Glacial-interglacial variability in the eastern tropical North Pacific oxygen minimum zone recorded by redox-sensitive trace metals

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ABSTRACT

Changes in the intensity of the oxygen minimum zone (OMZ) in the eastern tropical North Pacific over the past 140 kyr are recorded as enrichments and depletions of redox-sensitive metals in sediments of two piston cores, one within and one below the modern OMZ, from the continental margin off Mazatlán, Mexico (22°41'N, 106°28'W). Concentrations of Al (7.7±0.6 %), Ti (0.37 ± 0.03 %), Fe (3.1 ± 0.25 %), Mn (320 ± 31 ppm), and Ba (560 ± 82 ppm) in core NH15P (within the OMZ at 420m water depth) were relatively constant over the last 110 kyrs. In contrast, concentrations of Cd (4.8 ± 2 ppm), Cu (29.8 ± 9.1 ppm), U (9.1 ± 3.7 ppm), Mo (12.1 ± 5.0 ppm), V (138.2 ± 51.9 ppm) and Re (45.8 ± 25.5 ppb) were all at least 30% higher in interglacial stages compared to glacial stages. Concentrations of Al (7.4 ± 0.3%), Ti (0.35 ± 0.03%), Fe (3.5 ± 0.4%) and Mn (385 ± 77 ppm) in core NH22P (below the OMZ at 2025 m water depth) were comparable to those in core NH15P, while concentrations of Ba (1662 ± 292 ppm) were about a factor of three higher. In contrast, concentrations of Cd (0.9 ± 0.3 ppm), U (6.6 ± 0.9 ppm), Mo (3.2 ± 1.2 ppm), V (81.8 ± 10.1 ppm), and Re (25.4 ± 12 ppb) were lower in sediments of comparable age than the concentrations of these same metals in the OMZ core and the differences in their concentrations over glacial-interglacial cycles were less pronounced than those in shallower core. Comparison of the non-lithogenic fraction of metals in the sediments with their estimated contribution from plankton suggests that organic matter is probably the major source of Cu, Ba, and Cd to the sediment, whereas the indirect effect of organic carbon on sediment redox state appears to be a more important control on the distributions of U, Re, Mo, and V. Changes in the depth at which Re and Mo precipitated in the sediments and in the Re/Mo ratio suggest that sediment redox state at both core depths varied over time. Re and Mo removal depths were shallower and Re/Mo ratios were lower at the OMZ site than in deeper water,

suggesting that a more reducing sedimentary environment prevailed over time at the shallower site. Although the redox state of surface sediments at both sites varied over glacial-interglacial cycles, the OMZ likely was never anoxic in the last 140 kyr. This variability in sediment redox state could be attributed to changes in regional export productivity, changes in ocean circulation, or a combination of both processes. A paleoproductivity reconstruction from biogenic Ba data suggests that glacial productivity was considerable lower than it was during interglacial cycles. Model results suggest that the oxygen penetration depth, an indicator of sediment redox state, changed less than 1 cm as a result of the change in productivity. Changes in oxygen penetration depth estimated from Re and U removal depths are significantly larger, suggesting that changes in ventilation are a more important control on sediment redox state. Overall, trace metal results confirm the tight coupling between ocean circulation, marine productivity, and global change.

INTRODUCTION

The sedimentary concentrations of several minor and trace metals, such as Mn, Fe, Cd, U, Mo, V and Re, have been used successfully to characterize the redox state of modern depositional environments [*Calvert and Pedersen*, 1993; *van Geen* et al., 1995; *Crusius* et al., 1996; *Gobeil* et al., 1997; *Morford and Emerson*, 1999; *Nameroff* et al., 2002 and others]. These metals, which are commonly referred to as redox-sensitive metals due to their different geochemical behaviors under a range of redox states, also should be useful for detecting changes in redox conditions of past depositional environments [*van Geen* et al., 1996; *Crusius* et al., 1999; *Zheng* et al., 2000b; *Pailler* et al., 2002].

The fundamental control on sediment redox state is the balance between the flux of organic matter to the sea floor and the flux of oxidants to the sediments from overlying seawater [*Emerson* et al., 1985]. Thus, variations in sedimentary redox state are linked to changes in the magnitude of biological export productivity and the rate of ocean circulation. Some fraction of metal present above background lithogenic concentrations is due to the delivery to the sediment of metals associated with settling biological material [e.g., *Zheng* et al., 2000b; *Nameroff* et al., 2002], but most enrichment results from the changing redox conditions that occur as organic matter is degraded by the thermodynamically predictable sequence of oxidants (O_2, NO_3^-, Mn(IV), Fe(III) and SO_4^{2-}) [*Froelich* et al., 1979]. Consequently, under optimal conditions one should be able to use enrichments and depletions of individual trace metals to identify the redox conditions that prevailed when a layer of sediment was deposited. The reality is that we have imperfect knowledge of the phases that control metal enrichment and the kinetics of their formation, and an incomplete understanding of the tranport of metals by sinking particles and of the post-depositional diagenetic reactions that alter the distribution of metals in sediments.

Despite these limitations, the concentrations of Mn, Fe, Cd, U, Mo, V and Re in marine sediments are promising tracers of sediment redox state. Manganese is enriched in oxic (O_2 present) sediments in the form of Mn(IV) oxyhydroxides and is reduced and remobilized early in the redox progression and released as dissolved Mn(II) species into the pore water. Thus, its concentration is usually low in suboxic (O_2 and HS^- absent) and in anoxic (HS^- present) sediments. When Mn enrichment occurs in oxic sediments as solid phase oxyhydroxides, it may lead to sorption enrichment of other metals such as Mo and V. Iron also is often enriched as iron oxyhydroxide in oxic sediments but is not reduced (Fe(III) → Fe(II)) until later in the redox sequence, usually just before SO_4^{2-} reduction. Iron oxyhydroxides are also known to sorb V. In general, Cd, U, and V are enriched in anoxic sediments ($>1\mu M$ H_2S) but are not enriched in oxic sediments (>10 μM O_2). Molybdenum can have enrichments in both oxic sediments, such as the near surface manganese-rich horizons in continental margin environments with intense diagenetic recycling [*Shimmield and Price*, 1986] and in anoxic sediments. The behavior of Cd, Re, U and V is more complicated in environments under suboxic conditions ($<1\mu M$ H_2S and $<10\mu M$ O_2). Cadmium, U, and Re accumulate in sediments under suboxic sediment conditions whether the water column is either oxic or suboxic [*Klinkhammer and Palmer*, 1991; *Rosenthal* et al., 1995; *van Geen* et al., 1995; *Crusius* et al., 1996; *Nameroff* et al., 2002] and when anoxic conditions prevail [*Anderson* et al., 1989a,b; *Emerson and Huested*, 1991; *Colodner* et al., 1993, 1995]. In an ideal sequence, U reduction and precipitation as $UO_2(s)$ should start close to the redox potential of Fe(III) reduction, but poorly understood kinetic factors appear to result in slow removal. Free sulfide is not required to precipitate U, and probably not Re, in reducing sediment. Since authigenic Cd formation requires nanomolar HS^- concentrations, Cd removal theoretically should occur after U. However, several field studies have suggested that Cd is removed at a

shallower depth than U [*Klinkhammer and Palmer.,* 1991; *Rosenthal* et al., 1995]. Vanadium is

depleted in suboxic sediments when Mn reduction occurs within 1 cm of the sediment-water

interface [*Hastings*, 1994; *Morford and Emerson*, 1999]. Reduced V does not form sulfides but

instead adsorbs strongly onto particle surfaces [*Wehrli and Stumm*, 1989]. Because Mo

precipitates in the presence of free sulfide [*Bertine*, 1972; *Zheng* et al., 2000a] it is sometimes

used as a proxy for anoxia [*Piper*, 1994; *Dean* et al., 1997; *Crusius* et al., 1996]. However,

significant Mo enrichments can occur in sediments when free sulfide is not detectable in the

water column or in pore water [*Nameroff* et al., 2002]. Rhenium is usually the element most

enriched in anoxic sediments relative to seawater but its removal mechanism is poorly known.

Our study site is the continental slope of the eastern tropical North Pacific where the

OMZ impinges on the sea floor. The OMZ, one of the most intense in the world, reflects a

balance between oxygen consumption due to respiration of export productivity and the rate of

ocean circulation or ventilation at mid-depths. The region is located in the southern reaches of

the California Current, and is the site of moderately high upwelling-induced primary. The waters

throughout the OMZ have both northern and southern sources. Past variations in either biological

production or ocean circulation could have resulted in paleo-variations in the intensity or depth

range of the OMZ, and sediments accumulating beneath this region should provide a high-

resolution record of this variability.

