Glacial-interglacial variability in denitrification in the world's oceans: Causes and consequences

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Abstract. The late Quaternary history of water-column denitrifcation of the eastern Pacific margins and the Arabian Sea is reconstructed using sedimentary $\delta^{15}N$ measurements. The $\delta^{15}N$ values in six piston cores raised from these regions show remarkably similar cyclic variations, being heavy (9-10.5‰) during the interglacials and 2-3‰ lighter during the glacials. This implies that denitrification in these regions decreased substantially during the glacial periods. The glacial decline in denitrification is attributed to reduced upwelling and flux of organic material through the oxygen minimum zone. Since water-column denitrification in these areas accounts for about half of the fixed-nitrogen loss in the modern ocean, the inferred decrease in denitrification should have increased the oceanic nitrate inventory during glacial periods. Because nitrate is a limiting nutrient, oceanic productivity and attendant changes in CO_2 may therefore have been modulated on glacial-interglacial timescales by variations in the oceanic NO_3^- content.

1. Introduction

The biological pump has been identified as being a key governor in the modulation of atmospheric pCO_2 over glacial-interglacial timescales [*Berger et al.*, 1989; *Broecker and Henderson*, 1998]. Strengthening the biological pump by increasing the oceanic nitrate inventory and biological production in surface waters is one mechanism that could explain the drawdown of glacial CO_2 levels, as this would lead to an increase in the pool of inorganic carbon stored in the glacial ocean [*McElroy*, 1983; *Altabet and Curry*, 1989; *Ganeshram et al.*, 1995, *Falkowski*, 1997; *Broecker and Henderson*, 1998]. The inventory of oceanic fixed nitrogen (occurring mostly as nitrate) may change significantly on glacial-interglacial timescales because of its short residence time of ~3000 years [*Codispoti*, 1995]. Fixed nitrogen is supplied to the ocean mainly by in situ N fixation of cyanobacteria, and the major sinks are denitrification in oxygen-deficient waters and in margin sediments [*Codispoti and Christensen*, 1985]. Thus it is the balance between these two processes that determines the nitrogen content of the ocean on glacial-interglacial time scales.

In the absence or near absence of O_2, nitrate is used as an electron acceptor in the bacterially mediated degradation of organic matter, resulting in denitrification. When denitrifica-tion occurs in the water column, the gaseous products of deni-trification (N_2O and N_2) are to a large extent lost to the atmosphere; it is this process that constitutes the net loss of fixed nitrogen from the ocean [*Codispoti and Richards*, 1976]. Water-column denitrification occurs today primarily in three areas: the eastern tropical North Pacific (ETNP), the eastern tropical South Pacific (ETSP), and the Arabian Sea (AS) and accounts for almost one half of the total oceanic N loss of 200 Tg N yr^{-1} [*Codispoti*, 1995]. These three regions host large oxygen-deficient water masses with near-zero oxygen concentrations (Figure 1) and upwelling-induced primary production leading to a large settling flux of organic detritus that sustains high rates of denitrification in subsurface waters [*Codispoti*, 1989]. Nitrate reduction in these areas is largely confined to relatively shallow depths (typically 100-500 m) in the upper part of the oxygen minimum where the settling flux of organic matter is high [*Brandes et al.*, 1998]. As a consequence, deni-trification rates in these zones are sensitive to climate-induced changes in upper ocean circulation and upwelling intensity [e.g., *Codispoti*, 1989].

In the oxygenated waters of the open ocean, the isotopic composition of the nitrate that is mixed into the photic zone from deep waters is ~4-6‰ [Sigman et al., 1999]. However, in oxygen-depleted waters, denitrification renders the isotopic composition of source NO_3^- heavy. Isotopic fractionation associated with denitrification discriminates against $^{15}NO_3^-$ (isotopic fractionation is estimated to be 22-30 ‰), and as a result $^{14}NO_3^-$ is preferentially converted to gaseous products of denitrification [*Cline and Kaplan*, 1975; *Brandes et al.*, 1998; *Altabet et al.*, 1999a]. As denitrification proceeds, the residual nitrate in the oxygen-deficient subsurface waters be-comes progressively enriched in $^{15}NO_3^-$. Nitrate highly enriched in ^{15}N ($\delta^{15}N$ values as high as +18‰; see *Cline and Kaplan* [1975] and *Brandes et al.*, [1998]) is found in the sub-surface waters of all three regions discussed here, particularly near the highly productive continental margin where denitrifi-cation is the dominant biological respiration process in the oxygen minimum zone [*Codispoti and Packard*, 1980; *Garfield et al.*, 1983; *Codispoti*, 1989]. The isotopically heavy nitrate

