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Sediment Geochemical Records of Productivity and Oxygen Depletion Along the Margin of Western North America During the Past 60,000 Years: Teleconnections with Greenland Ice and the Cariaco Basin

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Sediment geochemical records of productivity and oxygen depletion along the margin of western North America during the past 60,000 years: teleconnections with Greenland Ice and the Cariaco Basin

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Abstract

Many sediment records from the margins of the Californias (Alta and Baja) collected in water depths between 60 and 1200 m contain anoxic intervals (laminated sediments) that can be correlated with interstadial intervals as defined by the oxygen-isotope composition of Greenland ice (Dansgaard–Oeschger, D–O, cycles). These intervals include all or parts of Oxygen Isotope Stage 3 (OIS3; 60–24 cal ka), the Bölling/Alleröd warm interval (B/A; 15–13 cal ka), and the Holocene. This study uses organic carbon (Corg) and trace-element proxies for anoxia and productivity, namely elevated concentrations and accumulation rates of molybdenum and cadmium, in these laminated sediments to suggest that productivity may be more important than ventilation in producing changes in bottom-water oxygen (BWO) conditions on open, highly productive continental margins. The main conclusion from these proxies is that during the last glacial interval (LGI; 24–15 cal ka) and the Younger Dryas cold interval (YD; 13–11.6 cal ka) productivity was lower and BWO levels were higher than during OIS3, the B/A, and the Holocene on all margins of the Californias. The Corg and trace-element profiles in the LGI–B/A–Holocene transition in the Cariaco Basin on the margin of northern Venezuela are remarkably similar to those in the transition on the northern California margin. Correlation between D–O cycles in Greenland ice with gray-scale measurements in varved sediments in the Cariaco Basin also is well established. Synchronous climate-driven changes as recorded in the sediments on the margins of the Californias, sediments from the Cariaco Basin, and in the GISP-2 Greenland ice core support the hypothesis that changes in atmospheric dynamics played a major role in abrupt climate change during the last 60 ka. Millennial-scale cycles in productivity and oxygen depletion on the margins of the Californias demonstrate that the California Current System was poised at a threshold whereby perturbations of atmospheric circulation produced rapid changes in circulation in the eastern North Pacific Ocean. It is likely that the Pacific and Atlantic Oceans were linked through the atmosphere. Warmer air temperatures during interstadials would have strengthened Hadley and Walker circulations, which, in turn, would have strengthened the subtropical high pressure systems in both the North Pacific and the North Atlantic, producing increased rainfall over the Cariaco Basin and increased upwelling along the margins of the Californias.

1. Introduction and background

1.1. North Pacific circulation

The California Current is the southward flowing, wind-driven eastern limb of the North Pacific subtropical gyre formed by the divergence of the West Wind Drift on the western margin of North America. This oceanic circulation is driven by atmospheric-pressure systems of the North Pacific and western North America (the North Pacific High, the Aleutian Low, and the North American Low). The seasonal strength and position of these pressure systems not only generate the weather and climate of the western US (Huyer and Kosro, 1987; Strub et al., 1987; Smith et al., 1988; Thomas and Strub, 1990), but are part of the atmospheric teleconnections that stretch across the northern hemisphere (e.g., Namias et al., 1988). Except for El Niño-Southern Oscillation (ENSO) events, the importance of the North Pacific in global climate change has been little appreciated.

The North Pacific between 30° and 60°N latitude is at least 60° of longitude wider than the North Atlantic. This

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large area of ocean contributes water vapor to the atmosphere and affects global atmospheric circulation. Because water vapor has a rapid response time and is a greenhouse gas, the North Pacific is a major contributor to climate change (Pierrehumbert, 1999, 2002). Recent studies suggest that sea-surface temperatures (SST) during the last glacial interval (LGI; 24–15 cal ka) may have been 3–4 °C cooler off Oregon and California than at present (e.g., Prahl et al., 1995; Sabin and Pisias, 1996; Doose et al., 1997, Ortiz et al., 1997; Mix et al., 1999; Herbert et al., 2001; Pisias et al., 2001), with an even greater difference off southern California (e.g., Kennett and Ingram, 1995; Mortyn et al., 1996; Hendy and Kennett, 2000). Barron et al. (2003) found that alkenone SSTs off northern California were as much as 4 °C cooler during the Younger Dryas cold interval (YD; 13–11.6 cal ka) than during the Bölling–Alleröd warm interval (B/A; 15–13 cal ka). Model simulations by Peteet et al. (1997) suggest that North Pacific SST changes of this magnitude would have cooled the entire northern hemisphere and affected the source regions of the Laurentide Ice Sheet. Changes in the position and strength of atmospheric systems that occurred as a result of the change from global-glacial to interglacial conditions obviously had large influences on the California Current, the western US, and perhaps the northern hemisphere. For example, Doose et al. (1997) concluded, based on alkenone SST estimates, that coastal upwelling on the California margin was significantly reduced or even completely shut down during the LGI.

The paleoceanography of the California Current is difficult to interpret because of the poor preservation of calcareous microfossils in the sediments of the northeast Pacific Ocean, and because of dilution by the influx of terrigenous clastic debris. However, it is known that the California Current has responded to historical short-term ENSO events (Johnson and O'Brien, 1990; Van Scoy and Druffel, 1993), as well as late Pleistocene intervals of intense upwelling (Anderson et al., 1987, 1989, 1990; Gardner et al., 1988, 1997; Lyle et al., 1992; Hemphill-Haley and Gardner, 1994; Dean et al., 1994, 1997; Ortiz et al., 1997; Cannariato and Kennett, 1999; Mix et al., 1999; Pisias et al., 2001; Kienast et al., 2002; Barron et al., 2003; Crusius et al., 2004). The high sedimentation rates generally preclude the collection of cores that document several glacial–interglacial cycles using conventional piston coring techniques. However, this same high sedimentation rate permits high-resolution reconstructions of younger intervals such as marine oxygen isotope stage 3 (OIS3; 60–24 cal ka), the LGI, the B/A, and the YD.

1.2. Productivity and bottom-water oxygen (BWO) concentrations

High organic productivity that develops in response to seasonal upwelling of nutrient-enriched water along the eastern margin of the southward-flowing California Current places a high biological oxygen demand on North Pacific Intermediate Water (NPIW). This water mass becomes depleted in dissolved oxygen (DO) producing an oxygen-minimum zone (OMZ) with values of DO <0.5 ml/L (<5 μmol/kg or μM) between about 600 and 1200 m (Fig. 1). Hydrographic time-series data indicate that the intensity of the OMZ off California is delicately balanced today with respect to variations in the relative contributions of low-DO water of equatorial origin delivered by the northward-flowing California Undercurrent, and high-DO water from the north (Lynn and Simpson, 1987; Van Scoy and Druffel, 1993; van Geen et al., 1996). The OMZ in the northeastern Pacific at 800 m water depth also contains the highest concentration of dissolved cadmium, a proxy for the nutrient phosphate, in the open ocean (van Geen et al., 1996). Although low, the DO concentrations in the OMZ are sufficient to support diverse benthic faunas that thoroughly mix the surface sediments where the OMZ intersects the continental slope. However, cores collected on the slope off northern and central California contain intervals of laminated sediment deposited during interstadials of OIS3 and the B/A, suggesting that NPIW was virtually anoxic when those laminated sediments were deposited (Gardner and Hemphill-Haley, 1986; Anderson et al., 1987, 1989; Dean et al., 1994, 1997; Hemphill-Haley and Gardner, 1994; Gardner and Dartnell, 1995; Cannariato and Kennett, 1999; Zheng et al., 2000a). In addition to laminated sediments, relatively high concentrations of some redox-sensitive trace metals, such as molybdenum (Mo), suggest that intermediate waters were anoxic, leading to the preservation of laminations (Dean et al., 1997; Zheng et al., 2000a; Nameroff et al., 2002). Zheng et al. (2000b) have shown that preservation of laminations requires a lower concentration of DO (<5 μM) than does the precipitation of authigenic Mo (5–10 μM).

Imposing a high biological oxygen demand is one way to produce an OMZ. Another mechanism to produce DO-depleted intermediate water is to bring in less oxygen, i.e., intermediate water from some source that was less well ventilated, and there is some evidence that this may have happened in the past (e.g. Lund and Mix, 1988; van Geen et al., 1996; Keigwin, 1998; Cannariato and Kennett, 1999; Zheng et al., 2000a; Kienast et al., 2002). Whereas most sediments deposited on the open slope of the California margin are bioturbated with low concentrations of redox-sensitive trace metals, Zheng et al. (2000a) found that thin intervals of laminated sediments deposited during the B/A in two cores from about 800 m water depth on the central California margin contained elevated concentrations of Mo and cadmium (Cd). They concluded that the reduced DO content of NPIW off California during the B/A was due to reduced ventilation because of greater stratification of the upper water column at high latitudes of the North Pacific Ocean.