Water column denitrification in the intense OMZs of the eastern tropical North and South

Pacific and the Arabian Sea may account for half of the total sink for oceanic nitrate [*Codispoti*,

1995]. Previous studies have pointed to decreased denitrification during glacial periods in this

region [e.g. *Ganeshram* et al., 1995], so that variations in the intensity of the OMZ in the past

could have had important implications for the oceanic nitrogen budget [*Codispoti*, 1995; *Gruber and Sarmiento*, 1997; *Middleburg* et al., 1998; *Ganeshram* et al., 2000; *Castro* et al., 2001].

The goal of this study was to use distributions of redox-sensitive metals to examine variations in the intensity of the OMZ over the past 140 kyr in two well-characterized piston cores from the continental margin near Mazatlán, Mexico (22° 41'N; 106° 28'W). The interpretation of the data is placed in the context of a previous study of the geochemistry of these metals in water column, settling particles and the modern sediments from the same area [*Nameroff* et al., 2002].

STUDY AREA

The oxygen minimum of the eastern tropical North Pacific is located in a linear T-S mixing zone between Subtropical Subsurface Water (SSW) from the south and Pacific Intermediate Water (PIW) from the north [*Wyrtki*, 1967; *Garfield* et al., 1983; *Rue* et al., 1997]. The SSW has the same temperature, salinity, and density properties as the "Pacific Equatorial 13°C Water" [*Tsuchiya*, 1981] that ultimately originates in the South Pacific as Subantarctic Mode Water [*Toggweiler* et al., 1991]. The northern extent of SSW is controlled by the influx of California Current Water, which transports Pacific Subarctic Water southward with lower salinity and higher oxygen content on any given density level. Along the west coast of North America, properties on characteristic density surfaces (e.g. $\sigma_t = 26.2$ (~150m); 26.9 (~450m) and 27.1 (~600m)) reflect end-member mixing between waters from these two sources. Thus, in any given region, and over time, the intensity of the OMZ and the location of its northern boundary should reflect this push-pull relationship between these water masses and the relative rates of ventilation from these two sources [*Castro* et al., 2001].

The "13º water" contains ~80 µM O_2 when it reaches the Galapagos Islands [*Lukas*, 1986]. Some fraction of this current (<50%) is deflected to the north along the western boundary of Central America. Also in this region, wind driven upwelling of nutrient-rich subsurface waters into the euphotic zone stimulates biological production. Directly measured productivity data in this region are sparse [*Zeitschel*, 1969] but net annual primary productivity on the order of 28 mol C m^{-2} y^{-1} was estimated using satellite radiometer data [*Longhurst* et al., 1995]. Respiration of exported organic matter consumes the remaining oxygen and leads to the formation of an OMZ with oxygen concentrations less than 5 µM. Influence of oxygen-poor PIW (~100 µM O_2) [*Reid*, 1965; *Tsuchiya*, 1982; *Talley*, 1993] at mid-depths helps to explain why the OMZ extends deeply into the water column.

In the study area off Mazatlán (Figure 1), the depths of the SSW and PIW end-members are approximately 150 m and 750 m, respectively. Dissolved oxygen concentrations are <5 µM in the water column between 235 and 785 m and no sulfide is detected [*Nameroff* et al., 2002]. 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 µM exist throughout this depth interval [*Castro* et al., 2001; *Nameroff* et al., 2002]. A secondary nitrite maximum is centered at 250 m, similar to that seen by *Garfield* et al. [1983]. The deficiencies in nitrate and the presence of a nitrite maximum suggest that denitrification is occurring at these depths [*Cline and Richards*, 1972; *Codispoti and Richards*, 1976; *Lipschultz* et al., 1990].

Modern surface sediments in contact with the OMZ on this part of the Mexican margin are finely laminated, organic rich (<10%), silty clays. Their geochemistry reflects the low oxygen conditions in the water column [*Nameroff* et al., 2002]. Benthic O_2, Fe, and Mn fluxes cannot be detected because bottom water oxygen is low and because Mn and Fe are remobilized

prior to burial [A. Devol, unpublished data; *Nameroff* et al., 2002]. Sedimentary sulfate reduction rates are surprisingly low considering the high organic carbon content [*Kristensen* et al., 1999].

The concentration of trace metals in OMZ sediments is influenced by the concentration of metals in settling particulate material as well as the diagenetic processes governing the cycling of metals within the sediment. In surface sediments, Cd, U, Mo, V, and Re are all enriched relative to crustal lithogenic matter [*Nameroff* et al., 2002]. Organic matter input from sinking particulate matter makes a significant contribution to the enrichment of Cd and Mo and U. Uranium, V, Mo and Re are enriched due to post-depositional redox reactions. Copper and Ba efflux from sediments shallower than 500 m water column depth, and are therefore not enriched relative to crustal abundances.

CORE DESCRIPTION

We selected two cores from a transect of cores from the NW Mexican margin southwest of Mazatlán, Mexico that were collected during R/V *New Horizon* cruise 90-5 in April, 1990 [*Lambourn* et al., 1991]. The cores were obtained from a range of depths that spanned the present day OMZ. The first core (NH15P) was from a site that is currently within the most intense portion of the OMZ (420 m water depth, $< 5\mu M$ O_2). Modern sediments at this site are organic rich with sub millimeter-scale laminations. The second core (NH22P) was from a site on the lower continental slope below the core of the OMZ (2025 m water depth, $\sim 100\mu M$ O_2). Laminated intervals occur between 425 and 535 cm. Modern sediments at this site are have lower organic matter contents than the OMZ site and they are fully bioturbated.

The chronostratigraphy for cores NH15P and NH22P was constructed by *Ganeshram and Pederson* [1998]. Ages for isotope stage boundaries 1/2 and 2/3 (~12.5 kyr and ~25 kyr, respectively) were determined by accelerator mass spectrometry (AMS) ^{14}C. The age scale for sediments older than Stage 3 was based on benthic foraminiferal oxygen isotope data correlated to the stacked isotopic stratigraphy of *Martinson* et al. [1987] and comparison of organic carbon profiles for sediments older than the Stage 4/5 boundary (~74 kyr). The sedimentary record in cores NH15P and NH22P covers 0 - 140 kyr and 0 - 115 kyr, respectively.

Core NH15P consists of alternately homogeneous and laminated olive-green clay. Interbedding of laminated and homogeneous intervals suggests that the oxygenation of the sea floor at this site varied in the past [*Savrda* et al., 1984; *Dean* et al., 1994]. The bulk sedimentation rate was relatively low during the last glacial maximum (LGM) (~8 cm kyr^{-1}) and increased to 17 cm kyr^{-1} during the Holocene. LGM sediments appear to have been subjected to intense winnowing, probably because of lowered sealevel [*Ganeshram and Pedersen*, 1998].

Core NH22P from the lower continental slope is mostly composed of alternately homogeneous and mottled olive- and pale-green clay, except for a reddish-brown interval that occurs between 12 and 20 kyr ago. Distinct laminations appear infrequently in mottled intervals. The alternating sediment facies suggest that seafloor oxygenation also varied at this site, but the lower frequency of distinct laminations compared to NH15P suggests that bottom water oxygen concentrations were higher at this water depth in comparable isotope stages. The sedimentation rate, however, was fairly constant (~6 cm kyr^{-1}), at least through Stages 1-3.

METHODS

The cores were split in half lengthwise after collection and cut into 1m sections, sealed in a vinyl polymer bag and stored at 4°C [*Ganeshram* et al., 1995; *Ganeshram and Pedersen*, 1998; *Ganeshram et al*., 2002]. Analytical methods for organic carbon, bulk sediment ^{15}N, and foraminiferal ; δ^{18}O determinations are described by *Ganeshram and Pedersen* [1998].

Additional subsamples were taken, avoiding contamination from the edges of the cores, for elemental analysis at the University of Washington (UW). Metal determinations by ICP-MS (Ba, Cu, Cd, Fe, Mn, Mo, Re, Ti, U, and V) and FAAS (Al) are described in *Nameroff* [1996]. Briefly, sediments were digested with an acid cocktail in a microwave oven using a slightly modified version of the procedure described by *Murray and Leinen* [1993]. Use of a flow-injection system with the ICP-MS allowed sample analysis with minimal matrix effects. Rhenium and U were quantified using isotope dilution, and the other metals by addition calibration. Detection limits were at least an order of magnitude lower than the determined concentrations of all metals. Precision (typically <5%) and accuracy (typically <6 %) were verified by repeated analysis of certified reference standards (National Research Council, Canada) throughout the course of this work as well as through inter-laboratory calibration [*Colodner*, pers. comm., 1995; *Crusius*, pers. comm., 1996].

