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Sediment Cd and Mo accumulation in the oxygen-minimum zone off western Baja California linked to global climate over the past 52 kyr

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[1] Concentrations of organic carbon (orgC), cadmium (Cd), and molybdenum (Mo) were measured in two sediment cores raised from depths of 430 and 700 m within the oxygen-minimum zone (OMZ) off southern Baja California at a temporal resolution of ~0.5 kyr over the past 52 kyr. These records are supplemented with diffuse spectral reflectance (DSR) measurements obtained on board ship soon after collection at a resolution of ~0.05 kyr. In the core from 700 m depth, a component extracted from the DSR data and the three geochemical proxies generally vary in concert with each other and over a wide range (4–22% orgC; 1–40 mg/kg Cd; 5–120 mg/kg Mo). Intervals of increased orgC, Cd, and Mo accumulation generally correspond to warm periods recorded in the oxygen-isotopic composition of Greenland ice, with the exception of the Bolling/Allerod which is only weakly expressed off Baja California. Concentrations of the biogenic proxies are higher in the core from 430 m depth, but erratic sediment accumulation before 15 ka precludes dating of the older intervals that are laminated and contain elevated orgC, Cd, and Mo concentrations. The new data provide further evidence of an intimate teleconnection between global climate and the intensity of the OMZ and/or productivity along the western margin of North America. On the basis of a comparison with Cd and Mo records collected elsewhere in the region, we conclude that productivity may actually have varied off southern Baja California by no more than a factor of 2 over the past 52 kyr.

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1. Introduction

[2] The California Current is one of Earth's four large and productive eastern boundary currents underlain by an intense oxygen-minimum zone (OMZ). The shape and intensity of the OMZ reflects a balance between oxygen consumption by decaying organic matter and advection of oxygenated intermediate water produced at high latitudes by cooling [*Wyrtki*, 1961]. A number of early studies have suggested that the intensity of the OMZ along the western margin of North America may have fluctuated in response to climate change in the past [*Anderson et al.*, 1987, 1989, 1990; *Dean et al.*, 1994, 1997]. The most spectacular demonstration of such a linkage, however, was provided by the discovery of a sequence of laminated and bioturbated sediments in cores from Ocean Drilling Program (ODP) Site 893 in Santa Barbara Basin, with laminated sections corresponding to warm climate intervals recorded in the oxygen-isotopic composition of Greenland ice over the past 60 kyr [*Behl and Kennett*, 1996]. The evidence for a link to global millennial-scale climate fluctuations has been reinforced by detailed faunal, isotopic, and geochemical analyses at ODP893 [*Cannariato et al.*, 1999; *Hendy and Kennett*, 1999; *Emmer and Thunell*, 2000; *Ivanochko and Pedersen*, 2004], as well as detailed analyses of cores from ODP Site 1017 on the open central California at a depth of about 1000 m [*Cannariato and Kennett*, 1999; *Hendy et al.*, 2004; *Hendy and Pedersen*, 2005].

[3] Despite the large quantities of high-quality data that have been generated for the region, the relative importance of productivity and ventilation in establishing the pattern of laminations in Santa Barbara Basin has still not been definitively determined. Moreover, the nature of the teleconnection(s) between temperature over Greenland and processes affecting ocean circulation and biogeochemistry of the California Current also remains largely speculative. This study presents new biogenic proxy data from a site on the southern Baja California margin, 500 km south of ODP893 and ODP1017 (Figure 1), where previous works has shown millennial-scale climate fluctuations also have been recorded over the past 52 kyr [*van Geen et al.*, 2003; *Ortiz et al.*, 2004].

2. Biogenic Proxies

[4] Three paleoproxies are the primary focus of this study. The first is the concentration and mass accumulation rate

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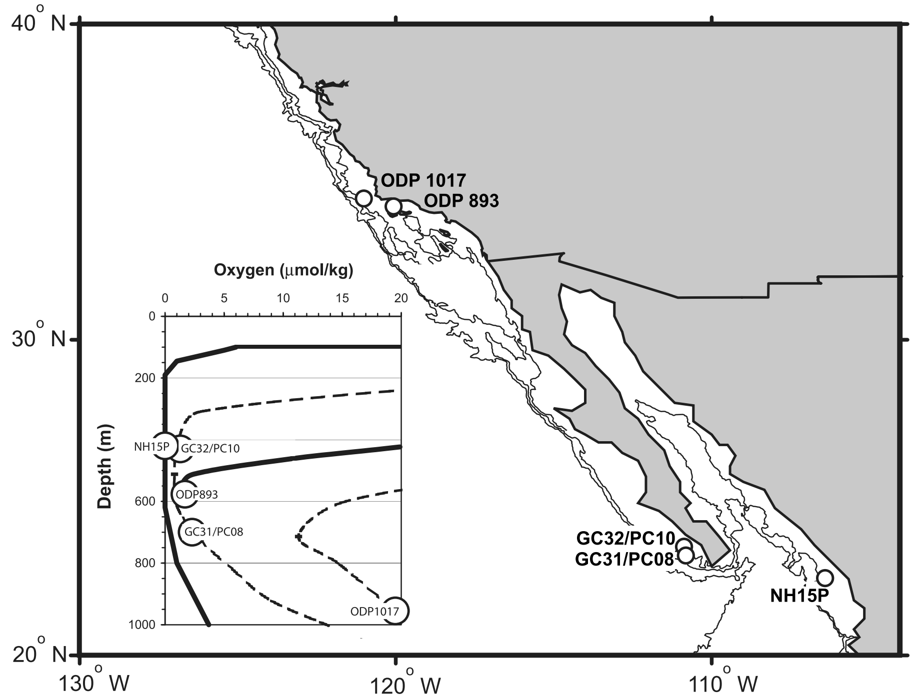

Figure 1. Map of the continental margins of North America from northern California to northwestern Mexico showing the location of the seven sites discussed in this paper. Depth contours on the continental slope are at 1000 m and 3000 m. Corresponding dissolved oxygen profiles from *Fine et al.* [2001], *Hartnett and Devol* [2003], and *van Geen et al.* [2003] are shown in the inset.

(MAR) of organic carbon (orgC) in the sediment. There is no doubt that sediment underlying productive regions of the ocean generally contain elevated concentrations of orgC [*Berger*, 1989]. Less clear is the extent to which orgC can be used as a reliable indicator of past productivity. This is because, first of all, only a small fraction of the orgC produced in surface waters reaches the sediment [*Suess*, 1980]. Further, decomposition of orgC is affected by a number of factors, including the sediment burial rate and, at least under certain conditions, bottom water oxygen (BWO) concentrations and the penetration of oxygen into pore waters [*Emerson and Hedges*, 1988; *Calvert et al.*, 1992; *Canfield*, 1994; *Dean et al.*, 1994; *Hedges and Keil*, 1995]. These factors have been combined by *Hartnett et al.* [1998] in the concept of oxygen exposure time as a major control on orgC preservation. The orgC that is preserved in the sediment is, by definition, also the most refractory component of the settling flux of plankton matter [*Canfield*, 1994; *Hedges and Kiel*, 1995]. The concentrations of this refractory fraction may therefore be only weakly connected to the level of primary production in overlying waters.

[5] Another factor complicating the interpretation of down core orgC records is that fine-grained sediments typically contain more orgC than coarse-grained sediments [*Mayer*, 1994; *Hedges and Keil*, 1995]. Compound-specific radiocarbon dating of marine sediment has shown that the history of deposition of fine-grained organic material can be very different from that of rapidly sinking tests of foraminifera [*Ohkouchi et al.*, 2002; *Mollenhauer et al.*, 2003; *Kienast et al.*, 2005]. Therefore variations in orgC content could also result from changes in the source of particles because of changes in bottom currents. In Santa Barbara Basin, *Berger et al.* [2004] recently proposed that orgC burial was influenced by tidally driven redistribution of fine-grained particles from the shelf, which may complicate the interpretation of the orgC record from ODP893 [*Hendy and Pedersen*, 2005].

