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Suboxic trace metal geochemistry in the eastern tropical North Pacific

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Abstract—We analyzed Al, Ti, Fe, Mn, Cu, Ba, Cd, U, Mo, V, and Re in water column, settling particulate, and sediment (0 to 22 cm) samples from the intense oxygen minimum zone (OMZ) of the eastern tropical North Pacific near Mazatlán, Mexico. The goal was to determine how the geochemistry of these elements was influenced by suboxic water column conditions and whether the sediments have a unique "suboxic" geochemical signature.

The water column was characterized by a Mn maximum, reaching ~8 nmol kg^{-1} at 400 m. Concentrations of Cu, Ba, Cd, Mo, Re, U, and V were unaffected by the low O_2 conditions and were comparable to those of the open ocean. Sinking particles were composed of lithogenic particles of detrital origin and nonlithogenic particles of biogenic origin. Al, Ti, and Fe are mostly (at least 79%) lithogenic. About 75% of the Mn was nonlithogenic. Significant amounts (at least 58%) of Cu, Ba, Cd, and Mo were nonlithogenic.

Sediment geochemistry varied across the continental shelf and slope. Cadmium, U, and Re have prominent maxima centered at 310 m, with 12.3 ppm, 10.9 ppm, and 68.3 ppb, respectively, at the core top. High values of Mo (averaging 6.8 ppm) and V (averaging 90 ppm) are seen in OMZ surface sediment. Additional down-core enrichment occurs for all redox-sensitive elements in the top 10 cm. For U, Mo, V, and Re, surface sediments are a poor indicator of metal enrichment. Comparison of the nonlithogenic composition of sediments with sinking particles suggests that direct input of plankton material enriched in metals makes a significant contribution to the total composition, especially for Cd, U, and Mo.

We evaluated Re/Mo and Cd/U ratios as tracers for redox environments. Rhenium and Mo concentrations and Re/Mo ratios do not lead to consistent conclusions. Concurrent enrichments of Re and Mo are an indicator of an anoxic depositional environment. In contrast, high Re/Mo ratios are an indicator of suboxic conditions. Cadmium is enriched in surface sediments, while U has considerable down-core enrichment. The concentrations of Cd and U and the Cd/U ratio do not follow patterns predicted from thermodynamics. Though the water column is suboxic, these four redox-sensitive elements indicate that the sediments are anoxic. The implication for paleostudies is that a trace metal sediment signature that indicates anoxic conditions is not necessarily attributable to an anoxic water column. *Copyright © 2002 Elsevier Science Ltd*

1. INTRODUCTION

The sedimentary records of trace metals such as Cd, Cu, Mo, Re, U, and V provide important clues to how the redox state of depositional environments has changed over time. The history of redox environments can be reconstructed by interpreting variations in the concentrations of these metals in recent sediments (e.g., Thomson et al., 1993; Morford and Emerson, 1999) and sedimentary rocks (e.g., Brumsack, 1986; Shultz, 1989) using what we know about their sensitivity to changes in redox conditions (Table 1).

To use chemical distributions in sedimentary rocks to reconstruct ancient water column depositional environments (Piper, 1994; Dean et al., 1997) we need to understand the geochemistry of these redox tracers at modern sites that are well characterized. Ideally, one could point to enrichments or depletions of an individual metal in the sedimentary record and pinpoint the redox conditions in the water column that prevailed when a layer of sediment was deposited. To do this, one would use the speciation-dependent pE values that characterize the metals' reduction potentials (Piper, 1994) and the sulfide concentrations that determine their solubilities (Emerson et al., 1983;

Helz et al., 1996). Unfortunately, for most of these tracers, we have inadequate knowledge of the phases that control their enrichment or the kinetics of their formation.

Because uncertainties remain in our understanding of their geochemistry, interpretations of Cd, Cu, Mo, Re, U, and V in the sedimentary record essentially have been constrained by differences in the metals' behavior in the end-member depositional environments, defined here as oxic (>10 μmol/L O_2) and anoxic (>1 μmol/L H_2S). Previous studies have shown that Cd, Cu, Mo, Re, U, and V are enriched in anoxic sediments and are not enriched in those that are oxic (e.g., Veeh, 1967; Bertine and Turekian, 1973; Jacobs and Emerson, 1982; Colodner et al., 1993; Calvert and Pedersen, 1993). Much less is known about the effect of suboxic (<10 μmol/L O_2 and <1 μmol/L H_2S) depositional environments (e.g., Froelich et al., 1979; Murray et al., 1995; van Geen et al., 1995; Rosenthal et al., 1995a, b; Rue et al., 1997) on distributions of these metals in the water column, settling particulate material, and sediments. Progress has been hampered by the fact that a suite of redox-sensitive metals is seldom analyzed on the same samples. Previous data indicate that differences in metal geochemistry between suboxic and anoxic conditions in sediments may be significant. The lack of data for suboxic depositional environments limits our ability to interpret distributions of these metals in the sediment record. Evaluating whether geochemical differences exist in their behavior in oxic, suboxic, and anoxic

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Table 1. Geochemistry of trace elements used to characterize the redox state of sedimentary depositional environments. Data sources: Bertine (1972), Bruland (1983), Collier (1984), Emerson and Huested (1991), Breit and Wanty (1991), Wehrli and Stumm (1989), and Colodner et al. (1993).

| Element	Oxidation state in oxic sea water	Speciation in oxic sea water	Major processes that control distribution in oxic sea water	Oxidation state when reduced	Speciation in reducing environment	Major processes that control accumulation in sediments
Cd	Cd(II)	$CdCl^+(aq)$	Nutrient cycling	Cd(II)	$CdS(s)$	Released during diagenesis of organic matter. Complexes strongly with bisulfide. Likely precipitates in the presence of micro quantities of free sulfide.
Cu	Cu(II)	$CuCl^+(aq)$	Nutrient cycling, scavenging	Cu(II), Cu(I)	$CuS(s)$, Cu_2S	Released during diagenesis of organic matter. Precipitates as disseminated sulfides.
Mo	Mo(VI)	$MoO_4^{2-}(aq)$	Conservative behavior	Mo(V), Mo(IV)	$MoO^{2+}(aq)$, $MoS_2(s)$	Diffuses across sediment-water interface to precipitation depth. Free sulfide required to accumulate. Removal as a mixed Mo-Fe-S begins at ≈ 0.1 μmol/L sulfide. Direct Mo-sulfide precipitation occurs at above 100 μmol/L.
Re	Re(VII)	$ReO_4^-(aq)$	Conservative behavior	Re(IV)	$ReO_2(s)?$, $ReS_2(s)?$, $Re_2S_7(s)?$	Diffuses across sediment-water interface to precipitation depth. Removal mechanism is poorly understood
U	U(VI)	$UO_2(CO_3)_3^{4-}(aq)$	Conservative behavior	U(IV)	$UO_2(s)$	Diffuses across sediment-water interface to precipitation depth. Removal appears controlled by kinetic factors.
V	V(V)	$HVO_4^{2-}(aq)$; $H_2VO_4-(aq)$	Nearly conservative, perhaps some nutrient cycling	V(IV), V(III)?	$VO^{2+}(aq)$, $VO(OH)_3^-(aq)$, $V(OH)_3(s)$	V is released from sediments when Mn reduction occurs near the sediment-water interface (where oxygen penetrates <1 cm). Accumulates in anoxic sediments via diffusion across sediment-water interface to removal depth. Reduced V(IV) species are strongly scavenged.
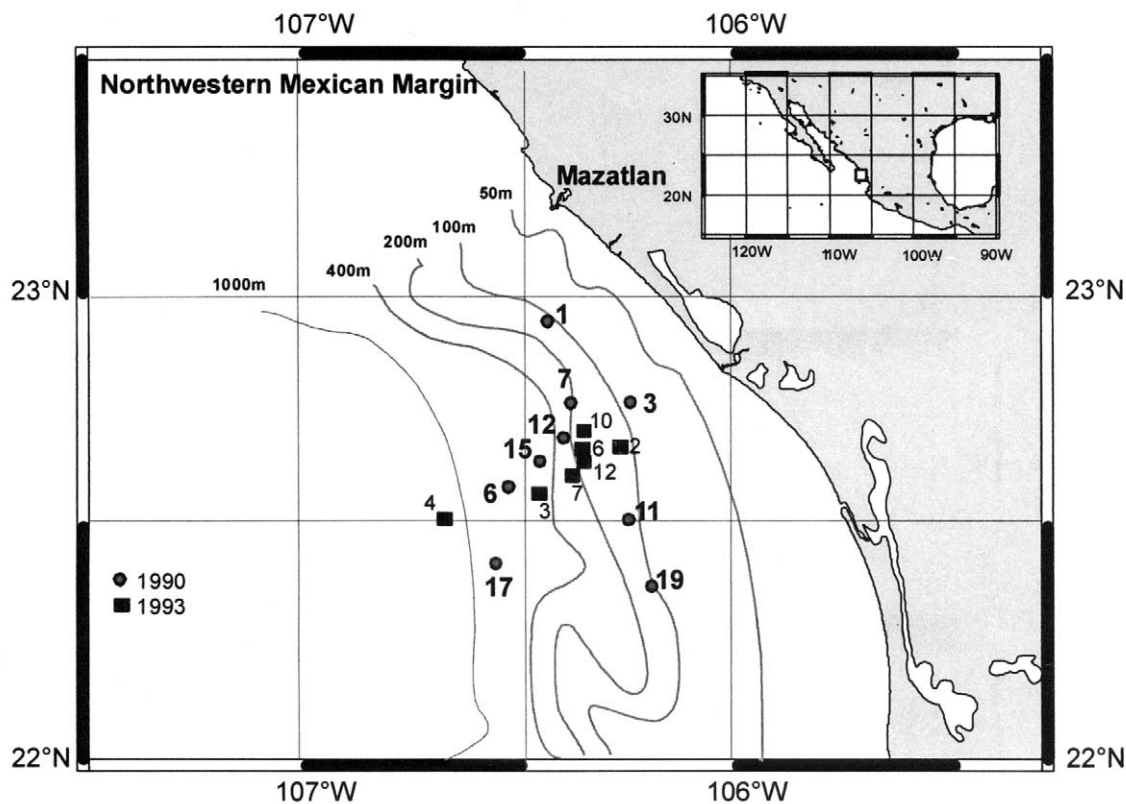
Fig. 1. Station locations occupied during the 1990 (filled circles) and 1993 (filled squares) R/V *New Horizon* cruises.

depositional environments would strengthen these interpretations.

Two factors complicate utilization of metal enrichments for evaluation of the redox state of the water column of a depositional environment. First, the sinking particle flux contributes metals to the sediments. Significant supply of redox-sensitive tracers with plankton matter would mean that changes in biologic productivity could affect levels of metal enrichment beyond the consequences of the more reducing conditions that a high-C_{org} flux can induce. Second, diagenesis can be extensive after deposition, frequently modifying the original extent of metal enrichment that occurs in the upper layer of sediment (Calvert and Pedersen, 1993; Crusius et al., 1996; Gobeil et al., 1997, 2001). The tracers that are preserved in the geological record may reflect the redox conditions of this diagenetic modification in the sediments rather than those of the overlying water. The effect of early diagenesis on redox-sensitive metal concentrations buried into the geological record has not been well documented.