It is difficult to separate the relative contributions of oxidation of organic matter and ventilation of the water column, because the concentration of DO in NPIW represents a balance between the two. However, studies

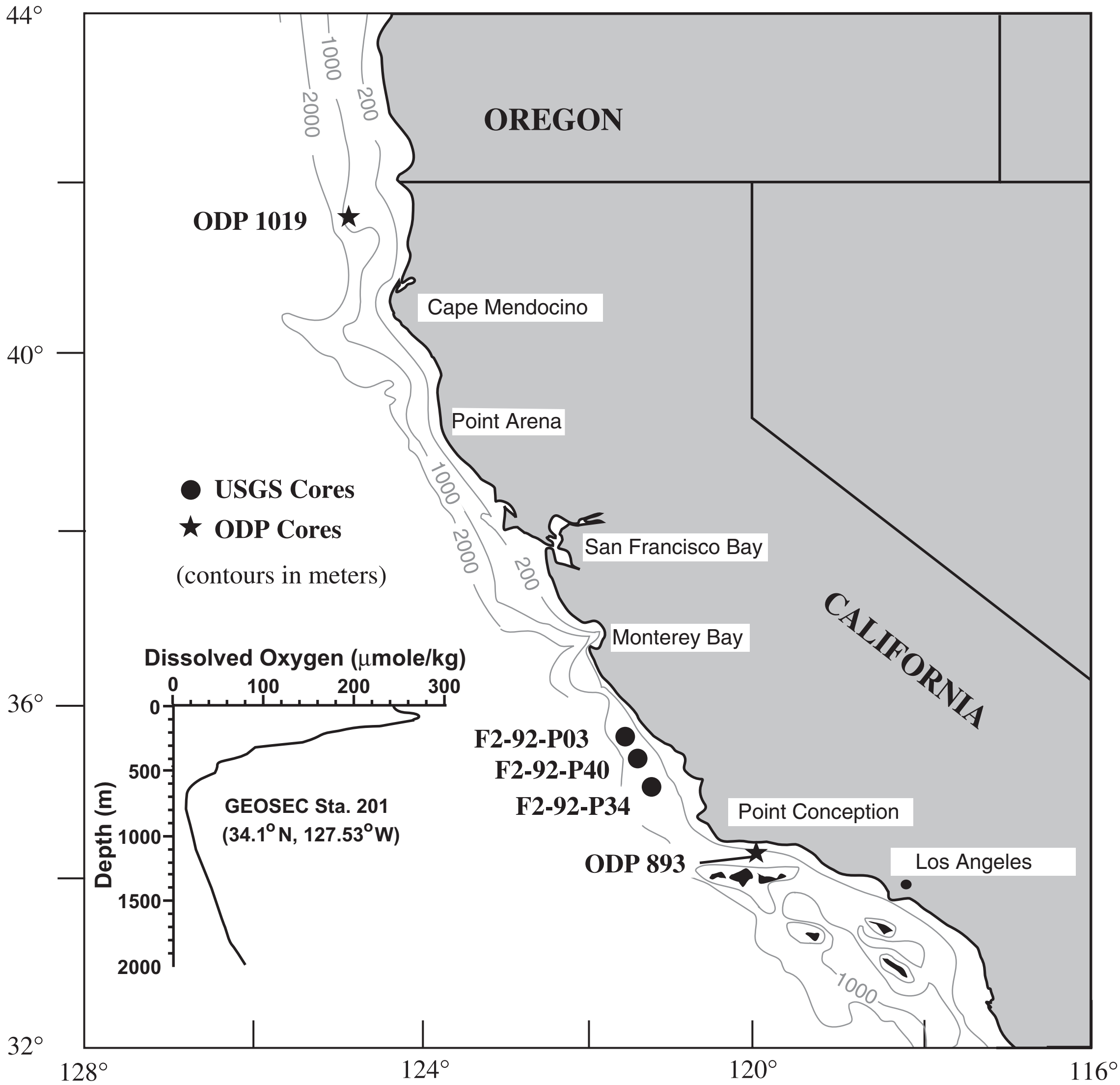

Fig. 1. Index map of the continental margin of California showing locations of cores discussed in this report. Actual coordinates and water depths of the cores are given in Table 1. Contours are in meters.

of the biogenic components in those cores with laminated OIS3 and B/A sediments indicate that there have been distinct differences in productivity within the California Current upwelling system over time. Productivity changes have been documented by fluctuations in concentrations and mass accumulation rates (MAR) of biogenic carbonate ($CaCO_3$), biogenic silica (biopal), organic carbon (Corg), and biogenic barium (Ba) (Lyle et al., 1992; Dean et al., 1997; Gardner et al., 1997; Lyle et al., 2000a; Barron et al., 2003), in the concentration and MAR of Cd (Zheng et al., 2000a; Hendy and Pedersen, 2005), and in diatom abundance and species composition (Sancetta et al., 1992; Barron et al., 2003). These paleoproductivity proxies suggest that organic productivity along the California margin was lower during cold intervals (LGI and YD) and higher during warmer intervals (OIS3, B/A, and Holocene).

The application of trace metals to track variations in productivity and redox conditions in the ocean is relatively new. Several trace metals, such as rhenium (Re), uranium (U), vanadium (V), nickel (Ni), zinc (Zn), Cd, and Mo, are concentrated in Corg-rich sediments where sulfate reduction has occurred (e.g., Jacobs et al., 1985; Emerson and Huested, 1991; Crusius et al., 1996; Morford and Emerson, 1999). These elements may have two sources: (1) a biogenic source represented by trace elements taken up mostly in the photic zone by phytoplankton, and (2) a hydrogenous fraction derived from bottom water and (or) sediment pore water by adsorption and precipitation reactions under low DO, sulfate-reducing conditions (Piper, 1994; Piper and Dean, 2002).

As a measure of sulfate reducing conditions, I focus on Mo in this study because of the elements for which I have data, it is *the* diagnostic element in sediments that accumulate under seawater sulfate-reducing conditions (Bruland, 1983; Jacobs et al., 1985; Emerson and Huested, 1991; Piper, 1994; Crusius et al., 1996, Piper and Dean,

Table 1
Core locations

Core number	Latitude N	Longitude W	Water depth (m)	Year collected
USGS Cruises				
F2-92-P03	35°37.20′	121°36.45′	803	1992
F2-92-P34	35°01.85′	121°13.54′	610	1992
F2-92-P40	35°25.09′	121°24.95′	760	1992
1999 R/V Melville				
MV99-GC31	23°28.03′	111°35.91′	705	1999
MV99-PC08	23°28.01′	111° 35.91′	705	1999
Ocean Drilling Program				
Site 893	34°17.25′	120°02.20′	576	1992
Site 1019	41°40.90′	124°55.80′	980	1997

2002). Piper and Dean (2002) calculated that hydrogenous Mo MAR contributed 97% of the total Mo MAR in surface sediments in the anoxic Cariaco Basin. Elevated concentrations of Mo (above 1 ppm) usually, but not always, are associated with laminated sediments, another indicator of anoxic or near anoxic bottom-water conditions. Elevated concentrations of Cd (above 0.1 ppm) might also be used as a geochemical indicator of low-DO bottom-water conditions. However, because Cd, along with Cu, Ni, and Zn, are found in high concentrations in plankton (Martin and Knauer, 1973; Collier and Edmond, 1984; Brumsack, 1986), Cd likely has a biogenic source that dominates over a hydrogenous source. Nameroff et al. (2002) found that most of the Cd in surface sediments on the Mazatlan margin could be attributed to input from plankton (nonlithogenic particulates in sediment traps). Piper and Dean (2002) found that 86% of the total Cd in Cariaco Basin sediments was from phytoplankton. Therefore, the concentration of Cd can be used, with some caution, as a qualitative measure of primary productivity.

In this paper I re-examine the Mo and Cd data from two cores on the central California margin presented by Zheng et al. (2000a), together with Mo data from other cores from the California margin (Gardner et al., 1997; Dean et al. 1997) and from Ocean Drilling Project Site 1019 (ODP 1019) as proxies of primary productivity and water-column redox conditions. Emphasis is on the B/A and the YD time intervals, but is extended to OIS3 in a few cores. Upper Quaternary sediments recovered at ODP Site 1019 were deposited at a high rate (40–80 cm/ka) so that high-resolution proxy records may be highly reliable. Interpretations of paleoclimate and paleoceanography for this site have been presented by Mix et al. (1999), Lyle et al. (2000a, b), Pisias et al. (2001), and Barron et al. (2003).

2. Materials and methods

2.1. Cores and samples

Cores F2-92-P03, -P34, and -P40 are part of a suite of cores collected on the California margin between Monterey Bay and the Mexican border (Fig. 1; Table 1), which are described in Gardner et al. (1992). The sediments in most cores were mainly bioturbated, but Gardner et al. (1992) noted laminated sediments at depths of 2.0–2.1, and 3.5–3.7 m in P03 and P40, respectively (Fig. 2), which later were interpreted by Zheng et al. (2000a) to be correlative with the B/A. Results of geochemical analyses of samples every 10 cm from these and other cores from the northern, central, and southern California margins are presented in Gardner et al. (1997), Dean et al. (1997), and Dean and Gardner (1998). Calibrated radiocarbon ages for these cores are from Gardner et al. (1997). Additional ages for P03 and P40 are from Zheng et al. (2000a).

