

# Redox Gradients in the Vicinity of the Santa Barbara Basin: Application of Techniques Developed within the San Francisco Bay Toxics Study

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## ABSTRACT

Methodology for trace sulfide determinations, developed within the San Francisco Bay-Estuary Toxics Study, was applied in an investigation of redox gradients in the suboxic Santa Barbara Basin. Water-column distributions of dissolved oxygen, sulfide and nitrate, and pore-water distributions for dissolved sulfide and iron indicate very different redox conditions between the coring sites within the Santa Barbara Basin and its vicinity, and provide a contrast to the more-oxidizing conditions just north of the basin's sill. For example, pore-water sulfide concentrations exhibited a range of 5 orders of magnitude, indicating a primary sulfide source from the deep basin (that is from depths greater than 500 m). An estimate for sulfide flux out of the basin using water-column data ( $9$  to  $138$   $\text{nmoles}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ) is consistent with spatial and temporal variability of pore-water gradients near the sediment-water interface ( $-4$  to  $13,000$   $\text{nmoles}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ). This variability in pore-water gradients affects the authigenesis and mobility of trace elements in the Santa Barbara Basin.

## INTRODUCTION

A number of reasons motivate interest in coastal-zone redox gradients. First, there is paleoceanographic interest in how these redox gradients are established as a result of changes in water column productivity and subsequent deposition, and also as a result of ocean ventilation due to natural hydrodynamic events (Thunell and others, 1995; Zheng, unpublished doctoral dissertation). Of related interest are the effects of redox gradients on nutrient cycling (Murray and others, 1978; Klump and Martens, 1981; Thamdrup and others, 1994a). Yet another reason is to understand how the authigenic formation of metals in the ocean sediments proceeds (Calvert and Pederson, 1993; van Geen and others, 1995; Piper and Isaacs,

1996; Zheng, unpublished doctoral dissertation). Finally, there has been some consideration of waste disposal strategies (some involving radionuclides) for deposition on the sea floor. One obvious management question would be, "What processes are going to control the mobility of any toxic or hazardous substance?" One might expect that the partitioning and hence mobility of many inorganic and organic solutes would be affected by the range of redox conditions in these environments.

Santa Barbara Basin is considered asuboxic, that is, intermediate between conditions in permanently anoxic systems such as the Black Sea and oxygenated open-ocean water. Water-column hydrogen sulfide ( $\text{H}_2\text{S}$ ) concentrations range from  $<1$  to  $\sim 20$   $\mu\text{M}$  in

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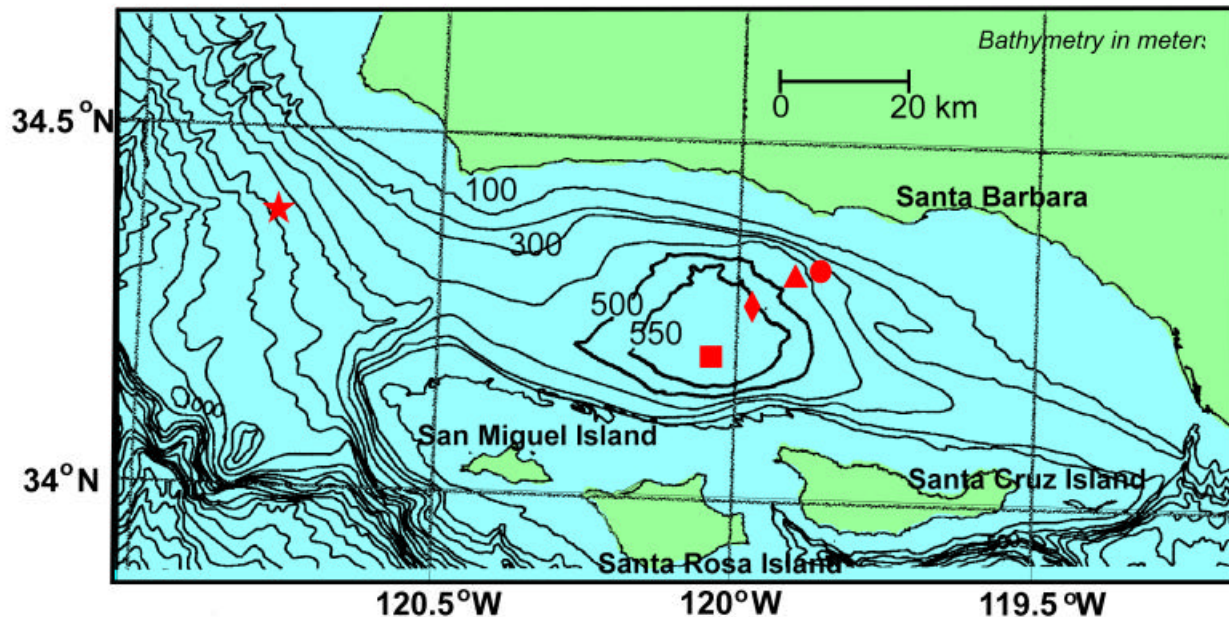