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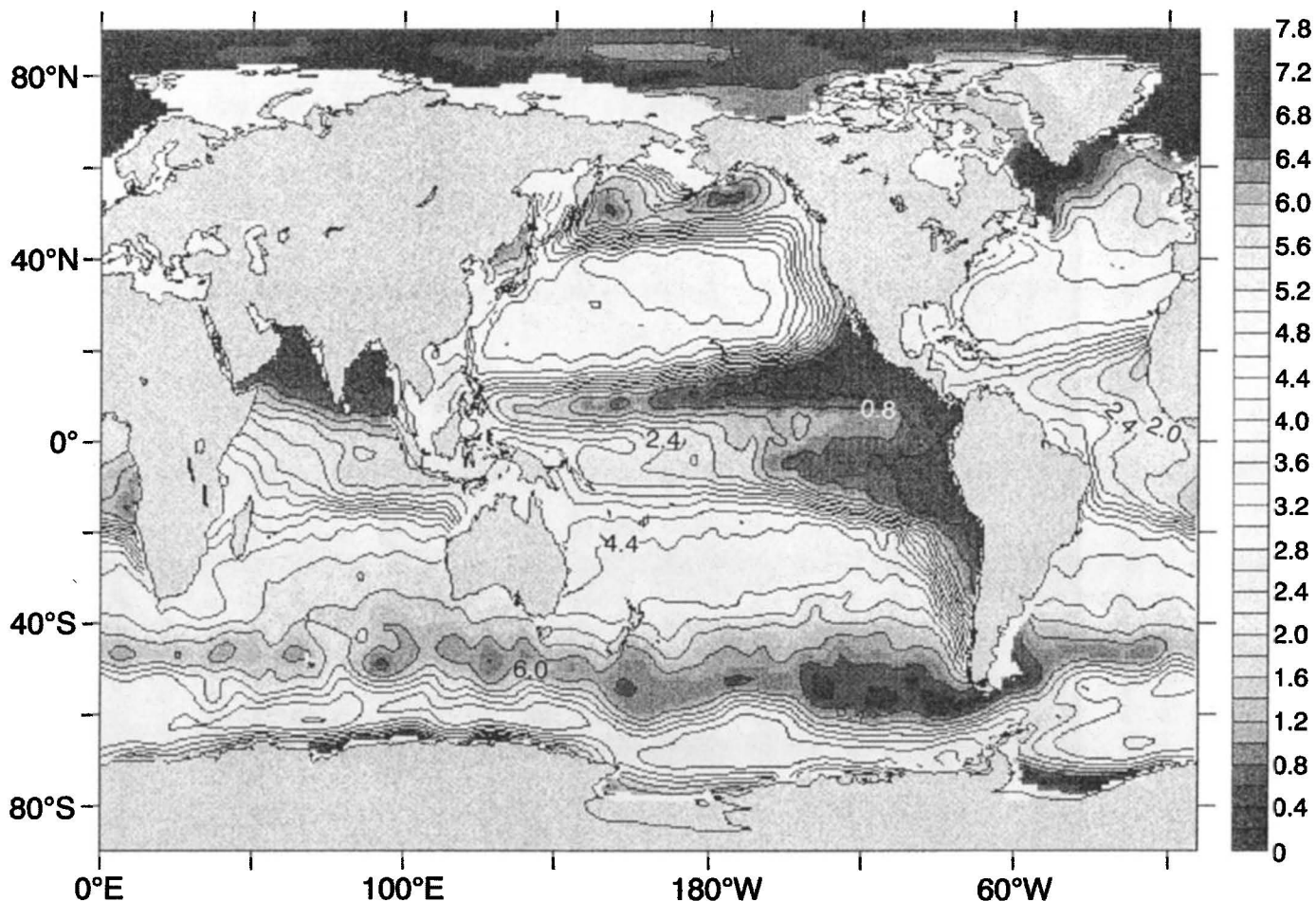[5] Laboratoire Mixte, Centre des Faibles Radioactivites, CNRS-CEA, Gif-sur-Yvette, France.