Comparison of the results reported here with data obtained by *Ganeshram* [1996] using XRF methods showed [*Nameroff*, 1996] statistically indistinguishable values for Al, Ti, Mn, and Fe, whereas concentrations of Ba and Cu were 20% and 14% higher, respectively, in the UW data set. The cause of these differences is not known, but our interpretation of the distributions of Cu and Ba would be the same if either data set were used.

All organic carbon data illustrated in the figures are from *Ganeshram and Pedersen* [1998]. We also determined organic carbon at UW using a Carlo Erba Model 1106 Elemental Analyzer after removal of carbonate carbon to check the consistency of the correlation between C_{org} and metal concentration in the actual sub-samples that we analyzed [*Hedges and Stern*, 1984]. The precision of the measurement was 5%.

RESULTS

Core NH15P. Downcore changes in sedimentary organic carbon (OC) are closely correlated with the glacial-interglacial stratigraphy. OC contents are two to four times higher in interglacial periods relative to glacial isotope stages (Figure 2). The organic-rich sediments are also laminated. The highest OC concentrations (about 9% by weight) are found in Holocene sediments. Highest $\delta^{15}N$ values (9 - 10‰) in interglacial intervals and lower values (ca. 7‰) in glacial intervals record increases in the intensity of denitrification in the OMZ [*Ganeshram* et al., 1995] or the import of isotopically heavier nitrate via the California Undercurrent [*Kienast* et al., 2002] during interglacials.

Concentrations of Al, Ti, Fe and Mn are relatively constant downcore (Al: 7.7 ± 0.6% (w/w), Ti: 0.37 ± 0.03%, Fe: 3.2 ± 0.2%, Mn: 320 ± 30 ppm). Changes in Al and Ti vary inversely with %$CaCO_3$, reflecting dilution of the aluminosilicate fraction by biogenic carbonate [*Ganeshram*, 1996]. Barium showed somewhat higher variability (560 ± 80 ppm), but this did not correlate significantly with the stratigraphy. The standard deviations of these data exceed the analytical precision of the measurement, indicating some unresolved natural variability in abundance. The concentrations of Al, Ba, Fe, Mn, and Ti were significantly correlated with each other (Table 1).

Concentrations of Cd, Cu, U, Mo, V and Re are highest in laminated interglacial intervals, with maximum values of 10.5 ppm Cd, 50.2 ppm Cu, 23.4 ppm U, 23.4 ppm Mo, 271.3 ppm V and 110.8 ppb Re, and lowest in unlaminated glacial age horizons. The concentrations of these metals were significantly correlated with each other and with organic carbon.

Core NH22P. Concentrations of OC in core NH22P (Figure 3) are lower than in core NH15P and are slightly higher in interglacial than in glacial stage intervals. As observed in the OMZ core, maximum $\delta^{15}N$ values are found during interglacial stages.

Concentrations of Al, Ti, Fe and Mn (Al: $7.4 \pm 0.3\%$, Ti: $0.35 \pm 0.03\%$, Fe: $3.5 \pm 0.4\%$, Mn: 380 ± 80 ppm) are comparable to those in core NH15P, while concentrations of Ba (1660 ± 290 ppm) are about a factor of three higher. Once again, the variability of Ba concentrations is higher than that of the other metals. Aluminum, Ti and Fe show subtle variations downcore, generally being lower in Stages 2 and 6 (Al) and 4 and 6 (Ti and Fe). On the other hand, Mn is slightly higher in Stages 2, 4 and at the base of Stage 5.

Concentrations of redox-sensitive metals in core NH22P generally are lower than in NH15P, and the concentration changes over glacial-interglacial cycles also tend to be smaller than in NH15P. Copper distributions are similar to those of Ba, with higher values in Stages 1, 3 and 5. Concentrations of Cd are lowest in isotope stage 2 (0.4 ppm) and reach a maximum of 1.5 ppm in stage 5. Rhenium and U concentrations ranged from 8.1-70 ppb and 4.6-9.7 ppm, respectively, with lower concentrations generally occurring in glacial stages. Molybdenum concentrations were lowest in isotope stage 2 (1.1 ppm) and reached a broad maximum through stages 3 and 4, reaching a maximum of 6.4 ppm. The maximum V concentration (103 ppm) was coincident with the Cu maximum.

DISCUSSION

Changes in the depth and intensity of the OMZ over glacial-interglacial timescales may be the result of variations in the magnitude of export production, the rate of ocean circulation, or both processes. Changes in organic matter fluxes at the sea floor affect the depth of the redox boundaries within the sediments. Changes in bottom water oxygen concentrations alter both the depth of the redox boundaries and the concentration gradient of dissolved O_2 below the sediment surface. These changes may be recorded in sediments that are in contact with and below the depth of the oxygen-deficient water column as enrichments (or depletions) of Mn, Fe, Cd, U, Mo, Re, and V. Our analysis of the trace metal data presented here has three goals:

1. To assess whether changes in trace metal concentrations are coherent with glacial-interglacial timescales.

2. To relate changes in metal concentrations to changes in sediment redox state of the sediments over these timescales;.

3. To evaluate the relative importance of changes in productivity and circulation on sediment redox state at the two sites over glacial-interglacial timescales.

To meet these goals, we first define and examine metal enrichments and depletions in both piston cores to elucidate the contributions of lithogenic material, planktonic organic matter, and post-depositional processes to the observed metal concentrations. Next, we constrain changes in sediment redox state over glacial-interglacial timescales by examining the depths at which Mo and Re precipitate in the sediment and by comparing the ratio of sediment Re/Mo concentrations observed in other locations. We use a three-step approach to evaluate the last question. Organic carbon data constrain potential changes in productivity and export production

over glacial-interglacial timescales and thereby determine the burial flux of the organic

component of the sediment. We then assess how the diagenesis of this buried material affects

sediment redox state and trace metal removal depths. The difference (if any) between these

estimated removal depths and observed metal removal depths can then be attributed to changes

in bottom water oxygen levels or ocean ventilation.

Factors controlling trace metal enrichments and depletions. The flux of settling

lithogenic (e.g., continental) material, the flux of settling biological material (plankton), and the

rate of early diagenesis are the three major processes that control trace metal enrichments and

depletions in sediment. The latter two processes are responsible for contributing the non-

lithogenic fraction of metals in sediment. We determine the fractions of the metals in the

sediments from lithogenic and non-lithogenic sources, and then assess the contributions of

settling organic material and the supply of metals by diffusion from seawater after deposition

through further analysis of the non-lithogenic fraction.

We calculated the lithogenic concentration of each metal at each sample depth as the

product of the Al content and the Me/Al ratio for average continental crust [*Turekian and

Wedepohl*, 1961]. These data are shown as dashed lines in Figures 2 and 3. Although average

shale is a commonly used proxy for the lithogenic fraction of marine sediments and sedimentary

rocks [*Calvert and Pedersen*, 1993; *Piper*, 1994], the composition of terrigenous material can

vary regionally depending on the source rock [*Klump* et al.*, 2000]. The Sonoran Basin and

Range province of Mexico (the region adjacent to our study area) contains a mix of source rocks

that is more like crust than shale [*de Cserna*, 1989]. Using crust as the proxy for the lithogenic

fraction in our dataset produced fewer instances (compared to shale) where the calculated non-

lithogenic value is higher than the total metal concentration [*Nameroff* et al., 2002]. This choice

of reference material also appears to be more consistent with the regional geology.

Variable metal enrichments and depletions relative to crust are evident in both cores. In

NH15P (Fig. 2), the Ti content is similar to Ti concentrations reported for modern sediments

from the same region [*Nameroff* et al., 2002] and from the continental margin west of Baja

California [*Shimmield and Price*, 1986]. Iron is slightly depleted and Mn is strongly depleted

relative to lithogenic values. Copper is at or slightly enriched relative to lithogenic levels in

laminated sediments and depleted in homogeneous sediments, while Ba is essentially identical to

crustal values throughout the core. The highest Cd enrichments occur in Holocene (stage 1)

sediments. Uranium, Re and Mo share similar patterns of enrichment and their concentrations are

higher than crust throughout the core. All these metals have especially large enrichments in

stages 1 and 5. Vanadium is enriched in the laminated sediments.