To address these questions, we investigated the geochemistry of the water column, sinking particles, and sediments from the eastern tropical North Pacific southwest of Mazatlán, Mexico (22°41'N, 106°28'W), where the oxygen minimum zone (OMZ) (Wyrtki, 1967) impinges on the continental shelf and slope. We evaluated the contribution of metals in the sinking particle flux and the extent of subsurface diagenetic enrichment.

The goals of this work are to describe the geochemistry of a suite of redox-sensitive metals (Cd, Cu, Mo, Re, U, and V) and to identify whether they leave a recognizable "suboxic" signature in the sediment record. Manganese, Fe, Ba, Ti, and Al were also analyzed to provide information about sediment redox state and input of biogenic and terrigenous material. We utilize these data to evaluate the Re/Mo and Cd/U ratios proposed as tracers for oxic, suboxic, and anoxic redox environments.

2. SAMPLES AND METHODS

2.1. Sample Collection

Samples were collected on R/V *New Horizon* cruises in April 1990 and in December 1993. Station locations for both cruises are indicated in Figure 1. Water column depths and bottom water oxygen values are summarized in Table 2. The shelf-slope transition is gradual, and scarps or ridges do not interrupt sediment deposition. The 3.5-kHz bottom profiles suggest that no sediment slumping has occurred at this location.

2.2. Sampling Methods

Water column nutrient and dissolved oxygen samples were collected using 5-L, acid-cleaned Niskin bottles hung on stainless steel hydrowire. Trace metal samples were collected at stations 3 and 4 on the 1993 cruise. Trace metal clean techniques were employed throughout the cruise (Nameroff, 1996). Niskin bottles were acid cleaned before collection of samples for trace metal analysis. These samples were stored in acid-cleaned, 250-mL, high-density polyethylene bottles and acidified to pH < 2 with quartz-distilled HCl. Hydrographic data were acquired using a Seabird Seacat profiling CTD.

Sediment traps were deployed for 4-d periods at stations 3 and 4 in 1993. Samples for trace metal analysis were collected with acid-cleaned particle interceptor traps of Martin and Knauer's (1984) design,

Table 2. Station depths for R/V *New Horizon* cruises in 1990 and 1993. Dissolved oxygen concentration in the water column at the station depth is indicated for reference. The data reports for these cruises are Lambourn et al. (1991) and Lambourn and Devol (1994).

Cruise station	Depth (m)	Bottom water oxygen (μmol/L)
90-19	97	40
90-03	100	32
90-01	110	36
90-11	135	16
93-02	140	12
90-07	190	8
93-11	220	7
93-10	235	<5
93-06	250	<5
93-12	310	<5
90-12	322	<5
93-07	350	<5
90-15	420	<5
93-03	510	<5
90-06	620	<5
90-17	785	<5
93-04	1020	17

modified to allow filtration through the bottom of the trap (Jannasch, 1990). Trap frames were attached to a synthetic polymer line and deployed on a bottom-moored array. Duplicate samples were collected at each depth. Traps were fitted with 0.40-μm, preweighed, acid-washed Nuclepore filters and were gravity filled before deployment with filtered seawater. Brine (50 g NaCl L^{-1}) was placed in the bottom 10 cm to repel swimmers and trap any metals remineralized during deployment. Both brine and filtered seawater were run through Chelex 100 (Na^+ form) ion exchange resin to remove metals before use. Trap solution blanks were collected for each deployment. After recovery, filters were rinsed with 10 mL of distilled and deionized water buffered to pH = 8 to remove salts. Swimmers were handpicked from the filters under 10× magnification using acid-cleaned plastic tweezers in a laminar flow hood. The filters were folded and transferred to plastic petri dishes and stored in plastic bags before analysis. They were dried and weighed before analysis.

Sediment cores were collected on both cruises over a range of depths that spanned the OMZ. Sediment and pore water samples were collected from Soutar box cores and sectioned at 10°C in a nitrogen-filled glove box (Sawlan and Murray, 1983). Pore water was separated by centrifugation. Solid sediments extracted from each sample were dried to constant weight at 60°C and ground with an agate mortar and pestle after each cruise. Salt-corrected sediment porosity was determined by weight difference between wet and dry samples on separate subcores taken from the same box core used to collect pore waters and sediments. Porosity data are reported in Lambourn and Devol (1994). An additional subcore was used for sedimentary organic carbon determinations (Hartnett, 1998).

2.3. Analytical Methods

Dissolved oxygen concentrations were determined using the method of Broenkow and Cline (1969). Methods for nutrients were described in Whitledge et al. (1981). The analytical approach developed for trace metal analysis (Nameroff, 1996) relied on flow injection (FI) and inductively coupled plasma mass spectrometry (ICP-MS) to analyze Ti, Cd, Cu, Mn, Fe, Mo, V, Re, and U in marine waters and sediments. Cadmium, Cu, and Mn in seawater were analyzed using online preconcentration on 8-hydroxyquinoline (Beauchemin and Berman, 1989; Chapin, 1997). The isotope-dilution (ID) method of Klinkhammer and Chan (1990) was adapted to analyze Mo and U in seawater by FI-ICP-MS. The dilution factor reported by Klinkhammer and Chan (1990) was reduced to a factor of five so that both elements could be measured in the same sample. The method of Shabani and Masuda (1992) was used to analyze Re in seawater and marine sediments by isotope

dilution. The FI configuration reported by these workers was altered to accommodate the valve system available for the present work; identical reagents were employed. Electrothermal vaporization ID-ICP-MS (Hastings et al., 1996) was used to analyze V in seawater.

Microwave digestion procedures for sediments and sediment trap filters were comparable to those reported by Murray and Leinen (1993) and Chapin (1997). The composition of the acid cocktails used by these workers was changed slightly to accommodate the higher concentrations of organic material in these sediments and larger proportion of terrigenous material on the sediment trap filters. Aluminum in marine sediments and settling particulate material was analyzed by flame atomic absorption spectrophotometry. Titanium, Cd, Cu, Mn, Fe, Mo, V, Re, and U in sediments were analyzed by ICP-MS (McLaren et al., 1987; Alaimo and Censi, 1992; Hastings, 1994). The dilution factor of digested sediments was adjusted to allow sample introduction by flow injection. Detection limits were at least an order of magnitude lower than concentrations of metal in samples. Samples were run in duplicate or triplicate, depending on sample availability. Accuracy (typically <6%) was verified by repeated analysis of certified reference seawaters (NASS-3, CASS-2; National Research Council, Canada) and sediments (BCSS-1, PACS-1, MESS-1; National Research Council, Canada) as well as through interlaboratory calibration (D. Colodner and J. Crusius, personal communication) throughout the course of this work. Several seawater and sediment samples were analyzed repeatedly to estimate overall analytical precision (typically <5%, $n > 10$). Comparison of sediment samples analyzed independently by ICP-MS and X-ray fluorescence (XRF) (R. Ganeshram, personal communication) was used to assess the accuracy of the ICP-MS method. In general, the ICP-MS data were statistically indistinguishable from the XRF data (Nameroff, 1996).

Organic carbon was determined using a Carlo-Erba CHN Analyzer by the method of Hedges and Stern (1984).

3. RESULTS

3.1. Water Column

Distributions of dissolved oxygen, phosphate, silica, nitrate, and nitrite in the water column are illustrated in Figure 2. Temperature and salinity data from the study area are available in Lambourn and Devol (1994).

Dissolved O_2 concentrations were less than 5 μmol/L in the water column between 235 and 785 m (Table 2), and no sulfide was detected. Nitrate deficiencies (the difference between nitrate distributions predicted from phosphate data using a Redfield ratio of N/P = 16:1 and observed nitrate) of up to 15 μmol/L exist throughout this interval. A secondary nitrite maximum was centered at 250 m, similar to that seen by Garfield et al. (1983). The distributions of nitrate and nitrite suggest that denitrification is occurring at these depths (Cline and Richards, 1972; Codispoti and Richards, 1976; Lipschultz et al., 1990).

The oxygen minimum of the eastern tropical North Pacific is located in a linear *T-S* mixing zone between the salinity maximum ($S = 35.1$; $T = 13.0°C$) of the subtropical subsurface water (SSW) and the salinity minimum ($S = 34.8$; $T = 6.0°C$) of the Intermediate Water (Wyrtki, 1967; Garfield et al., 1983; Rue et al., 1997). The depths of these end-members at this site are approximately 150 and 750 m, respectively. The SSW has the same temperature, salinity, and density properties as the "Pacific Equatorial 13°C Water" (Tsuchiya, 1981) that originates in the South Pacific as Subantarctic Mode Water (Toggweiler et al., 1991). The northern extent of the SSW is controlled by the influx of California Current Water from the north, which has higher oxygen content on any given density level. Thus, temporal variability in the intensity of the oxygen minimum and its northern boundary reflects the relative strength of
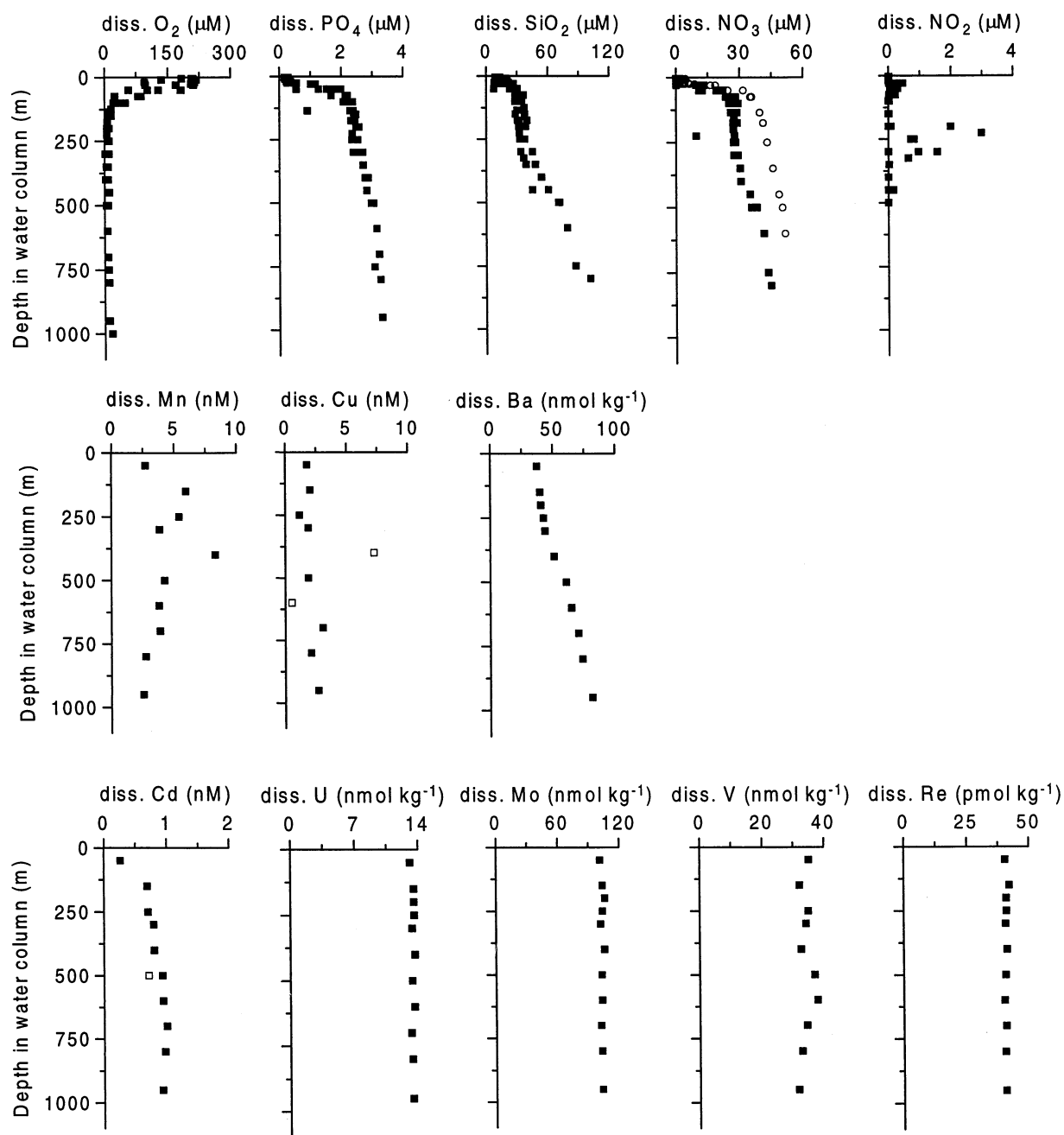
Fig. 2. Oxygen, nutrients (phosphate, silicate, nitrate, nitrite), and total acid-soluble metals (Mn, Cd, Cu, Ba, Re, U, Mo, and V) in the water column of the study area. Dissolved oxygen was <10 μmol/L between 175 and 900 m. The nitrate deficit due to denitrification was indicated by the nitrite maximum and the comparison between observed concentrations (filled circles) and concentrations predicted from phosphate data (open circles), assuming a Redfield ratio of 16:1. Data are from Lambourn et al. (1991) and Lambourn and Devol (1994). Open data points in the Cu and Cd profiles may reflect contamination or analytical artifacts.