[6] The concentrations and MARs in sediment of the two other proxies used in this study, cadmium (Cd), and molybdenum (Mo), are also related to primary production in overlying waters, but through a sequence of steps that presently preclude simple quantitative interpretation. Enrichments of Cd in sediment underlying productive waters are thought to reflect the enrichment of this trace element in plankton matter [*Knauer and Martin*, 1981], retention of this fraction in surficial sediments, and additional precipitation in pore waters [*McCorkle and Klinkhammer*, 1991]. The distribution of Cd in the water column of Santa Barbara Basin exemplifies both the nutrient-like properties of this trace element, in the sense that surface waters are depleted, as well as its affinity for sediment under reducing conditions reflected by a depletion of dissolved Cd in bottom waters [*van Geen et al.*, 1995]. *Rosenthal et al.* [1995] hypothesized that nanomolar sulfide concentrations might be sufficient to trap dissolved Cd onto particles; such sulfide concentrations have been measured in pore waters of surficial sediments in

Table 1. Setting of Key Cores Along the Western Margin of North America

Site	Latitude, °N	Longitude, °W	Depth, m	BWO, μmol/kg	Sediment Rate, cm/kyr	References
ODP1017	34°32′	121°06′	955	20	18	*Kennett et al.* [2000] and *Hendy and Pedersen* [2005]
ODP893	34°17′	120°02′	577	~1	140	*Behl and Kennett* [1996] and *Hendy et al.* [2002]
MV99 GC32/PC10	23°47′	111°34′	430	~1	22[a]	*van Geen et al.* [2003]
MV99 GC31/PC08	23°28′	111°36′	700	3	30	*van Geen et al.* [2003] and *Ortiz et al.* [2004]
NH15P	22°41′	106°28′	420	<5	17[a]	*Ganeshram and Pedersen* [1998]

[a]Holocene.

Santa Barbara Basin [*Kuwabara et al.*, 1999] that are also enriched in Cd in the solid phase [*Bruland et al.*, 1981]. The combination of these processes cause significant enrichments of Cd up to ~2 mg/kg in sediment within the oxygen-minimum zone (OMZ) off central California, 2 mg/kg in the bottom of Santa Barbara Basin, and 12 mg/kg along the Mexican margin off Mazatlan [*van Geen et al.*, 1995; *Nameroff et al.*, 2002].

[7] The behaviors of Cd and Mo in suboxic environments, though related, differ in several ways. First, Mo is not particularly enriched in plankton matter, as illustrated by nearly conservative behavior of this oxyanion in surface waters [*Collier*, 1985]. Indeed, Mo is not highly enriched in sinking plankton matter in Santa Barbara Basin [*Zheng et al.*, 2000a]. Analysis of sediment trap material from this location also shows that nonbiogenic Mo associated with Mn oxides reaching the sediment with the OMZ is probably released to the water column [*Zheng et al.*, 2000a]. This would tend to further attenuate initial enrichments of Mo in surface sediment underlying the OMZ. On the other hand, *Nameroff et al.* [2002] did document a weak association of Mo with plankton matter in the particularly intense OMZ off Mazatlan, Mexico.

[8] A simple consideration of mass balance underlines another significant difference between Cd and Mo. Assuming a sediment porosity of 80%, precipitation of Cd out of a volume of pore water, starting from bottom water concentrations of ~1 nmol/kg, corresponds to an enrichment of 0.2 mg/kg, i.e., ~2 × crustal concentrations [*Taylor and McLennan*, 1985]. The precipitation Mo from a bottom water concentration of 120 nmol/kg, instead, is equivalent to an enrichment of 23 mg/kg, which corresponds to ~20 × crustal levels. This difference, and pronounced precipitation of Mo in pore waters at micromolar sulfide concentrations [*Emerson and Huested*, 1991; *Zheng et al.*, 2000a], leads to postdepositional enrichment of Cd that is typically restricted to the upper few cm of the sediment whereas significant additional precipitation of Mo can occur deeper in the sediment. Such divergent distributions of Cd and Mo have been observed in short sediment cores off Mazatlan [*Nameroff et al.*, 2002]. Whereas the above calculation neglects diffusion of Cd and Mo across the sediment-water interface, it illustrates that Cd enrichments predominantly reflect the retention of Cd contained in plankton matter, whereas Mo enrichments are postdepositional and linked to the reducing power of organic matter that drives sulfate reduction. In anoxic Cariaco Basin, *Piper and Dean* [2002] indeed estimated that 86% of Cd accumulating in the sediment was attributable to settling plankton matter, whereas the accumulation of hydrogenous Mo linked to sulfate reduction within the sediment contributed 97% of the total amount of Mo in the solid phase.

[9] Satellite data show that the intensity and width of the coastal band of elevated chlorophyll concentrations narrows considerably along the southerly flow path of the California Current [*Thomas et al.*, 1994]. Instead of weakening, however, the intensity of the OMZ increases in the same direction [e.g., *Hartnett and Devol*, 2003]. The accumulation of biogenic proxies along the margin could therefore be expected to reflect the combination of these two opposing meridional trends of plankton atter generation in surface water and preservation in bottom water, respectively. A recent study of the distribution of chlorofluorocarbons along the western margin of Baja California has demonstrated that the OMZ, despite its intensity, is ventilated from the north on decadal timescales [*van Geen et al.*, 2006]. This is countered by northward eddy transport of low-oxygen water along the coast that has been documented to a depth of 600 m by numerous float deployments [*Collins et al.*, 2004].

3. Materials and Methods

3.1. Sediment Cores

[10] The two new records of orgC, Cd, and Mo accumulation presented here were obtained from an area where oxygen depletion of the water column and elevated productivity combine to limit bioturbation of the sediment under present climate conditions. Further north along the margin, laminations are not preserved within the OMZ today although they have been occasionally in the past [*van Geen et al.*, 2003]. The study relies on two sets of overlapping gravity and piston cores from the open slope off Baja California at ~23°N and water depths of 430 (MV99 GC32/PC10) and 700 m (MV99 GC31/PC08; Figure 1 and Table 1) that were collected on board R/V *Melville* in 1999 [*van Geen and R/V Melville Scientific Party*, 2001; *van Geen et al.*, 2003]. The cruise label is not included hereon in the designation of the *Melville* cores. The tops of the piston cores typically were missing 1–1.5 m of sediment. Overlap with the gravity cores was determined within 1 cm by comparing the patterns of laminations. Radiocarbon dating indicates that the upper laminated sediments are Holocene in age and were deposited at an average rate of 22 and 30 cm/kyr in GC32 and GC31, respectively [*van Geen et al.*, 2003]. Additional time control points, based on a visual correspondence between a component of the diffuse spectral reflectance data collected on board ship and the Greenland isotope record, indicate that the lower laminated sections in the deeper of the two cores (PC08) were deposited between 35 and 50 kyr ago [*Ortiz et al.*, 2004]. The age of sections older than 15 ka at the shallow site

(PC10) is unconstrained because of a probable hiatus [*van Geen et al.*, 2003].