ODP Site 1019, in the Eel River basin off northern California, was one of a series of sites cored from northern Baja California to southern Oregon on ODP Leg 167 (Lyle et al., 2000a). The sediments were mainly bioturbated, but laminated sediments were noted at approximately 5, 7, and 9.5 m in cores from Hole 1019C (Lyle et al., 2000b, c; Fig. 2). The sediments at Site 1019 were described as being extremely "gassy" (Lyle et al., 2000a). In fact, all sites on the slope that were drilled on Leg 167 had high concentrations of methane (up to 160,000 ppm) in headspace samples (Lyle et al., 2000b). Although no methane hydrates were found in any of the cores collected at Site 1019, this was the only site on the ODP 167 site survey cruise where bottom-simulating reflectors (BSR) were detected, indicating the presence of methane hydrates or clathrates (Lyle et al., 2000b). The Eel River basin has long been known to have methane hydrates (Field and Kvenvolden, 1985). Samples in cores from Hole 1019C were collected every 5 cm for carbon analyses (Lyle, 2000a). Samples for diatom, alkenone, and pollen analyses also were collected from cores from Hole 1019C (Barron et al., 2003). Samples for inorganic geochemical analyses were collected every 5 cm from the top 12 m of section in cores from Hole 1019E. Calibrated radiocarbon ages are from Mix et al. (1999) with additional calibrated ages from Barron et al. (2003). For this paper, an age model was calculated as a second-order polynomial through all calibrated ages.

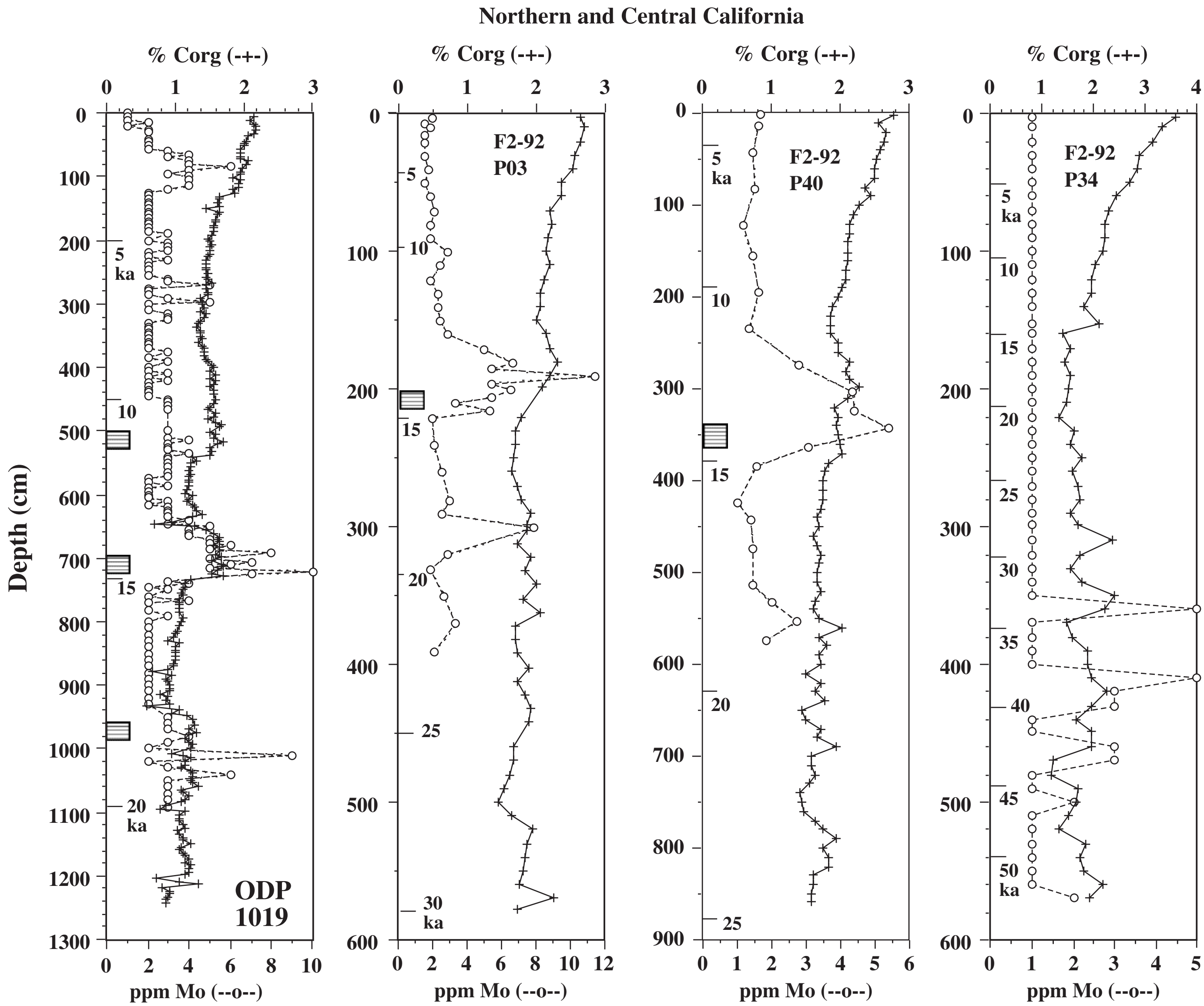

Fig. 2. Profiles of % Corg and, where available, ppm Mo versus depth in centimeters below sea floor in samples from cores from the continental margins of northern and central California (see Fig. 1 and Table 1 for locations). Calibrated radiocarbon ages (in cal ka) are given to the right of the depth scale. Stratigraphic locations of laminated sediments in cores from ODP Site 1019, P04, and P40 are indicated by the laminated box-symbols to the right of the depth scale.

Cores GC31 and PC08 were collected on the Pacific side of southern Baja California (Table 1) as part of a 1999 *R/V Melville* coring cruise in the OMZ off Baja (van Geen et al., 2001, 2003). The Holocene sections in these cores are laminated, and parts of the OIS3 section in PC08 are laminated. Samples for inorganic geochemical analyses were collected every 5 sm from GC31 and every 10 cm from PC08. The age model, based on 16 accelerator mass spectrometry radiocarbon dates on benthic foraminifera, is from van Geen et al. (2003) and Ortiz et al. (2004).

2.2. Analytical methods

Samples were analyzed for weight percentages of total carbon (TC) and total inorganic carbon (IC) using a carbon-dioxide coulometer (Engleman et al., 1985). Percent organic carbon (Corg) was calculated as the difference (TC−TIC). 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 for both TC and TIC, determined from hundreds of replicate standards (reagent grade $CaCO_3$ and a Cretaceous Corg-rich marlstone), usually are better than 0.10 wt%. Two standards were run at the beginning of a sample run and one at the end.

Samples were analyzed for 40 major, minor, and trace elements by inductively coupled, argon-plasma, atomic emission spectrometry (ICP-AES) by SGS Laboratories, Toronto, Canada. Rock standards (USGS) were included with the sediment samples, and 10% of the samples were analyzed in duplicate. The precision, determined by analyzing rock standards and duplicate sediment samples, is better than 10%. Only results for molybdenum (Mo) and, where available, cadmium (Cd) will be discussed here. Concentrations of both elements were often close to or below the limit of detection for the ICP-AES method used (1 ppm for both elements). However, as I hope to demonstrate, concentrations above 1 ppm are environmentally significant. Some geochemical results from the USGS cores listed in Table 1, and other cores, are discussed in Dean et al. (1997).

All cores in Table 1 were logged at sea with a Geotek multi-sensor logger that includes sensors for gamma-ray attenuation porosity evaluator (GRAPE), p-wave velocity, and magnetic susceptibility. Dry bulk density (DBD) was calculated from GRAPE wet bulk density (WBD) as

$$\mathrm{DBD} = 1.563\mathrm{WBD} - 1.560.$$

This equation was derived from linear correlation between GRAPE-WBD and measured DBD on samples from ODP Leg 167 cores (Lyle et al., 2000a). When this equation is applied to earlier USGS cores (F2-92) for which DBD was calculated from GRAPE-WBD using a different equation (Gardner et al., 1997), the correlation coefficient between the two estimates is 0.999.

The data from the USGS cores described in this paper and in Gardner et al. (1997) and Dean et al. (1997) are available in digital form at the World Data Center-A for Paleoclimatology, NOAA/NGDC 325 Broadway, Code E/CC23, Boulder, CO 80303-3328 (phone: 303-497-6280; Internet: www.ngdc.noaa.gov/paleo/).

3. Results—northern and central California

3.1. Northern California

The Corg concentrations in northern California ODP Site 1019 generally increase from about 1% in sediments deposited during the LGI to 2% in upper Holocene sediments. The Corg contents of sediments at ODP 1019 exhibit distinct maxima of % Corg and ppm Mo in and around laminated sediments at about 500, 700, and 1000 cm (Fig. 2). The maximum in % Corg in laminated sediments at about 700 cm (ca 15–13 cal ka) corresponds in time to the B/A warm interval, and the following minimum corresponds in time to the YD cold interval.