Figure 1. Bathymetric map of the coning and hydrocast stations within the basin at 500 m (square), 550 m (diamond), 430 m (triangle), and 340 m (circle), and outside the basin (590 m, star). Symbols on this map are used in later figures to indicate data from corresponding sampling locations.

seasonally anoxic marine systems such as Saanich Inlet (Richards, 1965; Emerson and Husted, 1991). In previous studies in the Santa Barbara Basin using standard colorimetric procedures, micromolar sulfide concentrations were measured in pore waters in the basin sediments at a distance of <10 cm below the sediment-water interface (Reimers et al, 1990). Such observed gradients suggest a sulfide flux into the water column

In this study, a voltammetric technique developed for use in the oxic water column of San Francisco Bay (Kuwabara and Luther, 1993) was used to measure total dissolved (0.2 $\mu$ m-filtered) sulfides in pore waters and in the water column aboard ship during three separate cruises conducted between February 1995, and April 1997. Dissolved-oxygen and nitrate profiles in the water column inside and outside (northwest) of the basin, as well as iron pore-water profiles also are presented to facilitate the interpretation of the sulfide data. Association of sulfide gradients with authigenic metal production is discussed. It is, to our knowledge, the first instance where both water-column and pore-water sulfide gradients are presented together, thus allowing closer examination of interfacial processes.

## METHODS

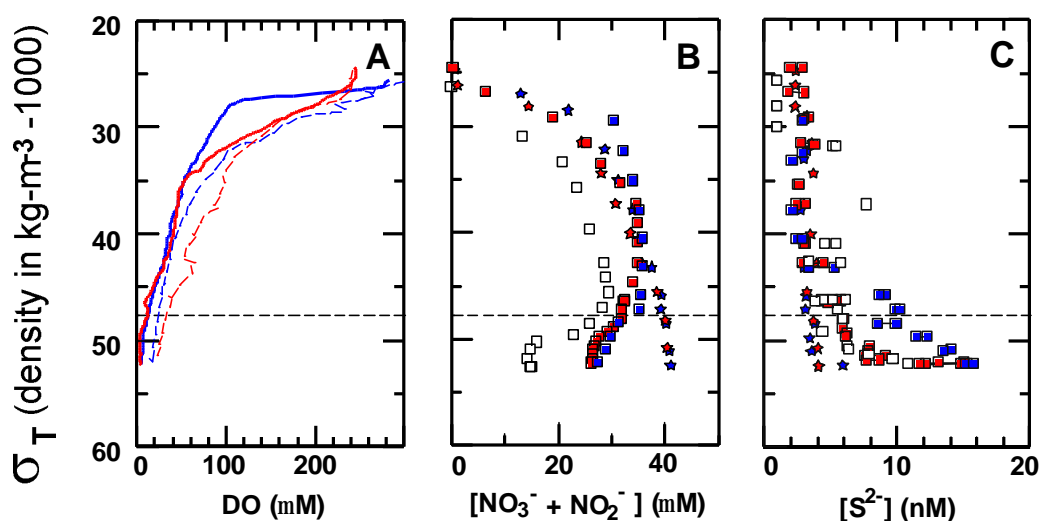
In February 1995, the Research Vessel (R.V.) Robert Gordon Sproul was used to obtain Soutar box cores from sites within the Santa Barbara Basin at 590 and 550 m (fig. 1). In November and December 1995, and later in April 1997, the R.V. Pt. Sur was used to sample 4 sites (590, 550, 430 and 340 m) within the basin and an exposed site to the northwest of the basin = sill (fig. 1). From the Pt. Sur, a multicorer was used to collect 8 simultaneous cores at a site with each deployment. The cores were processed under nitrogen in a refrigerated container at  $6 \pm 2$  °C. Hydrocasts were also taken at the 590 m deep-basin site and northwest of the basin to provide comparative water column information.