Figure 1. Oxygen concentrations in mL L^{-1} at 300 m water depth. Large subsurface water masses with oxygen concentration <1 mL L^{-1} occur in the eastern tropical North Pacific, the eastern tropical South Pacific, and the Arabian Sea.

is supplied to the surface waters by upwelling and is utilized by biota, resulting in unusual $\delta^{15}N$ enrichments (8-10‰) in particulate organic material and the underlying modern sediments [*Saino and Hattori*, 1987; *Libes and Deuser*, 1988; *Shafer and Ittekkot*, 1993; *Altabet et al.*, 1999a]. In contrast to denitrification, nitrogen fixation produces photosynthate that is isotopically similar to atmospheric nitrogen [*Brandes et al.*, 1998].

In this paper, we examine sedimentary records of glacial-interglacial variability in denitrification and changes in export on the continental margins of northwest Mexico (ETNP), southern California (ETNP), Peru (ETSP), and western India (AS) (Figures 2a-2d; Table 1). Temporal variations in denitrification are assessed using records of the $\delta^{15}N$ in bulk sediments, while the productivity history for each of these areas is assessed using the concentrations of biogenic components (weight percent organic carbon and Ba/Al ratios). Inferences on the type of organic matter present is derived from $\delta^{13}C_{org}$ values. The possible causes and the consequences of these fluctuations are then discussed in the context of global impacts of changes in whole-ocean nitrate inventories.

2. Methods

Total carbon was determined by flash-combustion gas chromatography on a Carlo-Erba elemental analyzer, as described by *Ganeshram and Pedersen* [1998]. The 1σ relative standard deviation (RSD) of these measurements was 1.25%. Carbonate carbon was determined by coulometry after acid evolution of CO_2 with a precision of 3% (1σ RSD), and organic carbon (OC) was estimated by difference (total minus carbonate C) with a combined precision of 3.3% (1σ RSD). Barium and aluminum were determined X-ray fluorescence spectrometry by employing methods described by *Calvert et al.* [1985]. The precision for both elements was better than 5% (1σ RSD).