In core NH22P, Ti and Mn concentrations are similar to those in NH15P, except for a Mn

peak at the isotope stage 5/6 transition in NH22P. Iron concentrations are at or above crustal

concentrations and generally are higher than in NH15P. Titanium is typically enriched in coarser

sediment size fractions [*Spears and Kanaris-Sotiriou*, 1976], suggesting that the sediment in both

piston cores is relatively fine grained. Iron and Mn oxides that form in surface sediments usually

are reductively dissolved as sediment is buried and oxygen is consumed [*Sawlan and Murray*,

1983; *Shaw* et al., 1990]. On the other hand, layers rich in Mn or Fe oxides can be preserved

under non-steady state conditions when the zone of reduction moves rapidly to a shallower level

[*Froelich* et al*.,* 1979*; Murray* et al*.,* 1984]. The concentrations of Fe and Mn in these layers

typically are much higher than concentrations in other layers. On this evidence, the absence of

significant enrichments of Fe and Mn in both piston cores suggests that steady state conditions likely have predominated over the past 140 kyr at the two sites investigated here.

Copper and Ba are significantly enriched relative to crust throughout NH22P and both metals have maxima in interglacial stages 1, 3 and 5. These metals frequently are used as proxies for organic matter input to sediments. Copper behaves like a micronutrient in the surface ocean, but is progressively enriched by scavenging in the deep sea [*Boyle* et al., 1977]. It is released from sediments during early diagenesis of organic matter [*Sawlan and Murray*, 1983; *Shaw* et al., 1990]. Barium is supplied to sediments as barite ($BaSO_4$) [*Dehairs* et al., 1980; *Bishop*, 1988]. Barite is stable under oxic conditions, and although it can dissolve when sulfate is depleted during sulfate reduction [*Church and Wolgemuth*, 1972; *Brumsack*, 1986; *Shimmield*, 1992; *Dean* et al., 1997], sulfate reduction alone is unlikely to control barite saturation [*McManus* et al., 1994]. The high Ba and Cu concentrations in NH22P compared to NH15P likely reflect the systematic increases in the concentration of these metals in sinking particles with increasing water depth [*Dymond* et al., 1992]. Similar patterns were observed for Ba off the Chilean margin [*Klump* et al., 2000].

The maximum Cd enrichment in core NH22P is reached in isotope stage 5. Uranium and Re share similar patterns of enrichment and their concentrations are higher than crust throughout NH22P. Molybdenum is slightly enriched relative to crust, while V concentrations are similar to those of crust.

The small or non existent nonlithogenic fractions of Ba (in NH15P), Mn, Fe, and Ti indicate that the concentrations of these metals appear to be controlled by aluminosilicate materials in both cores. In contrast, the nonlithogenic fractions of Cd, U, Re, Mo, and V(in

NH22P) are at least 2-3x greater than the potential contribution from aluminosilicate sources, suggesting that other processes likely control their distributions in sediment.

Smaller enrichments of Cd, U, Re, Mo and V in core NH22P compared to core NH15P suggest a smaller source of non-lithogenic material over the last 140 kyr as a result of lower particulate matter input and/or higher bottom water oxygen concentrations. To assess these options, we have examined the variation in the non-lithogenic fraction of the sediment samples in both cores. The non-lithogenic (NL) fraction is calculated as the difference between the total and lithogenic composition:

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

This calculation assumes that all Al is lithogenic rather than the result of scavenging [*Orians and Bruland*, 1986] or biogenic production [*Mackenzie* et al., 1978], and is a reliable indicator of aluminosilicate materials [*Calvert*, 1976]. These are reasonable assumptions given the near-shore location of this study area and likelihood of significant terrigenous input.

The concentrations of the non-lithogenic fractions of several metals (e.g., Cu, U, Mo, V and Re) correlate strongly with each other and with OC in both NH15P and NH22P (Tables 1 and 2), whereas Cd correlates with OC only in NH15P and Ba correlates positively with OC only in NH22P. The $\delta^{13}C$ and lignin biomarker data from both piston cores suggest that sedimented organic matter in both laminated and bioturbated sediments is overwhelmingly marine [*Ganeshram* et al., 1999]. These correlations therefore could reflect direct input of plankton material enriched in metals or they could result from the indirect effect of organic carbon on sediment redox state. High organic input can make the sediments more reducing and thus more likely to sequester the redox sensitive metals (except perhaps Ba) [*Morford and Emerson*, 1999].

To evaluate whether the non-lithogenic metal enrichments are attributable to variations in biologic productivity and input of biogenic material over time, we compare the concentrations with literature estimates of the trace metal content of marine organic matter. The available data from studies of plankton, colloids, sinking particles, and suspended particulate matter collected by large volume filtration in several locations, as well as sediment trap data from the study area [*Nameroff* et al., 2002], are presented in Table 3. The range of values reported reflects a wide range of plankton species, production rates, food web structure, and ambient metal concentrations in the various locations, all of which could affect the metal content of marine organic matter [e.g. *Cullen* et al., 1999]. The Mexican margin data represent only one time point in what is surely a highly variable system, but they do provide an indication of the local plankton source. Comparison of these data to the other studies from the literature, although qualitative, shows relatively small differences except in the case of Mn.

Changes in the non-lithogenic concentrations of metals in piston cores NH15P and NH22P over time are shown in Figure 4. The range of metal concentrations for biogenic matter and Mexican margin sediment trap samples (Table 3) are indicated on the top axis of the figure. The non-lithogenic Ti concentration is generally less than Mexican margin sediment trap and biogenic matter concentrations while Fe in both cores is close to the organic matter concentration and Mexican margin sediment trap concentrations. The negative values of non-lithogenic Mn in both cores are consistent with the conclusion that Mn of plankton origin is not preserved in the sediment. Copper and Ba concentrations in NH15P are slightly lower than the range of published values in plankton. Enrichments of Cu and Ba in NH22P may reflect increased addition with water column depth by addition through scavenging and barite formation, respectively, to settling particles. Variability in the delivery of plankton material therefore could explain all of

the changes in Cu and Ba concentrations in both cores. Although the range of published Cd concentrations in plankton is large, it suggests that plankton could contribute a significant amount of this metal to the sediment. Higher non-lithogenic U in both cores compared to biologic matter suggests this metal is mostly added after deposition. Molybdenum and V also are clearly enriched relative to a plankton origin in NH15P, but not in NH22P. If the Black Sea deep-water sediment trap data are representative for Re, this metal also appears to be added after deposition. Rhenium has not been measured in plankton-rich samples collected from the open ocean. *Crusius* et al. [1996] found a flux-weighted average of 6.5 ppb Re in one deep-water sediment-trap sample from the Black Sea. Although not directly comparable to other data, it suggests that Re is not likely enriched in biologic matter.

Ganeshram et al. [2002] found that sediment P concentrations averaged 0.33 wt% in the laminated layers of core NH15P. They proposed that carbonate fluoroapatite (CFA) precipitated in these layers as disseminated grains. A number of studies [summarized in *Calvert*, 1976 and *Altschuler*, 1980] have shown that the CFA lattice incorporates many trace metals, including Cd, Cu, Mo, U, and V, where their concentrations may be significant (average concentration Cd: 18 ppm, Cu: 75 ppm, Mo: 9 ppm, U: 120 ppm, V, 120 ppm; *Altschuler,* 1980]. If 25% of the sedimentary P in NH15P is incorporated into CFA [*Ganeshram* et al., 2002], then authigenic formation of this mineral could account for a significant fraction of the total sediment enrichments of these metals observed in these layers.

Our analysis shows that enrichments and depletions of several trace metals vary over glacial-interglacial timescales. Variability of Ti, Fe and Mn may be attributed to variability in the aluminosilicate fraction. Variations in the flux of plankton material over time are a plausible explanation for the distributions of Cu, Ba and Cd in both cores. Variability in U, Mo, V, and Re,

on the other hand, cannot be explained solely by direct addition of plankton to sediments. The indirect effect of the burial flux of organic material on sediment redox state [e.g., *Froelich* et al., 1979; *Emerson* et al., 1985] appears to be a more important control on the distributions of these metals.