Dissolved oxygen (DO) was determined using a dissolved oxygen probe mounted on the sampling rosette on R.V. Point Sur cruises only. To complement oxygen-probe determinations, discrete micro-Winkler DO analyses were also performed on bottom waters (Broenkow and Cline, 1969). Seawater density was calculated from pressure, temperature, and salinity measurements (i.e., data from the probe assemblage or CTD) taken from additional probes

on the rosette (Fofonoff and Millard, 1983). Dissolved sulfide concentrations were determined immediately after pore-water samples were processed by square-wave voltammetry (Kuwabara and Luther, 1993) and by mixed diamine spectrophotometry (Cline, 1969). The voltammetric technique provided nanomolar detection limits in contrast to micromolar detection limits of more conventional spectrophotometric methods. Due to the concentration range of interest in this suboxic environment (nanomolar to millimolar), and the decision not to store samples, the method that was used here did not discriminate between dissolved sulfide species (sample manipulation would otherwise be required).

Flow injection analysis (Johnson and Petty, 1983) was used to measure dissolved

nitrate+nitrite concentrations (hereafter referred to as nitrate) for all water-column samples. Pore-water iron concentrations were measured by graphite-furnace atomic absorption spectroscopy using standard addition methods. Particulate molybdenum concentrations were determined by isotope-dilution inductively coupled plasma-mass spectrometry after sediment digestion in concentrated  $\text{HClO}_4$  (Zheng, unpublished doctoral dissertation). Sediment trap analysis for molybdenum was performed on subsamples collected by Thunell and others (1995). Precision of the dissolved iron, nitrate and particulate molybdenum measurements was  $\pm 5$ , 5, and 4%, respectively.