3.2. Analyses

[11] The two cores were logged at sea at 1-cm resolution with a Geotek multisensor logger that includes sensors for gamma ray attenuated porosity estimation (GRAPE), P wave velocity, and magnetic susceptibility [*Gardner et al.*, 1992, 1995]. For converting orgC, Cd, and Mo concentrations to mass accumulation rates (MARs), dry bulk density (DBD) was calculated from wet bulk density (WBD) determined by GRAPE using the equation: DBD = 1.563WBD − 1.560. This equation was derived from a linear correlation between GRAPE-derived WBD and measured DBD on samples from ODP Leg 167 cores [*Lyle et al.*, 2000]. When this equation is applied to earlier U.S. Geological Survey (USGS) cores for which DBD was calculated earlier from WBD using a slightly different equation [*Gardner et al.*, 1997], the correlation coefficient between the two estimates is 1.0.

[12] Soon after splitting cores at sea, the sediment was analyzed at 1-cm resolution for diffuse spectral reflectance (DSR) with a Minolta CM-2022 spectrophotometer. A three-component R mode factor analysis of the first-derivative transform of the percent reflectance data accounts for >93% of the variance of the data. DSR factor 3 accounts for 10% of the variance and, in PC08, bears a striking resemblance to the organic carbon content of the core as well as the oxygen isotope record in Greenland ice over much of the past 52 kyr, with warm interstadials corresponding to high DSR factor 3 loadings [*Ortiz et al.*, 2004]. The DSR factor 3 record for the shallower core, GC32/PC10, is presented here for the first time.

[13] Dried and powdered samples were analyzed for weight percentages of total carbon (TC) and inorganic carbon (IC) by coulometric titration of CO_2 following extraction from the sediment by combustion at 950° C and acid volatilization, respectively [*Engleman et al.*, 1985]. Percent organic carbon (orgC) was calculated as the difference (TC − IC), and percent $CaCO_3$ was calculated as $CaCO_3$ = IC/0.12, where 0.12 is the fraction of carbon in $CaCO_3$. The accuracy and precision of this method, determined from several hundred replicate analyses of standards, usually are better than 0.1 wt% for both TC and for TIC.

[14] Concentrations of Cd and Mo were measured at ~5 cm resolution in GC31 and PC10, and at ~10 cm resolution in PC08, by inductively coupled plasma–atomic emission spectrometry (ICP-AES) in USGS laboratories in Denver [*Briggs*, 2002]. For most elements, the precision of the method, determined by analyzing USGS rock standards and duplicating 10% of the samples, was better than 10% and usually better than 5%, at a concentration of 10 × the detection limit of ~1 mg/kg for both Cd and Mo. Analyses of Cd and Mo in core GC32 at ~1 cm resolution followed a method described by *Zheng et al.* [2003] using inductively coupled plasma–mass spectrometry (ICP-MS) at Lamont-Doherty Earth Observatory. Comparison of ICP-AES and ICP-MS data in a subset of 67 samples collected from the same depths in GC31 indicates that Cd and Mo concentrations determined by ICP-MS were systematically 15 ± 2% higher. Only ICP-AES data were used to calculate mass accumulation rates (MARs) in GC31 and PC08. The ICP-MS data were adjusted to match the ICP-AES data to calculate MARs in GC32 and for plotting. Detailed interpretation of the higher-resolution Holocene records will be presented elsewhere (Y. Zheng et al., manuscript in preparation, 2006).

4. Results

4.1. Variations in Cd and Mo Concentrations at 700 m

[15] Concentrations of Cd and Mo ranging from 1 to 12 mg/kg and 5 to 40 mg/kg, respectively, closely track each other over the entire 16 m length of the GC31/PC08 record (Figure 2). The parallel variations of both proxies, combined with low Mn concentrations (<300 mg/kg) observed throughout the record, indicate that the observed Mo enrichments are not associated with Mn oxide layers [*Shimmield and Price*, 1986]. Concentrations ≥4 mg Cd/kg and ≥15 mg Mo/kg are sustained over the entire 3.3. m length of the upper laminated section, previously shown to cover the past 11.5 kyr (i.e., essentially the Holocene [*van Geen et al.*, 2003]). This section contrasts with the next interval down core between 3.3 and 7.0 m depth, which is bioturbated and dated at 11.5–25 ka, where concentrations rarely exceed 2 mg Cd/kg and 10 mg Mo/kg, respectively. Although these concentrations are lower than in the Holocene section, they still indicate considerable enrichment throughout the Last Glacial Interval (LGI, 25–12 ka) compared to crustal levels of ~0.1 mg Cd/kg and ~1 mg Mo/kg [*Taylor and McLennan*, 1985]. Between 7.0 and 15 m depth, variations in Cd and Mo concentrations span the entire range (Figure 2), with maxima and minima that are often defined by more than a single point. *Ortiz et al.* [2004] showed that sediments in this interval were deposited between 52 and 25 ka, when millennial-scale fluctuations in climate were recorded in the oxygen-isotopic composition of Greenland ice [*Grootes et al.*, 1993]. The laminated sections in PC08 deposited between 52 and 25 kyr ago all contain elevated Cd and Mo concentrations, but bioturbated or partially laminated sections are also occasionally elevated in Cd and Mo (Figure 2).

[16] Millennial-scale fluctuations in Cd and Mo concentrations closely resemble the variations in orgC levels between 5 and 15% over the past 52 kyr (Figure 2). Concentrations of all three proxies are elevated during the Holocene and during warm interstadials between 52 and 25 ka, and low during the LGI and cold stadials. There is a difference between orgC, Cd, and Mo, however, when changes in the rate of accumulation of sediment are taken into account. The shipboard logger data show that the DBD of cores GC31/PC08 increases steadily from 0.2 g/cm^3 at top of the section to 0.6 g/cm^3 at 5 m depth (Figure 2). The general trend in this upper section reflects at least in part compaction. Excursions in DBD deeper in the core also indicate lower bulk densities for laminated sediments that accumulated during earlier warm intervals, which is related to the higher orgC content. As a result of the changes in bulk sediment MARs, there is little if any change in MAR

