Geochemical Evidence for Enhanced Upwelling and Organic Productivity During the Late Quaternary on the Continental Margin of Northern California

Walter E. Dean, James V. Gardner, and Roger Y. Anderson

ABSTRACT: The present upper water mass of the northeastern Pacific Ocean off California has a well developed oxygen-minimum zone between 600 and 1000 meters wherein concentrations of dissolved oxygen are less than 0.5 ml/L. Even at such low concentrations, benthic burrowing organisms are abundant enough to destroy millimeter-scale laminations by thoroughly bioturbating the surface and near-surface sediments. These organisms also consume large quantities of organic carbon produced by large seasonal stocks of plankton in the overlying surface water that are supported by high concentrations of nutrients in the California Current upwelling system. The result is that concentrations of biogenic silica in surface sediments are highest in the oxygen-minimum zone, reflecting the high diatom production in the overlying water, but concentrations of residual organic carbon are lower in sediments in the oxygen-minimum zone than in sediments above and below it.

Laminated sediments are preserved in upper Pleistocene sections of cores collected on the continental slope at water depths within the present oxygen-minimum zone from at least as far north as the Klamath River and as far south as Point Sur. Comparison of sediment components in the laminae with those delivered to sediment traps as pelagic marine "snow" show the dark/light lamination couplets are indeed annual (varves). These upper Pleistocene varved sediments contain more abundant lipid-rich "sapropelic" (Type II) organic matter than the bioturbated and oxidized Holocene sediments. The stable carbon-isotopic composition of the organic matter does not change with time, indicating the greater abundance of Type II organic matter in the varved sediments is not due to a change in source but, rather, represents a greater degree of preservation of organic matter. The organic-carbon-rich varved sediments also contain higher concentrations of sulfide-sulfur, indicating a higher rate of sulfate reduction due to the presence of more "reactive" organic matter. Concentrations of several redox-sensitive trace elements, especially Cr, Cu, Ni, V, and Zn, also are enriched in the varved sediments. The presence of carbon-, sulfur-, and metal-rich sediments, as well as lack of bioturbation, all support the theory that the oxygen-minimum zone in the northeastern Pacific Ocean was more intense — in fact, anoxic — during the late Pleistocene in response to greater coastal upwelling and higher organic productivity.

Introduction

Marine environments that are effectively anoxic (*i.e.*, contain <0.1 ml/L dissolved oxygen) and that have preserved laminations occur in silled basins with bathymetric barriers and restricted circulation. Examples are:

- Guaymas basin in the Gulf of California (Calvert 1964 and 1966, Schrader *et al.* 1980, Schrader and Baumgartner 1983).
- Santa Barbara basin on the Southern California borderland (Hulsemann and Emery 1961, Soutar and Crill 1977, Pisias 1978, Thornton 1984).
- Bahia de Soledad along the Pacific coast of Baja California (Soutar *et al.* 1981).
- Saanich Inlet (Gross *et al.* 1963, Gucluer and Gross 1964).

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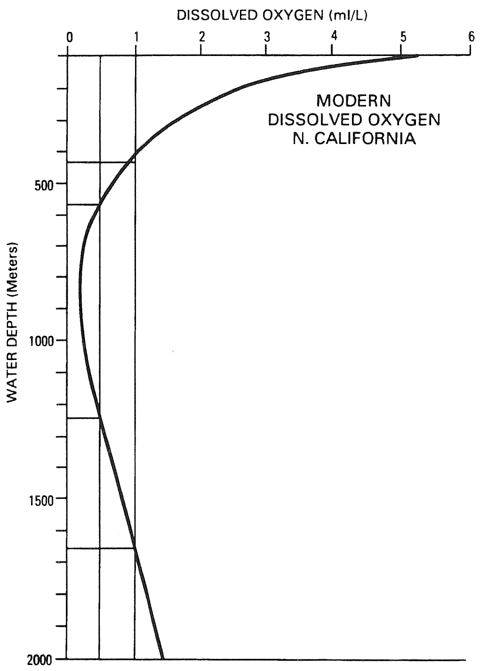
More rarely, open continental slopes in areas of strong coastal upwelling, such as off Peru (deVries and Schrader 1981, Reimers and Suess 1983), Namibia, southwest Africa (Calvert and Price 1983), and California (Mullins *et al.* 1985, Thompson *et al.* 1985, Gardner and Hemphill-Haley 1986, Anderson *et al.* 1987 and 1989), have a strongly developed oxygen-minimum zone (OMZ, <0.5 ml/L dissolved oxygen) and preserve laminated sediments **during times when the minimum was essentially zero** (<0.1 ml/L dissolved oxygen).

Figure 1
DISSOLVED OXYGEN CONCENTRATION VERSUS DEPTH OFF NORTHERN CALIFORNIA

The oxygen minimum zone has dissolved oxygen concentrations of <0.5 ml/L; the dysaerobic zone has dissolved oxygen concentrations of 0.5 to 1.0 ml/L. Data are from CalCOFI (1963).