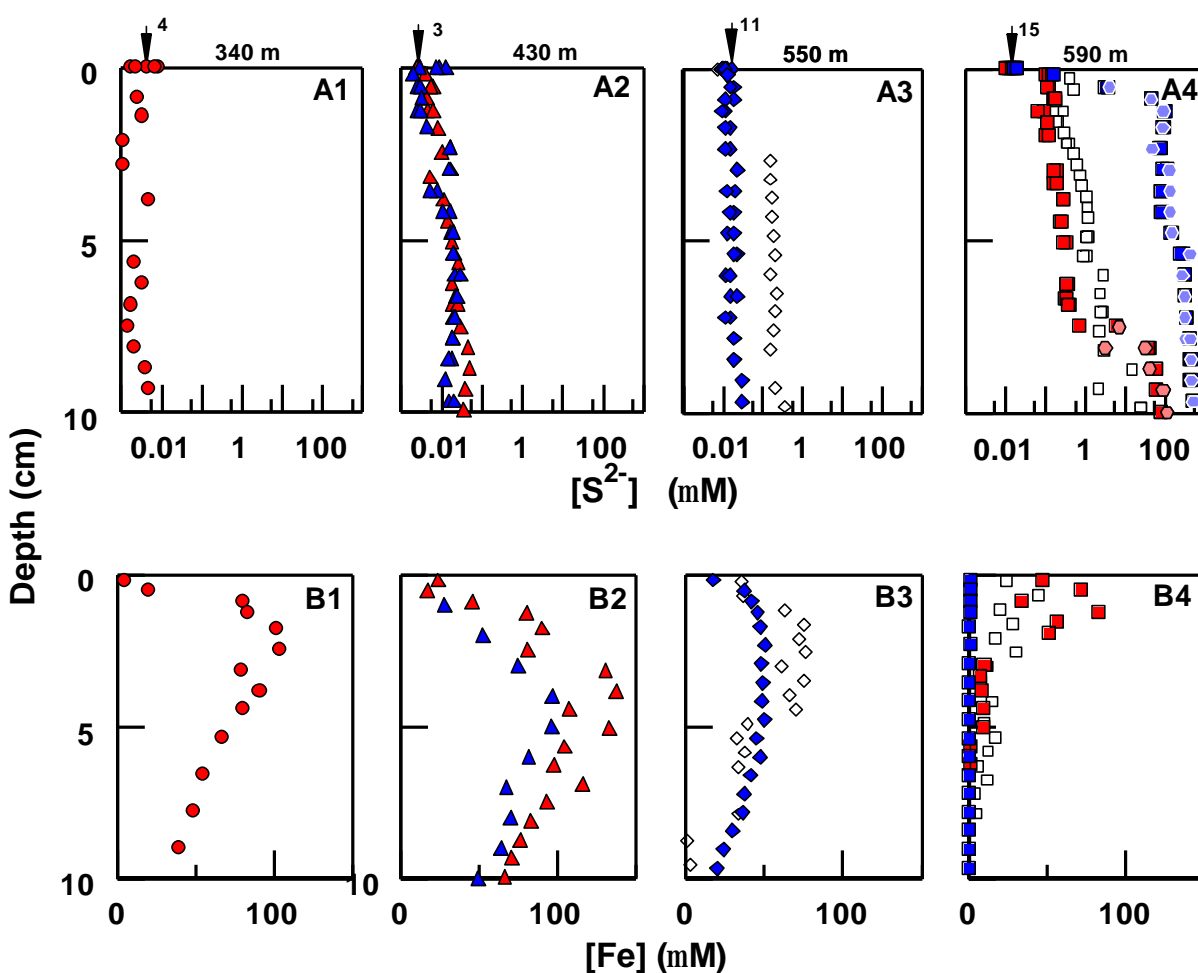


**Figure 2.** A comparison of water-column redox conditions at hydrocast stations within and outside the basin relative to seawater density for: 1) dissolved oxygen (DO), 2) nitrate and nitrite, and 3) sulfides (note nanomolar units). Open, shaded, and dark symbols or lines denote data from February 1995, December 1995 and April 1997 cruises, respectively. Squares and stars denote concentrations at the deep basin site and outside the basin, respectively. For DO measurements by oxygen probe, solid and hatched lines represent data from sites within and outside the basin, respectively. The horizontal hatched lines at a  $\sigma_T$  (density in  $\text{kg}\cdot\text{m}^{-3} - 1000$ ) of 48 indicate the density at the 480 m sill depth. In the absence of CTD (probe assemblage) data for February 1995, nitrate and sulfide profiles for February 1995 are plotted against estimated density from April 1997 CTD profiles.

## RESULTS

**Sedimentary Attributes:** At the 590 m site, the cores in February, 1995 had a brown surface layer of ~1cm thickness. In December, a thin orange veneer overlaid that brown surface layer. In contrast, the cores in April, 1997 exhibited tufts of the sulfide-oxidizing bacterium *Beggiatoa*, which had not been seen during the February and December 1995 cruises. These structures have been hypothesized to reflect an attempt by the colony to move into the more oxidizing environment just above the sediment-

water interface (Møller and others, 1985). Surface material overlaid anoxic varved sediments. Formation of these varves from seasonal changes in biogenic and lithogenic sources has been previously described (Sholkovitz and Gieskes, 1971; Reimers and others, 1990; Thunell and others, 1995). By contrast at shallower sites, cores exhibited thick (>2 cm), brown, oxidized layers without evidence of varving. The sedimentation rate in the basin is approximately 0.4 to 0.7 cm-yr<sup>-1</sup> (Reimers and others, 1990).



