984) and 2.0 in Saanich Inlet (Francois, 1988); we use a weight ratio of 2.0 for the following calculation. If $25 \pm 15\%$ of the dissolved Mo river flux is accumulating in anoxic sediments, and the anoxic sinks contain the above ratios, then the fraction of the river flux of U and V (Table 1) that accumulates in these areas is $17 \pm 10\%$ and $8 \pm 5\%$, respectively. The uranium sink estimated using an average anoxic basin accumulation rate of $260 \mu\text{g U cm}^{-2}$ (Cochran, 1982) multiplied by 0.3% of the ocean's area is 14–28% of the dissolved river inflow, which indicates that our estimate is reasonable. An independent check for vanadium cannot be made because of the large detrital component.

To complete the sensitivity analysis, let us assume that all removal mechanisms operating in the oxic portion of the ocean remain unchanged and that the anoxic sink is proportional to the area of sediments overlain by anoxic or near-anoxic water. The predicted change in seawater concentration for an increase in area of a factor of 10 (to 3% of the total ocean bottom area) for half

a glacial cycle (50 000 years) is presented in Table 5. The changes are rather large. The critical question now is the time frame for response of seawater concentration to changes in the sediment sink.

Given the relatively long residence times with respect to river inflow for these elements (Table 1), one must be concerned with the response of the seawater concentrations to changes in forcing of a 50 000 year duration. If the elements extracted from seawater during expanded bottom water anoxia, say during glacial times, were buried permanently, then one would expect a return to interglacial conditions on the time scale of the residence time with respect to river inflow. The response between periods of anoxia would be of the order of a few per cent in 50 000 years for Mo and U (assuming the situation summarized in Table 5). A nearly steady seawater concentration would then be controlled by removal during the periods of expanded anoxia (i.e. today's fluxes would not be in balance—river inflow would exceed currently identifiable sinks). If, on the other hand, sediments that accumulate these metals are reoxidized at the close of glacial times, returning the spoils of bottom water anoxia to seawater, then the full response predicted in Table 5 would be realized.

One might expect the latter scenario to be true for uranium, as Anderson et al. (1989b) demonstrated that uranium bound in anoxic sediments is released to the porewaters extremely rapid in the presence of oxygen; this complicates the determination of porewater U concentrations from anoxic sediments. Shaw and Klinkhammer (1989) demonstrated that uranium accumulation in the Chesapeake Bay sediments during periods of seasonal anoxia was released to the water when bottom waters became oxidized. Remnants of a similar process are observed in marine sediments as uranium and vanadium maxima caused by reoxidation of glacial organic-rich sediments (Colley et al., 1984; Jarvis and Higgs, 1987).

The process is certainly feasible to at least some extent, and the sedimentary signal would exist in only a few per cent of the ocean's sediments depos-

TABLE 5

Estimates of the change in seawater concentration of molybdenum, vanadium and uranium if the sink to areas overlain by anoxic water increased by a factor of 10 (to 3% of the total ocean area) for 50 000 years (half a glacial cycle); present fluxes to the anoxic sink are taken to be 25%, 8% and 17% respectively of the Mo, V and U river inflow

Element	Seawater inventory ($\times 10^{-12}$ mol)	Anoxic sink ($\times 10^{-6}$ mol year $^{-1}$)		% Change in concentration
		Today	10 \times increase	
Mo	144	46	460	16
V	55	44	440	40
U	19	10	100	26

ited during the periods of anoxia, if it remained at all. This type of deposit would be difficult to find by coring the ocean bottom and more difficult to interpret quantitatively. If a method for measuring the extent of variation in seawater concentrations of Mo, V and U in the past can be developed, it may provide a sensitive constraint on the changes in the area of sediments overlain by anoxic seawater. Much of the success of any such technique, however, will depend on a better understanding of the marine geochemistries of these elements.

CONCLUSIONS

Models developed to explain atmospheric CO₂ changes (Barnola et al., 1987) and variations in marine $\delta^{13}\text{C}$ and cadmium distributions (Boyle, 1986) in the last 100–1000 years predict concomitant changes in deep-water oxygen content to varying degrees (Knox and McElroy, 1984; Sarmiento and Toggweiler, 1984; Siegenthaler and Wenk, 1984; Boyle, 1988; Keir, 1988; Broecker, 1989). It is probably safe to rule out vast areas of complete anoxia for more than several tens of thousands of years during the entire Pleistocene simply because of the existence of fossil shells of benthic animals and lack of widespread laminated sediments. Boyle's (1988) model suggests that deep circulation in the last glacial age was rearranged, so that a decrease in the mean oxygen level of deep waters might have been compensated for by increased O₂ levels in areas that are near anoxia today. Thus, the area of sediments overlain by anoxic waters need not be directly correlated with the mean ocean O₂ content. The area of sediments overlain by anoxic waters would, however, be a powerful constraint on the degree of deep-water anoxia allowable in models of paleocean dynamics. We argue that the most sensitive indicator of this value is the seawater concentration of metals that are relatively conservative in ocean and concentrated in anoxic sediments.

Among the elements that are preferentially concentrated in anoxic basin sediments, molybdenum, vanadium and uranium are nearly conservative in seawater. We show here that Mo and V in the water column of anoxic basins are depleted much like distributions observed previously for uranium (Anderson et al., 1989a). It appears that removal of these metals from solution occurs in the sediments, although the mechanisms are probably different. Porewater measurements of molybdenum and vanadium from sediments with a wide range of redox conditions reveal large diagenetic changes strongly influenced by manganese cycling. Calculation of fluxes from the porewater data results in values that are inconceivably large, at least for vanadium. It is probable that single ion diffusion coefficients overestimate the mobility of V, and maybe Mo, because of complexation with porewater DOC. Studies of sediment–seawater exchange of these elements will require direct flux measurements.

The marine mass balance for molybdenum suggests that about 25% of the current river inflow is now accumulating in sediments overlain by oxygen-depleted water. Based on ratios of Mo/V and Mo/U in sediments from anoxic basins and organic-rich shales, roughly 8% and 17% of the vanadium and uranium dissolved inflow currently accumulates in these areas. If the area of sediments overlain by anoxic or near-anoxic water expanded by a factor of 10 (to 3% of the ocean bottom area) then seawater concentrations of these elements should decrease by 16, 40 and 26% (Mo, V and U). Because of the relatively long residence times for Mo and U (250 000–500 000 years), the short-term (50 000 year) response of these metals to changes in the area of the sedimentary sink depends on the extent of their release from the sediments when they are reoxidized at the close of the period of anoxia. Uranium should be remobilized based on known behavior in anoxic sediments, but whether Mo and V follow the same pattern is uncertain.

We have begun to investigate the concentration of uranium and vanadium in cleaned foraminiferal calcite dating from the past several glacial periods. Cleaning experiments indicate that lattice-bound metal concentrations can be obtained (Hastings et al., 1990; Russell et al., 1990). If vanadium and uranium are incorporated in foraminifera tests in proportion to the concentration in seawater, this approach should deliver a record of past changes in the dissolved concentration of these elements in the ocean.

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