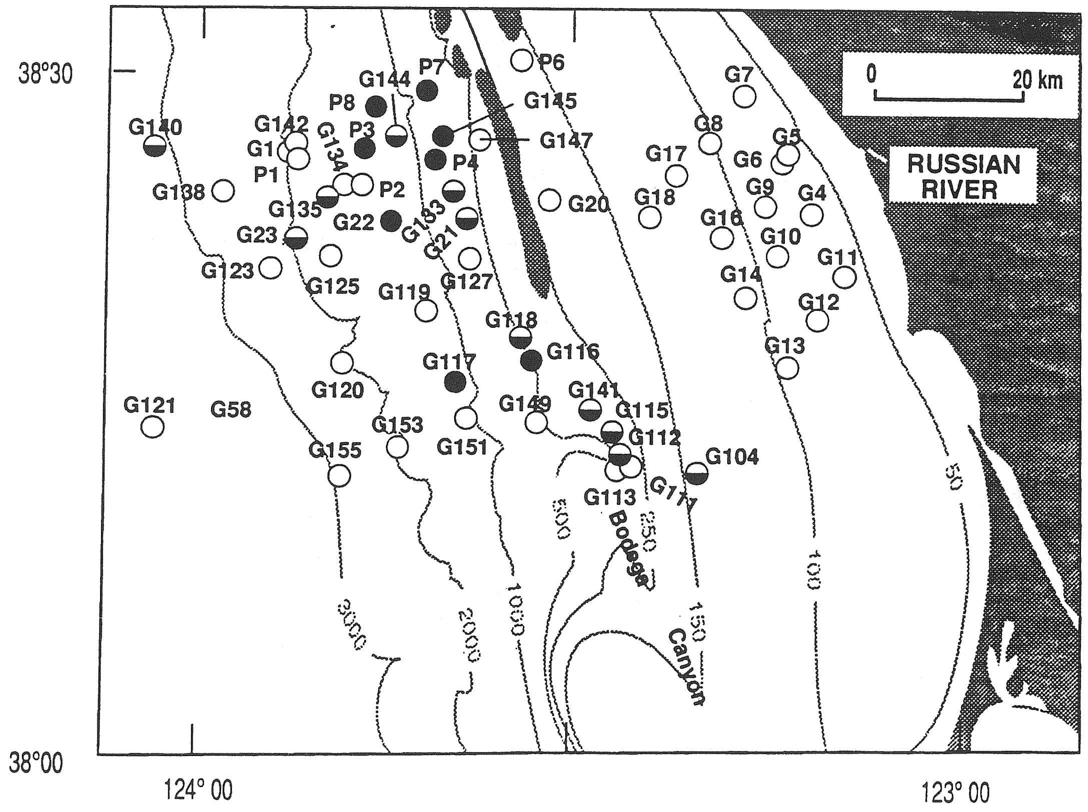
The continental margin off Northern California is characterized by high organic productivity in response to nutrients supplied by strong seasonal coastal upwelling, which, in turn, is driven by the southward-flowing California Current (Huyer 1983). Because of this high productivity, the present surface water mass off Northern California has an OMZ between 600 and 1200 meters, with concentrations as low as 0.2 ml/L at 800 meters (CalCOFI 1963) (Figure 1). The dysaerobic zone (0.5-1.0 ml/L dissolved oxygen) extends from about 400 to 1600 meters. These low concentrations of dissolved oxygen, even in the core of the OMZ, are sufficient to support a burrowing benthic fauna.

During 1980 and 1981 the U.S. Geological Survey conducted several cruises off the coast of Northern California to characterize sediments on the continental shelf, slope, and basin above, within, and below the OMZ. Gravity, piston, and box cores were collected as part of this investigation (Figure 2). Sediments recovered in most cores were bioturbated, greenish-gray diatom-bearing clays or silty clays, but cores collected on the upper slope between 500 and 1500 meters contained laminated sediment below a 5- to 80-cm-thick surface layer of bioturbated sediment (Gardner and Hemphill-Haley 1986, Anderson *et al.* 1987 and 1989). Sediments below the laminated/bioturbated contact are not continuously laminated but, rather, consist of interbeds of laminated and bioturbated sediment that alternate on a scale of centimeters to decimeters. The youngest dated laminations occur in core G117 (Gardner and Hamphill-Haley 1986). Since 1986, more work and dating have been done on this core, and it now appears the contact between the laminated and bioturbated sections of the core is an erosional unconformity that truncates the laminated sequence.

Three radiocarbon dates have been obtained from Core G117: one conventional ^{14}C date from above the unconformity and one conventional and one accelerator mass spectrometer (AMS) ^{14}C date from below the unconformity. The two conventional ^{14}C dates are from 8-cm-long samples of bulk sediment, and the AMS ^{14}C date is from a small sample of bulk sediment. Assuming a zero age for the top of the core, the calculated sedimentation rate for the bioturbated sediment above the unconformity is 0.8 cm/ky. The two ^{14}C dates below the unconformity give a sedimentation rate of 0.7 cm/ky. Interpolating to the unconformity from both sides suggests the unconformity separates sediment that is about 19 ky old from sediment about 14.5 ky old.

Figure 2
LOCATIONS OF GRAVITY (G) AND PISTON (P) CORES ON THE CONTINENTAL MARGIN OFF THE RUSSIAN RIVER, NORTHERN CALIFORNIA, USED IN THIS STUDY

Cores indicated by a solid circle contain some distinctly laminated sediments; cores indicated by a half-solid circle contain mostly bioturbated sediments but with some zones containing faint, indistinct, or discontinuous laminations; cores indicated by an open circle contain only bioturbated sediments. Bathymetric contours are in meters.



This exercise also suggests conditions that allowed preservation of varves at this site were active at 19 ka. In addition, the OMZ index for core G117, based on the style and type of trace bioturbation (Anderson *et al.* 1989), suggests conditions at 19 ka were strongly anoxic and not just dysaerobic. Consequently, sometime between about 19 and 14.5 ka, bottom conditions changed from fully anoxic to sufficiently aerobic to permit a burrowing benthic fauna.

Dark/light laminae couplets, where best developed, are about 1-mm thick and represent annual accumulations of sediment (varves) (for descriptions, see Gardner and Hemphill-Haley 1986, Anderson *et al.* 1987, 1989). Diatom assemblages in the laminae couplets can be matched to seasonal diatom data from a sediment trap of the type described by Anderson (1977) that was deployed 260 meters above the sea floor at a water depth of 2196 meters from September 16, 1980, to October 12, 1981. The summer upwelling diatom assemblage, dominated by *Skeletonema costatum*, is similar to that in the light laminae, and the winter, non-upwelling assemblage, dominated by *Thalassiosira pacifica*, is similar to that in the dark laminae (Gardner and Hemphill-Haley 1986).

Since the initial investigations in 1980 and 1981, more than two dozen cores have been identified that contain millimeter-scale laminations from as far south as Point Sur and as far north as the Klamath River area, a distance of more than 400 km (Anderson *et al.* 1987, 1989). Of the cores with locations shown in Figure 2, eight contain some distinctly laminated sediments and twelve contain mostly bioturbated sediments but with some zones of faint, indistinct, or discontinuous laminations. The varve laminae are best developed in two gravity cores that are the focus of this report: core G117, from a water depth of 695 meters, and core G145, from a depth of 698 meters. For reference, we also present data from a piston core from below the OMZ but within the dysaerobic zone (core P3, depth 1600 m) and two deep-water cores from well below the OMZ (core G121, depth 3580 m, and core G138, depth 2530 m).

Presence of laminated sediments in the subsurface in upper-slope cores suggests that during the late Pleistocene, the OMZ was more intense, with concentrations of dissolved oxygen low enough to eliminate burrowing organisms (Gardner and Hemphill-Haley 1986). A similar conclusion was reached by deVries and Schrader (1981) for termination of the laminated facies on the Peru margin. The purpose of this report is to present results of organic and inorganic geochemical investigations of laminated and bioturbated sediments in these cores, particularly as they relate to the origin, nature, and degree of preservation of the contained organic matter.