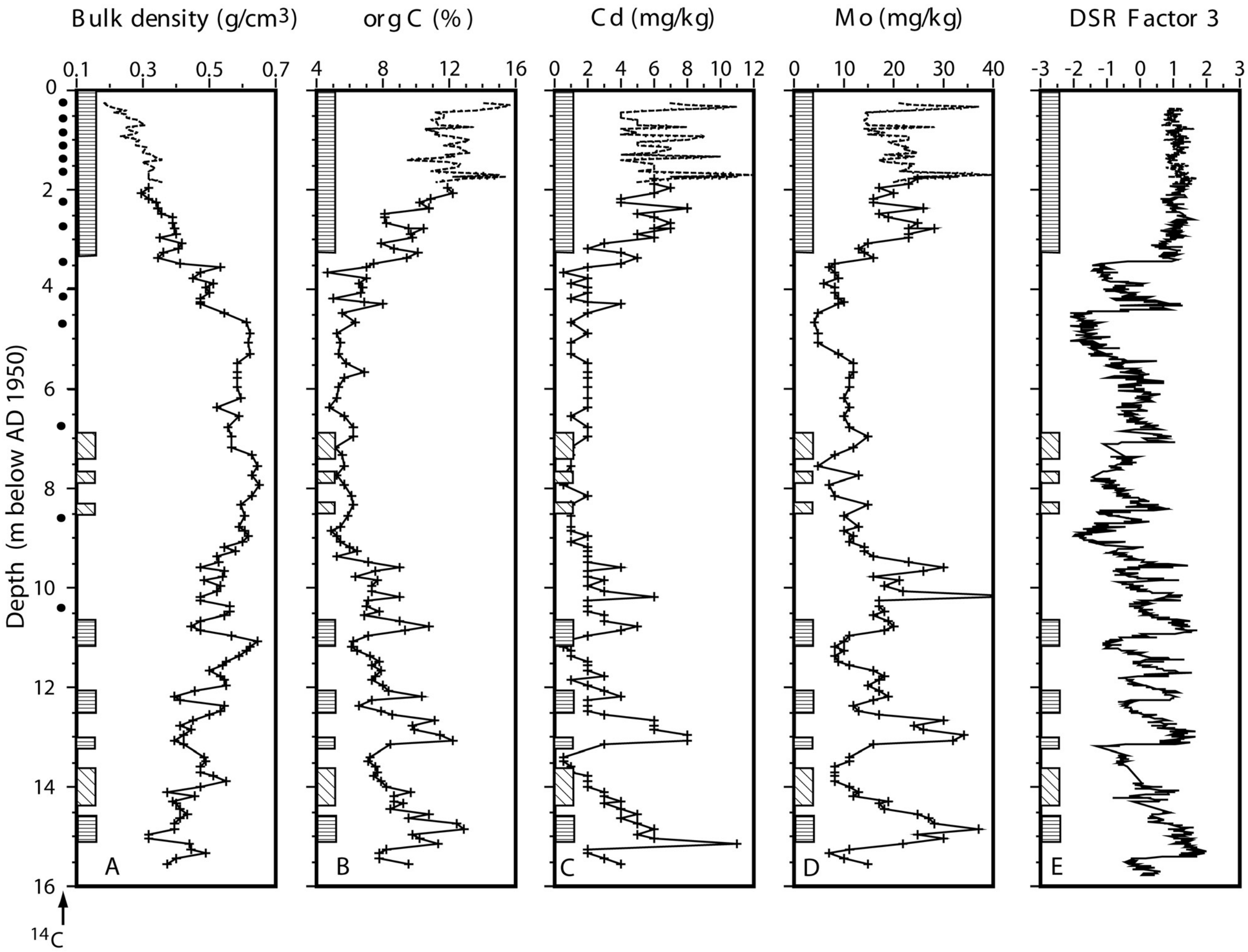

Figure 2. Profiles of wet bulk density, orgC, Cd, and Mo concentrations and DSR factor 3 [*Ortiz et al.*, 2004] as a function of depth in cores GC31 (adjusted ICP-MS data; dashed line) and PC08 (ICP-AES data, solid line) raised from 700 m depth off the margin of southern Baja California. Stratigraphic locations of laminated sediments are indicated by the laminated boxes to the right of the depth scale. Stratigraphic locations of disturbed, frothy sediments are indicated by the diagonally lined boxes to the right of the depth scale. Solid dots along the depth scale indicate the stratigraphic positions of ^{14}C dates [*van Geen et al.*, 2003].

of orgC during cold and warm periods, whereas MARs of Cd and Mo are significantly attenuated during cold periods.

4.2. Sedimentation and Paleoproxy Records at 430 m

[17] The age model for GC32/PC10 is well constrained over the past 15 kyr by 9 radiocarbon dates indicating a nearly constant sedimentation rate of 22 cm/kyr [*van Geen et al.*, 2003]. Between 4.5 and 5.1 m, however, there is a sharp jump in age from 15.6 to 34.2 ka. The sharp increase in age is not associated with a discontinuity that is detectable visually or a sharp change in wet bulk density (Figure 3). Benthic foraminifera dated from three additional intervals in PC10 all yielded ages >40 ka, which is beyond the practical limit for radiocarbon dating [*van Geen et al.*, 2003]. Unfortunately, DSR factor 3 cannot be used for chronostratigraphy of the laminated sections that dominate the record between 8.5 and 14.5 m in PC10 (Figure 3). Unlike PC08 from 700 m depth (Figure 4), there is no easily recognizable pattern in DSR factor 3 that can be linked with confidence to a portion of the Greenland isotope record.

[18] Whereas the DSR factor 3 record, collected at 1-cm intervals, does not provide any constraints for an age model for PC10 below ~4 m depth, the general correspondence with orgC measurements obtained at lower resolution (5 cm) is preserved. Particularly high factor 3 loadings observed in the deeper laminated sections of unknown age in PC10 are associated with orgC concentrations of ~14%, which are higher than in deeper laminated sections of PC08. Noticeably absent between 8.5 and 14.5 m depth in PC10 are sections of low DSR factor 3 loadings and reduced orgC content that occur in PC08 (Figure 2) and correspond to cold stadials recorded in Greenland ice. This suggests that sedimentation was sharply reduced at the site of PC10 not only during the LGI but also during previous cold climate intervals.