these two currents as well as O_2 consumption driven by local biologic new production.

Profiles of total acid-soluble Mn, Cd, Cu, Ba, Re, U, Mo, and V in the water column (0 to 1000 m) are shown in Figure 2. Total Mn in the water column exhibited a broad maximum between 150 and 700 m, reaching a maximum of 7.3 nmol kg^{-1} at 400 m. Murray et al. (1983), Johnson et al. (1992), and Rue

et al. (1997) previously reported similar values in the eastern tropical North Pacific OMZ. Cadmium concentrations increased with depth from 0.26 nmol kg^{-1} at 50 m to 0.95 nmol kg^{-1} below 400 m. The Cd:P correlation was highly significant ($r = 0.97$, $p < 0.01$; Taylor, 1982), and the slope of the Cd:P relationship (0.31 nmol/μmol) was the same as reported by Bruland et al. (1978) for other locations in the northeast Pacific.

Copper concentrations were ~2 nmol kg^{-1} and increased slightly with depth. Concentrations of Cu in the water column were comparable to those measured in the Santa Monica Basin by Johnson et al. (1988) and the northeast Pacific by Bruland et al. (1978) and Bruland (1980). Barium increased steadily from 37 to 87 nmol kg^{-1} and correlated with Si (r = 0.98). The concentration of Re in the water column was constant at 40.8 ± 0.8 pmol kg^{-1}, comparable to open-ocean values reported by other workers (Anbar et al., 1992; Colodner et al., 1993, 1995). Water column U concentrations were constant at 13.4 ± 0.3 nmol kg^{-1}. Concentrations of U measured here were comparable to open-ocean values (Ku et al., 1977; Chen et al., 1986) and show no indication of removal. Conservative U behavior was also observed in the Arabian Sea OMZ (Sarin et al., 1994). Total Mo concentrations in the water column were constant at 103.4 ± 2.1 nmol kg^{-1} and were comparable to open-ocean measurements (Collier, 1985). However, they were lower than the bottom water value of 120 nmol/L in the Santa Barbara Basin (Zheng et al., 2000) and values of 106 to 113 nmol kg^{-1} in the eastern North Pacific at 9°N 104°W (Tuit et al., 2000). Vanadium concentrations in the OMZ (32 to 38 nmol/L) were similar to those predicted using the open-ocean V:P relationship of Collier (1984).

3.2. Nonlithogenic Metals

Metal concentrations in excess of the lithogenic (e.g., continental) fraction are defined as nonlithogenic. Average shale is commonly used as a proxy for the lithogenic fraction when particulate and sediment samples from local rivers are not available (e.g., Calvert and Pedersen, 1993; Morford and Emerson, 1999; Zheng et al., 2000). If we use shale as the reference lithogenic material in our case, we get negative nonlithogenic values for several metals (e.g., Fe, Mn, Cu, Ba, and V). The geology of the Sonoran Basin and Range province of Mexico (the region adjacent to our study area) contains Tertiary volcanics that overlie Paleozoic schists, quartzites, and gneisses (de Cserna, 1989). This mix of source rocks is more like crust than shale. We have included both shale and crust (both from Turekian and Wedepohl, 1961) for comparison in relevant figures. For most metals, it makes little difference, but use of crust appears to be a better choice, as it is more consistent with the regional geology, and it removes negative values of nonlithogenic metal for Fe, Cu, and V.

3.3. Settling Particulate Material

Concentrations of metals and organic carbon in settling particulate material are shown in Figure 3. In most cases, the metals collected in the sediment trap remained in particulate form. The exceptions were Cd and U. Approximately 5% of U was found in the brine solution, while over 98% of the Cd was found in the trap brine solutions (Nameroff, 1996). Concentrations of metal in trap brine solutions and filter were summed to give total metal in each trap.

Most trace metal concentrations varied by less than 30% with depth at each station. Concentrations were slightly higher for station 4 than station 3. Settling particulate Al (2.5 to 6.2 wt.%) and Ti (0.20 to 0.37 wt.%) concentrations showed very slight increases with depth. In contrast, concentrations of set-

tling particulate Fe (1.9 to 3.2 wt.%), Cu (32 to 88 ppm), Ba (300 to 600 ppm), and V (31 to 59 ppm) increased with depth. Settling particulate Mn (ranging from 1100 to 1600 ppm) and U (ranging from 1.0 to 1.6 ppm) concentrations showed no significant trend with depth. Settling particulate concentrations of Cd decreased from a high of ~8 ppm at 150 m to ~1.9 ppm throughout the OMZ. Organic carbon decreased throughout the OMZ from 13 wt.% at 150 m to 7 wt.% at 900 m (Hartnett, 1998). Concentrations of Mo ranged from 3.4 to 9.5 ppm and decreased with depth at station 4. Insufficient quantities of settling particulate material were collected to measure Re in the trap samples.

3.4. Sediment Geochemistry

Surface sediments in contact with the OMZ were olive-green, silty clays and finely laminated, indicating that bioturbating organisms were absent. Surface sediment porosities were greater than 0.9 in all cores and reached values as high as 0.97 in some cases (Lambourn et al., 1991; Lambourn and Devol, 1994). Because bottom water oxygen concentrations were so low between water column depths of 190 and 785 m, no oxygen was available, and benthic oxygen fluxes were negligible (A. Devol, unpublished data). Benthic fluxes of NO_3^- showed that denitrification was occurring in the sediments. No benthic fluxes were detected for sulfate. Directly measured nitrate and sulfate reduction rates (expressed as carbon) integrated over the top ~15 cm of sediment were 1.2 ± 0.5 mmol C m^{-2} d^{-1} and 2.4 ± 1.0 mmol C m^{-2} d^{-1}, respectively (Kristensen et al., 1999). The maximum sediment sulfate reduction rates appeared to be unrelated to either the overlying bottom water oxygen concentration or the concentration of organic carbon in sediment. Iron and Mn were undetectable (<1 μmol/L) in the pore water. Increases in alkalinity and ammonia concentrations in the pore water (Lambourn et al., 1991; Lambourn and Devol, 1994) were consistent with the low rates of observed sulfate reduction (Murray et al., 1980; Emerson et al., 1980). The alkalinity and NH$_4$ gradients in the pore water suggested that the rates of organic carbon remineralization were highest in sediments at 140 m, while those at 97 and 1020 m were the lowest.

The concentrations of elements in surface sediment as a function of water column depth are shown in Figure 4. Aluminum and Ti concentrations in surface sediments ranged from 3.6 to 7.3 wt.% and 0.16 to 0.33 wt.%, respectively. Sedimentary Fe ranged from 2.5 to 3.5 wt.%. Manganese concentrations in surface sediments were low (~300 ppm) and relatively constant with water column depth. Surface sediments contained between 2.5 and 16.5 wt.% organic carbon (Lambourn et al., 1991; Lambourn and Devol, 1994; Hartnett, 1998). The organic carbon concentrations in surface sediment increased with water column depth from 100 to 500 m and then were constant to 1000 m (Fig. 4). Copper and Ba distributions in surface sediments generally increased with water column depth. The profiles of Cd, U, and Re in surface sediments were similar. All had a pronounced maximum in surface sediments at ~310 m, reaching concentrations of ~1 ppm, 3 ppm, and 20 ppb, respectively. Surface sediment within the OMZ showed a broad Mo maximum with more than 7.5 ppm. The distribution of V in surface sediments was somewhat similar to that of Mo.
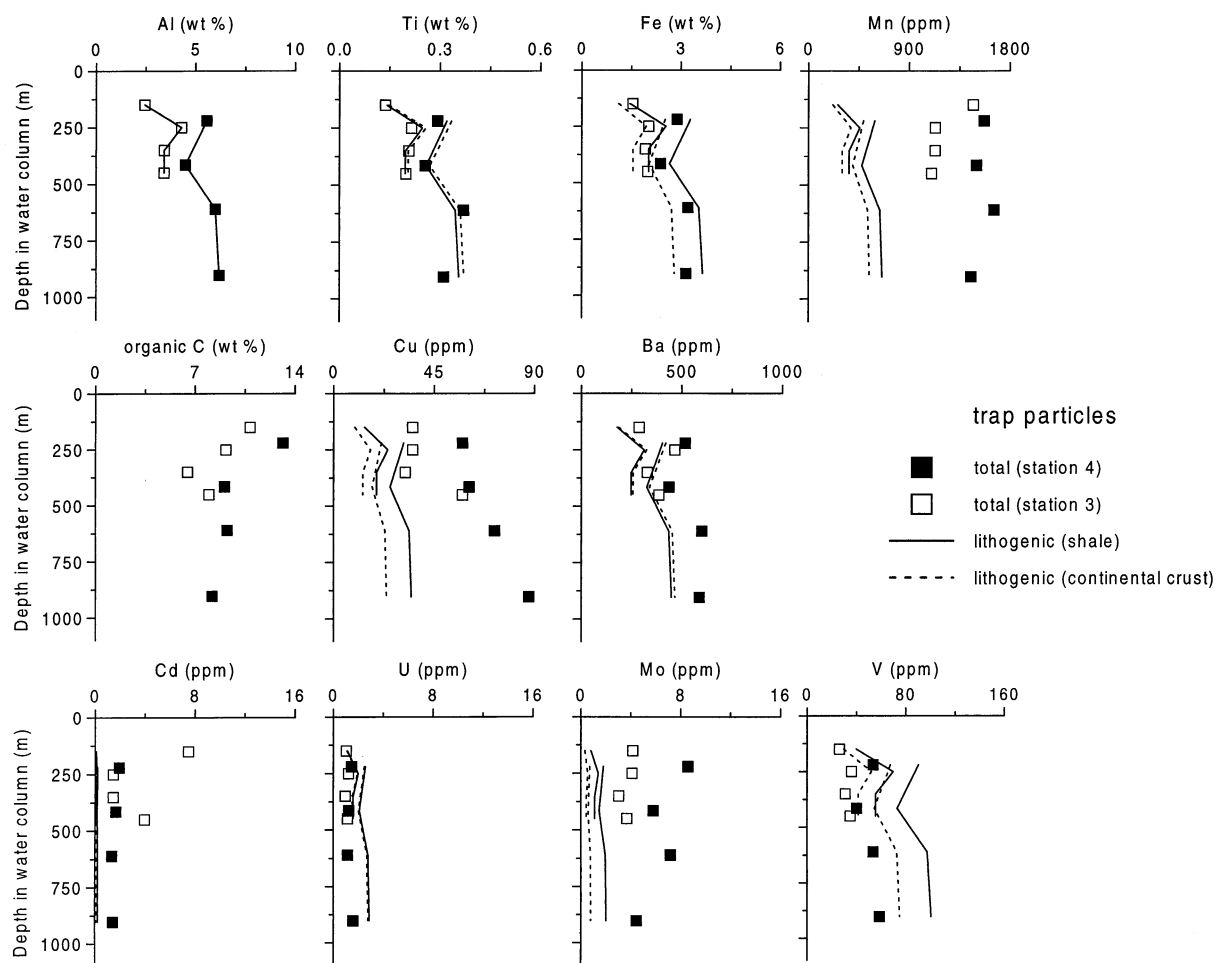
Fig. 3. Metal concentration in settling particulate material (Al, Ti, Fe, Mn, organic C, Cu, Ba, Cd, U, Mo, and V) collected during the 1993 *New Horizon* cruise. Data points represent the mean concentration for two traps deployed at each depth, station 3 trap deployment (□) and station 4 trap deployment (■). Reference lines represent lithogenic concentrations expected using shale (solid line) and crust (dashed line) as reference materials (Turekian and Wedepohl, 1961). The lines were calculated using the Al content of each sample times the Me/Al ratio in the respective reference material. Organic carbon values are from Hartnett (1998).