Methods

The type of organic matter in sediment samples from the two cores that contain laminated sediments taken within the OMZ (G117 and G145) and from the two deep-water reference cores that contain bioturbated sediments taken from well below the OMZ (G138 and G121) was determined by Rock-Eval pyrolysis. The Rock-Eval method provides a rapid determination of the hydrogen and oxygen richness and degree of preservation of sedimentary organic matter (for details, see Espitalie *et al.* 1977, Tissot and Welte 1984, and Peters 1986). Concentrations of free and adsorbed hydrocarbons and CO_2 released by programmed heating of the sample in a stream of helium are measured as areas under peaks on a pyrogram. These peak areas, when calibrated and normalized to percent organic carbon (C_{org}), yield a hydrogen index (HI) and oxygen index (OI), expressed as milligrams of hydrocarbons (HC) and CO_2, respectively, per gram of C_{org}. The Rock-Eval II instrument used for analyses also determines the percent C_{org}. Values of HI and OI correlate well with atomic $H:C_{org}$ and $O:C_{org}$ ratios determined in the same samples by other methods (*e.g.*, Tissot and Welte 1984).

Stable isotope ratios in organic carbon were determined by standard techniques described by Pratt and Threlkeld (1984) and Dean *et al.* (1986). Results are reported in the standard per mil δ-notation relative to the University of Chicago Pee Dee belemnite (PDB) marine-carbonate standard:

$$\delta \textit{ parts per mil} = ((R_{\text{sample}}/R_{\text{PDB}}) - 1) \times 10^3$$

where R is the ratio $^{13}C/^{12}C$.

Sediment samples for inorganic geochemical analyses were air dried and ground in a ceramic mill to pass a 100-mesh sieve. Concentrations of 10 major and minor elements (Si, Al, Fe, Mg, Ca, Na, K, Ti, P, and Mn) were measured by wavelength-dispersive X-ray fluorescence spectrometry (Baedecker 1987). Concentrations of 14 trace elements (Ba, Co, Cr, Cu, La, Ga, Li, Ni, Pb, Sc, Sr, V, Y, and Zn) were determined by inductively coupled, argon-plasma, emission spectrometry (Baedecker 1987). Total carbon and total sulfur were determined by the LECO induction-furnace gasometric method. Carbonate carbon was determined by coulometry (Engleman *et al.* 1985). Values of C_{org} determined by difference between total carbon and carbonate carbon agree well with values of C_{org} determined with the Rock-Eval II instrument, but the Rock-Eval results will be used in our discussions.

Results and Interpretations

Rock-Eval Pyrolysis and Organic Carbon

Samples from the laminated zones in cores G117 and G145 contain more organic matter (higher concentrations of C_{org}) that is distinctly enriched in hydrogen (higher values of HI) relative to the bioturbated sediments (Figures 3 and 4). The organic matter preserved in the deep-water reference cores (G121 and G138) has characteristics in terms of amount (% C_{org}) and richness (HI) that are very similar to the organic matter in core G145. Variations in hydrogen richness of organic matter may be due to variations in degree of preservation of the organic matter or due to mixing of H-rich marine organic matter with H-poor terrestrial organic matter (Tissot and Welte, 1984). The distinct trend of increasing H-richness in surface sediments from the mouth of the Russian River to the basin (Figure 5) suggests variations in HI may be due to mixing of organic matter types from marine and terrestrial sources. Isotopic composition of the organic carbon can help to distinguish between mixing and preservation.

Stable-Carbon Isotope Composition of Organic Matter

The isotopic composition of modern marine phytoplankton and terrestrial plants and the organic matter derived from them often provide distinct signatures that can be used to determine source of organic matter in sediments. Ten samples of plankton from the North Pacific between 20° and 40°N, analyzed by Rau *et al.* (1982), had values of $\delta^{13}C$ ranging from about –19.8 to –23.4 parts per mil, and eight of the ten samples had values between –19.8 and –22 parts per mil (Figure 6). Values of –20 to –22 parts per mil are typical of marine plankton from intermediate latitudes (Deines 1980).

Values of $\delta^{13}C$ of particulate organic matter (POM) derived from marine plankton tend to be lower than those of plankton by several per mil. For example, samples of North Pacific POM reported by Rau and others (1987) have $\delta^{13}C$ values that range from about –20 to –24 parts per mil, and samples from sediment traps in the VERTEX 5 experiment 1500 km west of Monterey, California, have values ranging from about –22.5 to –24 parts per mil (Rau *et al.* 1986). The isotopic composition of terrestrial vegetation can vary widely, but values of $\delta^{13}C$ for higher terrestrial vegetation (C3 plants) generally range from –22 to –32 parts per mil, and most are in the range of –24 to –28 parts per mil. In other words, marine organic matter tends to have $\delta^{13}C$ values in the low negative 20s terrestrial organic matter tends to be in the high negative 20s. With these values in mind, let us examine the isotopic composition of organic matter in the Northern California margin cores.

Values of $\delta^{13}C$ in cores G117 and G145 are mostly in the range of –22.5 to –23.5 parts per mil (Figures 3 and 4), almost exactly in the range of POM off Monterey (Figure 6). The fact that most $\delta^{13}C$ values in cores G117 and G145 are slightly lighter (more negative) than typical North Pacific plankton and POM may be due to a minor contribution of isotopically lighter terrestrial organic matter. By this argument, the distinctly lighter values of $\delta^{13}C$ in core G138 suggest that this locality on the basin floor receives an even larger contribution of terrestrial organic matter, probably transported down Bodega Canyon (Figure 2). In contrast, the heavier values of $\delta^{13}C$ in core P3 (water depth 1600 m), upslope from G138

Figure 3
PROFILES OF PERCENT TOTAL ORGANIC CARBON, VALUES OF $\delta^{13}C$ ORGANIC CARBON, PERCENT TOTAL SULFUR, ROCK-EVAL H-INDEX, PARTS PER MILLION Ni, AND PERCENT TOTAL Si VERSUS DEPTH IN CORE G117

Laminated intervals are indicated next to the depth scale at the left of the profiles.