Oxygen isotope ratio determinations on picked foraminifera in cores NH8P, NH15P, and NH22P were made following the methods outlined by *Pedersen et al.* [1991]. One sigma precision of replicate samples was better than 0.1‰. Carbon isotope ratios in organic matter in the Pacific Ocean cores were determined using a CHN elemental analyzer coupled to the Prism mass spectrometer, as described by *Pedersen et al.*
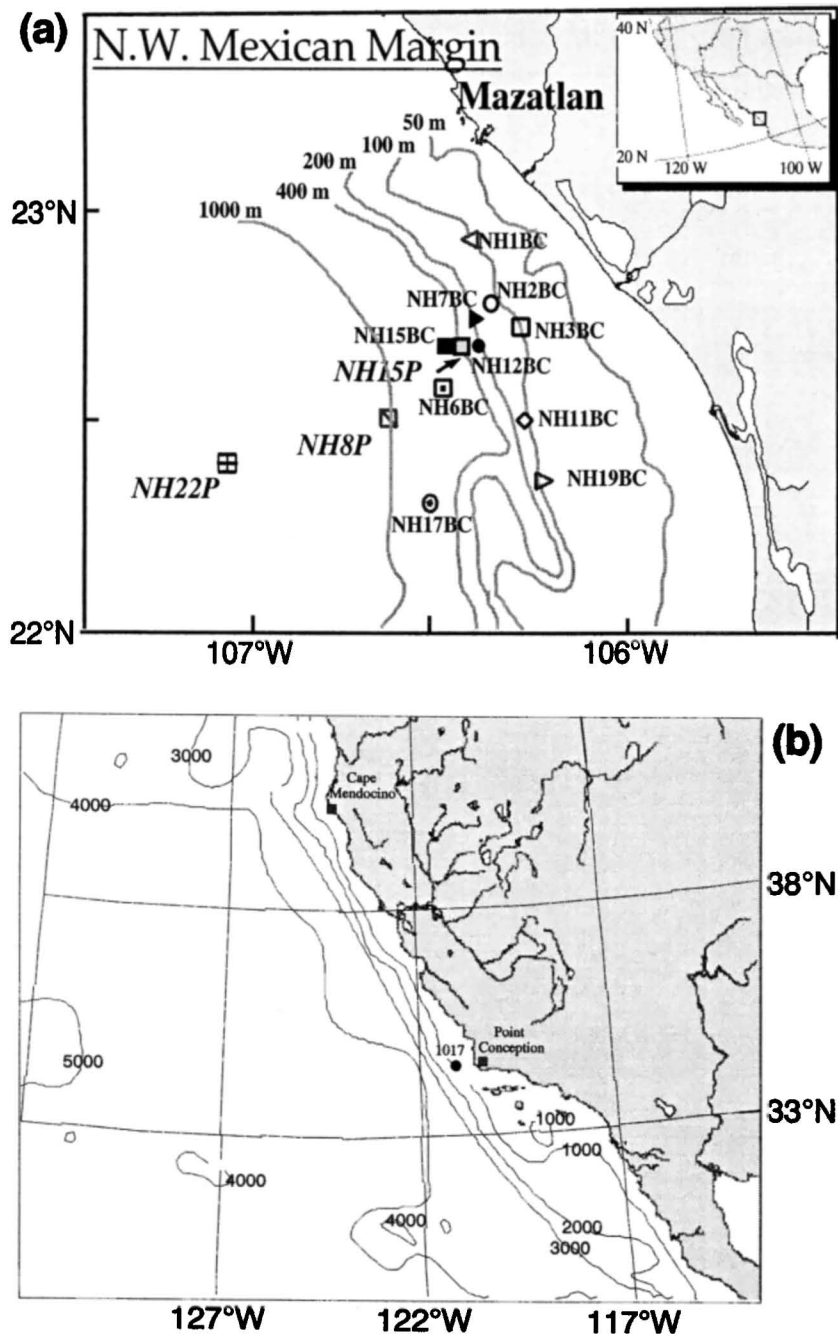
Figure 2. Maps showing bathymetry and the core locations: (a) NW Mexican margin, (b) southern California margin, (c) Peru margin, and (d) western Indian margin. Figure 2 also provides the locations of box cores presented in Figure 4.

[1991]. The precision of these determinations was better than 0.1‰ (1σ). Both $\delta^{18}O$ and $\delta^{13}C_{org}$ measurements are reported relative to the Peedee Belemnite (PDB) standard. Nitrogen isotope ratios were determined using an elemental analyzer directly coupled to the Prism mass spectrometer, as described by *Ganeshram et al.* [1995]. Analytical precision based on internal acetanilide standards was better than 0.2‰ (1σ). The $\delta^{15}N$ values are reported relative to air. The oxygen isotope stratigraphy and $\delta^{13}C_{org}$ were determined on the Arabian Sea core (MD76-131) at Gif-sur-Yvette as described by Fontugne [1983].