Additional metal enrichment occurred in subsurface sediments because of diffusion from bottom water to sites of authigenic enrichment in the sediments. Representative (0 to 20 cm) down-core profiles from our data set are shown in Figure 5 for Cd, U, Mo, V, and Re for a site above the OMZ at 140 m, in the core of the most intense part of the OMZ at 310 m, and at the lower boundary of the OMZ at 785 m. Most metals were enriched down core. Metal concentrations plateau by 10 to 20 cm. The down-core enrichments tended to be lower at the oxic site at 140 m.

The core bottom concentrations vs. water column depth are plotted in Figure 6. Core bottom data represent the deepest sample analyzed in each core, which ranged from 8 to 22 cm. The core bottom concentrations represent the amount buried into the geological record. In some cases, such as Cd, Mo, and V, the overall pattern vs. water column depth was similar to the pattern in surface sediments, although slightly enriched. In other cases, such as U and Re, sediment diagenesis creates a very different pattern. In most cases, the additional enrichment occurs in the sediments from 400 to 800 m in the deeper part of the OMZ.

4. DISCUSSION

We use this data set to evaluate the water column and sedimentary geochemistries of Fe, Mn, Cu, Ba, Cd, U, Mo, V, and Re under suboxic water column depositional conditions and compare them with oxic and anoxic environments. We then examine how metal enrichments in sediments depend on sinking particle composition and the extent of sedimentary diagenesis. We then assess the utility of metal concentrations and metal ratios as tracers for the redox state of the depositional environment.

4.1. Water Column

Trace metal distributions in the water column reflect a balance between conservative mixing of end-member water
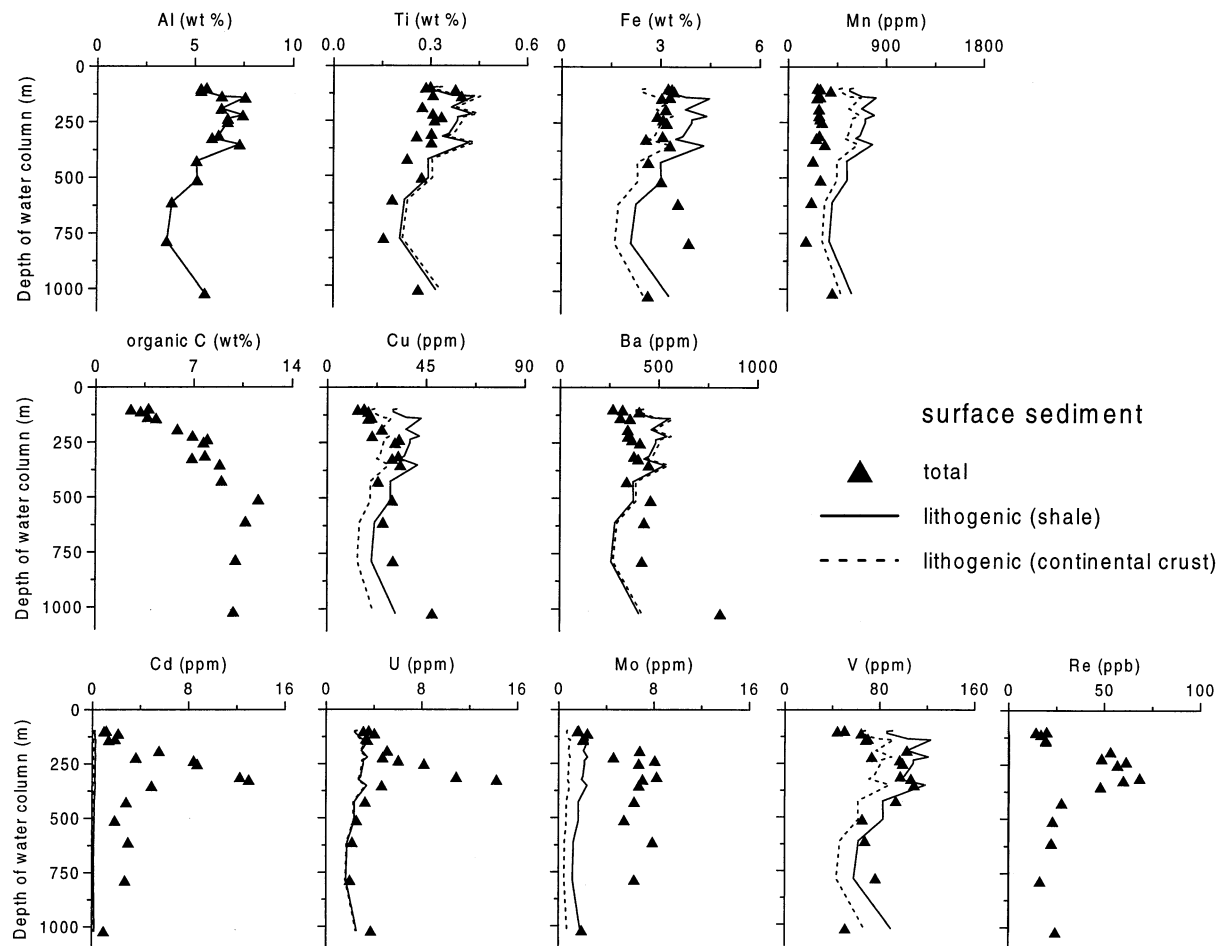
Fig. 4. Total concentrations of Al, Ti, Fe, Mn, organic C, Cu, Ba, Cd, U, Mo, V, and Re in surface sediment (0 to 0.5 cm or 0 to 1 cm depth interval) as a function of water column depth. Reference lines show the expected lithogenic concentrations using shale and crust as reference.

masses and nonconservative processes in the water column and sediments. Our data indicate that Mo, Re, and U are constant to within ±2% from the surface through 1000 m (Fig. 2). OMZ distributions of Cu, Ba, Cd, and V are similar to open ocean data. It therefore appears that in this location, low O_2 alone is not sufficient to make these elements more reactive. This observation contrasts with low-oxygen settings where circulation is restricted, and seawater has more time in contact with reacting sediments (van Geen et al., 1995). The concentrations of these elements cannot be used to distinguish between oxic and suboxic conditions in the water column.

The influence of suboxic conditions in the water column is seen prominently in the distribution of Mn (Fig. 2). Water column Mn maxima are one of the more scrutinized features in suboxic OMZs. The broad Mn maximum reaching ~8 nmol/L observed at this site is similar to previous results (Klinkhammer and Bender, 1980; Murray et al., 1983; Martin and Knauer, 1984; Johnson et al., 1992; Johnson et al., 1996; Rue et al., 1997).

Johnson et al. (1992, 1996) suggested that the highest Mn fluxes from the sediments occurred from the shallow shelf sediments, while the lowest Mn fluxes occurred from OMZ

sediments. The OMZ Mn profile is controlled by regeneration of plankton-associated Mn at the sediment-water interface rather than diffusion out of reducing pore waters. Our sinking particles have uniformly high values of nonlithogenic Mn (Fig. 3), while the sediments have very low Mn concentrations, even less than the predicted lithogenic values (Fig. 4). Our data suggest that at this site, remineralization of Mn must occur at the sediment-water interface before the sinking particles are buried.

Our Mo profile is uniform to within ±2%, which is possibly surprising given that denitrification is important at this site and that Mo is used in nitrate reductase, an enzyme required for reduction of NO_3 to NO_2 (Raven, 1988). A concentration anomaly may be difficult to see because the concentration of Mo is relatively high (~100 nmol/L). The conservative water column distributions of Mo also suggest that Mn and Mo cycles are not linked in the water column at this site.