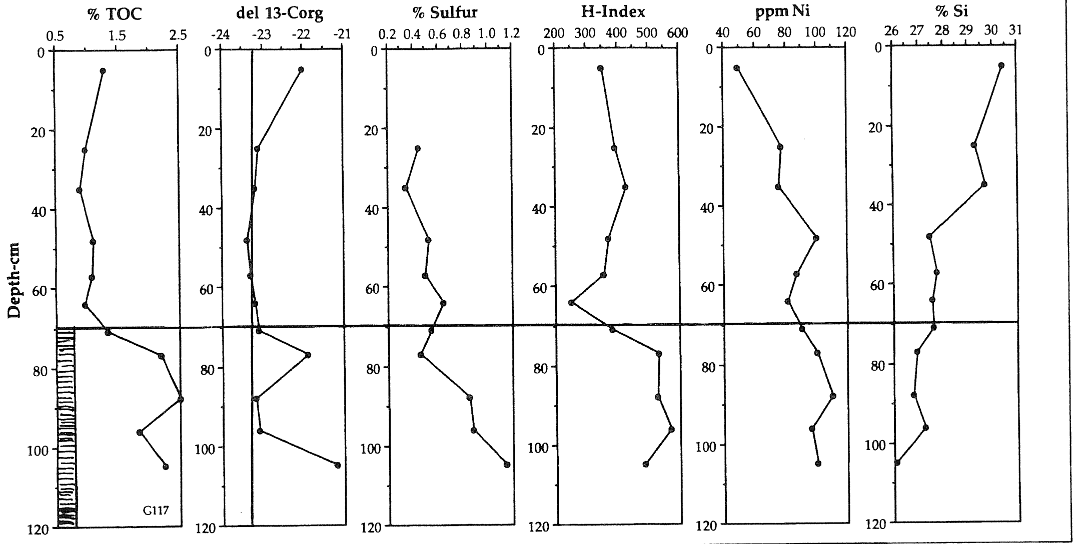


Figure 4
PROFILES OF PERCENT TOTAL ORGANIC CARBON, VALUES OF $\delta^{13}C$ ORGANIC CARBON, PERCENT TOTAL SULFUR, ROCK-EVAL H-INDEX, PARTS PER MILLION Ni, AND PERCENT TOTAL Si VERSUS DEPTH IN CORE G145

Laminated intervals are indicated next to the depth scale at the left of the profiles.

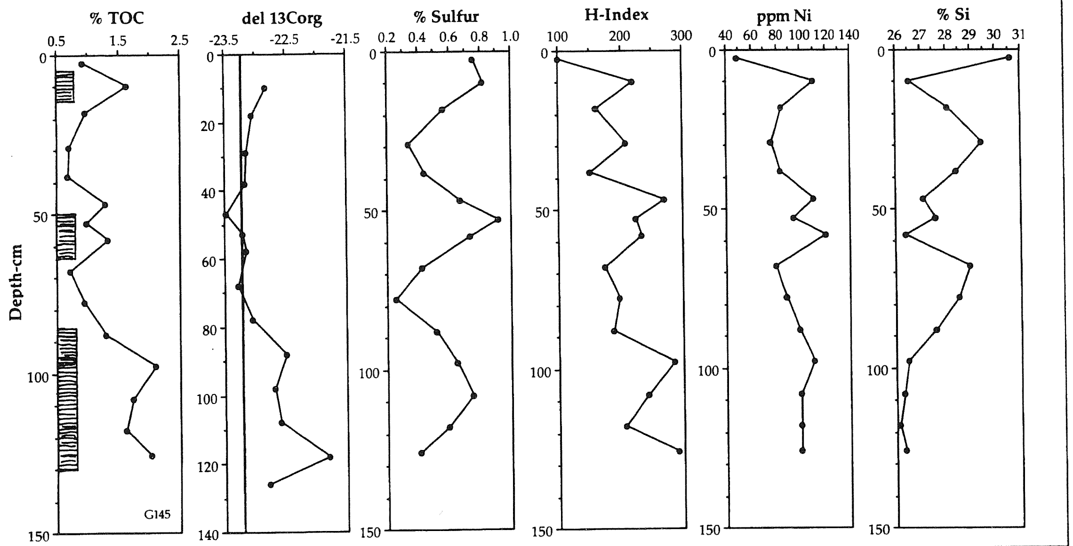


Figure 5
WATER DEPTH VERSUS
ROCK-EVAL H-INDEX IN
SURFACE SEDIMENTS (Top 5cm) ON THE
CONTINENTAL MARGIN OFF THE
RUSSIAN RIVER, NORTHERN CALIFORNIA

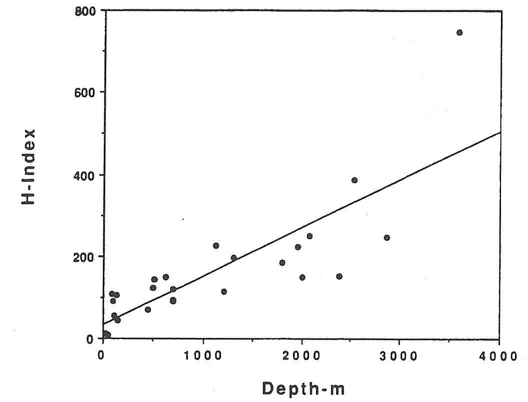
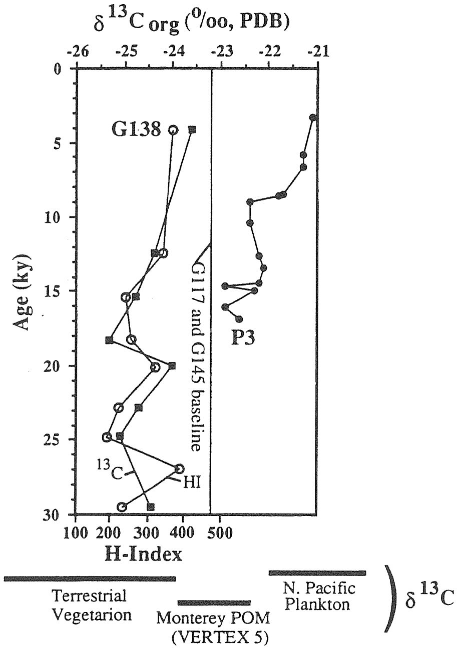


Figure 6
PROFILES OF $\delta^{13}C_{org}$ VERSUS AGE FOR
SAMPLES FROM CORES G138 AND P3 AND
H-INDEX VERSUS AGE FOR
SAMPLES FROM CORE G138
(open circles)



Data for core G138 are from Table 1.

Data for core P3 are unpublished data provided by Greg Rau.

Baseline for $\delta^{13}C_{org}$ in cores G117 and G145 are from Figures 3 and 4 respectively.

Ranges of $\delta^{13}C_{org}$ values for North Pacific plankton are from Rau et al. (1987).

Ranges of $\delta^{13}C_{org}$ values for VERTEX 5 particulate organic matter (POM) are from Rau et al. (1986).