3. Result

3.1. Eastern Tropical North Pacific (NW Mexican Margin)

Downcore records of sedimentary $\delta^{15}N$, the $\delta^{18}O$ of benthic foraminifera, $\delta^{13}C_{org}$, and OC concentrations (Figure 3a-3c) are presented in three piston cores comprising a shorenormal transect across the continental slope (Figure 2a; Table 1). These cores were raised from within the oxygen minimum (NH15P), below the oxygen minimum (NH8P), and on the continental rise in well-oxygenated water (NH22P). Details of the
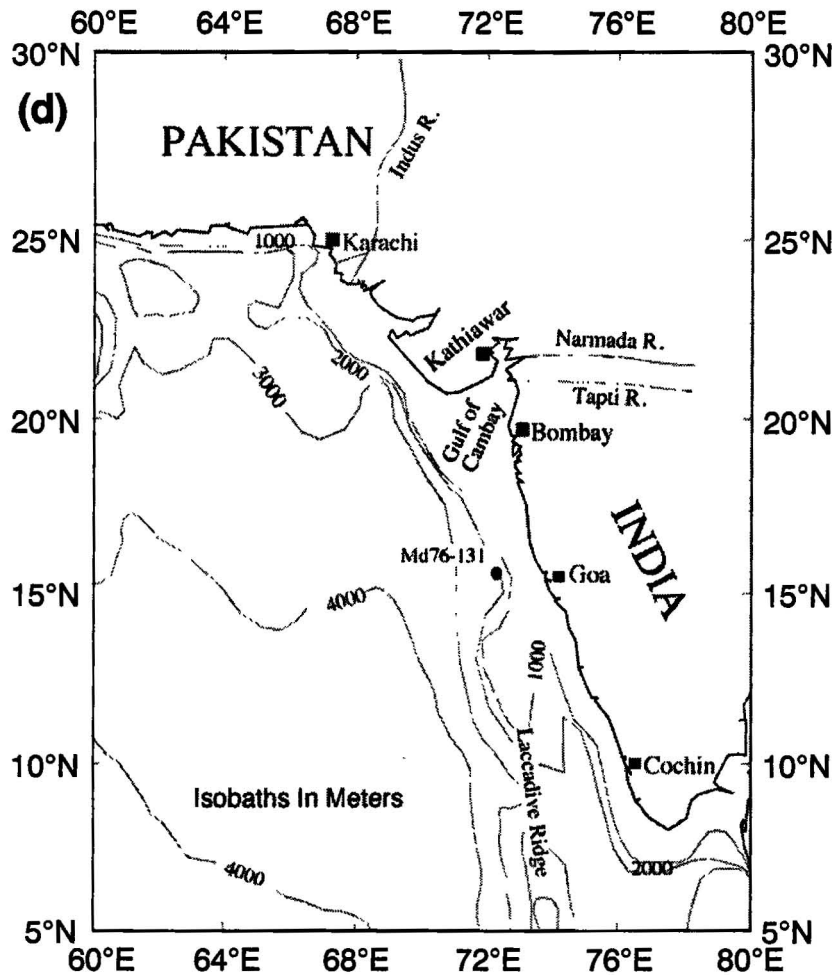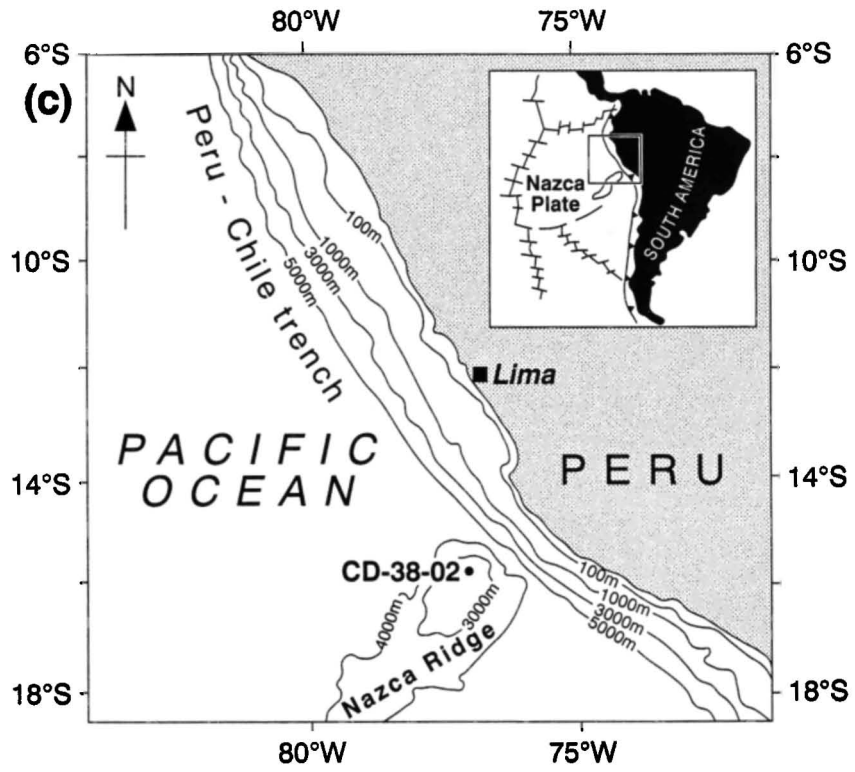
Figure 2. (continued)