4.2. Settling Particulate Material

Sinking particles are composed of lithogenic particles of detrital origin and nonlithogenic particles of biogenic origin.
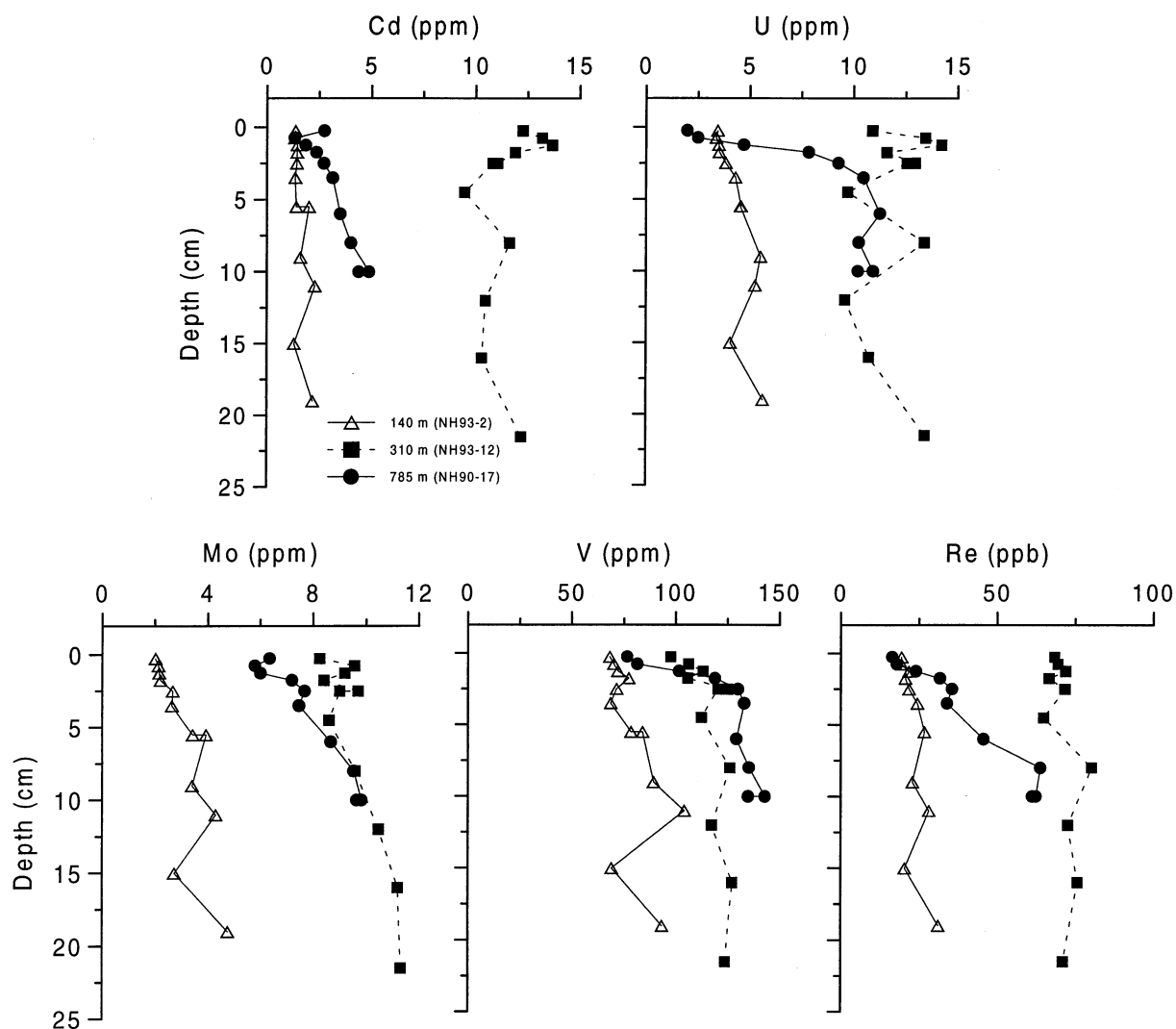
Fig. 5. Down-core profiles of total metal (Cd, U, Mo, V, Re) concentrations in cores from 140, 310, and 785 m.

Because our site is close to the Mexican coast, we expect that the lithogenic component should be relatively large and primarily due to particles of local riverine origin, although atmospheric transport may also be a source. Most particles may originate from resuspension of local sediments, perhaps going through multiple deposition and resuspension cycles. Resuspension of shelf sediments has been noted in other coastal environments, especially during the winter (e.g., Pak et al., 1980; Feely et al., 1981; Shiller, 1983).

We calculated the lithogenic composition for each sample as the product of the Al content times the Me/Al ratio for global average shale or crust (Turekian and Wedepohl, 1961). The calculated lithogenic content of the sinking particles is shown as solid (shale) and dashed (crust) lines in Figure 3. The nonlithogenic (NL) composition was calculated as the difference between the total and lithogenic composition:

$$Me_{NL} = Me_{total} - [Al_{total} (Me/Al)_{crust\ or\ shale}]. \qquad (1)$$

This calculation assumes that all Al is of lithogenic origin

rather than the result of scavenging (e.g., Orians and Bruland, 1986) or biogenic production (e.g., Mackenzie et al., 1978), a reasonable assumption at this near shore location. For some metals, the choice of the lithogenic reference material makes the nonlithogenic values negative.

Because we observed few systematic trends in the vertical profiles of the data, we averaged the total and nonlithogenic data sets (eight samples each) to get average values for the composition of sinking particles (Table 3). The limitation of this approach is that the data are from only one time point in what is surely a highly variable system. Nevertheless, these data provide a starting point for comparing the composition of sinking particles with underlying sediments.

Lithogenic material clearly is a significant fraction of settling particulate material because the absolute fluxes of Al and Fe are 100 to 1000 times larger than the nearest open-ocean locations for which comparable data are available (Landing and Bruland, 1987; Moore and Dymond, 1991; Nameroff 1996). We assume Ti has no biologic sources. The ability of Al to predict Ti using
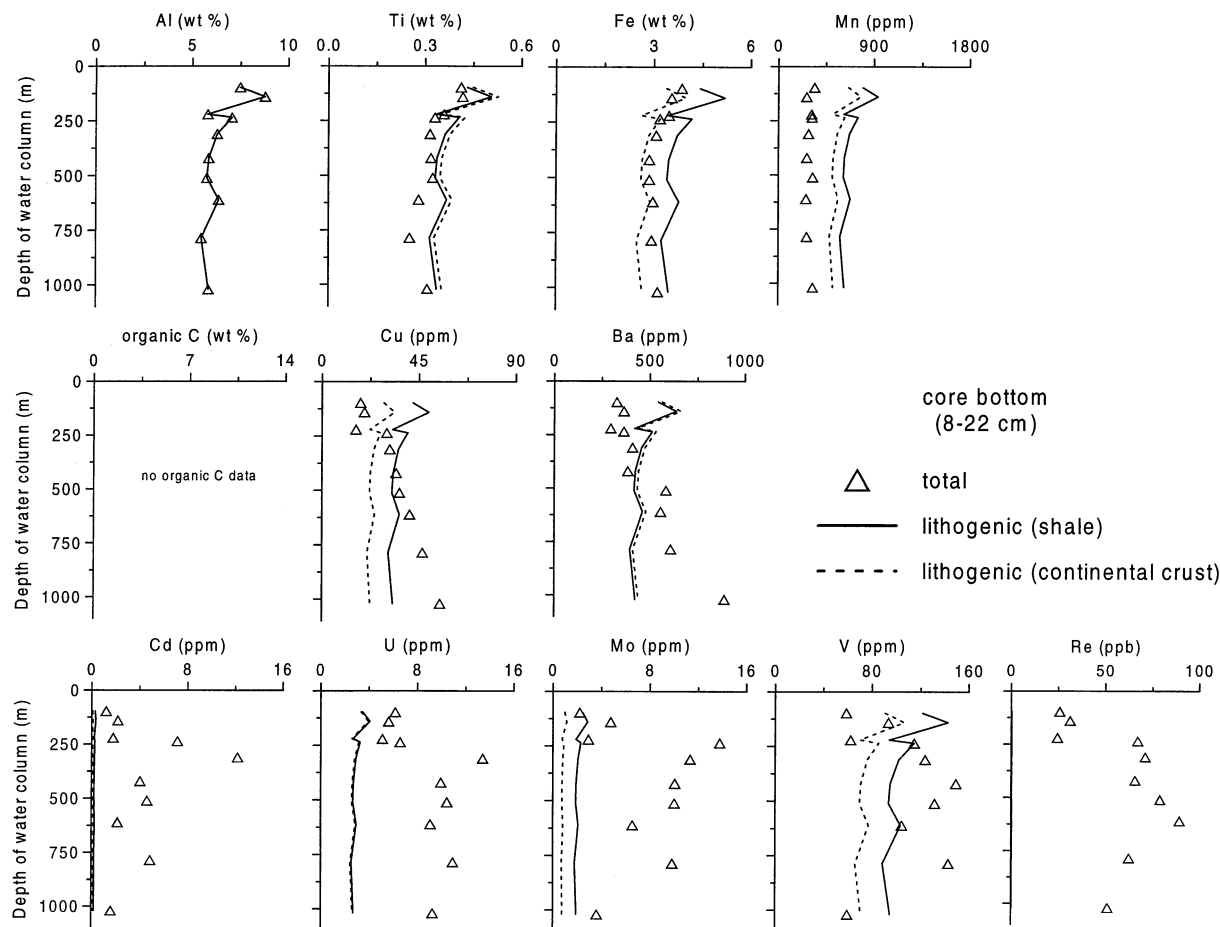
Fig. 6. Core bottom total sediment concentrations of Al, Ti, Fe, Mn, Cu, Ba, Cd, U, Mo, V, and Re as a function of water column depth. Reference lines show the expected lithogenic concentrations using shale and crust as reference.

Eqn. 1 supports our argument that Al in these samples is mostly lithogenic as well. Iron falls between the shale and crust estimates. If we use crust as the lithogenic reference, a small amount of nonlithogenic Fe is apparent (0.35 wt.%, Table 3). Approximately 75% of the total Mn is nonlithogenic and shows no systematic trend through the OMZ. There are also large values of nonlithogenic Cu, Ba, Cd, and Mo. Uranium is only slightly less than the crustal value. Vanadium is also mostly less than the crustal value. Most likely, these negative values reflect the fact that average crust is not totally representative of local detrital material. Hastings et al. (1996) and Morford and Emerson (1999) proposed that V and Mn distributions are closely coupled in sediments. That does not appear to be the case in the settling particles at this site.

Zheng et al. (2000) also observed nonlithogenic enrichments of both Mo and Mn in trap samples from the Santa Barbara Basin. Both Mo and Mn were partially released to the trap brine solutions and at the sediment water interface. They suggested that particulate Mn oxides in sinking particles scavenged Mo. We also observe significant enrichments for both Mo and Mn, but neither was released to the trap brine solutions. While the surface sediments have no nonlithogenic Mn, they have about the same amount of nonlithogenic Mo as the sinking particles.

Thus, at our site, Mo does not appear to be enriched in sinking particles because of scavenging by Mn oxides.

The nonlithogenic metal in sinking particles may be of biogenic (e.g., plankton) origin. The ability of plankton to concentrate trace metals is well known. To evaluate the biogenic fraction in the sinking material, we compared the nonlithogenic composition of our sinking particles with previous studies of the composition of plankton- and biogenic-rich particulate samples (Table 3). Such a comparison can only be qualitative because the composition of metals in plankton is highly variable and depends on rates of production, plankton species, food web structure, and ambient dissolved metal composition. Particles also remineralize at differential rates as they settle through the water column.

Few reliable studies of the trace metal composition of plankton material have been performed. We collected data from studies of plankton, sinking particles, and large volume particulate matter in the open ocean, the Baja California Coast, the eastern North Pacific, Monterey Bay, and Santa Barbara Basin (Martin and Knauer, 1973a, 1973b, 1975; Collier and Edmond, 1984; Sherrell and Boyle, 1992; Cullen et al., 1999; Zheng et al., 2000, in press). Comparison to our trap data suggests that concentrations of nonlithogenic Cu, Ba, Cd, and Mo in sinking

Table 3. Average total and nonlithogenic (NL) composition of bottom-moored sediment trap samples and comparison to literature estimates. The nonlithogenic composition was calculated as the difference between total Me and lithogenic Me. Lithogenic Me was calculated using the Al content of each sample and the Me/Al ratio in average crust (Turekian and Wedepohl, 1961). Reported values are the average of eight samples from 125 to 800 m. Insufficient quantities of material were collected to measure Re concentrations. The nonlithogenic composition of sinking particles is compared with estimates of plankton composition and other biogenic-rich samples from the literature. The nonlithogenic correction was not made for these literature samples, so they represent upper limits of the biogenic component. All concentrations in parts per million except where indicated.