3.2. Central California

Values of Corg in all of the northern and central California cores show a pronounced exponential decrease from the surface to about 200–300 cm at which point the exponential decrease becomes asymptotic with minimum Corg concentrations in sediments deposited during the LGI (Fig. 2). Dean and Gardner (1998) assumed that this exponential decrease in Corg that they observed in their cores from northern, central, and southern California that had a complete Holocene section was due to burial diagenesis or ‘‘burndown’’ of labile organic matter. At the asymptote, they assumed that burndown was complete, and that the value of Corg at that point represents the preserved value (e.g., Westrich and Berner, 1984; Gardner and Dartnell, 1995; Canuel and Martens, 1996). The composition of Corg at the asymptote is a mixture of refractory organic matter and labile organic matter that has been buried in the anoxic sediments below the depth of diagenesis. This mixture follows the models of Westrich and Berner (1984) and Tromp et al. (1995), which assume that the marine sedimentary organic matter consists of multiple organic phases of different reactivities. A mathematical calculation of burndown based on exponential decomposition of Corg with depth for ODP Hole 893A in the Santa Barbara Basin (SBB) is given by Gardner and Dartnell (1995). I have not calculated burndown of organic matter for the tops of the cores described in this paper, although this burndown should be considered when comparing Holocene Corg concentrations with those of older parts of the section where the organic matter has already been burned down. In other words, the Corg concentration that occurs at the tops of the Holocene sections in cores will not be the Corg concentrations in those sediments after burial diagenesis.

Laminations occur in sediments deposited about 14 cal ka in cores F2-92-P03 and -P40, and, within the limits of age models, these laminated intervals probably correlate to laminated sediments at ODP 1019 (Fig. 2) that correspond in time to the B/A warm interval. As in cores from ODP 1019 (Fig. 2), elevated concentrations of Corg and Mo in P03 and P40 begin in the laminated sediments deposited at about 15 cal ka, but increase above that horizon, reaching maximum values in bioturbated sediments overlying the laminated sediments (Fig. 2). Sediments deposited at about 15 cal ka in core P34 have only a slight increase Corg, but this core does have elevated concentrations of Corg and Mo (Fig. 2) in sediments deposited during OIS3, like OIS3 sediments in several other cores from within the OMZ on the central California margin (Dean et al., 1997).

4. Discussion: glacial–interglacial contrasts in productivity and oxygen depletion

4.1. Northern and central California margins

Sediment from ODP 1019 from the Eel River basin shows considerable variation in C_{org} and has several intervals of laminated sediments that contain elevated concentrations of Mo, particularly in sediments deposited during the B/A. The record from ODP 1019 resembles those from P40 and P03 from the central California margin (Fig. 2), which also have laminated sediments and elevated concentrations of Corg and Mo in the B/A (Zheng et al., 2000a).

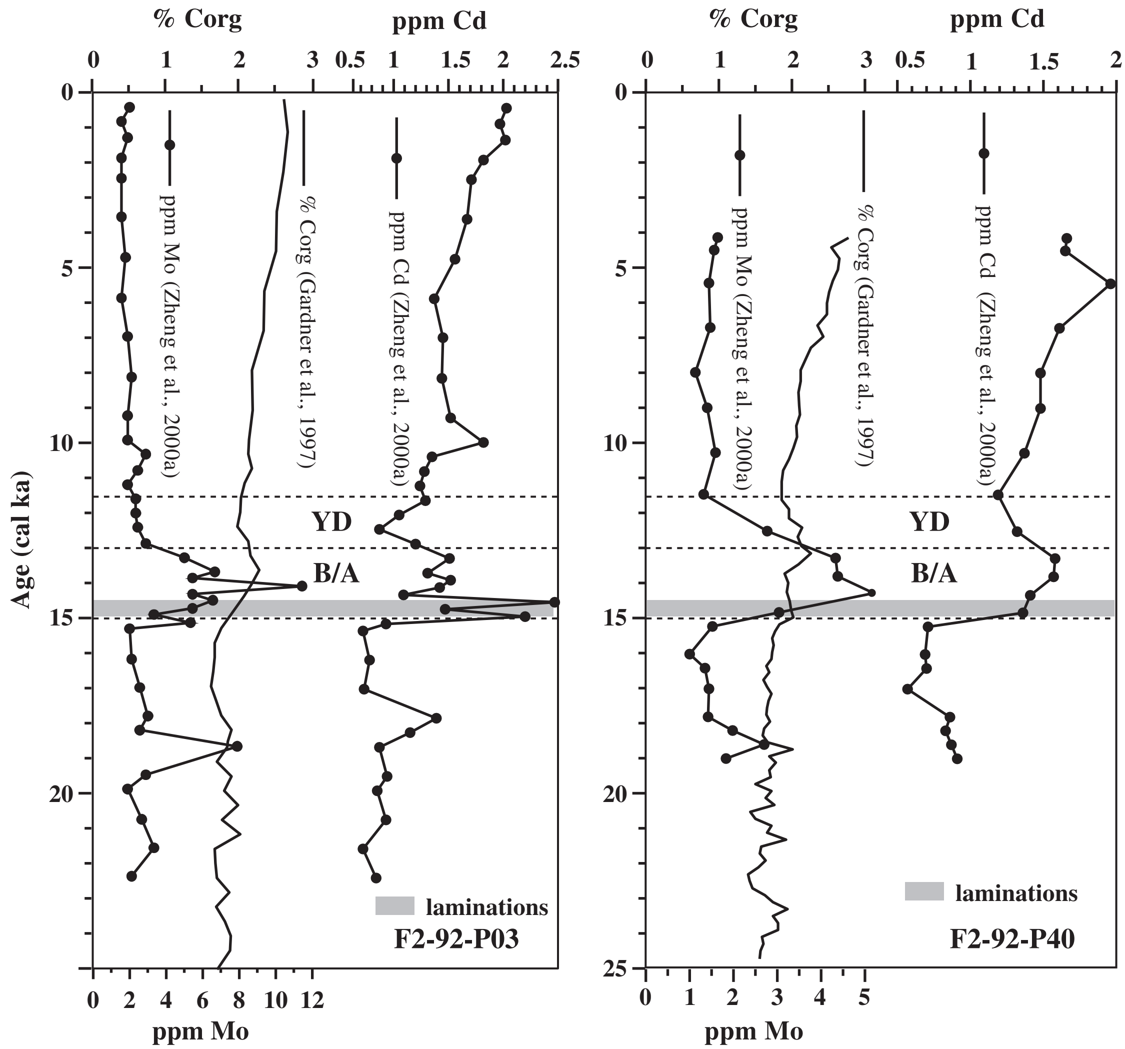

Fig. 3. Profiles of % Corg, ppm Mo, and ppm Cd versus age (in cal ka) in samples from cores F2-92-P03 and -P40 from the continental margin of central California (see Fig. 1 and Table 1 for locations). Stratigraphic locations of laminated sediments are indicated by shaded intervals. The timing of the global Bölling/Alleröd warm interval (B/A) and Younger Dryas cold interval (YD) are indicated by dashed lines.

In addition to elevated concentrations of Mo in B/A sediments, cores P40 and P03 have elevated concentrations of Cd (Fig. 3) in that interval, suggesting that the lower DO conditions, indicated by laminated sediments and elevated concentrations of Mo, are more likely due to a higher oxygen demand imposed by decomposition of higher amounts of produced organic matter than to poorer ventilation as suggested by Zheng et al. (2000a). Concentrations of Cd were below the limit of detection (1 ppm) of the ICP-AES method used for samples from ODP 1019. Based on benthic foraminiferal d^{13}C data at Site 1019, Mix et al. (1999) concluded that variations in NPIW ventilation were not responsible for the apparent variations in the OMZ on the California margin.

It is well known that B/A and Holocene sediments deposited in the SBB (ODP Site 893) are well laminated (e.g., Behl and Kennett, 1996), distinguishing them from bioturbated YD and LGI sediments. Some of the chemical characteristics of the SBB sediments have been documented, based mainly on the stable isotopes of carbon and oxygen (e.g., Cannariato and Kennett, 1999; Hendy and Kennett, 1999, 2000, 2003). Kennett and Ingram (1995) concluded that the laminated intervals in ODP 893 are the result of poorer ventilation in SBB because there was no evidence for higher productivity (e.g., no increase in % Corg in laminated B/A and lower Holocene sediments, Fig. 4). However, Hendy and Kennett (2003) state that during warm interstadials "high productivity along the eastern Pacific margin recommenced, causing 'southern component' intermediate water to become suboxic as the organic material rain rate increased". Also, maxima in the concentration of the upwelling foraminifer *Globigerina bulloides* during warm interstadials provide additional evidence for increased productivity. Ivanochko and Pedersen (2004) recently published trace metal data from ODP 893 showing elevated concentrations of Mo and Cd in B/A and Holocene sediments (Fig. 4). These elevated Cd concentrations indicate that increased productivity and