Ranges of $\delta^{13}C_{org}$ values for terrestrial organic matter are summarized from Deines (1980).

and downslope from G145, suggest this locality receives less terrestrial organic matter. The increase in $\delta^{13}C$ since the last glacial maximum in G138 and P3 suggests the influx of terrestrial organic matter to the basin floor was even greater during eustatic sea level low stands when the shoreline was about 40 km farther west.

With regard to interpreting HI and OI values in terms of source versus preservation, it is significant that, except for the laminated intervals at the bases of cores G117 and G145, there is not a good correlation between values of $\delta^{13}C$ and HI in these two cores. If decreasing HI values were due to mixing of marine with terrestrial organic matter, we would expect to find a concomitant decrease in $\delta^{13}C$ values, which is exactly what we find for core G138 where the organic matter has become more marine in character (higher HI, less negative $\delta^{13}C$) over the last 30 ky. There is no such correlation for cores G117 and G145, and there is an average $\delta^{13}C$ of about –23 parts per mil across the complete range of HI values. Therefore, we interpret $\delta^{13}C$ results in cores G117 and G145 as representing a fairly constant baseline of dominantly marine organic matter with average $\delta^{13}C$ values of about –23.2 parts per mil and with occasional intervals or "pulses" of higher marine productivity represented by $\delta^{13}C$ values of –21 to –22.5 parts per mil.

Iron-Sulfur-Carbon Systematics

The laminated sediments also tend to have higher concentrations of sulfur than the bioturbated sediments (Figures 3 and 4). This reflects a higher rate of sulfate reduction due to the presence of more "reactive", H-rich organic matter in the laminated sediments (*e.g.*, Berner and Westrich 1985). All samples have an average S:C ratio close to 0.4, which is the average ratio for Holocene "normal marine" sediments (those deposited under an oxic water column but that contain sufficient organic matter to cause pore waters to go anoxic after deposition) (Raiswell and Berner 1986). Such a relationship indicates the sediments were not iron-limited but availability of reactive carbon ultimately limited pyrite formation in these sediments (Dean and Arthur 1989).

Trace-Element Geochemistry

Results of major-, minor-, and trace-element analyses show that several trace transition elements, especially Cr, Cu, Ni, V, and Zn, are enriched in the C_{org}-rich laminated sediments. This relationship is shown by plots of ppm Ni versus depth in Figures 3 and 4. The greatest contrast is the difference between the concentration of Ni in the surface sediment and in the laminated intervals.

There is a tendency in the literature to attribute a causal relationship to the commonly observed correlation between metal concentration and C_{org} concentration, usually through some process of biological uptake, sorption, or "scavenging", although the fundamental physical, chemical, and biological processes involved in this scavenging are poorly understood (Honeyman *et al.* 1988). However, recent work has shown that trace-metal uptake is mainly controlled by particle concentration and surface chemistry, not by biological uptake (*e.g.*, Balistrieri *et al.* 1981, Collier and Edmond 1984, Wong and Wood 1984, Nyffeler *et al.* 1986; Honeyman *et al.* 1988).

A compilation of particle-concentration and Thorium adsorption-rate data by Honeyman *et al.* (1988) shows a linear correlation between the two variables over seven orders of magnitude of particle concentration and over a wide range of organic productivity. In other words, particles are particles, be they inorganic or organic. Data used by Honeyman *et al.* were for thorium, but the principle applies to many other metals. In highly productive areas (such as the continental margin off Northern California) many particles are of biological origin, but in terms of adsorption characteristics, they are still just particles.

This generality is modified somewhat by the types of particles and their surface chemistry, as demonstrated by Balistrieri *et al.* (1981) and Balistrieri and Murray (1982), who showed that iron and manganese oxides and, in particular, organic compounds with large, active surface areas can adsorb high concentrations of metals. In the data sets used by Honeyman *et al.* (1988), particles of silt and clay from the Amazon have a lower adsorption rate for a given particle concentration because these particles have a lower unit surface area. On the other hand, particles from the California Current (Coale and Bruland 1987) contain abundant organic compounds with large, active surface areas, and these particles have a slightly higher adsorption rate for a given particle concentration. The excellent correlation between organic productivity and Th-removal rate in the California Current system led Coale and Bruland to conclude that metal removal was by active biological uptake. However, the compilation by Honeyman *et al.* strongly suggests that flux rate of particles (marine snow) is the master variable governing metal adsorption rates.

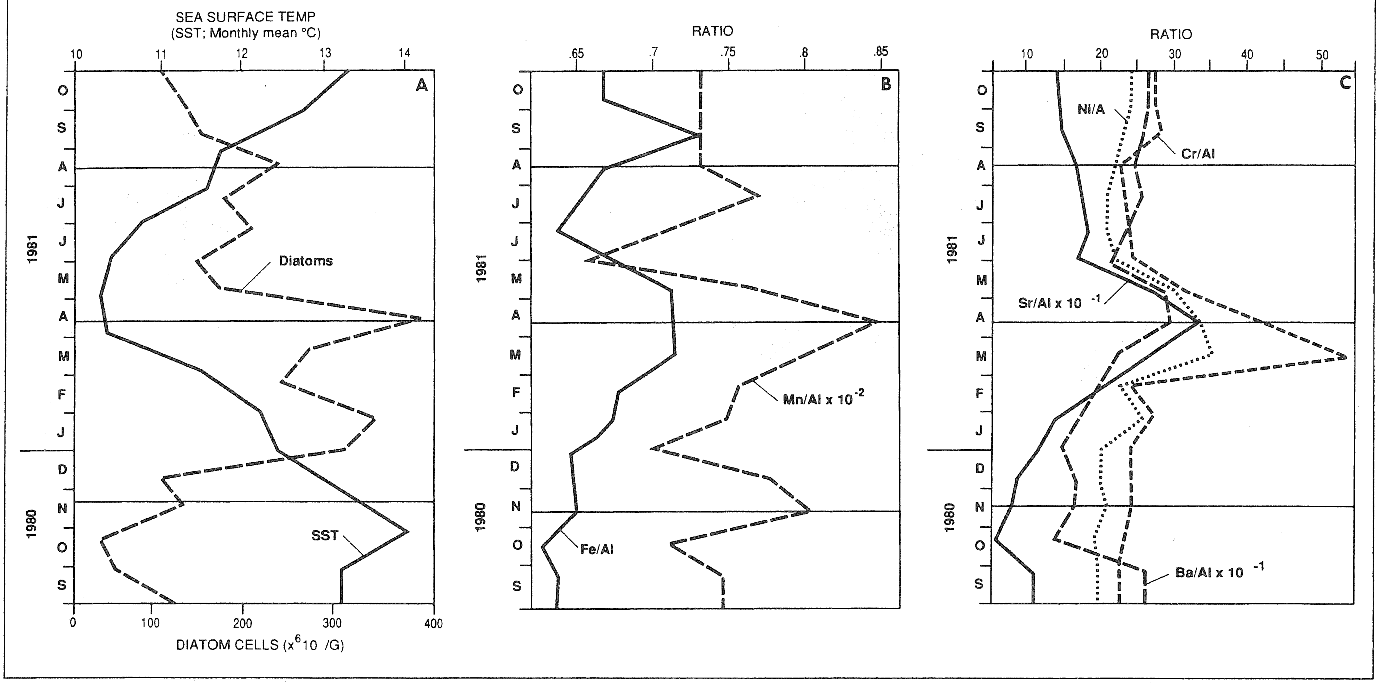
This relationship is demonstrated by our sediment-trap data, which show that highest flux rates of particles occur during spring diatom blooms (Figure 7), and this period also corresponds to highest concentrations of metals, expressed in Figure 7 as metal:Al ratios.