	Al	Ti	Fe	Mn	Cu	Ba	Cd	Mo	V	U
Avg. total	4.47 ± 1.26wt.%	0.25 ± 0.07wt.%	2.38 ± 0.58wt.%	1376 ± 207	54.8 ± 8.4	450 ± 107	2.59 ± 2.01	5.11 ± 1.78	41.7 ± 11.2	1.21 ± 0.19
Avg. NL trap	0	0.02 ± 0.01	3500 ± 100	982 ± 95	38 ± 13	113 ± 12	2.58 ± 2.00	4.53 ± 1.62	-12.6 ± 4.1	-0.78 ± 0.37
Brumsack (1986)	—			—	11	—	12	2	3	—
Martin and Knauer (1973a, 1973b, 1975)	38 to 44		231 to 1510	6.1 to 7.7	3 to 15	19 to 287	1.5 to 3.9	<2.0	<3.1	—
Sherrell and Boyle (1992), <100 m	9.7 to 1183		318 to 941	17 to 117	8 to 23	—	0.7 to 1.6	—	—	—
Collier and Edmond (1984)	22.4 ± 4.3		76.7 ± 3.4	5.3 ± 0.5	9.6 ± 1.9	—	16.4 ± 3.2	—	—	—
Zheng et al. (2000, in press)	—		—	—	—	—	—	1.3	—	1.3
Kuss and Kremling (1999)	238 ± 71		56.6 ± 16.2	19.8 ± 2.2	6.1 ± 1.0		13.4 ± 2.2			

particles are similar to that of plankton (Table 3). Vanadium and U are difficult to evaluate because our nonlithogenic values are negative. Anderson (1982) established that particulate nonlithogenic U is formed in surface waters. Other results suggest that U is completely regenerated under oxic conditions and at least partially preserved under low-oxygen conditions (Zheng et al., in press). Our observation of negligible nonlithogenic U is anomalous in this context. However, our absolute U concentrations compare well with other locations (Zheng et al., in press). Manganese and Fe are greatly enriched relative to plankton. The average lithogenic Al in our samples is 44,700 ± 12,600 ppm. Previous estimates of planktonic Al would fall in our noise level. We conclude that plankton material is likely a major source for certain elements to these sediments (e.g., Calvert and Price, 1970; Piper, 1994). This implies that variations in biologic productivity could affect levels of enrichment in recent sediments and through the paleorecord.

4.3. Trace Metal Enrichments in Surface Sediments

Trends in metal content of surface sediment with increasing water column depth show that the geochemical behavior of the elements varies across the continental shelf and slope where the OMZ contacts the sediments (e.g., Calvert and Price, 1970; Crusius et al., 1996). Surface sediments are composed of both lithogenic and nonlithogenic components and reflect the geochemical controls at work in the sediments and overlying water column. The surface sediment composition vs. water column depth for the Mexican margin OMZ sediments is shown in Figure 4. The total composition is compared with the calculated lithogenic composition (from Eqn. 1).

The Ti content is similar to that in average shale and crust and to concentrations reported for sediments located west of the Baja Peninsula (Shimmield and Price, 1986). This is expected because both sites have similar source rocks. Maximum Ti occurs above the shelf-slope break, while Ti of surface sediments in the OMZ is slightly lower. Titanium tends to be enriched in coarser sediment fractions (Spears and Kanaris-Sotiriou, 1976); thus, these data suggest that the sediments deposited on the slope under the OMZ (Ti < Ti_{crust}) are finer grained than those deposited on the shelf (Ti ≈ Ti_{crust}).

Iron is at crustal values down to 500 m but is slightly enriched in the surface sediments at 610 and 785 m, the lower boundary of the OMZ. These Fe enrichments are only seen in the surface samples and may reflect oxidation of mobilized reduced Fe(II) to solid Fe(III) phases. Solid-phase Mn is strongly depleted relative to lithogenic values at all depths. Because neither Fe nor Mn was detected (<1 μmol/L) in pore water samples, the processes controlling the enrichment of Fe and depletion of Mn probably occur at the sediment-water interface.

Copper and Ba are frequently used as tracers for biologic input. Copper behaves partly like a micronutrient in the water column (Boyle et al., 1977) and appears to be released from organic carrier phases in sediments (Sawlan and Murray, 1983; Shaw et al., 1990). Barium has been used as a tracer for paleoproductivity reconstructions (Dymond et al., 1992; Francois et al., 1995; Paytan et al., 1996). At this OMZ site, Cu and Ba in surface sediments increase with depth like organic carbon to 500 m. Cu and Ba continue to increase, while organic carbon

is constant below that depth. Copper is about equal to the crustal values, and Ba is slightly depleted relative to crust at depths shallower than ~500 m. Both Cu and Ba are slightly enriched relative to crust below 500 m.

Cadmium, U, and Re have similar distributions in surface sediments. All three show a strong enrichment centered on a water column depth of 310 m. Their similar distributions suggest a common control, perhaps due to more reducing sediments at these depths. However, this is not simply due to the availability of sulfide, as Cd is the only one of these three elements that is known to form sulfides. Uranium is close to crustal values above and below this maximum, while Cd and Re are enriched relative to crust at all depths. The sequence of enrichment relative to shale/crust is Re greater than Cd greater than U.

Molybdenum's distribution is different from other metals. It is broadly enriched relative to crust from 200 to 785 m. Sediment Mo composition probably has multiple controls (plankton, solid sulfide formation, scavenging by FeOOH). Vanadium is generally very similar to the shale/crust values, showing no prominent enrichments or depletions.

4.4. Down-Core Trace Element Enrichments

The importance of down-core trace element enrichment because of diagenesis varies from site to site and from metal to metal. To illustrate, we show the down-core data for the redox tracer elements Cd, U, Mo, V, and Re at an oxic site (140 m), at the most intense part of the OMZ (310 m), and at the lower boundary of the OMZ (785 m) in Figure 5. In most cases, down-core metal enrichment is complete within the upper 0 to 10 cm.

At the 140-m oxic site, all of these metals have relatively low concentrations and small down-core enrichments. The 310-m site shows the most enrichment from top to bottom for all elements, especially Cd, U, and Re. In fact, little additional down-core enrichment is apparent at this site. The 785-m site (which is representative for all cores below ~400 m) shows significant subsurface enrichment for all metals. Cadmium, Re, and Mo increase continuously from 0 to 10 cm, and the depths of removal of Re and Mo are not significantly different. The enrichments of V and U are mostly completed by 5 cm. Uranium enrichment occurs slightly before Cd. These trends do not give any new insights toward understanding removal mechanisms, especially because a diagenetic overprint is difficult to distinguish from a temporal change in redox conditions.

The enrichments of Cd, U, and Re that occur at 310 m are not linked clearly to sulfidic pore water. No free sulfide was detected (>1 μmol/L) in any OMZ sediments. Indeed, maximum sulfate reduction rates inferred from direct measurement and alkalinity and ammonium gradients do not appear to be related to the concentration of carbon in sediments or bottom water oxygen concentrations. If micro quantities of sulfide were present (<1 μmol/L), as observed by Kuwabara et al. (1999) in Santa Barbara Basin, we predict they would be found in sediments at and above the upper boundary of the OMZ (140 to 310 m), where the pore water alkalinity and ammonium gradients are steepest.

Metals are buried into the geologic record below the depth of

Table 4. Comparison of the non-lithogenic (NL) composition of sinking particles with estimates of plankton composition and other biogenic rich samples from the literature. The non-lithogenic correction was not made for these literature samples so they represent upper limits of the biogenic component. Non-lithogenic was calculated as the total minus the crustal component. All compositions given as ppm.

	Al	Fe	Mn	Cu	Ba	Cd	Mo	V	U
Avg. NL Trap	0	3500 ± 100	982 ± 95	38 ± 13 11	113 ± 12	2.58 ± 2.00 12	4.53 ± 1.62 2	−12.6 ± 4.1 3	−0.78 ± 0.37
Brumsack (1986)	—	—	—		—				—
Martin and Knauer (1973a,b; 1975)	38 to 44	231 to 1510	6.1 to 7.7	3 to 15	19 to 287	1.5 to 3.9	<2.0	<3.1	—
Sherrell and Boyle (1992), <100 m	9.7 to 1183	318 to 941	17 to 117	8 to 23	—	0.7 to 1.6	—	—	—
Collier and Edmond (1984)	—	—	5.2 to 9.0	8 to 14	—	16 to 54	—	—	—
Zheng et al (2000, in press)	—	—	—	—	—	—	1.3	—	1.3

diagenesis. To visualize the results of diagenesis, we plot the core bottom concentrations (ranging from 8 to 22 cm) vs. water column depth in Figure 6.

While some of the patterns at depth are similar to surface sediments (e.g., Mn, Cu, and Ba), surface sediment concentrations are a poor indicator of U, Mo, V, and Re enrichment. Down core, Re and U are more uniformly enriched throughout the OMZ rather than specifically at 310 m, as seen in the surface data. Molybdenum and V are more enriched down core inside the OMZ than outside it. Other workers have proposed that different forms of authigenic Mo can precipitate at two critical dissolved sulfide concentrations (Helz et al., 1996; Erickson and Helz, 2000; Zheng et al., in press). A mixed Mo-Fe-S phase may begin to form at ~0.1 μmol/L sulfide. Direct Mo-sulfide precipitation, the point at which Mo behavior switches from conservative to particle reactive, occurs above 100 μmol/L sulfide (Zheng et al., in press). Even though Mo was enriched, we detected no free sulfide. Vanadium shows significant nondetrital enrichment down core. Hastings (1994) and Morford and Emerson (1999) proposed that V could diffuse from sediments when Mn reduction takes place near the sediment-water interface (≤1 cm). Our observations indicate that V is effusing from sediments located above and below the OMZ but is enriched when O_2 < 10 μmol/L. Reduced V (possibly V[IV]) does not form sulfides but adsorbs strongly onto particle surfaces (Wehrli and Stumm, 1989).

Cadmium has a similar distribution in the surface and downcore data. A strong enrichment is evident at 310 m, and weaker enrichments occur in shallower and deeper cores. Van Geen et al. (1995) and Rosenthal et al. (1995b) simultaneously and independently showed that Cd is removed just below the depth at which oxygen becomes undetectable. Thus, the Cd distribution is consistent with Devol's (unpublished data) observation of no benthic oxygen flux.

4.5. Role of Sinking Particles in Producing Metal Enrichments

Settling organic material, adsorption and precipitation of metals at the sediment surface, and diffusion of metals to a

discrete depth below the sediment-water interface may all add metals to the sediment. The rates of the latter processes depend on sediment redox state. If organic material delivers most of a particular trace metal to the sediments, then it is difficult to relate changes in that metal's distribution to changes in sediment redox state rather than the organic input.

In Mexican margin sediments, organic carbon is correlated significantly with the total concentration of several redox-sensitive trace metals (Table 5). Vanadium, Cu, Ba, Mo, and Re are positively correlated with organic carbon, while Ti, Fe, and Al have negative correlations. The correlation between organic carbon and trace metals may reflect direct input of plankton material enriched in metals or common dilution of organic and redox-sensitive metal phases by lithogenic material. For example, both Cu and Ba correlate strongly with organic carbon. At the same time, nonlithogenic Cu and Ba are negligible. Organic carbon indirectly affects distributions of other metals via its influence on the sediment redox state (e.g., Froelich et al., 1979; Emerson et al., 1985). To evaluate these factors, we compare in Figure 7 the nonlithogenic metal in sediments to the range of nonlithogenic metal concentrations observed in the trap samples (Table 3, Fig. 3). This comparison suggests that sinking particles make an important contribution to the sediments, which varies from element to element.