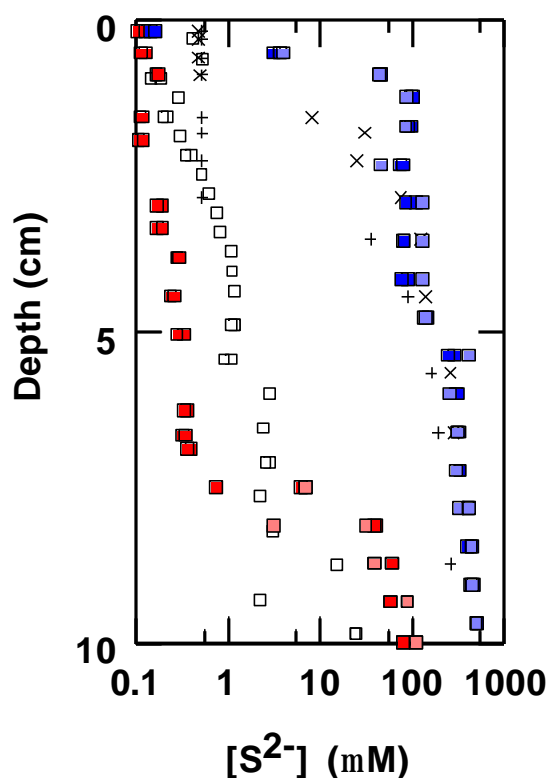
**Figure 3.** Pore-water profiles in the Santa Barbara Basin for dissolved sulfides (note log scale, panel A), and iron (panel B) from cores taken at various basin depths. Using symbols consistent with Figure 1, the panel columns 1, 2, 3, and 4 denote coring site depths 340 m (circle), 430 m (triangle), 550 m (diamond), and 590 m (square), respectively. Consistent with previous figures, open, shaded, and dark symbols denote data from February 1995, December 1995 and April 1997 sampling cruises, respectively. In plate A4, comparative colorimetric sulfide data at elevated concentrations (>1  $\mu\text{M}$ ) are

shown as hexagons. Arrows and adjacent numbers on the top border of each plot indicate mean bottom-water sulfide concentrations (nM). Bottom-water iron concentrations are not available.

**Water-column:** Contrasting redox conditions were evident in water-column profiles observed within and outside the Basin on the same density plane (fig. 2). The density of deep water within the basin ( $\sigma_T$  of 52.2 at 580 m) closely corresponds to a depth of approximately 575 m outside the basin. Dissolved oxygen (DO) concentrations within the basin decreased from  $>240 \mu\text{M}$  at the surface to approximately  $5 \mu\text{M}$  near the sediment-water interface. Although water-column DO concentrations outside the basin also decreased with depth, bottom-water (580 m) DO concentrations were 21 and  $16 \mu\text{M}$  in December 1995 and April 1997, respectively. In December 1995, Microwinkler DO analysis for the bottom water at 580 m, 430 m, and 340 m going upslope were 5, 15, and  $23 \mu\text{M}$ , respectively. That is, the bottom water DO concentration at the shallowest sampling site along the basin slope (340 m) was similar to that outside the basin at 580 m. Similarly in April 1997, bottom water DO concentrations at 590 m, 550m, and 430 m were 3, 5, and  $11 \mu\text{M}$ , while the bottom-water concentration just to the northwest of the basin was  $16 \mu\text{M}$ . The decrease in water-column nitrate concentration to  $<15 \mu\text{M}$  in February 1995 (fig. 2B), and to  $26 \mu\text{M}$  in November 1995 inside the basin, relative to  $40 \mu\text{M}$  on the same density surface outside the basin, is another indication of additional oxidant consumption within the basin due to organic matter decomposition (i.e., denitrification by facultative anaerobes or by anaerobes in water-column microenvironments (Robertson and Kuenen, 1984; Lloyd and others, 1987; Robertson and others, 1989).

During all three sampling periods, dissolved sulfide concentrations within the basin (fig. 2C) consistently showed a gradual increase below the sill depth ( $>480\text{m}$ ). Elevated dissolved sulfide concentrations observed in April 1997 below the sill depth relative to the other sampling dates is consistent with elevated pore-water profiles for sulfides observed in April 1997 (fig. 3A). By contrast, the water-column profiles outside the basin showed no evident increase in dissolved sulfides below sill depth (fig. 2C).