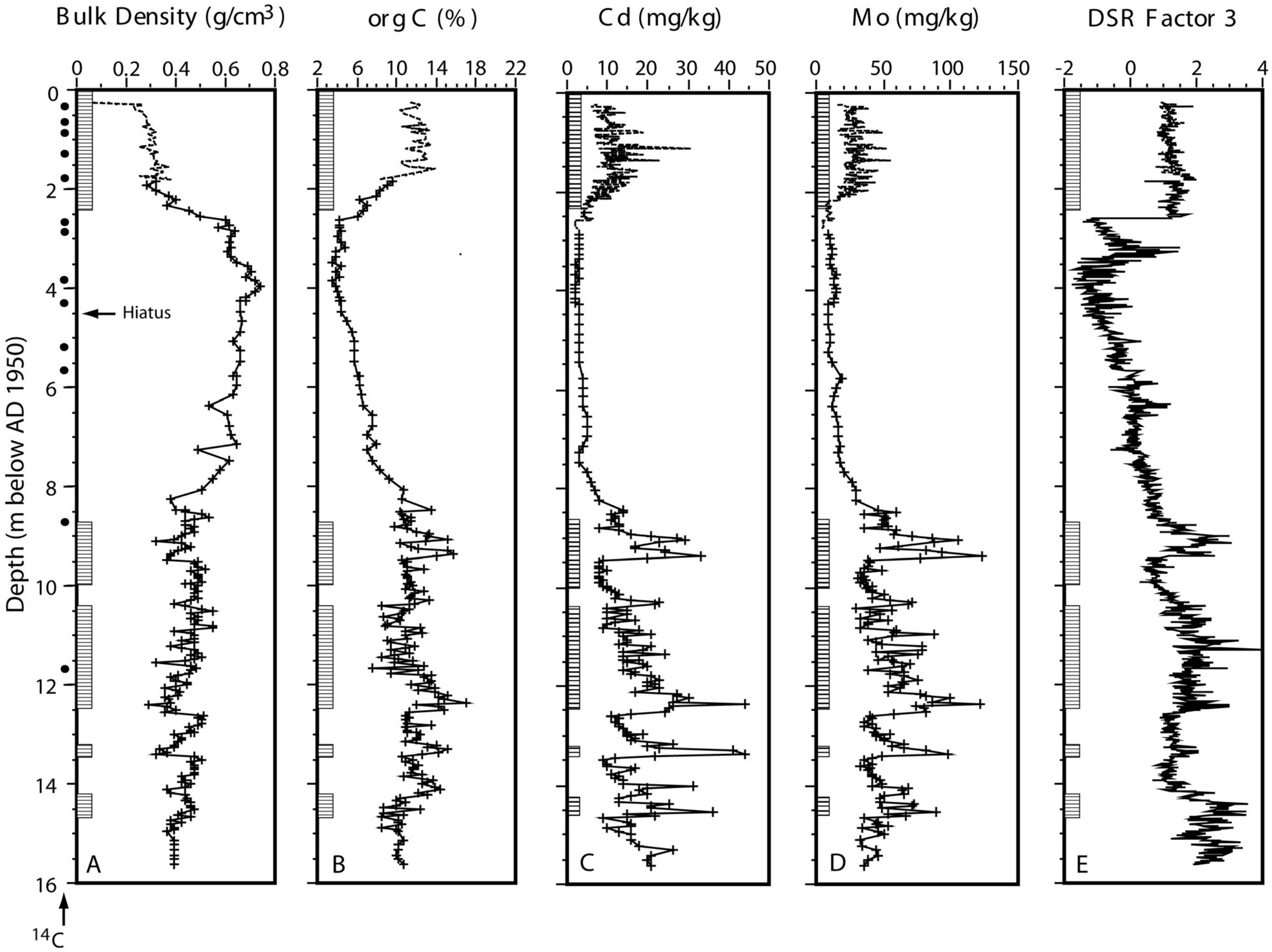

Figure 3. Profiles of wet bulk density, orgC, Cd, and Mo concentrations and DSR factor 3 as a function of depth in cores GC32 (adjusted ICP-MS data; dashed line) and PC10 (ICP-AES data, solid line) raised from 430 m depth off the margin of southern Baja California. Stratigraphic locations of laminated sediments are indicated by the laminated boxes to the right of the depth scale. Solid dots along the depth scale indicate the stratigraphic positions of ^{14}C dates [*van Geen et al.*, 2003].

[19] In contrast to orgC, authigenic metal concentrations vary over a wider range in GC32/PC10 compared to GC31/PC08. Concentrations of Cd and Mo range from 2 to 40 mg/kg and 2 to 130 mg/kg, respectively, with most of the highest values restricted to the deeper laminated section of undetermined age >40 ka. Within this section, several asymmetric sequences of increases and decreases in Cd and Mo concentrations in PC10 resemble the saw-tooth patterns observed in the records from PC08 and in the oxygen isotope record in Greenland ice We therefore speculate that, as in PC08, the Cd and Mo peaks in PC10 correspond to warm interstadials even if their age is undetermined, whereas cold stadial events apparently were not as well recorded at 430 m depth as they were at 700 m depth (Figure 2).

5. Discussion

5.1. Comparison of the Two Baja California Margin Records

[20] It is not clear why sediment accumulation at the 430 m site was interrupted during the LGI, to then resume during the Holocene. The distance of only 15 km separating the 430 and 700 m sites, compared to their distance of ~80 km from the coast, suggests that they are located within the same general regime in terms of surface productivity. SeaBeam bathymetry of the area, however, shows that the shallower site is located near the top of a ridge, whereas the 700 m site is at the bottom of a depression [*van Geen et al.*, 2003]. Sustained sediment focusing to the depression could therefore explain why lowering sea level by ~120 m during the LGI had little effect at this location, whereas it might have cut off or reduced the supply of settling particles to the considerably shallower ridge. Winnowing during the LGI inferred from a decrease in the sedimentation rate in core NH15P, raised from 420 m water depth off the mainland of Mexico near Mazatlan, accompanied by a coarsening of the grain size, may be related to the disturbance of sedimentation observed in PC10 [*Ganeshram and Pedersen*, 1998].

[21] Whereas the two records cannot be compared during the LGI and older intervals, the proxy data for the Holocene suggest similar biogeochemical conditions prevailed at the two sites over the past ~10 kyr. Today, BWO concentra-

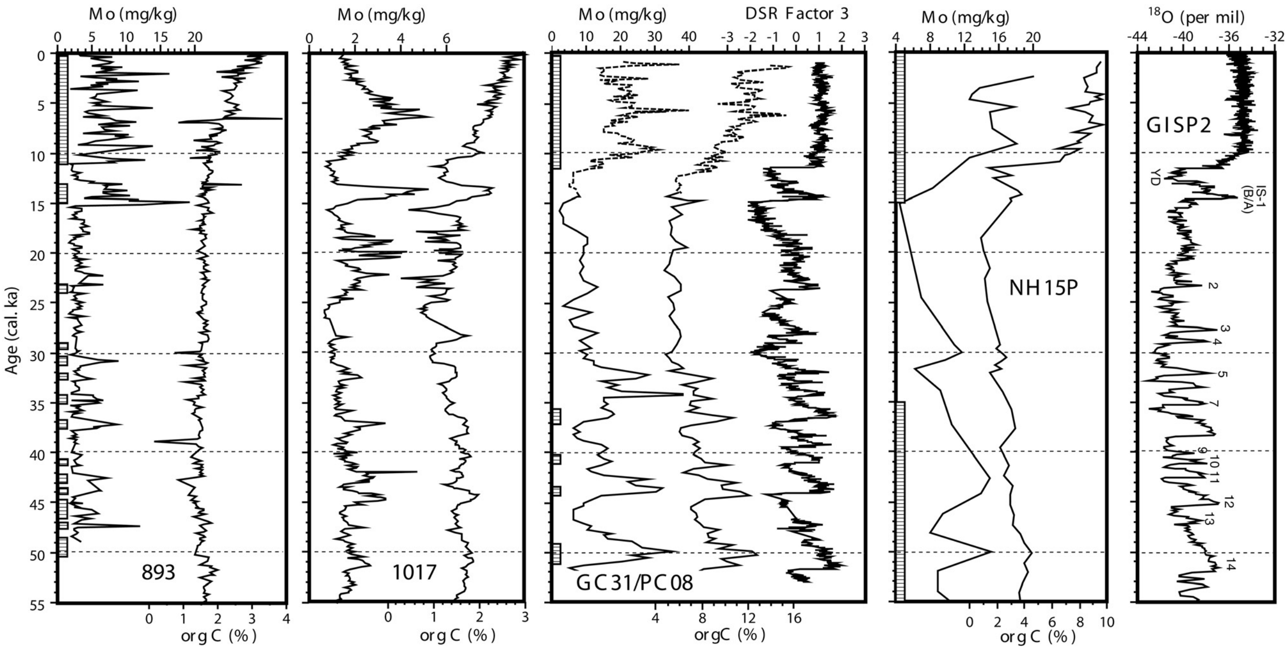

Figure 4. Concentrations of orgC and Mo measured at ODP Site 893 [*Gardner and Dartnell*, 1995; *Ivanochko and Pedersen*, 2004], ODP Site 1017 [*Hendy and Pedersen*, 2005], GC31/PC08 (this study), and NH15P [*Ganeshram and Pedersen*, 1998; *Nameroff et al.*, 2004] as a function of calendar age. Also shown are records of DSR factor 3 for GC31/PC08 [*Ortiz et al.*, 2004] and the variations of the oxygen isotope composition of Greenland ice [*Grootes et al.*, 1993]. Stratigraphic locations of laminated sediments are indicated by the laminated boxes to the right of the depth scale.

tions are rather similar: ~1 μmol/kg at 430 m versus 3 μmol/kg at 700 m (Figure 1). Concentrations of orgC, Cd, and Mo in sediments deposited during the Holocene are somewhat higher at the shallow site, but average MARs of the same constituents are comparable: 0.7 ± 0.2 versus 1.0 ± 0.1 g orgC/cm^2/kyr; 72 ± 26 versus 60 ± 16 μg Cd/cm^2/kyr; and 180 ± 54 versus 220 ± 60 μg Mo/cm^2/kyr at 430 and 700 m depth, respectively. Despite the difference in depth and depositional environment, the combination of moderate productivity and an intense OMZ in the area resulted in comparable fluxes of orgC, Cd, and Mo accumulating at 430 and 700 m depth during the Holocene. This suggests that the biogenic proxy records can be regionally representative and not merely the reflection of local changes in sediment focusing or bottom currents.