Table 1. Locations of Cores Used in this Study

	Latitude	Longitude	Depth, m
Long Cores			
NH15P	22°41.0'N	106°28.8'W	420
NH8P	22°23.3'N	107°04.5'W	1018
NH22P	23°31.1'N	106°31.1'W	2025
ODP 1017E	34°32.09'N	121°6.43'W	960
CD38-02	14°56'S	77°04'W	2525
MD76-131	15°31.8'N	72°34.1'E	1230
Short Cores			
NH1BC	22°56.3'N	106°26.2'W	110
NH2BC	22°43.2'N	106°21.6'W	133
NH3BC	22°43.5'N	106°17.4'W	107
NH6BC	22°36.7'N	106°31.1'W	620
NH12BC	22°41.7'N	106°27.8'W	322
NH15BC	22°41.3'N	106°29.0'W	425
NH11BC	22°30.5'N	106°17.5'W	135
NH19BC	22°22.2'N	106°15.2'W	97
NH7BC	22°42.9'N	106°25.7'W	190
NH17BC	22°18.0'N	106°33.1'W	785

construction of the timescales are given by *Ganeshram and Pedersen* [1998]. Timescales for isotope stages 1 and 2 are based exclusively on radiocarbon dates (corrected for a reservoir age of 400 years). Timescales for intervals older than isotope stage 3 are based on foraminiferal oxygen-isotope stratigraphy, and the age picks were determined by visual correlation with the normalized SPECMAP stack [*Martinson et al.*, 1987]. The $\delta^{15}N$ profiles of all three cores vary in general sympathy with glacial-interglacial stratigraphy: heavy values (means 9-10‰) characterize interglacials (isotope stages 1, 3 and 5),

While values 2-3‰ lighter occur during glacial isotope stages 2, 4, and 6. These glacial-interglacial variations in $\delta^{15}N$ occur almost synchronously in these cores during the last 60 kyr, indicating that the signal is regional in nature. The offsets between $\delta^{15}N$ records are on average <1‰ and lack consistent temporal patterns in intervals younger than 60 kyr. Some larger offsets in older intervals (>60 kyr), especially in isotope stage 5, are probably artifacts of age control which is poorly constrained in core NH15P due to the low resolution of the $\delta^{18}O$ record. OC concentrations show large cyclic variations that also conform to glacial-interglacial stratigraphy (Figures 3a-3c) for the last 140 kyr, with lower OC contents occurring with lighter glacial-age $\delta^{15}N$ values. The variations in OC concentration records are matched by opal and biogenic barium records, as well as variations in their accumulation rates [*Ganeshram and Pedersen*, 1998]. In contrast to $\delta^{15}N$ and OC contents, $\delta^{13}C_{org}$ values are invariant in all of the three cores with a mean value of approximately -21‰.

3.2. Eastern Tropical North Pacific (Southern California Margin)

Ocean Drilling Program Site 1017 off Point Conception (Figure 2b; Table 1) provides profiles of $\delta^{15}N$ and OC concentrations that span the last 30 kyr (Figure 3d). This site is located on the northern edge of the low-oxygen layer of the ETNP (see Figure 1). The timescale (reported in calendar years) is based exclusively on radiocarbon measurements made on monospecific planktonic foraminifera as described by *Kennett et al.* [2000]. Although complicated by intermittent deposition of sandy, organic-carbon-depleted turbidites [*Irino and Pedersen*, 2000], the profiles show that relatively low sedimentary $\delta^{15}N$ values and concentrations characterized the last

glacial period (OC <2 wt%). A general increase in OC content at the end of the glaciation (~16 kyr) is matched by a ~2‰ rise in $\delta^{15}N$ values of roughly 8‰, which persist throughout the last 15 kyr of deposition at this site. The timing and amplitudes of the shifts in $\delta^{15}N$ and OC abundance are very similar to the records from the NW Mexican margin.