**Core profiles:** At the 590 m site, within the top 10 cm of sediment depth, dissolved sulfide concentrations increased by 3 orders of magnitude from tenths to  $>100 \mu\text{M}$  (fig. 3A). Intercalibration between voltammetric and colorimetric methods for sulfide analyses during all three sampling trips showed good agreement ( $r^2 = 0.93$ ) over the effective concentration range for the colorimetric technique ( $>1 \mu\text{M}$ ). Sampling at shallower stations within the basin generated profiles that were typically orders of magnitude lower in sulfide concentrations for comparable core depths. Pore-water iron concentrations provide supporting evidence for this spatial variability within the basin (fig. 3B), with



**Figure 4.** Temporal variability in pore-water sulfide gradients near the sediment-water interface at 590 m are shown with profiles from 2 replicate cores taken in October, 1988 by Reimers and others (1990) shown with cross and Ax@ markers. Open, shaded and dark squares represent data from February 1995, December

1995, and April 1997 sampling cruises, respectively. The mean bottom-water concentration from three sampling cruises at this site was approximately 15 nM (fig. 3A4).

negligible concentrations at 590 m relative to shallower, more bioturbated sites (Kuwabara and others, 1999). The pore-water profiles consistently show the dynamic nature of the basin geochemistry even in the deepest areas (fig. 3).

## DISCUSSION

**Water Column:** Integrated studies of water-column and pore-water gradients for redox-sensitive solutes provides boundary conditions from which interfacial processes can be identified that regulate solute transport and distribution. An estimate of the dissolved sulfide flux from the basin can be made using water column data (fig.

2C). Dissolved sulfide concentrations outside the basin were consistently  $\leq 5\text{nM}$ , while at the 590 m deep basin site, concentrations increased to between 10 and 15 nM below 500 m with highest water-column concentrations observed in April 1997. Using bathymetric contours, the basin volume below 500 m is approximately  $29\text{ km}^3$ . Mean water residence times between 0.8 to 6 years have been determined for the basin (Berelson and others, 1987; Hammond and others, 1990; van Geen and others, 1995). A flux from the basin can therefore be crudely estimated as:

**Table 1.** Sulfide flux for various locations within the Santa Barbara Basin based on pore-water gradients. A diffusion coefficient of  $1 \times 10^{-5}\text{ cm}^2\text{-sec}^{-1}$  (Li and Gregory, 1974) was used with the pore-water gradient determined from an exponential fit of data near the sediment-water interface (<1 cm depth). Estimates for October 1988 are from representative pore-water profiles (upper 5 cm due to micromolar colorimetric detection limits for sulfides) from replicate cores by Reimers and others (1990) taken near our 590 m site. The number of data points (n) and coefficient of determination ( $r^2$ ) for each non-linear gradient determination are also tabulated.

Date	Core <sup>1</sup>	n; r <sup>2</sup>	Gradient ( $\mu\text{M}\text{-cm}^{-1}$ )	Flux ( $\text{nmoles}\text{-m}^{-2}\text{-h}^{-1}$ )
10/88A	-	10; 0.89	36	13000
10/88B	-	10; 0.59	16	6000
2/16/95	B590-1	3; 1.00	2.36	900
2/17/95	B550-1	3; 1.00	0.49	200
12/1/95	M580-2	9; 0.93	1.54	600
11/30/95	M430-2	8; 0.83	$6 \times 10^{-3}$	2
12/2/95	M340-2	9; 0.10	-0.01	-4
4/27/97	M550-3	8; 0.01	0.01	4
4/26/97	M430-3	9; 0.08	$9 \times 10^{-3}$	3

<sup>1</sup> Cores are indexed with the first letter designating the core type (B for Soutar box core, and M for multicore). The next three digits correspond to the site depth in meters. Finally the number after the hyphen indicates the cruise number (1 for February 1995, 2 for December 1995, and 3 for April 1997).

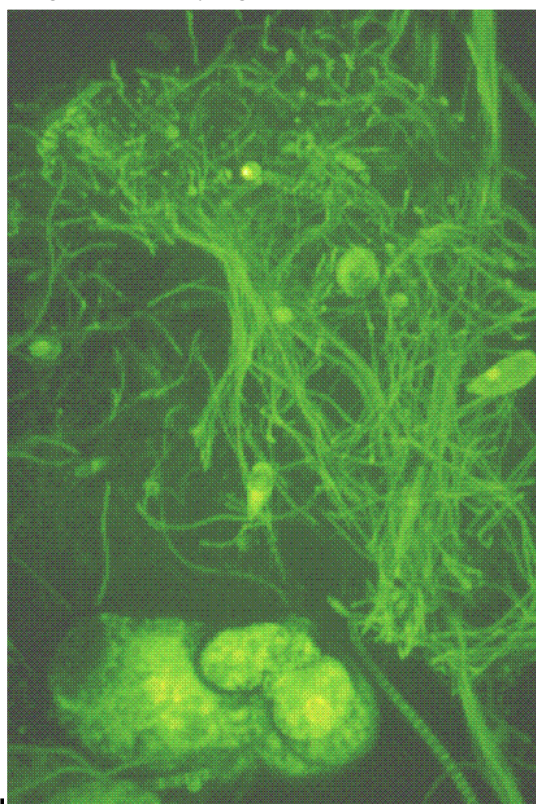
$$\text{Flux} = (\Delta C/\Delta t)(V/A),$$