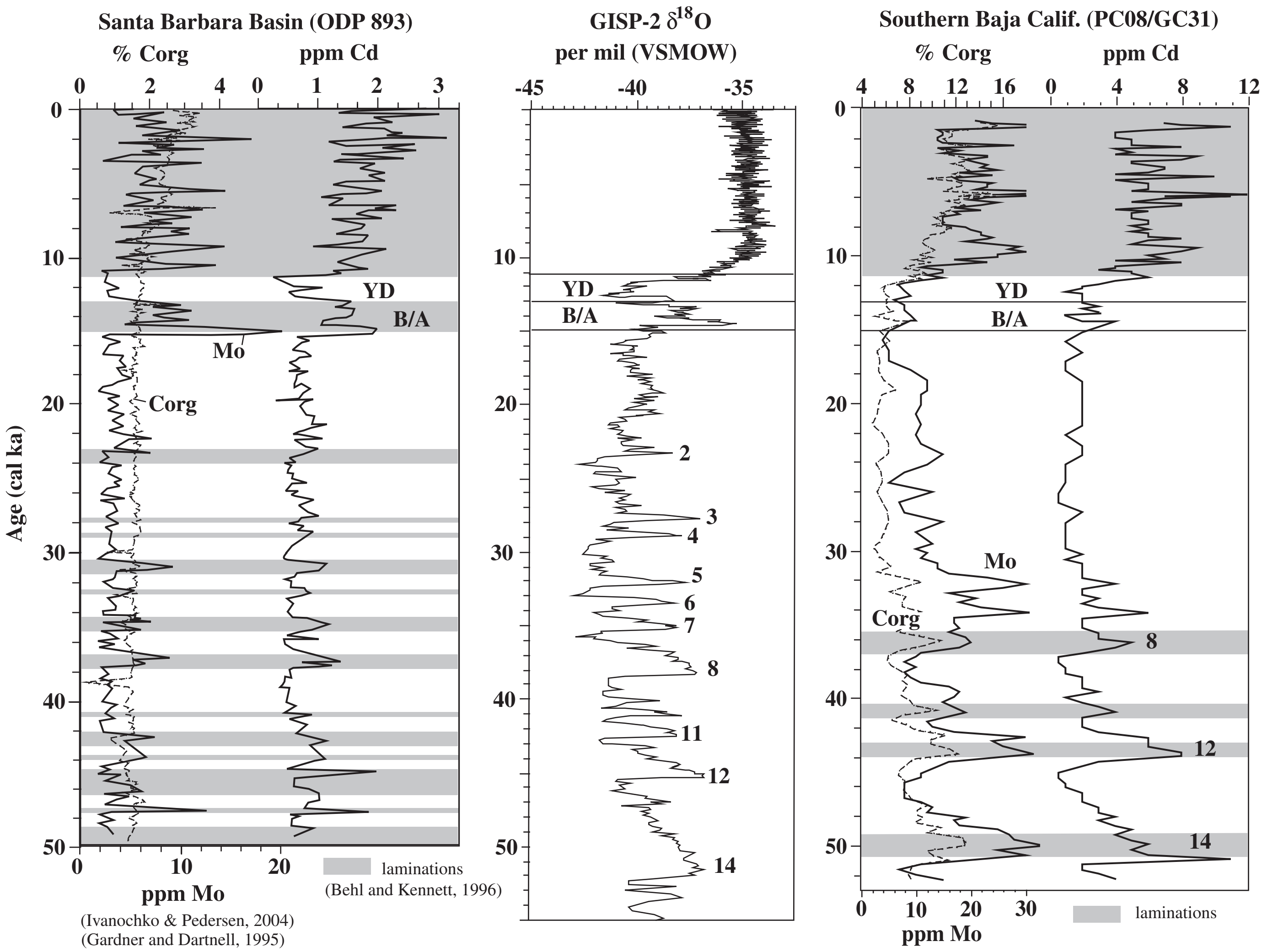

Fig. 4. Profiles of % Corg, ppm Mo, and ppm Cd versus age (in cal ka) in samples from cores from ODP Site 893 in the Santa Barbara Basin (left) and from overlapping gravity core (GC31) and piston core (PC08) from the continental slope off southern Baja California (right) (see Table 1 for locations). Stratigraphic locations of laminated sediments are indicated by shaded intervals; no shading indicates intervals of bioturbated sediment. Carbon data for ODP 893 are from Gardner and Dartnell (1995). Concentrations of Mo and Cd are from Ivanochko and Pedersen (2004). A profile of values of $\delta^{18}O$ in ice from Greenland Ice Sheet Project 2 (GISP-2) from Grootes et al. (1993) is shown in the middle. Numbers (2–14) identify interstadial events (IS) identified by Grootes et al. (1993). The timing of the global Bölling/Alleröd warm interval (B/A) and Younger Dryas cold interval (YD) are indicated by horizontal lines.

resulting biological oxygen demand, possibly in conjunction with poorer ventilation, contributed to lower mid-water DO concentrations.

4.2. Northwestern Mexico

Although a few sites on the open slope of the California margin have laminated B/A and OIS3 sediments, none cored so far have laminated Holocene sediments. However, laminated Holocene sediments were recovered in cores from within the OMZ off Mazatlan in northwestern Mexico (Ganeshram, 1996; Ganeshram and Pedersen, 1998; Ganeshram et al., 1999), and these laminated sediments contain elevated concentrations of Mo and Cd (Nameroff et al., 2004). It therefore seemed reasonable to extend the geographic coverage of the margins of the Californias southward to the Baja California margin, where the present day hydrographic data suggest that the OMZ is sensitive to the delicate balance between the supply of northern- and southern-sourced intermediate water (van Geen et al., 1996). To that end, a coring cruise was conducted in November, 1999 that collected a total of 55 gravity cores (GC), 16 piston cores (PC) and 18 sets of multicores (MC) along the western Baja California margin (van Geen et al., 2001, 2003).

Laminated Holocene sediments were not found on most of the Baja margin north of a latitude of about 23°30′N off southern Baja. However, south of that latitude, laminated Holocene sediments were recovered in numerous gravity and piston cores. Data from a piston core (PC08) and an overlapping gravity core (GC31) show that the laminated Holocene sediments contain high concentrations of Corg, Mo, and Cd (Fig. 4), indicating higher Holocene productivity relative to the LGI. These cores were collected from the base of the OMZ in 700 m water depth. Cores collected in the core of the OMZ at 400 m water depth had even higher concentrations of Corg, Mo, and Cd (Dean et al., in press) High concentrations of benthic foraminifera in sediments deposited during the Holocene and warm interstadials of OIS3, and low concentrations in LGI sediments, in PC08/GC31, suggest that productivity was considerably lower during the LGI (Ortiz et al., 2004). This Baja California site apparently did not record increased productivity and (or) reduced ventilation during the B/A, because those sediments are not laminated and have concentrations of Corg, Mo, and Cd comparable to LGI sediments (Fig. 6). This must reflect a difference in water-mass properties between offshore Baja California and Alta California. However, some sediments deposited during OIS3 off southern Baja California are laminated and contain elevated Corg, Mo, and Cd concentrations comparable to those in laminated Holocene sediments (Fig. 6). Laminated sediments also occur in OIS3 sediments in SBB, but concentrations of Mo and Cd are much lower than those in laminated Holocene sediments (Fig. 4).

Millennial-scale cycles in productivity and oxygen depletion on the margins of the Californias demonstrate that the California Current System, including its southern extension, was poised at a threshold whereby perturbations of atmospheric circulation produced rapid changes in circulation in the eastern North Pacific Ocean. With these changes in circulation came changes in degree of oxygenation of intermediate waters and rate of organic productivity, which may have acted together to produce extremely oxygen-depleted intermediate waters and preservation of laminated sediments where these intermediate waters impinge on the continental slope. In basins such as SBB where seawater circulation may be more restricted, oxygen depletion may be even more enhanced. A similar situation has been reported for the restricted basins of the Gulf of California (e.g., Keigwin and Jones, 1990).

4.3. Correlations with the GISP-2 Greenland ice core

The millennial-scale cycles of bioturbated and laminated sediments in SBB deposited before 10 cal ka have been attributed to cyclic variations in ventilation of intermediate waters in the basin associated with Dansgaard–Oeschger (D–O) stadial–interstadial cycles, as defined by the oxygen-isotope composition of Greenland ice (GISP-2; Grootes et al., 1993; Fig. 4) between 60 and 10 ka (e.g., Hendy and Kennett, 1999, 2000; Cannariato and Kennett, 1999). The laminated intervals have been attributed to a warming of SST of as much as 5 °C within a few decades. Expansion of the subtropical high and contraction of the Aleutian low over the North Pacific permitted northward expansion of southern-sourced intermediate water that was oxygen deficient (Hendy and Kennett, 2003; Hendy and Pedersen, 2005). During cool stadials, the Aleutian low expanded bringing in more cool, well-oxygenated North Pacific Intermediate Water that was ventilated in the Sea of Okhotsk (Talley, 1991).

Barron et al. (2003) correlated alkenone-derived SSTs at ODP site 1019 over the last 15 ka with the GISP-2 oxygen-isotope curve, and concluded that the YD at that site was 4 °C cooler than the B/A. Ortiz et al. (2004) correlated peaks in a diffuse spectral reflectance record (DSR) and % Corg from Baja core PC08 to the warm-cool D–O cycles in the GISP-2 ice core. The % Corg record for PC08 in Fig. 4 is the same one used by Ortiz at al. for this correlation. The corresponding peaks of ppm Mo and Cd in OIS3 sediments in core PC08 are even more pronounced than those of Corg (Fig. 4), and have a distinct saw-tooth distribution (abrupt increase followed by a gradual decrease) that is characteristic of the oxygen-isotope record in the GISP-2 ice core (Fig. 4). Elevated concentrations and MARs of Corg and Mo in laminated and even unlaminated OIS3 sediments also occur within the OMZ on the central California margin (Dean et al., 1997; Gardner et al., 1997). Core F2-92-P34 (Fig. 3) is an example of a record from the central California margin that has elevated concentrations of Corg and Mo but no laminated OIS3 sediments.

If these various correlations to GISP-2 D–O cycles are correct, it may provide a means of correlating millennial-scale variations recorded in OIS3 sediments of western North America with global events. Ortiz et al. (2004) suggested that higher productivity on the Baja California margin during warm intervals might be due to more La Niña-like conditions with a shallow nutricline. This interpretation is supported by nitrogen-isotope data presented by Kienast et al. (2002) that show enhanced denitrification during warm intervals all along the margins of North America from Oregon to northwestern Mexico.