Changes in sediment redox state over glacial-interglacial time scales. We assess the nature and extent of the changes that occurred in sediment redox state over time by examining changes in the depth at which Re and Mo precipitated in the sediments ("removal depth") and in the Re/Mo ratio. *Crusius* et al. [1996] proposed that estimates of the removal depth of these two metals could be used in combination with the authigenic Re/Mo ratio to determine whether a sedimentary environment was oxic, suboxic, or anoxic. Under this scheme, deep Re and Mo removal depths (calculated from Fick's first law and the accumulation rate of the metal in sediment) would imply an oxic environment. Shallow Re and Mo removal depths would imply an anoxic environment, with suboxic environments falling between these two limits. The Re/Mo ratio also would vary with the metal concentrations. Oxic conditions would be recorded as low Re and Mo concentrations with Re/Mo close to the crustal ratio (0.3 ng μg^{-1}). The ratio would increase in suboxic sediments where Mn oxide is not present because of Re enrichment relative to Mo. In anoxic sediments, the concentrations of both Re and Mo are high and the Re/Mo ratio would decrease to the ratio of seawater (~0.7 ng μg^{-1}) because both metals are quantitatively removed.

Nameroff et al. [2002] found that Re and Mo concentrations, removal depths, and Re/Mo ratios did not lead to consistent conclusions about redox conditions on the modern Mexican margin. They suggested that the scheme proposed by *Crusius* et al. [1996] only was useful for determining whether oxic or completely anoxic conditions were present. We therefore use the

approach of *Crusius* et al. [1996] to determine if the depositional environments recorded by the downcore metal profiles in cores NH22P and NH15P were oxic or anoxic.

We calculated removal depths (z) of Re and Mo for both cores assuming that sea water concentrations of these metals did not change appreciably over glacial to interglacial time [*Emerson and Huested*, 1991; *Morford and Emerson*, 1999]. Neglecting burial of pore water,

$$z = \{\varphi * SW * D_{eff}\} / \{Me_{NL} * S * \rho * (1 - \varphi)\} \tag{2}$$

where φ is sediment porosity from water content analysis, SW is the metal's sea water concentration, S is the sedimentation rate (cm kyr^{-1}), ρ is sediment density (2.4 g cm^{-3}) and D_{eff} (cm^{2} kyr^{-1}) is the molecular diffusion coefficient. Given the relatively coarse sampling interval for trace metals, correction for age of the host sediment and age of non-lithogenic enrichment would not change substantially the interpretation of the trace metal record. The uncertainties in each term in equation 2 are a more significant limit on the use of removal depths to characterize absolute change in sediment redox state [*Nameroff,* 1996].

In core NH15P, Re removal depths in glacial (2-7 cm) and interglacial intervals (2-10 cm) were comparable (Figure 5), whereas the Mo removal depths were 15-44 cm in glacial sediments and 8-44 cm in interglacial sediments. The Re/Mo ratios ranged from ~2 to ~8 ng μg^{-1} and the average ratio in glacial and interglacial horizons was the same, namely ~4 ng μg^{-1}. In core NH22P, Re removal depths ranged from 6-35 cm in glacial intervals and 2 – 24 cm in interglacial intervals. Molybdenum removal depths were more than 43 cm, and in some sediments sections were a factor of 3 higher, suggesting that seawater was not a significant source of Mo at this water depth. The Re/Mo ratios in interglacial and glacial intervals were comparable, falling between 1 and 6 ng μg^{-1}.

The differences between Re/Mo ratios and Re and Me removal depths within each core over time are smaller than the differences between the cores. This observation suggests that changes in redox state that occurred at each core depth were smaller than the differences in redox state that were a function of the relative position of the cores in the water column. In other words, the sediments in the shallower core (NH15P) appear always to have been more reducing than those of NH22P because the shallower core location was always either in contact with or closer to the depth of the OMZ.

Because the sediments in NH15P likely were in contact with or closer to the depth of the OMZ, changes in trace metal removal depths in this core are a better indicator than core NH22P of the magnitude of changes in the intensity of the oxygen minimum zone over glacial-interglacial timescales. Removal depths of Re and Mo and Re/Mo ratios throughout NH15P are comparable to estimates for Recent sediments within the modern OMZ at this site [*Nameroff*, 1996; *Nameroff* et al., 2002]. In contrast, significant variations in the rate of water column denitrification have been inferred from variations in $\delta^{15}N$ (Figure 2) [*Ganeshram* et al., 1995]. This comparison points to the sensitivity of $\delta^{15}N$ as a redox indicator and of the delicate balance between denitrification and water column oxygen concentrations. *Devol* [1978] estimated that denitrification begins in the water column of the ETNP when bottom water oxygen concentrations are < 2 μM. Hence, rather small changes in bottom water oxygen or the flux of carbon could substantially alter the rate of denitrification in the water column.

To constrain the observed changes in redox state, we compare these data to Re removal depths and Re/Mo ratios for other locations reported by *Crusius* et al. [1996] and to the seawater Re/Mo ratio (Figure 5). The Black Sea and Saanich Inlet both have anoxic water columns and bottom sediments. The Arabian Sea samples were collected from a region where both the

sediment and water column are suboxic. Our piston core data are most similar to the Japan Sea, which has an oxic water column and suboxic sediments. All Re/Mo values in the piston cores are higher than the sea water Re/Mo ratio. Given the limitations of this approach for distinguishing among suboxic depositional environments [*Nameroff* et al., 2002], these results suggest that the water column on the slope off NW Mexico probably was not anoxic over the past 140 kyr.

Our analysis of Re and Mo removal depths and Re/Mo ratios in sediments suggests that the sediments at 420 m depth off Mazatlán were more reducing because they were either in contact with or closer to the depth of the OMZ over the last 140 kyrs. Variability in Re/Mo ratios and in Re and Mo removal depths implies that the intensity of the OMZ has varied over glacial-interglacial cycles, but the OMZ was evidently never completely anoxic over this time period.

Glacial time-scale changes in productivity and ventilation. The observed changes in trace metal distributions in the piston cores studied here could be attributed to changes in regional export productivity, changes in ocean circulation, or some combination of both processes. Which of these of these two processes was dominant has been the subject of considerable debate. For example, *Lyle* et al. [1992], *Dean* et al. [1997], and *Ganeshram and Pedersen* [1998] attributed lower accumulation rates of biogenic Ba, organic carbon, and silica during glacial stages in the sediments of the ETNP and the California margin to reduced productivity. Changes in the wind-driven upwelling rate could decouple productivity from ocean circulation and the chemical composition of upwelled water. *Ganeshram and Pedersen* [1998] argued that the reduced contrast between land and sea temperatures during glacial stages weakened upwelling-favorable winds along the west coast of North America, which consequently diminished the supply of nutrients to surface waters, thereby causing a decrease in productivity.

Other evidence suggests that enhanced Pacific Intermediate Water (PIW) ventilation reduced the intensity of the OMZ during glacial stages due to enhanced production of young intermediate water in either the North Pacific [*Keigwin* et al., 1992] or the Equatorial Undercurrent (EUC). Reduced flux of older, less-oxygenated water into the Pacific as a consequence of reduced north Atlantic deep water formation [*Behl and Kennett*, 1996] also could reduce OMZ intensity. Sediment records from the Santa Barbara Basin suggested that during the last glacial period, oxygen levels in PIW may have been 60-80 µmol/kg lower than today [*Stott* et al., 2000]. *Keigwin and Jones* [1990], *Sancetta* et al. [1992], *Sancetta* [1995], *Kennett and Ingram* [1995], *Behl and Kennett* [1996], *van Geen* et al. [1996], *Pride* et al. [1999], and *Zheng* et al. [2000b] examined temporal and spatial variability of sediment geochemistry in the California Current upwelling system and the Gulf of California and suggested that changes in productivity and carbon flux were not the primary reason for variable oxygen levels over time.

Downcore trace metal data reported here provide additional insight into glacial to interglacial changes in water column oxygen content and export productivity. To evaluate the importance of changes in productivity on sediment redox state, we first constrain potential changes in the flux of carbon to the sea floor. We then calculate the effect of changes in productivity on trace metal removal depth. Differences between observed and calculated trace metal removal depths are attributed to changes in ventilation. This relatively simple approach allows us to assess the relative importance of each process.

Variations in the concentrations of organic carbon and Ba suggest that export production varied over glacial-interglacial timescales. The use of organic carbon accumulation rates to estimate paleoproduction [e.g., *Muller and Suess,* 1979*; Sarnthein* et al., 1988] is not necessarily reliable. A major variable used to establish these algorithms, the bulk sedimentation rate, varies

over many orders of magnitude in the ocean, while the OC contents of the same sediments is much less variable. *Middelburg* et al. [1997] demonstrated that randomly generated carbon burial rates correlate spuriously with sediment accumulation rates when these values span several orders of magnitude. We therefore estimate paleoproduction from biogenic Ba data using the method proposed by *Dymond* et al. [1992] and refined by *Francois* et al. [1995] to calculate changes in new production, P_{new}, over glacial to interglacial time:

$$P_{new} \ (\text{gC m}^{-2}\text{y}^{-1}) = 1.95 \times (F_{bioBa})^{1.41} \qquad (3)$$

In this equation, F_{bioBa} is the flux of biogenic barium (mg m^{-2}y^{-1}) estimated from the non-lithogenic Ba concentrations in sediment. Because barite may dissolve under reducing conditions [*Church and Wolgemuth*, 1972], we consider only the Ba data in NH22P. The coherence between the accumulation rates of organic carbon and biogenic Ba and Cu in NH22P [*Ganeshram and Pedersen*, 1998] indicates that the Ba concentration in the sediment at this depth probably does not suffer from severe dissolution artifacts.