Nonlithogenic fractions of Ti and Fe in sediment and sediment trap are similar, except for the enrichments in surface sediment Fe at 125, 600, and 785 m. Sediments contain much less nonlithogenic Mn than sinking particles, probably because of remineralization at the sediment-water interface, as discussed previously.

The organic carbon of the surface sediments is similar to sinking particles at depths greater than 250 m. At depths less than 250 m, organic carbon in sediments is less than in sinking particles, probably because of remineralization at the sediment-water interface and in the sediments. The distributions of Cu and Ba also decrease with depth in the sediment, from 125 to ~500 m for Ba and 785 m for Cu. The nonlithogenic Cu and Ba in sinking particles must be remineralized in the sediment as well. Copper and Ba must efflux from the sediments above
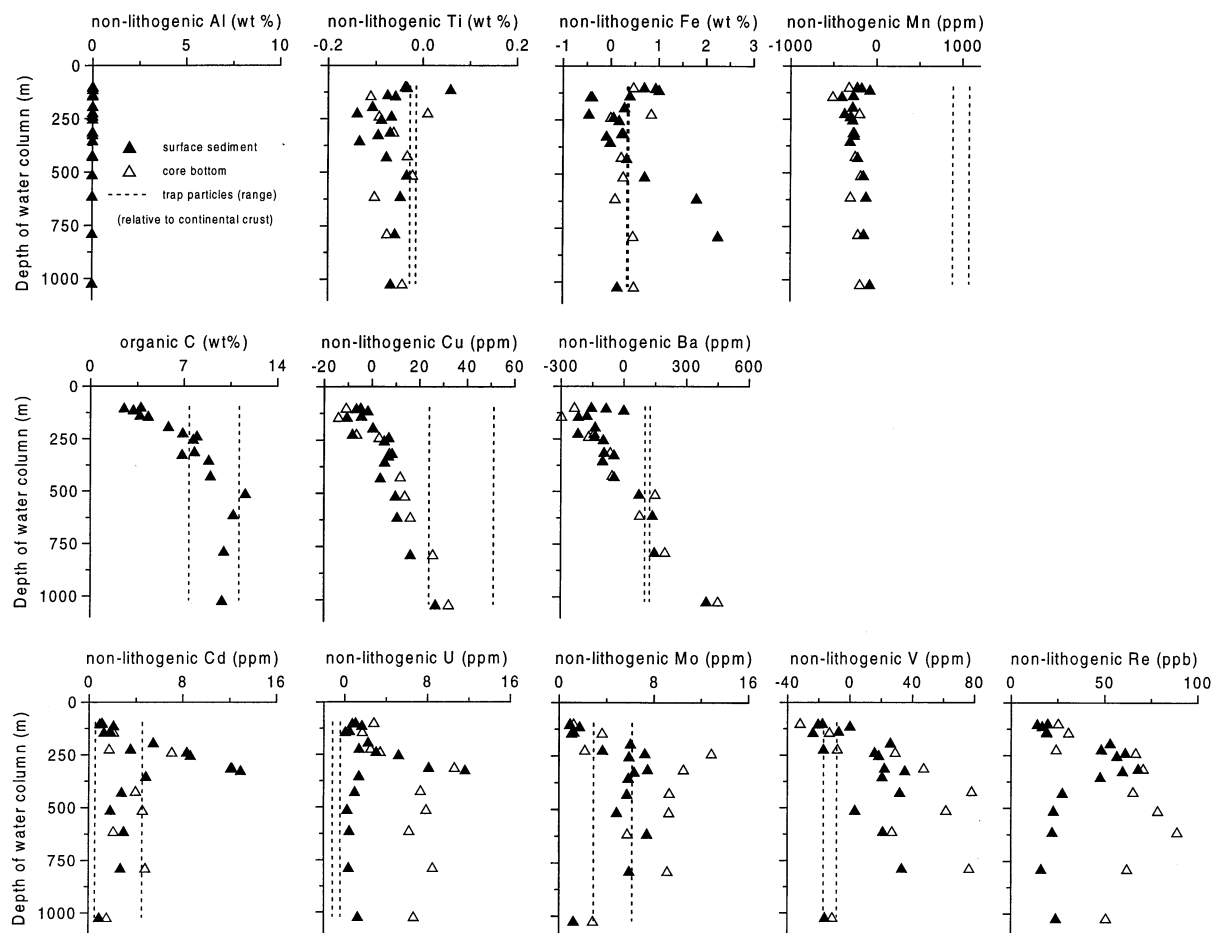
Fig. 7. Comparison of nonlithogenic sediment concentrations (both surface [filled triangles] and core bottom [open triangles]), with the range of nonlithogenic concentrations observed in sediment trap samples. Nonlithogenic is calculated from average crust.

500 m. Observed depletions of sedimentary Cu in Mexican margin sediments are consistent with results of Sawlan and Murray (1983) and Heggie et al. (1987), who used pore water gradients to calculate large benthic fluxes of Cu out of shallow continental margin sediments.

Much of the enrichment of nonlithogenic Cd and Mo (and possibly U) in surface sediments appears to be due to organic matter input from sinking particles. Nonlithogenic Cd in both surface and down-core sediments is equal to the sinking particles at all depths, except around 310 m. Thus, much of the nonlithogenic Cd enrichment could be attributed to input of plankton. Nonlithogenic U in surface sediments is only slightly greater than sinking particles, except around 310 m. Down-core U enrichment relative to sinking particles occurs at all depths, reflecting authigenic enrichment. Nonlithogenic Mo in surface sediments is similar to sinking particles, while down-core data shows enrichment for water depths greater than 250 m. Non-lithogenic V is enriched relative to sinking particles in both surface and down-core data. At core bottom depths, the enrich-ments of V, Mo, and U are clearly in excess of the input from sinking particles and due to early diagenesis. Definitive Cd

enrichments greater than particle input are limited to the 310-m depth horizon.

4.6. Redox-Sensitive Metals as Tracers for Redox Environments

Trace metal concentrations in sediments would be particu-larly helpful if they could be used to determine whether the overlying water at a depositional site was oxic, suboxic, or anoxic at the time of deposition. This may not be easy, how-ever, as we have shown that significant fractions of some metals may be contributed by sinking biologic particles. In addition, early diagenesis can produce down-core metal enrich-ment after initial sediment deposition as metals diffuse from seawater to removal sites below the sediment-water interface. The metal concentrations in sediments are preserved after early diagenesis is complete and sediments are buried. That signature may be very different than that initially deposited in surface sediments.

A metal's "removal depth," calculated from Fick's first law and the metal's accumulation rate in sediment, is a simple conceptual tool for understanding redox conditions (Crusius et

Table 5. Pearson correlation coefficient matrix for total trace metal data in all surface and down-core sediment samples ($n = 118$). Statistical significance ($p > 0.05$) is indicated when $r > 0.2$ and shown in boldface.

	Mn	Fe	Al	V	Cu	Ba	Mo	Cd	U	Re	C_{org}
Ti	**0.577**	**0.414**	**0.768**	−0.136	**−0.388**	**−0.220**	−0.158	0.034	0.045	−0.020	**−0.508**
Mn		0.158	**0.283**	**−0.335**	0.081	**0.288**	**−0.259**	−0.024	0.016	−0.026	−0.106
Fe			**0.358**	**−0.392**	**−0.558**	**−0.379**	**−0.297**	**−0.263**	**−0.498**	**−0.252**	**−0.537**
Al				−0.008	**−0.397**	**−0.299**	−0.054	0.091	−0.004	0.044	**−0.497**
V					**0.274**	−0.117	**0.856**	**0.448**	**0.557**	**0.700**	**0.452**
Cu						**0.880**	**0.221**	0.011	**0.292**	**0.307**	**0.794**
Ba							−0.189	**−0.253**	0.084	−0.012	**0.555**
Mo								**0.651**	**0.547**	**0.806**	**0.442**
Cd									**0.698**	**0.655**	0.087
U										**0.644**	0.159
Re											**0.489**

al., 1996). Shallow removal depths for metals that accumulate in sediments when oxygen is depleted imply a reducing environment. This approach is limited, however, because it requires a well-determined sedimentation rate. Steady state, a single removal pathway, and the absence of additional sources or sinks above a discrete removal depth must be assumed.

Metal ratios also have been proposed as tracers for redox environments. The metals in these ratios ideally are conservative in seawater and are removed in the sediments at different points in the redox sequence by well-understood geochemical pathways.

Crusius et al. (1996) proposed that the authigenic Re/Mo ratio could be used in tandem with a calculation of Mo and Re removal depths to determine whether a sedimentary depositional environment was oxic, suboxic, or anoxic. Rosenthal et al. (1995b) suggested that down-core changes in Cd/U could be used as a qualitative indicator to assess the role of steady-state metal accumulation relative to enrichments created by post-depositional change in sediment redox state. As our Mexican margin data set includes all four of these elements, we can evaluate the variability in the ratios.

4.7. Re and Mo

Rhenium and Mo are conservative in seawater, are strongly enriched in reducing sediment, and may be removed from seawater at different redox potentials. Crusius et al. (1996) proposed that the fractions of Re and Mo in particulate material are small and that their enrichments in sediments are controlled primarily by diffusion from seawater to removal depth in the sediment.

Oxic sediments typically are characterized by enrichment in Mn (~0.5 to 1 wt.%); Mo is enriched because of scavenging by MnO_2 (Table 6). Re is not scavenged under oxidizing conditions and remains close to crustal values (0.1 to 1 ppb). In suboxic sediments, MnO_2 is reduced and adsorbed Mo is released. The remaining Mn and Mo should be present at crustal values ($Mn_{crust} = 690$ ppm; $Mo_{crust} = 1$ ppm). Rhenium, on the other hand, is strongly enriched in suboxic sediments (e.g., 10 to 20 ppb in Japan Sea sediments and up to 25 ppb in Pakistan margin OMZ surface sediments; Crusius et al., 1996). Thus, in suboxic sediments, the Re removal depth is shallower than that of Mo. Anoxic sediments are enriched in both Re (30 to 50 ppb) and Mo (20 to 40 ppm), and Mo enrichment sometimes can occur at shallower depths than Re (Crusius et al., 1996).

The systematics of the Re/Mo ratio should reflect the metals' concentrations (Table 6). In the sediment record, the ratio would be close to the crustal ratio (0.3 ng μg^{-1}) if sediments were deposited under oxic conditions. The ratio would be less than the crustal ratio if MnO_2 enriches Mo because of adsorption. The Re/Mo ratio should increase because of Re enrichment when sediments are suboxic. Under anoxic conditions, the ratio should decrease to the Re/Mo ratio in seawater (0.7 ng μg^{-1}) because both Re and Mo are quantitatively removed.

In the sediments from the Mexican margin, Mn concentra-

Table 6. Summary of expected metal concentrations and tracer ratios for oxic, suboxic, and anoxic conditions compared with observations of Mexican margin sediments.