Biogenic Silica and Organic Carbon Production

Figures 3 and 4 show that the down-core variation in concentration of total Si in cores G117 and G145 is exactly opposite to that of C_{org}; that is, values of total Si are lowest and concentrations of C_{org} are highest in the laminated sediments. If laminated sediments with higher concentrations of C_{org} record periods of increased upwelling and organic productivity, and if that increased productivity is due mainly to diatoms, then we would expect total Si to be highest in the laminated sediments. The modern distribution of total Si in surface sediments (top 5 cm) in the study area (Figure 8A) shows total Si concentrations are highest in sediments within the OMZ, which is what we expected because of increased diatom production in surface waters of this area. All of this reasoning assumes, of course,

Figure 7
PLOTS OF DIATOM CONCENTRATION (A) AND METAL-TO-ALUMINUM RATIOS (B AND C) VERSUS TIME FROM SEPTEMBER 1980 TO OCTOBER 1981 FOR SAMPLES FROM A SEDIMENT TRAP ON THE CONTINENTAL SLOPE OFF NORTHERN CALIFORNIA

Sea surface temperature also is shown on plot A.



that the higher values of total Si are due to biogenic Si above some background level of detrital, nonbiogenic Si.

To obtain an estimate of the background level of detrital Si, we assumed the lowest Si:Al ratio in each core represents the background detrital Si:Al. These background Si:Al values are 3.6 for G117 and 3.4 for G145. The average Si:Al ratio for the deep-water reference cores are 3.6 for G121 and 3.4 for G138. These ratios can then be used to compute the detrital Si fraction. We call the difference between total Si and detrital Si "excess Si", and we assume most of this excess Si is biogenic. Results of these calculations for G117 and G145 are shown in Figure 9. The shaded area between the plots of total and detrital Si represents biogenic Si with lowest concentrations in the laminated sediments. If we apply the excess calculation to total Si in surface sediments (Figure 8A), using a "detrital" Si:Al ratio of 3.5, the resulting pattern of excess Si (Figure 8B) shows a much more restricted distribution than does total Si. Highest concentrations of excess Si (assumed to be biogenic Si) occur between 150 and 500 meters (Figure 8B) and rapidly decrease with increasing water depth (Figure 10).

We are still left with questions of why the concentration of biogenic silica decreases so rapidly with depth within a core and why it is lowest in the laminated sediments. Our answer to both questions is excess alkalinity, although we do not have pore water data to prove it. The diatoms dissolve in anoxic, alkaline pore waters, and the most alkaline pore waters would be in the laminated sediments where anaerobic decomposition of organic matter by sulfate reduction would have produced the greatest concentrations of H_2S and HCO_3^-, thereby increasing the alkalinity. Anaerobic decomposition in the laminated sediments may have proceeded to methanogenesis, which would further increase alkalinity. This same phenomenon occurs in Black Sea sediment, where a large flux of biogenic

Figure 8
ISOPLETHS OF PERCENT TOTAL Si AND BIOGENIC Si IN SURFACE SEDIMENTS ON THE CONTINENTAL MARGIN OFF THE RUSSIAN RIVER, NORTHERN CALIFORNIA

Triangles are locations of box cores (B); closed circles are locations of gravity cores (G); open circles are locations of piston cores (P).

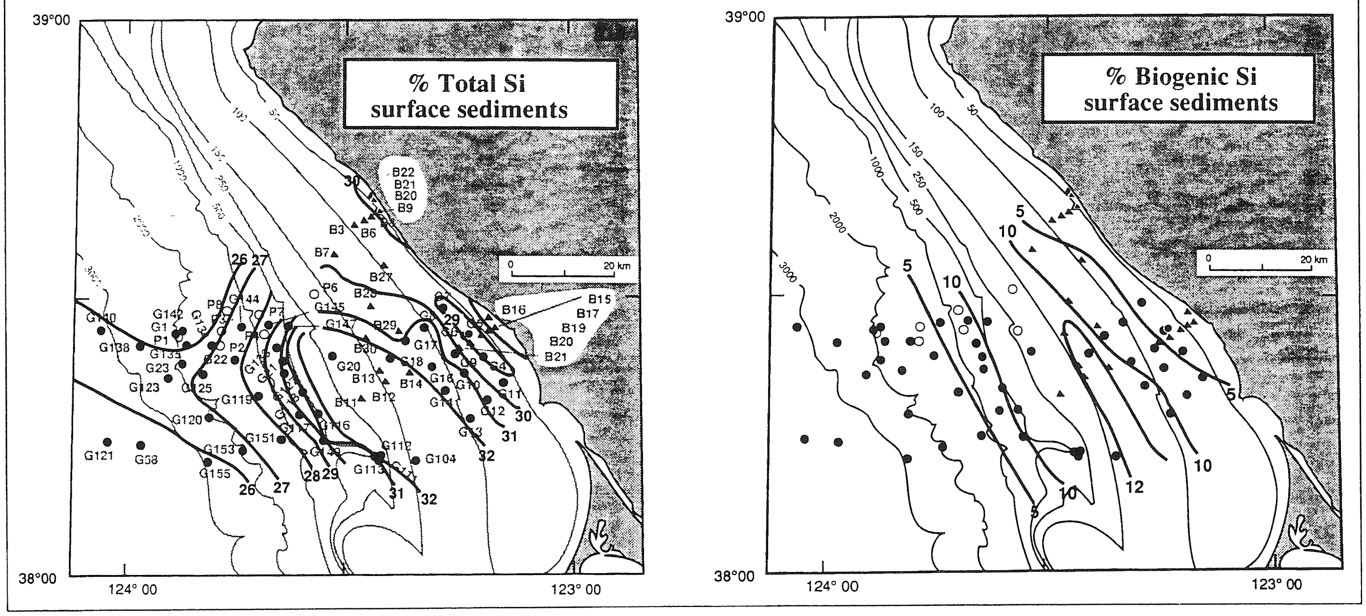


Figure 9
PERCENT TOTAL Si AND PERCENT DETRITAL Si VERSUS DEPTH FOR SAMPLES FROM CORES G117(A) AND G145 (B)

The difference between total and detrital Si (shaded areas) is excess Si and is mainly biogenic Si.