The estimated new production for interglacial times (isotope stages 1, 3, and 5) is 31 ± 16 mol C m^{-2}y^{-1} and is 18 ± 7 mol C m^{-2}y^{-1} during glacial periods (isotope stages 2, 4, and 6). Additional error that stems from an imperfect understanding of the relationship between the flux of biogenic Ba to the sediments and new production is small relative to the range of the new production estimates. The calculation of new production (25 mol C m^{-2} y^{-1}) from the Ba content of Recent (0-3 kyr) NH22P sediments is in excellent agreement with the estimate of net annual primary productivity (28 mol C m^{-2} y^{-1}) for the modern ETNP from satellite radiometer data [*Longhurst* et al., 1995].

The flux of carbon to the sea floor resulting from the estimated new production can be calculated from a predictive equation of *Sarnthein* et al. [1988]:

$$F_c = 20.563 * (P_{new})^{0.6648} * z^{-0.5537} \qquad (g\ C\ m^{-2}\ y^{-1}) \quad (4)$$

Sarnthein et al. [1988] showed this relationship is robust over a range of new production data ($r = 0.92$). Using our P_{new} estimates, the average interglacial flux of carbon to the sea floor was 1.2 ± 0.4 mol C $m^{-2}y^{-1}$ and was 0.9 ± 0.2 mol C $m^{-2}y^{-1}$ during glacial stages.

The diagenesis of exported material at the sea floor affects trace metal removal depths via the consumption of oxygen in the sediment. The relationship between diagenesis and trace metal removal depth is not completely understood. However, models have been developed that link export production and consumption of oxygen in the sediment. Model results and literature data can be used to develop a relationship between oxygen consumption and trace metal removal.

The magnitude of the change in sediment redox state that results from a change in new production can be assessed using the relationship between carbon flux at the sediment-water interface (F_c mol $cm^{-2}\ s^{-1}$), bottom water oxygen (O_2°, 1×10^{-9} mol cm^{-3}) and depth of oxygen zero (z cm) in the sediment pore water [*Emerson*, 1985]:

$$(\varphi * O_2^{\circ} * D_s * ß)/(\gamma * F_c) = (e^{ßz} + e^{-ßz} - 2)/(e^{ßz} - e^{-ßz}) \qquad (4)$$

D_s is the sediment diffusion coefficient for oxygen at 1°C (6×10^{-6} $cm^2\ s^{-1}$), and γ is the stoichiometric ratio of moles oxygen reduced to moles carbon oxidized (138/106). Because the oxygen flux at 420 m is not detectable, we again rely on NH22P data. The term $ß = (k/K)^{1/2}$ captures the effects of bioturbation, K (5×10^{-9} $cm^2\ s^{-1}$, based on similarity of oxygen concentrations at 2025m and at MANOP M), and the carbon degradation rate constant, k. Because the sediment carbon contents in NH22P are high (between 1.7 and 4.6 wt%) and at the

upper end of values that Emerson used to develop his model, we selected a slow degradation rate, 1×10^{-10} s^{-1}. Although this value is somewhat arbitrary, it is the relative difference between oxygen penetration depth in glacial and interglacial sediments that is important for this exercise. Using a constant degradation rate eliminates uncertainty in the assessment of relative changes. Model calculations suggest that given the estimated 40% change in the flux of carbon to the sea floor, the oxygen penetration depth, z, changed by less than one cm.

The distribution of the trace metals in core NH22P records changes in sediment redox state induced by changes in both productivity and ventilation. To assess which variable might be more important, we can compare the magnitude of productivity-induced change in oxygen penetration depth to the total change in oxygen penetration depth inferred from trace metal data. We use literature data to develop a relationship between the accumulation of Re and U in sediment and the depth at which pore water oxygen is completely consumed in the sediment. We selected these metals because they have the largest non-lithogenic enrichments in NH22P (49% for U and 99% for Re, on average). Reduction potentials for Re and U predicted from thermodynamic relationships are close to that of Fe [*Davenport* et al., 1969; *Langmuir*, 1978]. Sediment studies suggest that both these metals may accumulate in sediments at the depth of iron reduction [*Klinkhammer and Palmer*, 1991; *Colodner* et al., 1993].

We use pore water data to develop a relationship between oxygen penetration depth and Fe reduction, which serves as a proxy for precipitation of Re and U (Figure 6). Since the availability of these data is limited, we also use NO_3^- and Mn pore water data where possible. Complete consumption of nitrate in pore water is an indicator that iron reduction has started [*Froelich* et al., 1979]. Similarly, Mn reduction begins after complete consumption of pore water oxygen. Because pore water chemistry is well understood, the greatest limits on this proxy are

the uncertainty in the relationship between Fe reduction and Re and U precipitation in the
sediment [*Nameroff,* 1996] and the calculation of the metal precipitation depth (equation 2).

The proxy relationship is significant (r=0.90) and suggests that the depth dependence
between oxygen zero and the onset of metal reduction is not constant (slope is not 1:1). The
implication is that the trace metal removal depth will be less sensitive to changes in redox state
as sediments become less reducing. The observed, average differences in Re and U precipitation
depths between each glacial-interglacial couple in NH22P are 7 and 10 cm, respectively
(equation 2). From Figure 6, we find that the oxygen penetration depth would need to change
about 3 cm to induce this difference in metal precipitation depths.

Our results provide additional insight into changes that occurred in the California Current
system over glacial to interglacial stages. Comparison of indicators of productivity (% opal,
%OC, and Ba/Al) and denitrification in sediments ($\delta^{15}N$) from the Mexican, California and
Oregon margins, suggests that both oxygen input by the Equatorial Undercurrent and local
organic matter flux have controlled denitrification rates (and by inference subsurface dissolved
oxygen concentrations), in the eastern tropical North Pacific over the last 120 kyr [*Kienast* et al.,
2002]. Indicators of primary production and denitrification are in phase off central North
America, but changes in productivity lag changes in denitrification in Mexican margin sediments
by several kiloyears. The fact that the proxies are slightly out of phase off Mexico shows that
both factors, ventilation and organic flux, are involved in setting the oxygen concentrations at the
depth of the OMZ. The magnitude of change in oxygen zero depth inferred from trace metal
removal depths in the Mexican margin sediment is significantly larger than the change in oxygen
zero depth inferred from Ba data. The difference in new production between glacial and
interglacial periods would need to be an order of magnitude larger in order for the relative impact

of changes in productivity to approach that of changes in ventilation. Trace metal data therefore suggest that, in addition to a decrease in surface productivity, PIW ventilation also had to intensify to increase removal depths of Re and U in glacial sediment to the extent observed in the sediment record. Changes in ventilation appear to be the more important variable.

CONCLUSIONS

Patterns of enrichment and depletion of redox-sensitive trace metals in Mexican continental margin sediments reflect several processes at work in the ocean and in the sediment. Concentrations of Cd, Cu, U, Mo, V and Re in sediments in contact with the OMZ are significantly higher in interglacial stage sediments compared to glacial stage sediments and vary in a similar pattern. Further analysis of the distributions of these metals confirms the important role of biological production in delivering metals to the sediment. Comparison of the non-lithogenic fraction of trace metals to their estimated contribution from plankton suggests that organic matter likely is a major source of Cu, Ba, and Cd. However, sediment redox state appears to be a more important control on the distributions of U, Re, Mo, and V.

Changes in the depth at which Re and Mo precipitated in the sediments and in the Re/Mo ratio suggest that the intensity of the eastern tropical North Pacific's OMZ varied over the past 140 kyr. Re and Mo removal depths were shallower and Re/Mo ratios were lower in core NH15P than NH22P, suggesting that NH15P sediments consistently were more reducing because they were either in contact with or closer to the depth of the OMZ over the last 110 kyr. Relatively small differences in Re and Mo removal depths and Re/Mo ratios in sediments in the shallower core contrast strongly with the significant variations in the rate of water column denitrification

inferred from $\delta^{15}N$. The trace metal data underscore the delicate balance between denitrification and water column oxygen concentrations.