where  $\Delta C/\Delta t$  is equivalent to the solute concentration change over the period of residence,  $V$  is the basin water volume where the solute is elevated, and  $A$  is area of exchange, assumed here to be 300 km<sup>2</sup>, the projected area at 500 m. The calculation yields a sulfide flux range of 9 to 138 nmoles-m<sup>-2</sup>-h<sup>-1</sup>.

**Pore-water:** Sulfide flux from the sediments can alternatively be determined from pore-water gradients near the sediment-water interface using an exponential model (Klump and Martens, 1981; Table 1). Clearly, benthic flux determinations for sulfides based on diffusion gradient methods yield widely disparate estimates (-4 to 13,000 nmoles-m<sup>-2</sup>-h<sup>-1</sup>) based on easily observable differences in the pore-water gradients between 1988, 1995, and 1997 profiles (Table 1). This variability, consistent with profiles for other redox-sensitive solutes (Kuwabara et al, 1999), suggests that the deep basin was characterized by more reducing conditions in 1988 and 1997 relative to 1995. It should be noted that <sup>210</sup>Pb and <sup>234</sup>Th profiles suggest a removal of about 12 cm of sediment from the 590 m core a few months to weeks before the April 1997 cruise at the 590 m site (Zheng, unpublished doctoral dissertation). However, the surficial microbial population was already reestablished by April 1997.

Temporal and spatial differences in sulfide flux within the basin (fig. 4) have been linked to an iron-sulfide trapping mechanism (Reimers and others, 1996; Kuwabara and others 1999). Further retardation of sulfide flux near the sediment-water interface is indicated by lower water-column based flux estimates (9 to 138 nmoles-m<sup>-2</sup>-h<sup>-1</sup>) relative to pore-water gradient estimates at the 590 m site (600 to 13,000 nmoles-m<sup>-2</sup>-h<sup>-1</sup>). This interfacial retardation has been attributed to sulfide oxidation by the benthic microbial layer (fig. 5; Kuwabara and others 1999). Sulfate reduction rates are consistently >2mM -y<sup>-1</sup> at sediment depths <10 cm near our deep-basin site (Reimers and others, 1996). If this rate even approximated the net microbial sulfide production rate, then it would take only a few weeks to shift the shallow gradient observed in February and December 1995 to that observed in October 1988 and April 1997. The composition of benthic biota within the basin is regulated by bottom-water redox conditions

(Bernhard and Reimers, 1991). It is therefore reasonable to assume that physical and biological events that alter redox gradients at the sediment-water interface could result in periods of transition for the benthic community. Using colorimetric techniques, Reimers and others (1996) could not detect pore-water sulfides (<0.5 μM) near the sediment-water interface in spite of high rates of sulfate reduction. Results presented herein provide resolution of the redox gradient in this ecologically and geochemically significant zone.



**Figure 5.** Confocal micrograph of the benthic microbial community near the sediment-water interface in the deep basin (~590 m). Filamentous sulfide-oxidizers and foraminifera that predominate under conditions of low dissolved oxygen (i.e., DO < 10 μM) are shown.