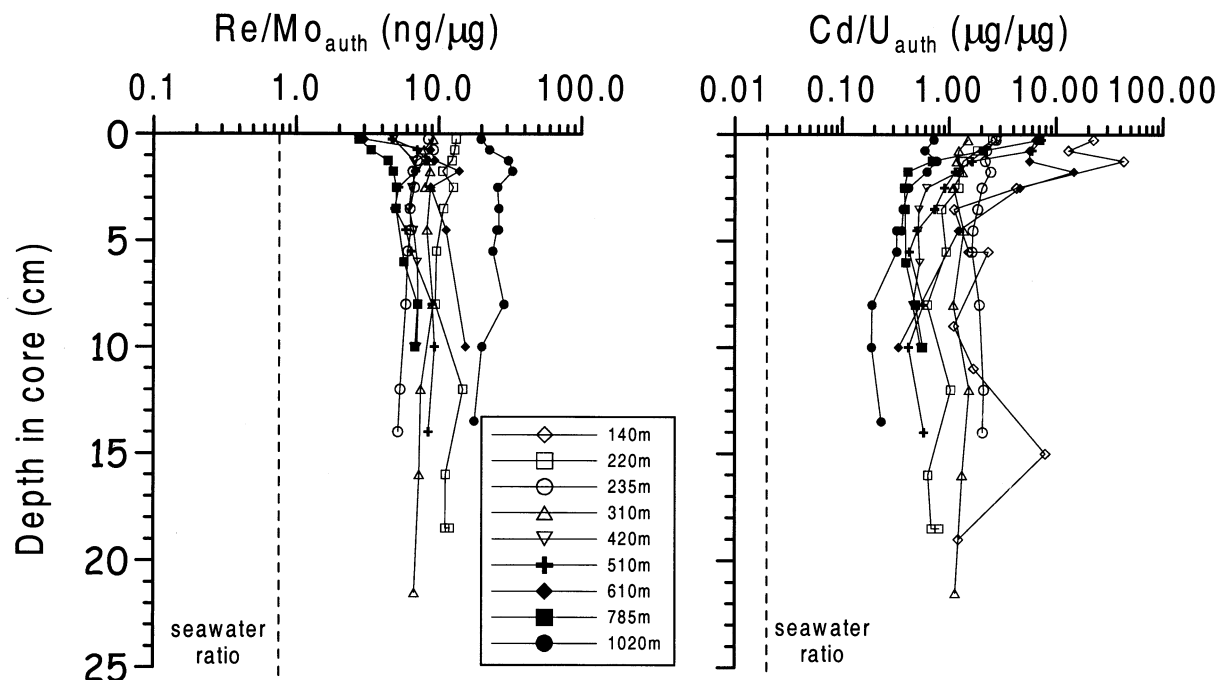|	Re	Mo	Cd	U	Re/Mo	Cd/U
Oxic	Low	High (with Mn)	Low	Low	Low (≤crust)	Medium (~Crust)
Suboxic	Very high	Low	Low	High	Very high (>crust)	Low
Anoxic	High	Very high (without Mn)	Very high	High	=SW	=SW
Mexican margin (≈310/m)	Very high	Very high	Very high	High	Very high	Very high (constant with depth)
Mexican margin (</>310 m)	High	High	High	Low	Very high	Very high (decrease with depth)

SW = seawater.

Fig. 8. Down-core variations in the authigenic Cd/U and Re/Mo ratios in Mexican margin sediments. These authigenic ratios were calculated assuming average crust for the lithogenic component. The ratios for seawater are shown for comparison.

tions are always low (even less than the crustal value), and Re concentrations are always high (Figs. 4 and 6). Thus, none of these sediments would be identified as oxic, even when they are overlain by oxygenated seawater. Re reaches values as high as 70 ppb at the surface (at 310 m) and 90 ppb at the core bottom. Mo is also enriched to 8 to 12 ppm, even though free sulfide is not measurable. We also do not observe an offset in the removal depths of Re and Mo, as did Crusius et al. (1996) in the Pakistan margin OMZ. The removal depths of Re and Mo are shallow (2 to 3 cm) and appear to coincide (Nameroff, 1996). The nonlithogenic Re/Mo ratios range from 2 to >30 ng μg^{-1} and appear to converge on values of ~6 to 20 ng μg^{-1} by depths of 15 to 20 cm. (Fig. 8). These ratios are higher than those in Black Sea sediments (≤0.7 ng μg^{-1}) and the seawater ratio and are consistent with ratios expected for suboxic conditions.

Re and Mo concentrations, removal depths, and Re/Mo ratios do not lead to consistent conclusions about the Mexican margin redox environment. The concentrations of both Re and Mo are enriched (anoxic signature), while the Re/Mo ratios are high (suboxic signature). The removal depths for both metals are consistent with an anoxic signature. Under the scheme of Crusius et al. (1996), one would classify these sediments as being deposited under oxic water and suboxic sediment conditions, which is not the case. We suggest that the classification scheme does not adequately distinguish suboxic depositional environments. It remains useful, however, for determining whether oxic or completely anoxic conditions were present.

4.8. Cd and U

Concentrations of Cd and U and the authigenic Cd/U ratio are tightly coupled to early diagenesis of organic matter. Use of the concentrations of these elements and their ratio is complicated because of their association with plankton material (Bruland et al., 1978; Anderson, 1982). Because our understanding of the removal mechanisms and kinetics for both metals is poor, it is not entirely clear how U and Cd concentrations and the Cd/U ratio should change through the redox sequence.

Under oxic conditions, the sediment concentrations of Cd and U are determined by their concentrations in lithogenic material and planktonic organic matter. Crustal concentrations of Cd and U are 0.1 and 3.5 ppm, respectively, with Cd/U = 0.03 μg μg^{-1} (Table 6). Uranium is conservative in seawater, but Cd is not. Because Cd is enriched in plankton material, its concentrations are linked to the uptake and regeneration cycles of P and carbon (van Geen et al., 1995).

Previous work has shown that Cd is enriched relative to U in reducing sediments. In modern sediments, Cd is provided primarily by decomposing organic matter and to a lesser extent from overlying seawater. Cadmium is probably removed as CdS(s) (Rosenthal et al., 1995a) or a mixed Fe-Cd-S phase (Framson and Leckie, 1978; van Geen et al., 1995) at sulfide concentrations below analytical detection by colorimetry (<1 μmol/L). Thus, Cd enrichment above the amount provided by plankton indicates the onset of sulfate reduction.

Uranium removal involves reduction of U(VI) (as the conservative species $UO_2[CO_3]_3^{4-}$) to U(IV) (as the nonconservative species $UO_2[s]$) (Anderson et al., 1989a, 1989b). Equilib-

rium calculations indicate that U(VI) reduction should occur after Mn(IV) reduction and just before Fe(III) and SO_4 reduction (Langmuir, 1978). While microbial reduction of U(VI) to U(IV) by Fe- and sulfate-reducing bacteria has been observed in culture experiments (Lovely et al., 1991, 1993; Lovely and Phillips, 1992), field studies of U geochemistry have given inconsistent results. McKee et al. (1987), Klinkhammer and Palmer (1991), and Barnes and Cochran (1993) concluded that U was enriched after Fe reduction and was coupled to sulfate reduction. Zheng et al. (in press), on the other hand, suggested that U is reduced and enriched primarily in the zone of iron reduction. Because observations indicate that U may not be removed at the point predicted by equilibrium calculations, kinetic factors likely play an important role. If both Cd and U are removed in association with sulfate reduction, they would not be useful for distinguishing redox environments.

The Cd/U in oxic sediments should be close to the crustal value ($0.03 \ \mu g \ \mu g^{-1}$) (Table 6). Prediction of how the ratio will vary under suboxic conditions is problematic. Assuming that U is removed during Fe(III) reduction, the ratio would initially decrease, then increase to the seawater ratio (Cd/U = $0.02 \ \mu g \ \mu g^{-1}$) as Cd is removed during SO_4^{2-} reduction. If the kinetics of U removal are slow, the ratio would increase initially, then decrease.

In the Mexican margin, Cd is enriched in surface sediments (Fig. 4). The largest enrichments, to ~12 ppm, occur around 310 m. Generally, little additional enrichment occurs at depth (Figs. 5 and 6). Uranium, on the other hand, has considerable down-core enrichment. Like Cd, large values of nonlithogenic U are only seen in surface sediments around 310 m. But by the core bottoms (8 to 22 cm), U has become considerably more enriched at water column depths greater than 250 m. Thus, U is enriched considerably deeper in the sediments than Cd.

The Cd/U ratio is greater than crust and seawater in surface sediments ($\geq 20 \ \mu g \ \mu g^{-1}$), reflecting the immediate Cd enrichment (Fig. 8). Except at 310 m, the ratio decreases with depth in the sediments to values ranging from 0.2 to 2 $\mu g \ \mu g^{-1}$, reflecting down-core enrichment of U. The Cd/U ratio never approaches the seawater ratio. Because the Cd/U ratio is highly variable in a suboxic depositional environment, it does not appear to be a sensitive method for assessing the role of steady-state metal enrichment relative to transient postdepositional processes.

The concentrations of Cd and U and the Cd/U ratio in Mexican margin sediments do not follow thermodynamic predictions. Because Fe(III) reduction is not occurring in these sediments, and the rates of sulfate reduction are slow (Kristensen et al., 1999), the absence of bacterial catalysis may slow the removal of U.

5. CONCLUSIONS

We determined the geochemical distributions of Al, Ti, Mn, Fe, Cu, Ba, Cd, Mo, Re, U, and V in the water column and sediments on the continental margin southwest of Mazatlán, Mexico. This region is characterized by an intense OMZ, so the sediments are deposited under "suboxic" conditions. One goal was to evaluate whether redox-sensitive trace metals provide a unique suboxic signature in the sedimentary record. The important conclusions from this work are as follows:

1. Dissolved concentrations of Cu, Ba, Cd, Mo, Re, U, and V in the water column were unaffected by the low-O_2 conditions in the OMZ. Dissolved Mn is enriched in the water column apparently because of remineralization at the sediment/water interface.
2. The composition of settling particulate material varied little in any systematic way. Manganese, Mo, Cu, Cd, and Ba had significant nonlithogenic concentrations, calculated relative to average crust. Uranium and V had essentially zero nonlithogenic concentrations.
3. The nonlithogenic composition for several metals (e.g., Cu, Ba, Cd, and Mo) in settling particles was similar to plankton material, within the constraints of available data. This comparison is more difficult for V, U, and Re because the composition of these elements in plankton material is not well known. The composition of Cd and Mo (and possibly U) in surface and down-core sediments reflects the composition of sinking particles; hence, changes in productivity could affect levels of enrichment in the sediments. The paleorecord of these metals should be viewed in this context as well.
4. The nonlithogenic composition of surface sediments in the Mexican margin is overprinted by sediment diagenesis, especially around 310 m, where Cd, U, and Re are strongly enriched. The cause of this authigenic enrichment is unclear because the distribution of organic carbon and pore water composition (e.g., sulfide, alkalinity or ammonia) does not indicate that these sediments are any more reducing than shallower or deeper sediments. Trace sulfide could play a role for Cd and Re, but its role in the removal of U is unknown.
5. The nonlithogenic composition of down-core sediments reflects additional enrichment due to sediment diagenesis. Rhenium and U are much more uniformly enriched throughout the OMZ in the down-core data than the surface data. Molybdenum and V show slight additional enrichments in down-core data. Surface sediment concentrations of these metals are a poor indicator of final enrichment. The down-core patterns for Mn, Cu, Cd, and Ba are similar to surface sediments.
6. The concentrations of Re and Mo and the Re/Mo ratios do not give consistent conclusions about the redox condition of the depositional environment. The large Re and Mo enrichments point to anoxia, while the high Re/Mo ratio indicates suboxic conditions. The concentrations of Cd and U and the Cd/U ratio are more confusing. The high concentrations of Cd and U suggest anoxic conditions, while the Cd/U ratio is not consistent with predictions from equilibrium chemistry. Uranium is enriched after Cd in these sediments.

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