3.3. Eastern Tropical South Pacific (Peru Margin)

Core CD 38-02 raised from the Nazca Ridge off Peru (Figure 2c; Table 1) provides records of $\delta^{15}N$, $\delta^{18}O$ of benthic foraminifera, $\delta^{13}C_{org}$, and Ba/Al ratios spanning 275 kyr (Figure 3e). The timescale is constructed by visual correlation with SPECMAP as described by *McNeill* [1993]. The $\delta^{15}N$ profile shows cyclic variations, with heavier values being largely confined to interglacials (mean 8‰); glacial values are up to 3‰ lighter. Ba/Al variations show a clear glacial-interglacial pattern with ratios >0.03 (indicating enhanced productivity [*Dymond et al.*, 1992]) occurring predominantly during the interglacial periods. In highly reducing sediments, such as those accumulating in contact with the oxygen minimum off NW Mexico, sulfate reduction can result in diagenetic Ba remobilization [*Ganeshram and Pedersen*, 1998]. However, Core CD 38-02 was raised from depths well below the oxygen minimum and therefore the largely coherent variations seen in Ba/Al ratios cannot be attributed to diagenetic effects. Also, changes in mass accumulation rates of biobarium follow downcore variations in the Ba/Al ratio, indicating that this profile is largely independent of differential dilution effects [*McNeill*, 1993]. In contrast to $\delta^{15}N$ and Ba/Al ratios, the $\delta^{13}C_{org}$ values are almost invariant (approximately -21‰) with little glacial-interglacial contrast.

3.4. Arabian Sea (Western Indian Margin)

Core MD76-131 collected at 1230 m water depth on the western Indian margin (Figure 2d; Table 1) shows large glacial-interglacial variations in $\delta^{15}N$. Heavy $\delta^{15}N$ values (mean 9-10‰) are confined to the interglacials, and glacial values are 2-3 ‰ lighter (Figure 3f). With the exception of early stage 2, OC contents vary in a similar fashion, showing highest values (mean 2-3 wt. %) in the interglacial intervals. Unlike these other parameters, $\delta^{13}C_{org}$ values are close to -19‰ in stages 2-4, with a small decrease to ~20‰ in stage 1 (Figure 3f).

In summary, in all of the four regions reported here, there is a consistent pattern in which glacial intervals are characterized by lighter $\delta^{15}N$ values coupled with declines in the concentrations or rates of accumulation of biogenic sedimentary components.

4. Discussion

4.1. Possible Causes for the Downcore Variability in $\delta^{15}N$

We discuss five factors that could have caused the observed downcore cyclical variations in N isotopic composition in the three regions considered in this work.

4.1.1. Terrestrial organic matter. Mixing of marine organic matter with isotopically lighter terrestrial organic matter (~ $\delta^{15}N$ = 2‰ [*Sweeney and Kaplan*, 1980]) can produce lighter $\delta^{15}N$ values in marine sediments [*Peters et al.*,