4.4. Cariaco Basin

The teleconnections between the GISP-2 oxygen-isotope record and various proxies in sediments on the margins of the Californias from Northern California to Baja California appear to be well established. Another well-established teleconnection between the GISP-2 record and the sediments in another anoxic setting is with the gray-scale record in the Cariaco Basin off northern Venezuela (Hughen et al., 1996a, 1998; Lea et al., 2003). During boreal winter and spring, the Intertropical Convergence Zone (ITCZ) in the western Atlantic is located south of the equator. Strong northeast trade winds produce intense upwelling and elevated primary productivity. Remains of plankton are preserved in the sediment as a light-colored lamina. During summer and autumn, the ITCZ shifts north of the equator, trade winds weaken, and upwelling is reduced. The northward shift of the ITCZ increases rainfall along the northern coast of South America, resulting in an increase in the flux of terrigenous debris into the basin that is deposited as a dark lamina, which together with a light

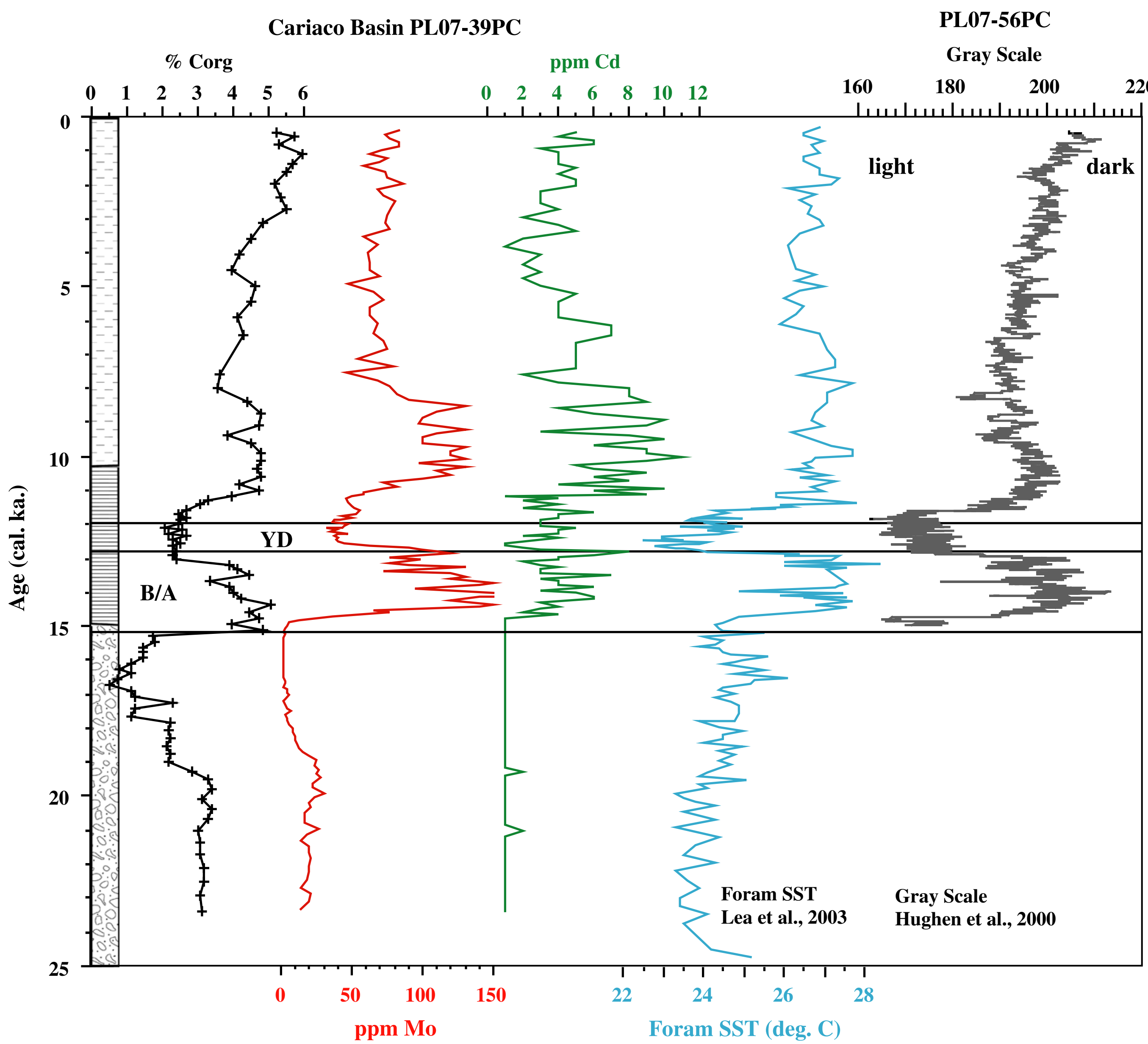

Fig. 5. Profiles of % Corg, ppm Mo, and ppm Cd versus age (in cal ka) in samples from core PL07-39PC from the Cariaco Basin. Continuous laminated symbol for the Cariaco Basin core indicates distinct laminations; discontinuous laminated symbol indicates indistinct laminations; conglomerate symbol indicates bioturbated sediments. The timing of the global Bölling/Alleröd warm interval (B/A) and Younger Dryas cold interval (YD) are indicated by horizontal lines. Also shown are foram-estimated sea-surface temperatures (SST) for core PL07-39PC (Lea et al., 2003), and gray-scale reflectance for core PL07-56PC (Hughen et al., 2000).

winter lamina, forms an annual couplet, or varve (Peterson et al., 1991; Hughen et al., 1996b).

The gray-scale record in cores of Cariaco Basin sediments follows the annual changes in light/dark laminations. Light-colored sediments were deposited during cold, dry periods such as the YD (Fig. 5), the LGI, and stadials of OIS3 (Peterson et al., 2000; Peterson and Haug, 2006). Dark-colored sediments were deposited during warm, rainy periods such as the Holocene, the B/A, and warm interstadials of OIS3. The dark sediments are also laminated, and are enriched in Corg and river-borne terrigenous debris (as proxied by high concentrations of Ti and Al; Haug et al., 2001; Peterson and Haug, 2006). These interstadials were times of higher sea level and higher productivity as a result of a greater influx of nutrients from the open Caribbean and from the land (Haug et al., 1998). The light, bioturbated sediments represent times of lower sea level when the Cariaco Basin was largely isolated from open communication with the Caribbean and its supply of nutrients, and calcareous and siliceous plankton accumulated relatively undiluted by riverine terrigenous debris. These were periods of enhanced upwelling, but productivity may have been lower than during interstadials because of lower nutrient concentrations.

Peterson et al. (1991) interpreted the lithologic change from bioturbated to laminated sediments about 15 cal ka as reflecting the onset of elevated primary productivity in the photic zone and establishment of sulfate-reducing conditions in the bottom water. Their record went back to about 25 ka, and they did not have the benefit of the longer record from ODP Site 1002 that also contains dark, laminated sediments deposited during the interstadials of OIS3 (Peterson et al., 2000).

The geochemical transition is equally abrupt with increases in Corg, Mo, and Cd indicating onset of anoxia and a rapid increase in productivity at about 15 cal ka (Fig. 5). As mentioned earlier, Piper and Dean (2002) calculated that 86% of the Cd MAR in Cariaco Basin sediments was biogenic, whereas 97% of the Mo MAR was hydrogenous formed by bottom water and (or) sediment pore-water reactions. Therefore, Cd is responding mainly to surface-water nutrients, whereas Mo is responding to bottom-water anoxia and sulfate reduction. The distinct laminations continue through the YD interval until about 10 cal ka when the laminations become thinner and weakly defined (Peterson et al., 1991; Hughen et al., 1996b) even though anoxic, sulfate-reducing bottom waters continued to the present (Richards, 1975). Although the Mo concentration decreased during the YD interval, it was still fairly high (ca 50 ppm, Fig. 5) indicating, along with the distinctly laminated sediments, that bottom waters were still anoxic. Surface waters of the Cariaco Basin were as much as 4 °C cooler during the YD than during the B/A based on foraminiferal Mg/Ca ratios (Lea et al., 2003), similar to the difference observed in ODP 1019 based on alkenone-derived SSTs (Barron et al., 2003). Values of gray-scale were lightest (Fig. 5) due to an increase in the thickness of light-colored, plankton-rich laminae suggesting that the seasonal length of upwelling might have been longer (Lea et al, 2003). The concentration of Cd did not decrease significantly during the YD interval (Fig. 5) suggesting that upwelled nutrients sustained fairly high productivity. Although the concentrations of Corg and Mo decreased during the YD interval, their rates of accumulation remained high in agreement with the presence of distinctly laminated sediments (Piper and Dean, 2002). Thus, all proxies support the interpretation that bottom waters during the YD interval were still anoxic, but productivity remained relatively high due to upwelled nutrients. Hughen et al. (1996a) attributed changes in upwelling and productivity in the Cariaco Basin to changes in strength of the trade winds, which, in turn, is dictated by thermohaline circulation. The dissimilar responses of Mo and Cd during the YD interval suggest that there was a certain level of independence between the rates of bottom-water advection of DO and upwelling of nutrients into the photic zone. Concentrations of Corg, Mo, and Cd were all high again by 10 cal ka (Fig. 5).