Variability in sediment redox state could be attributed to changes in regional export productivity, changes in ocean circulation, or some combination of both processes. A paleoproductivity reconstruction from organic C data suggests that productivity changes averaged 17% over glacial to interglacial cycles. Model results suggest that the oxygen penetration depth, an indicator of sediment redox state, would have changed less than 1 cm as a result of the change in productivity. Changes in oxygen penetration depth estimated from Re and U removal depths are significantly larger, suggesting that changes in ventilation are a more important control on sediment redox state.

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Table 1. Pearson-coefficient correlation matrix for non-lithogenic fraction in NH15P (n = 47). Statistical significance (p>0.05; Taylor [1982]) is indicated when |r| > 0.27 and indicated in boldface.

	Al	Ti	Fe	Mn	OC	Cu	Ba	Cd	U	Mo	V	Re
Al	**1.00**	**0.47**	**0.80**	**0.59**	-0.09	-0.01	**0.53**	-0.15	0.15	0.11	0.23	-0.02
Ti		**1.00**	**0.69**	**0.42**	-0.16	**-0.32**	**0.41**	-0.08	-0.05	-0.08	0.04	-0.12
Fe			**1.00**	**0.77**	0.04	0.00	**0.39**	-0.03	0.00	0.04	0.20	0.07
Mn				**1.00**	0.03	0.04	**0.30**	0.09	-0.14	-0.11	-0.06	0.05
OC					**1.00**	**0.81**	**-0.48**	**0.66**	**0.52**	**0.66**	**0.76**	**0.96**
Cu						**1.00**	**-0.60**	**0.47**	**0.59**	**0.71**	**0.73**	**0.81**
Ba							**1.00**	-0.21	**-0.32**	**-0.37**	**-0.35**	**-0.48**
Cd								**1.00**	0.18	**0.42**	**0.40**	**0.64**
U									**1.00**	**0.78**	**0.77**	**0.54**
Mo										**1.00**	**0.79**	**0.69**
V											**1.00**	**0.74**
Re												**1.00**

Table 2. Pearson-coefficient correlation matrix for non-lithogenic metals in NH22P (n = 41). Statistical significance (p>0.05; Taylor [1982]) is indicated when $|r| > 0.30$ and indicated in boldface.

	Ti	Fe	Mn	OC	Cu	Ba	Cd	U	Mo	V	Re
Al	**0.33**	0.20	0.04	0.12	**0.35**	**0.38**	**0.47**	0.17	**0.37**	**0.36**	0.16
Ti	**1.00**	**0.75**	0.05	0.22	**0.49**	**0.39**	0.29	0.29	-0.12	**0.62**	0.20
Fe		**1.00**	-0.11	**0.36**	0.57	**0.50**	0.16	0.25	-0.17	**0.69**	0.23
Mn			**1.00**	**-0.79**	**-0.46**	**-0.47**	**0.33**	-0.08	-0.19	**-0.37**	**-0.38**
OC				**1.00**	0.67	**0.59**	-0.07	**0.34**	0.31	**0.58**	**0.55**
Cu					**1.00**	**0.80**	0.24	**0.32**	0.19	**0.77**	**0.41**
Ba						**1.00**	0.09	0.24	0.16	**0.57**	**0.36**
Cd							**1.00**	**0.37**	0.29	0.30	0.20
U								1.00	0.29	**0.42**	**0.34**
Mo									**1.00**	0.11	0.16
V										**1.00**	**0.33**
Re											**1.00**

Note: The leftmost diagonal entry 1.00 for Al appears before the Ti column; each subsequent row begins with a diagonal 1.00 value.

Table 3. Estimates of plankton composition and other biogenic-rich samples from the literature. The non-lithogenic correction was not made for the literature samples so they represent upper limits of the biogenic component. The lithogenic fraction was subtracted from the Mexican margin data. All compositions given as ppm.

		Al	Ti	Fe	Mn	Cu	Ba	Cd	Mo	V	U
Mexican margin	Nameroff et al. [2002]	0	2000 ± 1000	3500 ± 100	982 ± 95	38 ± 13	113 ± 12	2.58 ± 2.00	4.53 ± 1.62	-12.6 ± 4.1	-0.78 ± 0.37
Gulf of California	Brumsack [1986]	-	-	-	-	11	-	12	2	3	-
Monterey Bay, Baja California	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	-
Tropical Atlantic, <100 m	Sherrell and Boyle [1992]	9.7 to 1183	-	318 to 941	17 to 117	8 to 23	-	0.7 to 1.6	-	-	-
Open ocean	Collier and Edmond [1984]	-	-	-	5.2 to 9.0	8 to 14	-	16 to 54	-	-	-
Santa Barbara Basin, Northwest Atlantic	Zheng et al. [2000a, 2002]	-	-	-	-	-	-	-	1.3	-	1.3
Gulf of Mexico, Mid-Atlantic Bight, Galveston Bay	Guo et al. [2000]	8.5 ± 7.6 7.8 ± 3.6 16.8 ± 16.5	- - -	145 ± 35 536 ± 807 309 ± 228	1.4 ± 1.0 5.06 ± 3.70 5.09 ± 3.45	15.4 ± 4.8 13.3 ± 4.2 47.4 ± 18.3	0.49 ± 0.16 1.24 ± 0.81 26.3 ± 44.5	0.16 ± 0.08 0.82 ± 0.76 0.193 ± 0.049	- - -	1.28 ± 0.94 1.96 ± 2.63 2.53 ± 2.13	- - -
North Atlantic	Kuss and Kremling [1999]	238 ± 71	-	56.6 ± 16.2	19.8 ± 2.2	6.1 ± 1.0	-	13.4 ± 2.2	-	-	-

Figure captions.

Figure 1. Locations of piston cores NH15P (420m water depth; 22º 4.0'N, 106º 28.8'W) and NH22P (2025m water depth; 22º 31.1'N, 106º 31.1'W) collected during the 1990 R/V *New Horizon* cruise.

Figure 2. Total concentration of Al, Ti, Fe, Mn, organic C, Cu, Ba, Cd, U, Mo, V, and Re in NH15P sediment as a function of calendar age. Glacial stages indicated by stippled pattern. Laminated intervals indicated by the stripes to the right of each block of plots. Dashed reference line shows the expected lithogenic concentrations using crust [*Turekian and Wedepohl*, 1961] as a reference. Isotope stages indicated by numbers at the right side of the $\delta^{18}O$ profile. $\delta^{18}O$, organic C, and $\delta^{15}N$ data from *Ganeshram* [1996].

Figure 3. $\delta^{18}O$, $\delta^{15}N$, total concentration of Al, Ti, Fe, Mn, organic C, Cu, Ba, Cd, U, Mo, V, and Re in NH22P sediment as a function of calendar age. Glacial stages indicated by stippled pattern. Laminated intervals indicated by the stripes to the right of each block of plots. Dashed reference line shows the expected lithogenic concentrations using crust [*Turekian and Wedepohl*, 1961] as a reference. Isotope stages indicated by numbers at the right side of the $\delta^{18}O$ profile. $\delta^{18}O$, organic C , and $\delta^{15}N$ data from *Ganeshram* [1996].
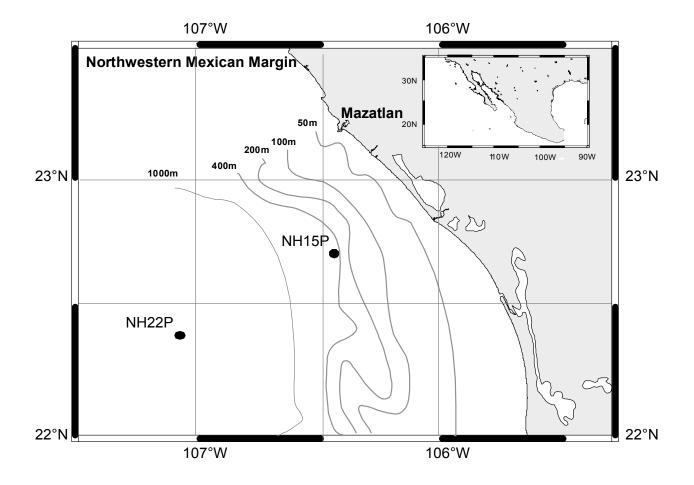
Figure 4. Comparison of non-lithogenic metal concentrations in NH15P (■) and NH22P (●) sediment with the range of non-lithogenic metal concentrations reported in Table 3 for biogenic matter (x) and Mexican margin sediment trap material (□). The mean value for biogenic matter is plotted and the error bars indicate the range of values in Table 3. The non-lithogenic