### Implications on Metal

**Authigenesis:** Redox gradients can have pronounced effects on metal authigenesis. For example, the authigenic formation of molybdenum minerals has been thought to be controlled by the reduction of molybdate (that is, Mo(VI)) and the formation of thermodynamically stable disulfide precipitates, Molybdenite and Jordisite (Emerson and Huested, 1991; Calvert and Pederson, 1993). Recent sediment analyses by Extended X-ray



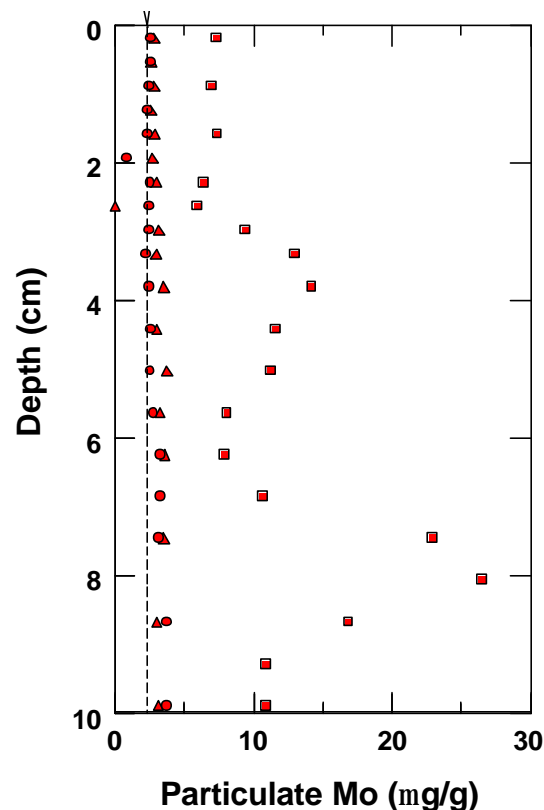
Absorption Fine Structure, EXAFS, have indicated a Mo - Fe interaction that results in the formation of Mo-Fe sulfides (Helz and others, 1996). Only at the deep basin site is molybdenum authigenesis clearly indicated by the elevated particulate molybdenum concentrations in the sediment profile relative to sediment trap concentrations (i.e., particulates advected from the water column to the bottom-sediment surface; fig. 6). Authigenic formation is therefore favored under the more reducing conditions of the deep basin relative to the shallower basin-slope sites (fig. 3A and 6; Zheng, unpublished doctoral dissertation). Helz and others (1996) have suggested that the sulfidation of molybdate would place bisulfide in the role of a geochemical switch, shifting molybdenum between conservative and particle-reactive species. Reimers and others (1996) observed a pH shift from 7.5 to 8.0 in the top 2 cm near our 590 m deep-basin site. Over this pH range, Helz and others (1996) indicated a bisulfide switch point of the order of  $10^{-4}$ M, where the activities of  $\text{MoO}_4^{2-}$  and the particle-reactive  $\text{MoS}_4^{2-}$  would be equivalent. It is therefore noteworthy that the observed porewater pH transition was coincident with an increase in dissolved sulfides to  $>10^{-4}$ M in 1988 and 1997, and also in 1995 at a lower depth (fig. 4). The enrichment of other metals (e.g., Cd) in suboxic sediments also has been linked to the formation of insoluble metal sulfides, but without a valence change (Calvert and Pederson, 1993).

### Summary Points:

(1) Distributions of dissolved oxygen, sulfide and nitrate in the water-column, and dissolved pore-water sulfide and iron indicate very different redox conditions between the coring sites within the Santa Barbara Basin and its vicinity, and certainly provide a contrast to the more-oxidizing conditions just north of the basin.

**Figure 6.** Authigenesis of molybdenum in Santa Barbara Basin sediments. Site markers are consistent with previous figures: 590 m (square), 430 m (triangle), and 340 m (circle). The vertical hatched line at  $2.5 \mu\text{g}\cdot\text{g}^{-1}$  indicate the particulate molybdenum concentration in the sediment trap.

A concentration range of 5 orders of magnitude for pore-water sulfide was observed.



(2) Our results indicate more oxidizing conditions in the basin in 1995 than in 1988 when previous pore-water studies were conducted. Temporal variability between studies can be explained by net sulfide-reduction rates.

(3) In contrast to the deep basin, micromolar pore-water sulfide peaks are absent at the shallower sites below observed peaks for dissolved Fe and appear to reflect changes in bottom-water chemistry at these more-oxidized sites as well as the magnitude of bioturbation.

(4) Observed spatial and temporal variability in pore-water gradients affect the authigenesis and mobility of trace elements in the Santa Barbara Basin.

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