Data from core PL07-39PC do not go back beyond 24 cal ka, so records of Mo and Cd in the Cariaco Basin during OIS3 can only be speculated upon. Results from the longer record at ODP Site 1002 indicate that the interstadial intervals in OIS3 consist of dark, Corg-rich, laminated sediments (Peterson et al., 2000), much like those in core PC08 off Baja California (Fig. 4). Thus, the laminated, Corg-rich interstadial OIS3 sediments likely also contain high concentrations of Mo and Cd.

The ranges of concentrations of Corg, Cd, and, especially, Mo in Cariaco Basin sediments are extremely large (Fig. 5). Concentrations of Mo range over more than two orders of magnitude, with a maximum of 150 ppm in a piston core from 400 m water depth (Dean et al., in press), comparable to the maximum concentration in Holocene sapropel from the anoxic Black Sea (Arthur and Dean, 1998). Concentrations of Corg and Mo are much lower in California margin sediments. Nevertheless, the Corg and Mo records from the Cariaco Basin are strikingly similar to those from ODP 1019 on the open slope of northern California (Fig. 6). This correlation would appear to complete the triangle: margins of the Californias to Greenland, Cariaco Basin to Greenland, and now California to Cariaco Basin. Such teleconnections cannot be by thermohaline circulation and must be through the atmosphere.

4.5. Regional differences in productivity and anoxia

Regional and temporal differences in geochemical indicators of productivity and anoxia can be seen in a series of histograms of average MARs of Corg, Cd, and Mo for three time slices in six cores from northern and central California, southern Baja California, and the Cariaco Basin (Fig. 7). All three MARs are distinctly lower for all time slices in cores from the central California margin (P03, P40, and P34). The surprising record from the California margin is that from ODP 1019, where high MARs of Corg and Mo relative to the other California margin sites occur throughout the section (Dean et al., 1997; Gardner et al., 1997). The high MARs at Site 1019 likely result from the high sedimentation rate at that site that made it such a promising site for a high-resolution paleoclimatic record (Mix et al., 1999). The Corg MAR at Site 1019 is comparable to those from southern Baja California (GC31/PC08) and the anoxic Cariaco Basin (core 39PC). The Mo MAR at Site 1019 is comparable to that from southern Baja California. That the Corg and Cd MARs on the open slope of southern Baja California are comparable to those in the anoxic Cariaco Basin suggests that the two areas have similar levels of productivity.

4.6. Climate forcing

Earlier it was suggested that higher productivity on the Baja California margin during warm intervals that correlated with warm interstadials in the GISP-2 ice core might be due to more La Niña-like conditions with a shallow nutricline (Ortiz et al., 2004). This in line with the

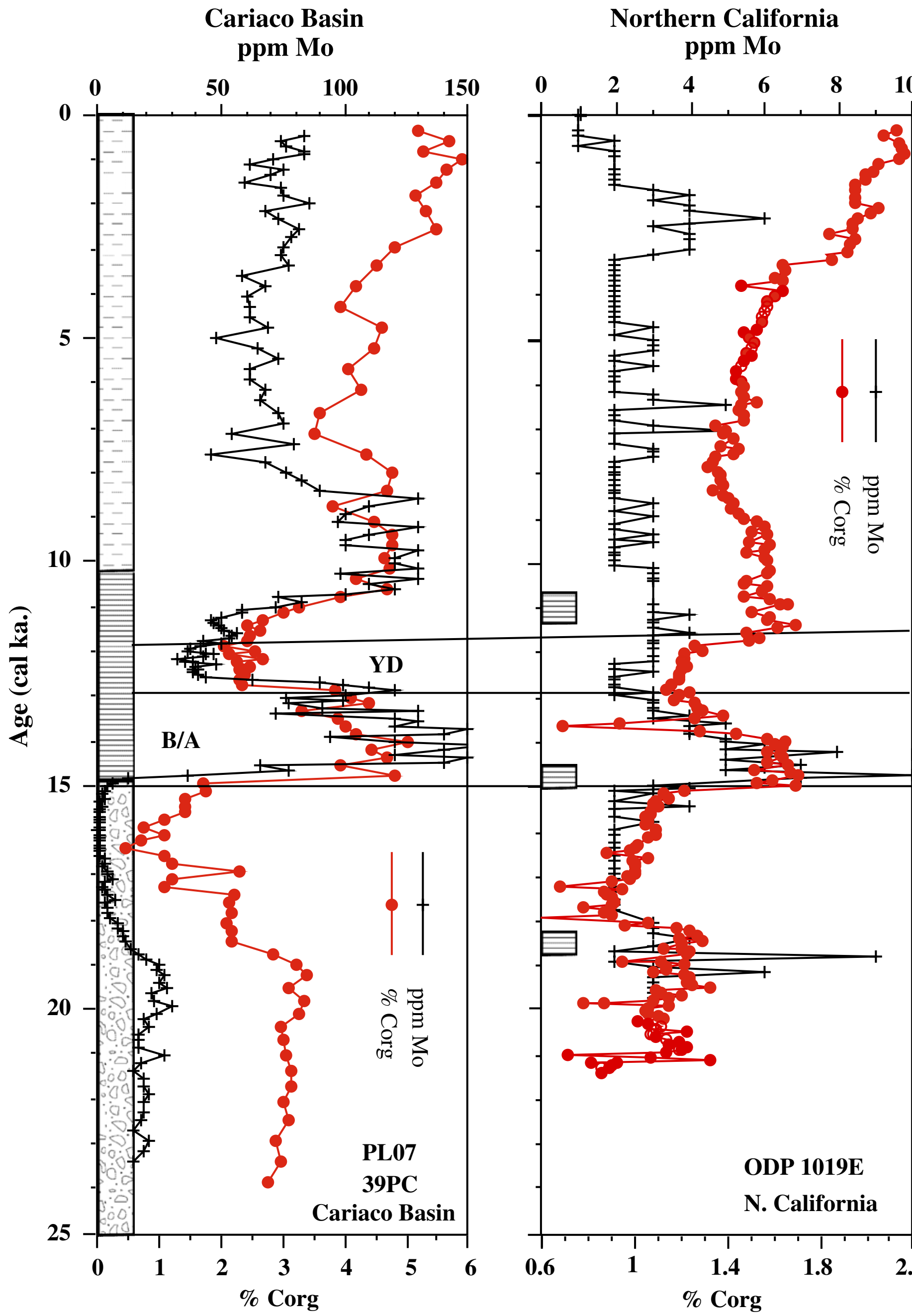

Fig. 6. Profiles of % Corg, ppm Mo, and ppm Cd versus age (in cal ka) in samples from core PL07-39PC from the Cariaco Basin and from cores from ODP Site 1019 (repeated from Fig. 2). Stratigraphic locations of laminated sediments are indicated by the laminated box-symbols to the right of the depth scale. Continuous laminated symbol for the Cariaco Basin core indicates distinct laminations; discontinuous laminated symbol indicates indistinct lamination; conglomerate symbol indicates bioturbated sediments. The timing of the global Bölling/Alleröd warm interval (B/A) and Younger Dryas cold interval (YD) are indicated by horizontal lines.

observation based on oxygen isotopes, alkenone SST measurements, and Mg/Ca ratios in foraminifera that the eastern and western tropical Pacific had La Niña-like conditions during warm interstadial, and El Niño-like conditions during cool stadials (Koutavas et al., 2002; Stott, et al., 2002). Variations in El Niño/La Niña conditions are known to have far-reaching climatic effects downstream from the Pacific Ocean (e.g., Bjerknes, 1969; Golderberg and Shapiro, 1996; Pielke and Landsea, 1999). Based on modern ENSO teleconnections, La Niña conditions in the tropical Atlantic usually result in wet conditions over northern South America like those postulated for the Holocene, B/A, and warm, wet OIS3 interstadials (Peterson and Haug, 2006). Barron et al. (2003) found that the alkenone SSTs during the YD at ODP Site 1019 were 4 °C cooler than during the B/A, and a similar difference occurs in the Cariaco Basin (Lea et al., 2003). Barron et al. suggested that the model of Peteet et al.