concentrations of metal in the Mexican Margin data were calculated using Eqn. 1 and the metal concentrations in average crust.
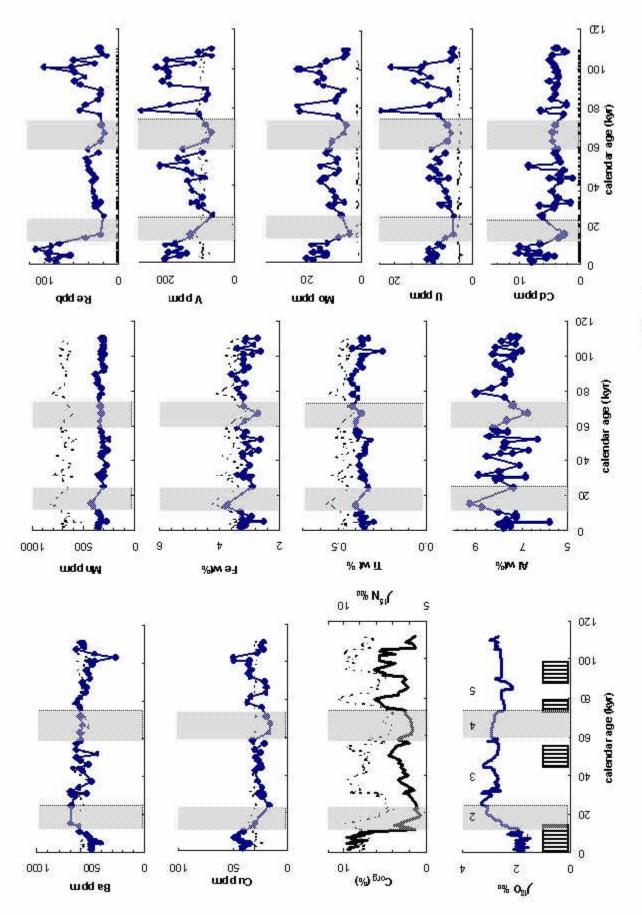
Figure 5. Comparison of changes in the Re removal depth (cm) and Re/Mo ratio (ng ug^{-1}) in glacial and interglacial sediments in the piston cores. Other data reported in *Crusius* et al. [1996] are indicated for comparison.
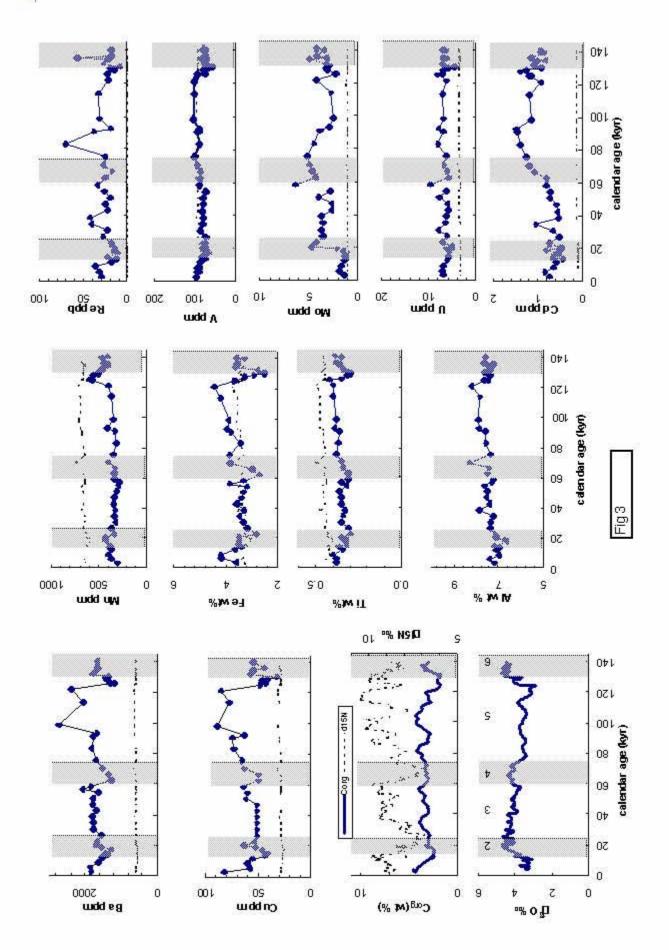
Figure 6. Observed relationships between the depth of the onset of Mn remobilization (assumed to coincide with the depth of O_2 zero) and the depth of NO_3 zero (assumed to coincide with the Fe remobilization depth). Data are from *Rutgers van der Loeff* [1990] (□), *Murray and Kuivila* [1990] (●), *Sawlan and Murray* [1983] (X), and *Emerson* et al. [1985] (▲).
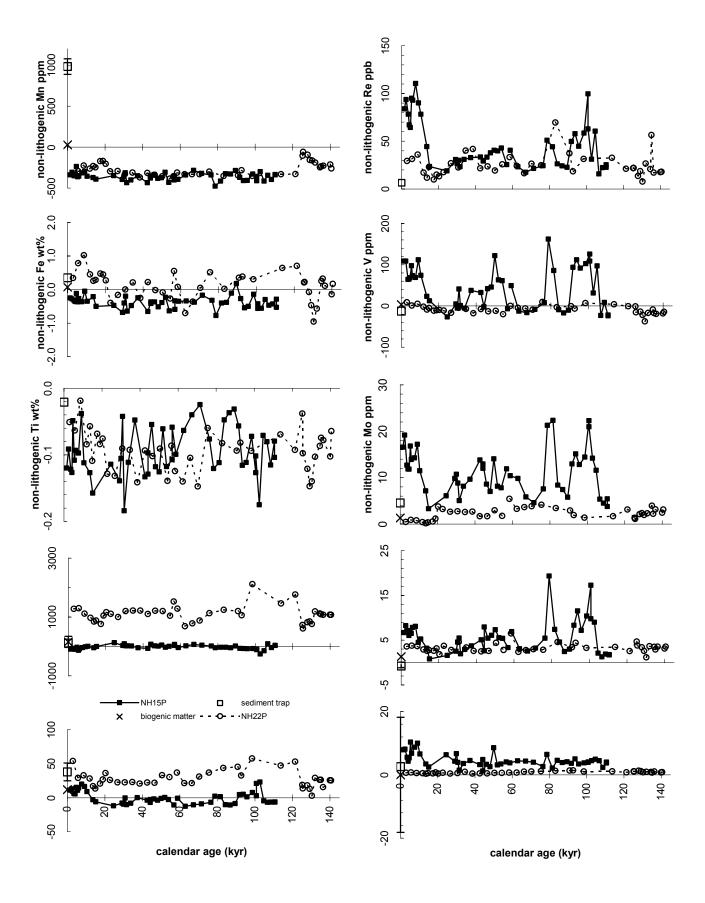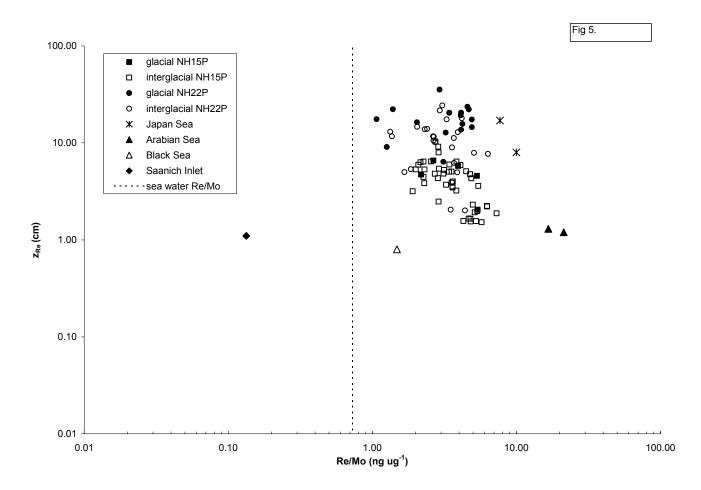
Figure 1

Fig 2

Fig 3

Fig 5.

100.00

■ glacial NH15P
□ interglacial NH15P
● glacial NH22P
○ interglacial NH22P
✳ Japan Sea
▲ Arabian Sea
△ Black Sea
◆ Saanich Inlet
---- sea water Re/Mo

z_{Re} (cm)

10.00

1.00

0.10

0.01

0.01   0.10   1.00   10.00   100.00

Re/Mo (ng ug^{-1})

Fig 6