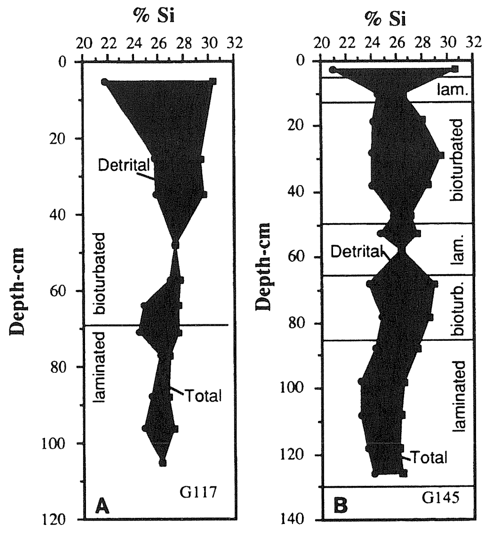
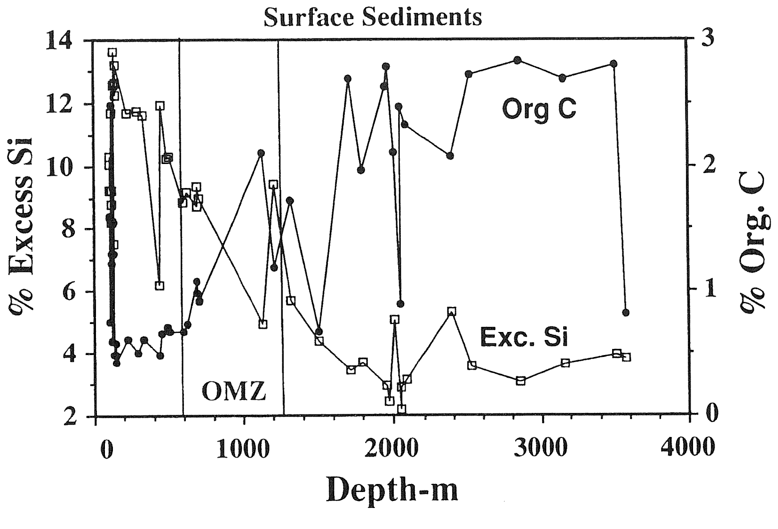


Figure 10
PERCENT EXCESS SILICA AND PERCENT ORGANIC CARBON IN SURFACE SEDIMENTS VERSUS WATER DEPTH FOR THE CONTINENTAL MARGIN OFF THE RUSSIAN RIVER, NORTHERN CALIFORNIA

Because of the extreme variation in concentration of Si and, particularly, organic carbon in shallow-water cores, data were plotted only for cores taken in water depths of >100 meters.



silica from diatoms and silicoflagellates is dissolved within the top 4-5 centimeters, the so-called "fluff" layer (Pilskaln 1990).

If excess Si in surface sediments (Figures 8B and 10), where Si dissolution has not occurred, is indeed biogenic Si and, therefore, the differences in surface distribution of excess Si shown in Figure 8B represent differences in diatom productivity in the overlying water, then a plot of excess Si versus water depth (Figure 10) can be interpreted to represent the average position of the core of highest diatom productivity. The surprising observation is that the maximum concentration of C_{org} does not correspond to the maximum concentration of excess Si. In fact, concentrations of these two parameters show opposite distribution patterns. Excess Si concentration is *greatest* between 150 and 500 meters and *decreases* offshore, whereas C_{org} concentration is *lowest* between 150 and 500 meters and *increases* offshore. This distribution suggests that less C_{org} is being preserved in sediments in the same area where it is being produced in greatest quantities in the overlying water.

A similar distribution of C_{org} content is in the data of Thompson *et al.* (1985) for sediments in a high-productivity upwelling area off Monterey Bay, although they did not discuss this distribution. One possible explanation for lowest concentration of C_{org} beneath areas of highest production is that sedimentation rate is higher under the high-productivity zone and this would tend to dilute the C_{org} content. Another possible explanation is that where C_{org} production is greatest, C_{org} consumption, both in the water column and by benthic organisms, also is greatest. This is why there is an OMZ in the first place. It may be that benthic consumption of C_{org} per unit area of sea floor is much greater under a shallow, high-productivity area than in a deeper area.

Part of the reason for higher C_{org} concentrations in deeper water may be textural; that is, the deeper sediments generally contain a higher proportion of clay that adsorbs more organic matter. On average, however, coarser sediments contain about the same range of C_{org} concentrations as clay-rich sediments. Consequently, most of the depth distribution of C_{org} concentration must be due to some other cause, whereby C_{org} is being consumed in greater quantities on the sea floor under where it is being produced in greatest quantities in the overlying water. Probably the main cause for the reduced C_{org} concentration is greater consumption by benthic organisms at the top of the OMZ. The implication is that as long as the OMZ is not anoxic, benthic organisms have plenty of food. A corollary to this implication is that if the bottom waters become anoxic and eliminate the benthic community, the excess C_{org} pool will be better preserved, reduced only by anaerobic decomposition, resulting in higher concentrations of C_{org}, which is what we observe in the laminated sediments.

The increased C_{org} consumption at the top of the OMZ may be a consequence of the *edge effect* described by Thompson *et al.* (1985) and Mullins *et al.* (1985) for the OMZ off Monterey. They found the abundance of all major invertebrate groups greatest in the upper part of the OMZ. Some invertebrates, such as echinoderms, were most abundant in sediments under the core of the OMZ (O_2 concentrations as low as 0.3 ml/L), and richness of benthic Foraminifera species also was greatest in the core of the OMZ.

Dissolved oxygen concentrations in the OMZ in the Santa Cruz basin are as low as 0.19 ml/L at 700 meters, yet the sediments support a surprisingly large epifaunal population (Edwards 1985). Mullins *et al.* (1985) point out that the edges of the OMZ, in addition to being highly productive benthic communities, also are "hot spots" of biogeochemical activity, where nitrite produced by denitrification in the core of the OMZ is reoxidized to biologically usable nitrate (Anderson 1982). The upper part of the OMZ is, thus, a region of increased nutrient cycling and can support bacteria-based benthic communities such as bacterial mats (Williams and Reimers 1983) that provide additional sources of food for benthic invertebrates.