[22] The MARs of Cd and Mo are quite large compared to the diffusive fluxes that have been estimated independently elsewhere from pore water gradients near the sediment-water interface. Translated in terms of Fick's law, the Cd MARs at 430 and 700 m during the Holocene, if derived entirely from diffusion and starting at a bottom water concentration of ~1 nmol Cd/kg, would result in complete removal of Cd from pore waters at a depth of only ~0.3 cm. This is a considerably steeper gradient than observed at the limited number sites where pore water Cd concentrations have been measured, albeit under less intensely reducing conditions than the OMZ off southern Baja California [*McCorkle and Klinkhammer*, 1991; *van Geen et al.*, 1995]. The implication is that Cd initially contained in plankton organic matter may have contributed much if not most of the enrichment observed in Holocene sediment off southern Baja California. The MARs of Mo at 430 and 700 m depth during the Holocene correspond to depletion at a depth in the sediment of ~8 cm from typical bottom water concentrations of 120 nmol/kg, which is consistent with observation elsewhere, including Santa Barbara Basin [*Zheng et al.*, 2000a]. In contrast to Cd, it therefore appears that postdepositional precipitation of Mo dominates the enrichments observed in OMZ sediments off southern Baja California.

[23] It is worth pointing out that the behavior of the three biogenic proxies is also occasionally decoupled. During the Holocene, for instance, the concentration of orgC rises steadily from the LGI to the present in GC31 (but not in GC32), whereas Cd and Mo concentrations fluctuate around a relatively constant mean throughout the Holocene (Figures 2 and 3). This may be due to mineralization of organic matter at a depth in the sediment where precipitation of Cd and Mo out of pore waters no longer occurs. Cd and Mo concentrations also rise and fall slightly within the LGI in a fashion that resembles the DSR factor 3 record, whereas orgC concentrations do not. Most striking is the decoupling between biogenic proxies during the warm Bolling/Allerod interval (B/A; ~15–13 ka) when a clear rise in DSR factor 3 in both PC08 and PC10 is accompanied by little if any increase in orgC, Cd, and Mo concentrations (Figures 2 and 3). By and large, however, the behavior of the biogenic proxies is remarkably similar over much of the past 52 kyr.

[24] If the processes leading to orgC, Cd and Mo enrichments in OMZ sediments are related but not identical, why

are variations in concentrations of biogenic proxies so closely coupled? The simplest, but not the only, explanation is that all three signatures were modulated primarily by-productivity changes in overlying waters. In the case of orgC and Cd, the linkage could be directly associated with the supply of both these constituents with sinking plankton matter. For Mo, covariations with orgC and Cd suggest that sulfate reduction leading to postdepositional enrichment is also closely linked to the supply of plankton matter. Whereas the scenario is plausible, two alternative explanations cannot be ruled out. The first is that fluctuations in BWO concentrations modulated the preservation of orgC and Cd contained in plankton matter in the water column and in surficial sediments and, in parallel, BWO concentrations also regulated the intensity of sulfate reduction leading to precipitation of Mo. The other is that variations in focusing of organic-rich fine-grained sediment to the 700 m site could conceivably have varied orgC and Cd concentrations in tandem, while at the same time also changing the oxidant demand leading to sulfate reduction. Further interpretation therefore requires consideration of similar records reported previously for different sites along the western margin of North America.

5.2. Comparison With Biogenic Records at Other Northeast Pacific Margin Sites

[25] We compare the paleoproxy data from GC31/PC08 with high-resolution records from ODP893 and ODP1017 to the north, as well as lower resolution records from site NH15P off the coast of Mazatlan, Mexico (Figures 1 and 4). For the last 30 kyr at each location, the latest age model based on radiocarbon is used [*Hendy et al.*, 2002; *Hendy and Pedersen*, 2005; *Ganeshram and Pedersen*, 1998]. For horizons older than 30 ka, the age models at all four locations assume that recognizable stadial/interstadial maxima/minima in the oxygen isotope composition of planktonic foraminifera or, for PC08, DSR factor 3, are synchronous with the same events recorded in Greenland ice [*Grootes et al.*, 1993] or the stacked oxygen isotope record for benthic foraminifera [*Martinson et al.*, 1987]. In PC08, such a match is obtained within ~1 kyr by simply extrapolating the average ^{14}C-based sedimentation rate [*Ortiz et al.*, 2004], whereas additional changes and/or inconsistencies are observed in the age models of ODP893, ODP1017, and NH15P. Of these four sites, therefore, the sedimentation rate at the site of GC31/PC08 is the only one that has remained essentially constant over the past 52 kyr [*Ortiz et al.*, 2004], in spite of large changes in the orgC content of the sediment.

[26] Within the limitations of the various age models, it appears that many of the laminated sections in ODP893 were deposited at the same time as high orgC and high Mo intervals in ODP1017 and GC31/PC08 between 52 and 25 ka. As first pointed out by *Behl and Kennett* [1996], these intervals correspond to warm interstadials recorded in the GISP2 oxygen isotope record (Figure 4). Laminated sediments and Mo enrichments also have been documented in several cores from the OMZ off central California within the 60–24 ka interval, but at lower temporal resolution and with lower Mo concentrations [*Dean et al.*, 1997]. The fluctuations in Mo concentrations at ODP893 and ODP1017 are significantly attenuated relative to those at GGC31/PC08, particularly in sediments deposited between 52 and 25 ka. The Mo record from the OMZ off Mazatlan (NH15P) shows significant enrichments between 30 and 50 kyr that are consistent with the other observations but only in a broad sense because of the temporal resolution of only ~2 kyr. The match with the Greenland isotope record is particularly striking on the southern Baja California site because of the wide range of variations in the biogenic proxies and the similarity in the saw-tooth pattern characteristic of Dansgaard-Oeschger cycles documented also by the higher-resolution DSR factor 3 record.

[27] There are also some differences between the various proxy records along the margin. The most obvious is the absence of a large increase in Mo and orgC concentrations at the southern sites of GC31/PC08 and NH15P during the B/A compared to well-developed maxima in Mo and orgC at ODP1017 and Mo (only) at ODP893 (Figure 4). Laminated sections and sharp increases in Mo and Cd concentrations during the B/A have previously been reported at two additional sites within the OMZ off central California [*Zheng et al.*, 2000b] and as far north as off the coast of northern California at ODP Site 1019 [*Ivanochko and Pedersen*, 2004]. The particularly intense OMZ that prevailed during the B/A was recently attributed by *Crusius et al.* [2004] to enhanced productivity at high latitudes of the North Pacific that reduced the initial oxygen content of intermediate waters that ventilate the OMZ. This explanation is consistent with results from a simple model of ventilation of the OMZ, calibrated with the penetration of man-made chlorofluorocarbons, indicating that the preservation of laminations off central California would probably require a reduction in the initial oxygen content of intermediate waters, as well as a reduction in ventilation and an increase in productivity [*van Geen et al.*, 2006]. If the imprint of the B/A on the sedimentary record was at least in part advective in nature, and driven from the north, the effect of the lowering the initial oxygen content of ventilating waters could have had little additional impact off southern Baja California because BWO concentrations were already very low. A possible implication of such a scenario for the B/A is that the pronounced maximum in δ^{15}N observed in sediments deposited during the B/A at ODP893 and ODP1017 may have been due to strong denitrification extending to higher latitudes than today, rather than a signal emanating from northward advection of equatorial waters [*Kienast et al.*, 2002; *Ivanochko and Pedersen*, 2004].