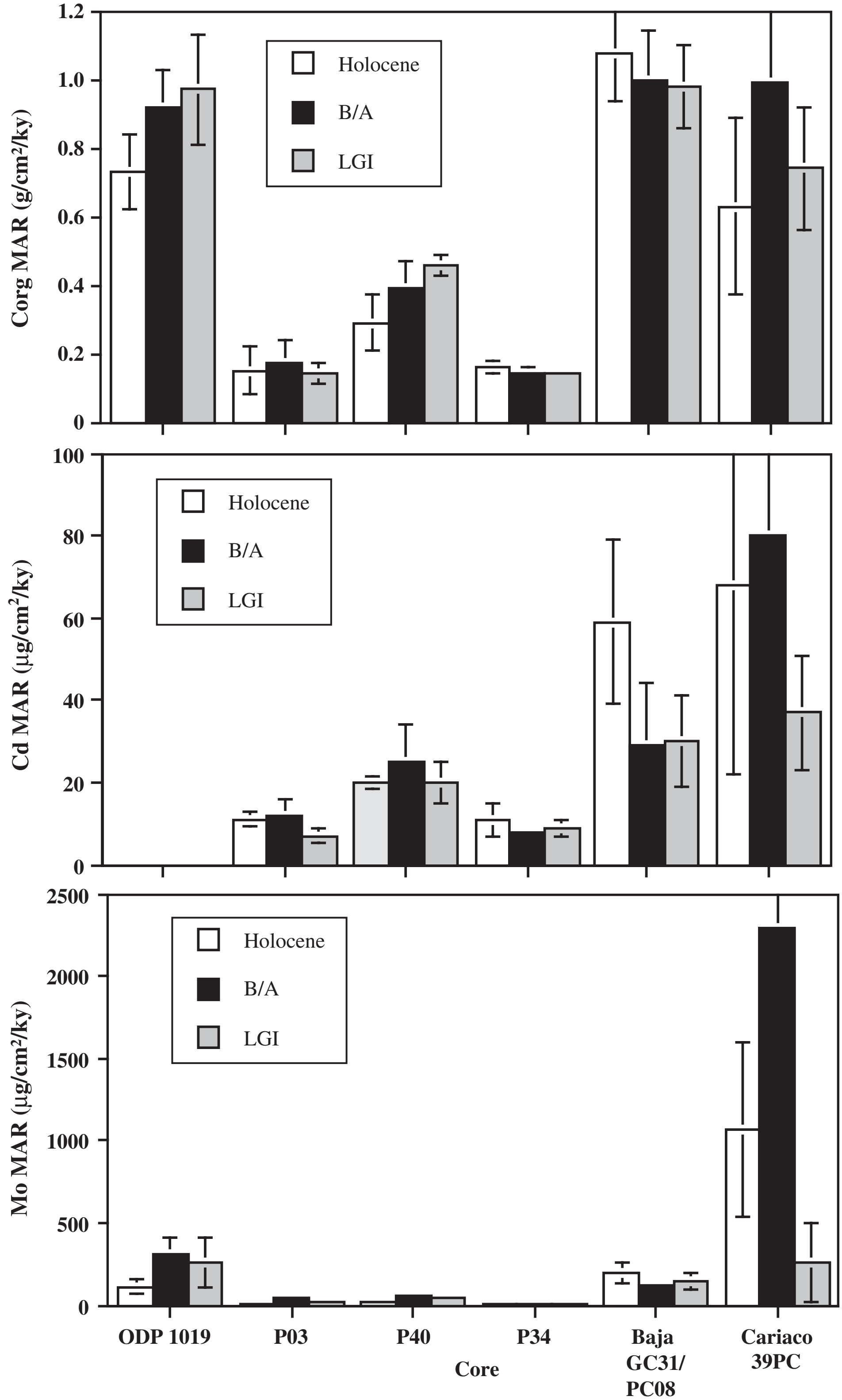

Fig. 7. Histograms of mass accumulation rates (MAR) of Corg, Cd, and Mo for three time slices in cores from the northern and central California margins, the margin of southern Baja California, and from the Cariaco Basin. See Fig. 1 and Table 1 for locations of cores. Time slices are: Holocene, 10-0 cal ka; Bölling/Alleröd warm interval (B/A), 15–13 cal ka; and Last Glacial Interval (LGI), 24–16 cal ka.

(1997) might apply in that such lower SSTs would result in cooler, drier air over North America and possibly over the entire northern hemisphere.

Kennett and Ingram (1995) point out that the flux of North Atlantic Deep Water (NADW) was high during the B/A and Holocene and reduced during the LGI and YD.

Modeling studies by Chiang et al. (2003) suggest that thermohaline circulation can have a strong effect on the position of the Atlantic ITCZ. They suggested that thermohaline variations were the cause of the observed covariation between the Greenland and Cariaco Basin records. Switching on and off of NADW formation is probably the best-studied candidate mechanism for millennial-scale climate fluctuations, but cannot produce a strong response outside the North Atlantic (Pierrehumbert, 1999), particularly on such short time scales. Changes in deglacial SST in the Cariaco Basin are synchronous within 30–90 years with those in Greenland air temperatures suggesting that there was an active tropical feedback to high latitude changes (Lea et al., 2003) through changes in atmospheric convection and (or) water vapor transport (Lea et al., 2003). Based on foraminiferal data, Mix et al. (1999) concluded that there must be transmission through the atmosphere of millennial-scale warming and cooling cycles between the Atlantic and Pacific. Kennett and Ingram (1995) concluded that synchronous inter-ocean paleoceanographic changes are likely transmitted through the atmosphere. Hendy and Kennett (1999) argued that the correlation of cycles of bioturbated and laminated sediment in SBB with D/O cycles in the GISP-2 ice core was evidence for tightly coupled ocean–atmosphere circulation switches and a strong interdependence between atmosphere and ocean. They suggested that during OIS3 the global climate system was at a threshold such that perturbations in the climate system were amplified into rapid, major climate shifts. Cannariato and Kennett (1999) further suggested that these climate oscillations had a profound impact on the Earth's biosphere as indicated by rapid changes in benthic foraminiferal assemblages in SBB. Within the same laminated high Corg, Mo, and Cd sediments in core P08 that have been correlated with interstadials in GISP-2 (Fig. 4), concentrations of benthic foraminifera are as much as two orders of magnitude higher than in adjacent bioturbated sediments (Ortiz et al., 2004). Ortiz et al. (2004) suggested that the much higher benthic foraminifera concentrations in laminated OIS3 sediments was due to higher surface-water productivity, also indicated by the geochemical proxies, perhaps due to more La Niña-like conditions with a shallower nutricline.

It is most likely, then, that the Atlantic and Pacific Oceans were linked through the atmosphere; warmer air temperatures during interstadials would have strengthened Hadley and Walker circulations, which, in turn, would have strengthened the subtropical high pressure systems in both the North Atlantic and North Pacific, producing increased rainfall over the Cariaco Basin and increased upwelling along the margins of the Californias. Increased Hadley and Walker circulations also would have increased the amount of water vapor in the atmosphere which potentially could have had a large effect on the global climate system over short time scales (e.g., Pierrehumbert, 1999).

5. Conclusions

1. Sediments deposited during the B/A warm interval in cores from several sites on the northern and central California margins are laminated, have considerable variation in Corg, and have elevated concentrations of Mo and Cd. No cores recovered from within the oxygen minimum zone (OMZ) on the open margin of central and northern California have laminated Holocene sediments, but several cores from the central California margin have sediments deposited during OIS3 that are laminated and (or) have elevated concentrations of Corg and Mo indicating more productive surface waters and less oxygenated intermediate waters.
2. Laminated Holocene sediments do not occur on most of the Baja California margin until south of a latitude of about 23°30′ off southern Baja. The laminated Holocene sediments off southern Baja contain high concentrations of Corg, Mo, and Cd indicating higher Holocene productivity relative to that of the LGI.
3. Millennial-scale variations in productivity and oxygen depletion on the margins of the Californias demonstrate that the California Current System was often poised at a threshold whereby perturbations of atmospheric circulation produced rapid changes in circulation in the eastern North Pacific Ocean. With these changes in circulation came changes in degree of oxygenation of intermediate waters and rate of organic productivity, which may have acted together to produce extremely oxygen-depleted intermediate waters and preservation of laminated sediments where these intermediate waters impinge on the continental slope.
4. Millennial-scale cycles of bioturbated and laminated sediments in the Santa Barbara Basin (SBB) have been attributed to cyclic variations in ventilation of intermediate waters in the basin associated with Dansgaard–Oeschger (D–O) stadial–interstadial cycles, defined by the oxygen-isotope composition of Greenland ice (GISP-2). Alkenone-derived SSTs at ODP Site 1019 have been correlated with the GISP-2 oxygen-isotope curve. Peaks in a diffuse spectral reflectance record (DSR) and % Corg from Baja core PC08 have been correlated to OIS3 D–O cycles in the GISP-2 ice core. The correspondence of peaks of ppm Cd in OIS3 sediments in the OMZ on the Baja California margin with OIS3 D–O cycles are even more pronounced than those of Corg, and have a distinct saw-tooth distribution characteristic of the oxygen-isotope record in the GISP-2 ice core. If these various correlations to GISP-2 D–O cycles are correct, it provides a means of correlating millennial-scale variations recorded in OIS3 sediments of western North America with global events.
5. Another well-established teleconnection between the GISP-2 record and the sediments in another oxygen deficient marginal setting is between GISP-2 and the gray-scale record in the Cariaco Basin off northern

Venezuela. Concentrations of Corg and Mo are much higher in Cariaco Basin sediments than in California margin sediments, but the Corg and Mo records for the B/A and YD intervals from the Cariaco Basin are strikingly similar to those from ODP Site 1019 on the open slope of northern California. This correlation completes a triangle of margins of the Californias to Greenland, Cariaco Basin to Greenland, and California to Cariaco Basin. Such rapid teleconnections cannot be by thermohaline circulation and must be through the atmosphere.

6. It is likely that the Atlantic and Pacific Oceans were linked through the atmosphere. Warmer air temperatures during interstadials would have strengthened Hadley and Walker circulations, which, in turn, would have strengthened the subtropical high-pressure systems in both the North Atlantic and North Pacific, producing increased precipitation over the Cariaco Basin and increased upwelling along the margins of the Californias. Increased Hadley and Walker circulations also would have increased the amount of water vapor in the atmosphere, which potentially could have had a large effect on the global climate system.

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