Organic-Carbon Burial: Anoxia versus Productivity

Pedersen and Calvert (1990) stated that the fundamental control on the accumulation of organic carbon is primary productivity and not anoxia and that there is no evidence for enhanced preservation of organic matter in sediments deposited under oxygen minima. To illustrate their point, they cite examples where the maximum **residual** C_{org} concentration **in the sediments** does not always correspond to the position of the OMZ. We suggest that sediments on the Northern California margin in general and late Pleistocene sediments in particular are striking examples of enhanced preservation of organic matter in sediments deposited under a high-productivity upwelling area with a dysaerobic to anoxic oxygen-minimum zone.

Pedersen and Calvert (1990) overlooked two important points in the argument over productivity versus anoxia in the preservation of C_{org}-rich sequences.

The first point is that under oxic or even dysaerobic bottom waters (most OMZs) consumption of organic matter by benthic organisms may severely reduce the **residual** organic matter ultimately preserved, but overall these areas of high productivity that result in oxygen minima also result in accumulation of C_{org}-rich sediments. On face value, the observed distributions of residual C_{org} and excess Si concentrations **in surface sediments** off Northern California (Figure 15 of work cited) would tend to support Pedersen and Calvert's case, because the highest concentrations of **residual** C_{org} are not in sediments deposited within the OMZ. However, if our model is correct, one would not expect to preserve increased C_{org} concentrations in sediments beneath a zone of high organic production in the surface waters. Increased consumption by larger populations of benthic invertebrates and micro-organisms, particularly at the edges of an oxic or dysaerobic OMZ, would deplete C_{org} in the surface sediments, and higher sedimentation rate would dilute the C_{org} concentration. By trying to correlate maximum contents of C_{org} with minimum concentrations of dissolved oxygen, Pedersen and Calvert missed the point that the presence of an OMZ indicates high productivity and areas of high productivity, in general, are areas of enhanced preservation of C_{org}.

The second point Pedersen and Calvert missed, or at least failed to emphasize, is the importance of laminated sediments as an indicator of anoxia. Hence, they make statements such as "anoxic environments are not, *ipso facto,* sites where organic matter is preferentially preserved" [p. 458] and "The simple presence of anoxia does not foster burial of organic-rich sediments" [p. 464]. In a high productivity, oxygen-deficient environment, such as off Northern California, if organic productivity is increased through more vigorous upwelling and nutrient supply, then the concentration of O_2 in an OMZ may drop from, say, 0.5 ml/L to 0.1 ml/L or lower. As far as any benthic fauna is concerned, this is an anoxic environment and the benthic faunas disappear. Under these conditions, laminations are preserved, consumption of C_{org} is restricted to anaerobic decomposition, and a much larger proportion of the C_{org} flux is preserved as residual C_{org}. The point is, **laminated**

sediments do indicate anoxia that produced a benthic environment very different from the oxic environment with bioturbating epi- and infaunas.

Conclusions

High concentrations (up to 3% organic carbon) of well preserved, lipid-rich (H-rich) organic matter is accumulating in diatomaceous sediments on the continental margin off Northern California to depths of at least 3500 meters. This organic matter is derived from high organic productivity in response to active seasonal (summer) upwelling driven by the southward-flowing California Current. Today, there is sufficient dissolved oxygen at all depths to support a benthic fauna, even though there is a well developed oxygen-minimum zone (as low as 0.2 ml/L dissolved oxygen) between 600 and 1200 meters water depth.

During the late Pleistocene, laminated (varved) sediments were preserved within the present OMZ, indicating that at that time the OMZ was anoxic (<0.1 ml/L dissolved oxygen) and, therefore, lacked a burrowing epi- and infauna so that benthic consumption of organic matter was restricted to anaerobic decomposition. Higher concentrations of more hydrogen-rich marine organic matter were preserved in these laminated sediments. From this observation we infer that upwelling and organic productivity in this area were greater during the late Pleistocene. Because stronger upwelling under the California Current implies greater wind stress by atmospheric circulation on the northeast Pacific Ocean, the stratigraphic record of laminated and bioturbated sediments off Northern California should contain a detailed high-resolution paleoclimatic record of changes in atmosphere/ocean circulation.

Sediment-trap data show highest concentrations of metals are associated with higher particle flux rates during spring diatom blooms. Higher overall particle flux rates due to higher organic productivity during times of laminated sediment accumulation resulted in accumulation of higher metal concentrations in the laminated sediments relative to interbedded bioturbated sediment. The laminated sediments also contain higher concentrations of sulfur, indicating a higher rate of sulfate reduction due to the presence of more "reactive" H-rich organic matter in the laminated sediments. The concentration of biogenic Si is lower in the laminated sediments than in the interbedded bioturbated sediments, indicating greater dissolution of biogenic Si in more alkaline pore fluids of the anoxic laminated sediment.

Higher concentrations of biogenic Si from diatoms, but lower concentrations of organic carbon, are preserved in surface sediments near the top of the OMZ relative to both shallower and deeper sediments. This indicates less residual C_{org} is preserved in sediments in the same area where organic matter is produced in greatest quantities in the overlying water. This difference in apparent production and preservation of organic matter probably is due to higher benthic consumption by large populations of benthic microorganisms and invertebrates at the edges of an oxic or dysaerobic OMZ. This means accumulation of C_{org} should not necessarily be expected to be greatest within the OMZ, or at least at the upper edge of the OMZ. Regardless of the locus of maximum accumulation of organic carbon relative to the OMZ, the important points are that because of upwelling and high surface water productivity, **there is an OMZ** and **there is preservation of high concentrations of organic matter under this zone**. Sediments containing up to 3% organic carbon in water depths up to 3500 meters are organic-carbon-rich by almost anyone's definition.

Although modern sediments on the continental margin off Northern California represent an impressive accumulation of organic matter, under an oxic to dysaerobic OMZ, the upper Pleistocene sediments are a striking example of **enhanced** preservation of organic matter in sediments deposited under an **anoxic** OMZ. These sediments show that **laminated sediments do indicate anoxia** and that anoxia produced a benthic environment very different from the oxic environment with bioturbating epi- and infauna. We conclude that anoxic environments are indeed sites where organic matter is preferentially preserved and that anoxia does indeed foster the burial of organic matter. This study shows that it is important to distinguish between processes within oxic, dysaerobic, and anoxic OMZs.

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