5.3. Relating Holocene MARs of Biogenic Proxies to Oceanographic Regimes

[28] Productivity generally declines along the southerly flow path of the California Current, whereas the intensity of the OMZ increases in the same direction. The MARs of biogenic proxies in OMZ sediments along the margin during the Holocene might therefore be expected to reflect the net effect of these opposing geographic trends. A serious obstacle to making such direct comparisons, however, is the potential overprint of local conditions such as sediment

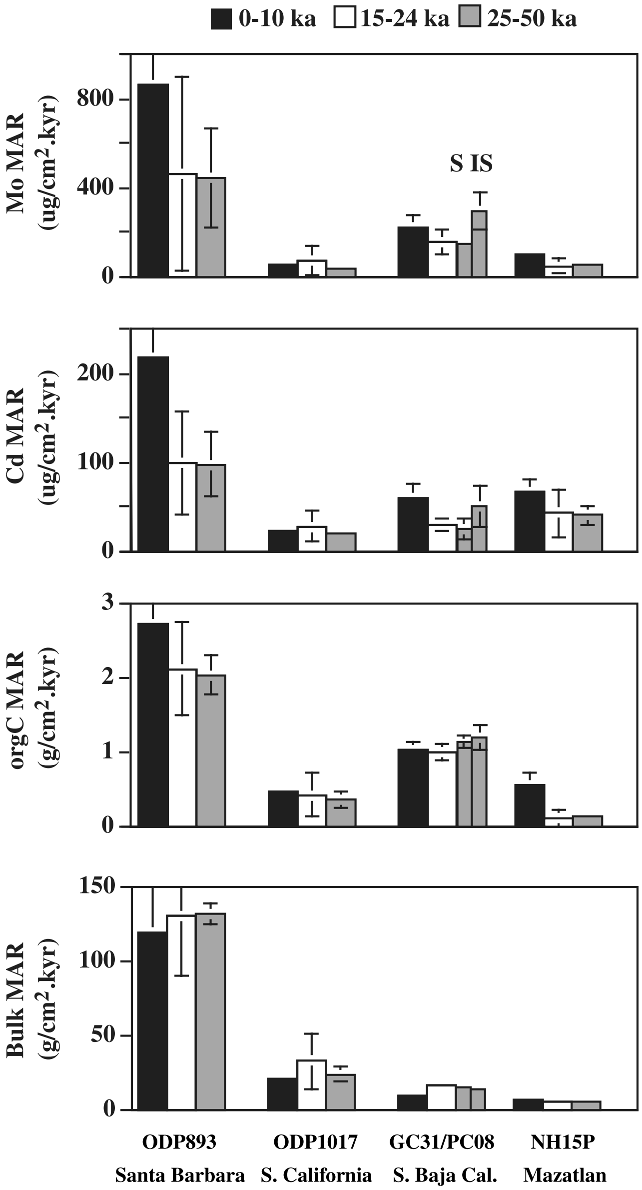

Figure 5. Bar graphs showing average and standard deviation of MARs for bulk sediment, orgC, Cd, and Mo at ODP893, ODP1017, GC31/PC08, and NH15P (references in caption of Figure 4) during 3 time intervals. Bar graphs for PC08 were split into stadials (S) and interstadials (IS).

focusing and bottom currents. A bias that must also be considered is that paleoceanographic reconstructions generally focus on sites where the sedimentation rate is particularly high because of the desirability of high temporal resolution. Santa Barbara Basin is an extreme example where detrital particles supplied by local streams as well as an important flux of biogenic matter are trapped. The result is a bulk MAR that is fivefold higher at ODP893 than at ODP1017, on the open margin (Figure 5). This complicates any direct of comparison between sites, even after conversion of the concentration of biogenic constituents to MARs because their preservation and postdepositional enrichment are probably not independent of the sedimentation rate. The bulk MAR of sediment at ODP1017 is only slightly higher than at GC31/PC08, however, and therefore offers a better basis for comparing biogenic proxy records (Figure 5). The bulk MAR at site NH15P to the south is somewhat lower than at these two open margin sites but probably still sufficient for comparison at least during the Holocene.

[29] The MAR of orgC in GC31 during the Holocene is twice the MAR of orgC in ODP1017 and NH15P on the open margin during the same interval (Figure 5). We cannot rule out that this pattern is determined primarily by local conditions and reflects particularly effective focusing of fine-grained sediment at the site of GC31/PC08. The comparable MAR of orgC at GC32 during the Holocene suggests this may not be the case, however. The location of the southern Baja California margin could therefore conceivably correspond to an optimum in terms of orgC accumulation between primary production, which is higher to the north, and preservation which should be higher to the south as the OMZ expands vertically (Figure 1).

[30] The average MAR of Mo during the Holocene is about a factor of 2 higher in GC31 compared to NH15P, and a factor of 3 higher than in ODP1017 (Figure 5). This suggests that there is a connection between the accumulation of refractory orgC and the intensity of sulfate reduction recorded by Mo across these sites. *Hartnett and Devol* [2003] point out that sulfate reduction, which is necessary for the accumulation of authigenic Mo, indeed accounts for the vast majority of remineralization of labile organic matter in margin sediments. *Zheng et al.* [2000a, 2000b], however, showed that precipitation of authigenic Mo does not occur under BWO concentrations >3 μmol/kg even in Santa Barbara Basin. The elevated MAR of Mo averaged over the Holocene at ODP1017, overlain today by BWO concentrations of ~20 μmol/kg (Figure 1), therefore probably reflects the presence of a more intense OMZ earlier during the early and middle Holocene. The inferred weakening of the OMZ at this location is consistent with a steady decline in Mo concentrations during the late Holocene in ODP1017, starting from a maximum a ~6 ka (Figure 4).

[31] The patterns of Holocene Cd MARs at the three sites are somewhat different from those of orgC and Mo. The MAR of Cd in GC31 during the Holocene, like those of orgC and Mo, is about twice as high as that in ODP1017 but similar to that in NH15P (Figure 5). It is worth noting that there is a systematic southward increase in Holocene Cd/Mo ratios from southern California to Mazatlan (Figure 6 and Table 2). Off southern Baja California, Holocene Cd/Mo ratios are also significantly higher at 430 m than 700 m depth. The reason for this pattern is unclear, but the particularly high Cd content of plankton off Baja California compared to central California was already pointed out by *Bruland et al.* [1978] and could therefore explain elevated Cd accumulation relative to Mo off the Mexican coast. An alternative explanation, or an additional factor, is that Cd may be preferentially mobilized relative to labile organic carbon in the water column and in surficial sediments when the OMZ is relatively weak. A role for water column

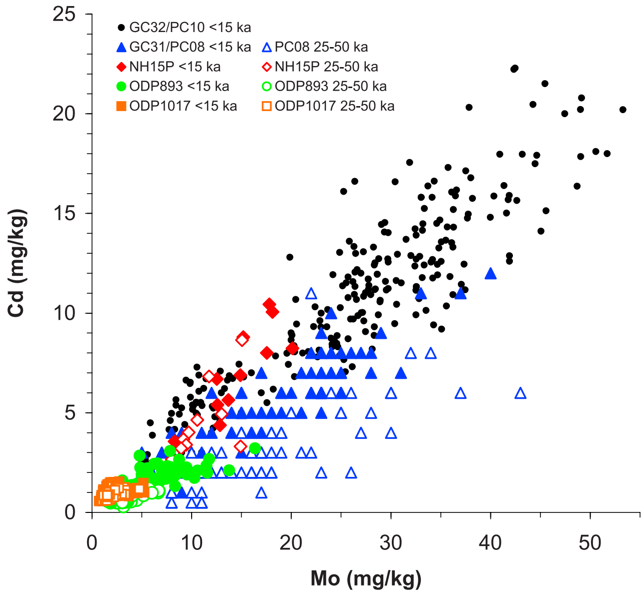

Figure 6. Comparison of relationship between Cd and Mo concentrations during the 0–15 ka and the 25–50 ka intervals at ODP893, ODP1017, MV99 GC32/PC10, MV99 GC31/PC08, and NH15P.

oxygenation has similarly been invoked to explain patterns in the transfer and accumulation of uranium [*Zheng et al.*, 2002].

5.4. Scaling MARs of Biogenic Proxies in the Past to Environmental Change

[32] How did biogenic proxy MARs respond to conditions prevailing during the LGI at the various sites? At the site of GC31/PC08 off southern Baja California, average Cd and Mo MARs during the LGI decline by up to half the corresponding Holocene fluxes, whereas the MAR of orgC was about the same (Figure 5). At ODP1017, very similar MARs of orgC, Cd, and Mo during the Holocene and the LGI suggest that mean conditions changed relatively little off central California. At NH15P, MARs of orgC, Mo, and Cd were also lower during the LGI compared to the Holocene, but *Ganeshram and Pedersen* [1998] point out that lower sea level during the LGI reduced the supply of fine-grained material to NH15P. For this reason, fluxes of biogenic proxies at this site before the Holocene are not considered further. Concentrations of Cd and Mo at all 3 open margin sites are well in excess of crustal levels throughout the LGI, which suggests that a significant OMZ was preserved during this period.

[33] Slightly higher BWO concentrations at the site of GC31/PC08 could have reduced the retention of Cd in plankton matter at the sediment-water interface and reduced the postdepositional enrichment of Mo. Therefore the modest reduction in MARs of these constituents suggest that the OMZ could have weakened slightly during the LGI whereas average productivity changed very little if at all. If on the other hand the intensity of the OMZ did not change, or if such a change had little impact on Cd and Mo, then average productivity may have differed by no more than a factor of 2 between the LGI and the Holocene if some degree of proportionality between Cd and Mo MARs and primary production is assumed. The absence of laminations in GC31/PC08 and NH15P during the LGI does not allow us to discriminate between the two scenarios because the preservation of laminations off southern Baja California appears to be sensitive to BWO as well as productivity and/or sediment focusing [*van Geen et al.*, 2003].

[34] The twofold difference in average Cd and Mo MARs at the site of GC31/PC08 between the LGI and the Holocene is equal to or larger than the difference in average Cd and Mo MARs between interstadials and stadials from 25 to 52 ka (IS and S in Figure 5). Cd/Mo ratios between 25 and 52 ka are significantly lower than during the Holocene, although not quite as low as off southern California (Table 2 and Figure 6). This suggests that the contrast between stadials and interstadials was smaller than between the Holocene and the LGI and that, on average, oceanographic conditions off southern Baja California between 25 and 52 ka may have shifted to conditions representative of the Holocene somewhat further north. One possible scenario is slightly elevated productivity during the 25–52 ka interval combined with a somewhat weakened OMZ off southern Baja California. *Ortiz et al.* [2004], however, previously documented 2 orders of magnitude variations in the concentration of benthic foraminifera between interstadials and stadials recorded in GC31/PC08 that were attributed to changes in productivity in overlying water. How can relatively modest changes in OMZ intensity and primary production inferred from Cd and Mo be reconciled with much larger changes in the benthic fauna? Ecosystems are known to be sensitive to modest but persistent changes in the environment, perhaps more so than larger changes of shorter duration [*McGowan et al.*, 2003]. For example, *Ruhl and Smith* [2004] recorded large changes in the deep ocean benthic community off southern California in response to relatively modest variation in the flux of organic matter reaching the seafloor linked to the El Niño–Southern Oscillation. We speculate that the concentration of benthic foraminifera off southern Baja California may also have

Table 2. Linear Regressions of Cd as a Function Mo Along the Western Margin of North America

	0–15 ka			25–50 ka			
	Cd/Mo	Intercept	n	Cd/Mo	Intercept	n	Source of data
ODP1017	0.04 ± 0.02	1.0 ± 0.0	107	0.19 ± 0.02	0.5 ± 0.0	171	*Hendy and Pedersen* [2005]
ODP893	0.10 ± 0.01	1.0 ± 0.1	91	0.12 ± 0.01	0.4 ± 0.0	107	*Ivanochko and Pedersen* [2004]
MV99 GC32/PC10	0.37 ± 0.01	1.0 ± 0.3	237				this study
MV99 GC31/PC08	0.25 ± 0.01	1.1 ± 0.2	337	0.19 ± 0.01	−0.6 ± 0.3	67	this study
NH15P	0.50 ± 0.08	−0.3 ± 1.2	11	0.50 ± 0.17	−1.0 ± 1.9	10	*Nameroff et al.* [2004]

amplified modest but persistent changes in food supply and therefore that the productivity changes suggested by the geochemical and faunal proxies are not necessarily inconsistent.

5.5. Implication of the California Margin Records for Global Climate

[35] The visual comparison of variations in orgC and Mo concentrations strengthens the notion of an intimate linkage between the processes that regulate the concentration of these proxies along west coast of North America (Figure 4). *Behl and Kennett* [1996] and *Cannariato et al.* [1999] initially postulated a teleconnection to global climate by invoking changes in ventilation affecting the oxygen content of the OMZ to explain interbedding of laminated and bioturbated sediments in Santa Barbara Basin. Without necessarily excluding changes in ventilation, more recent records from the open margin have shifted the interpretation toward changes in productivity along the margin or at higher latitudes [*Hendy et al.*, 2004; *Ortiz et al.*, 2004; *Crusius et al.*, 2004; *Hendy and Pedersen*, 2005]. Our new data from the southern margin of Baja California suggest that even if the exact driver of the signals recorded at several sites along the margin of North America remains poorly defined, the actual range in productivity and/or BWO concentrations spanned by the region under past warm and cold climate episodes may have been rather limited.

6. Conclusions

[36] Fluctuations in the orgC, Cd, and Mo content of southern Baja California margin sediment vividly demonstrate that millennial-scale variations in productivity of the northeast Pacific and/or the intensity of the OMZ have been linked to global climate variability over the past 52 kyr. Concentrations of these biogenic proxies are high in laminated sediments deposited during the Holocene and earlier warm interstadials, and low in bioturbated sediments deposited during the LGI and cold stadials. Over most of the last 52 kyr, variations in orgC, Cd, and Mo concentrations also parallel fluctuations in a factor extracted at higher resolution from the diffuse spectral reflectance of the sediment that closely resembles the Greenland oxygen isotope record.

[37] Within the limits of the different age models, the geochemical fluctuations recorded in sediment off southern Baja California appear to be synchronous with variations in orgC, Cd, and Mo concentrations on the open margin to the south (NH15P off Mazatlan, Mexico) and to the north (ODP1017, off central California), as well as the alternations between laminated and bioturbated sediments in Santa Barbara Basin (ODP893). The one exception is the B/A, which is strongly expressed at ODP1017, ODP893, and two additional sites within the OMZ to the north, but only weakly so off southern Baja California.

[38] Consideration of MARs shows that variations in orgC, Cd, and Mo concentrations off southern Baja California were actually driven to a significant extent by dilution with nonbiogenic matter. The MAR of orgC remained essentially constant between warm and cold climate intervals over the past 52 kyr, whereas the MAR Cd and Mo during warm climate intervals were no more than a factor of 2 higher than during cold intervals. Comparison of Cd/Mo ratios and Cd and Mo MARs with other margin sites suggests that productivity could plausibly have changed little over the past 52 kyr and that the limited range of variations in Cd and Mo MARs may have reflected at least in part a weakening of the OMZ during cold climate intervals relative to warm intervals.

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