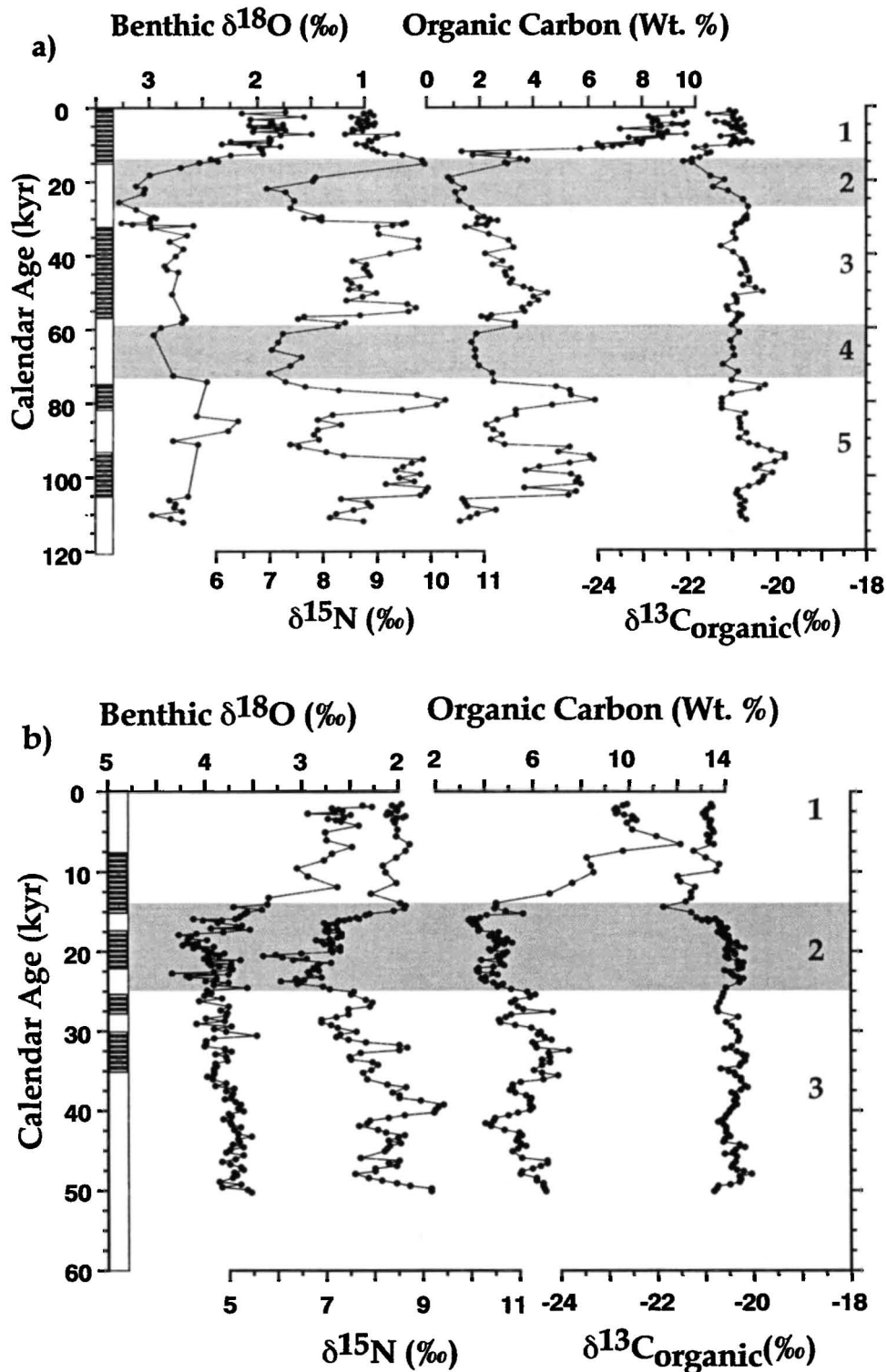**Figure 3.** Records of formaninferal $\delta^{18}O$, bulk sediment $\delta^{15}N$, weight percent organic carbon, Ba/Al weight ratios (Core MD76-131) and $\delta^{13}C_{org}$ from (a, b, and c) NW Mexican margin, (a) Core NH15P, (b) Core NH8P (c) Core NH22P, (d) southern California margin, Ocean Drilling Program Site 1017E, (e) Peru margin, Core CD38-02, and (f) the western Indian margin, Core MD-76-131. Isotope stages are indicated near the right margin of Figures 2a-2f, and glacial stages are shaded. The $^{18}O/^{16}O$ ratios were measured on *Uvigerina* spp. in NH22P and CD38-02, *Bolivina* spp. in NH8P, NH15P, and 1017E, and *Globigerinoides ruber* in MD76-131. Bars in the left margin of Figures 2a-2c indicate laminated (hatched) and massive (shaded) intervals. Data from Cores NH8P and NH22P were reported previously by *Ganeshram et al.* [1995] and *Ganeshram and Pedersen* [1998]. Organic carbon and $\delta^{18}O$ records from ODP 1017E have been reported by Kennett et al. [2000] and *Irino and Pedersen* [2000] respectively. The $\delta^{18}O$ and Ba/Al records from Core CD38-O2 were presented by *McNeill* [1993]. Organic carbon and $\delta^{18}O$ records from Core MD76-131 are from *Fontugne* [1983].
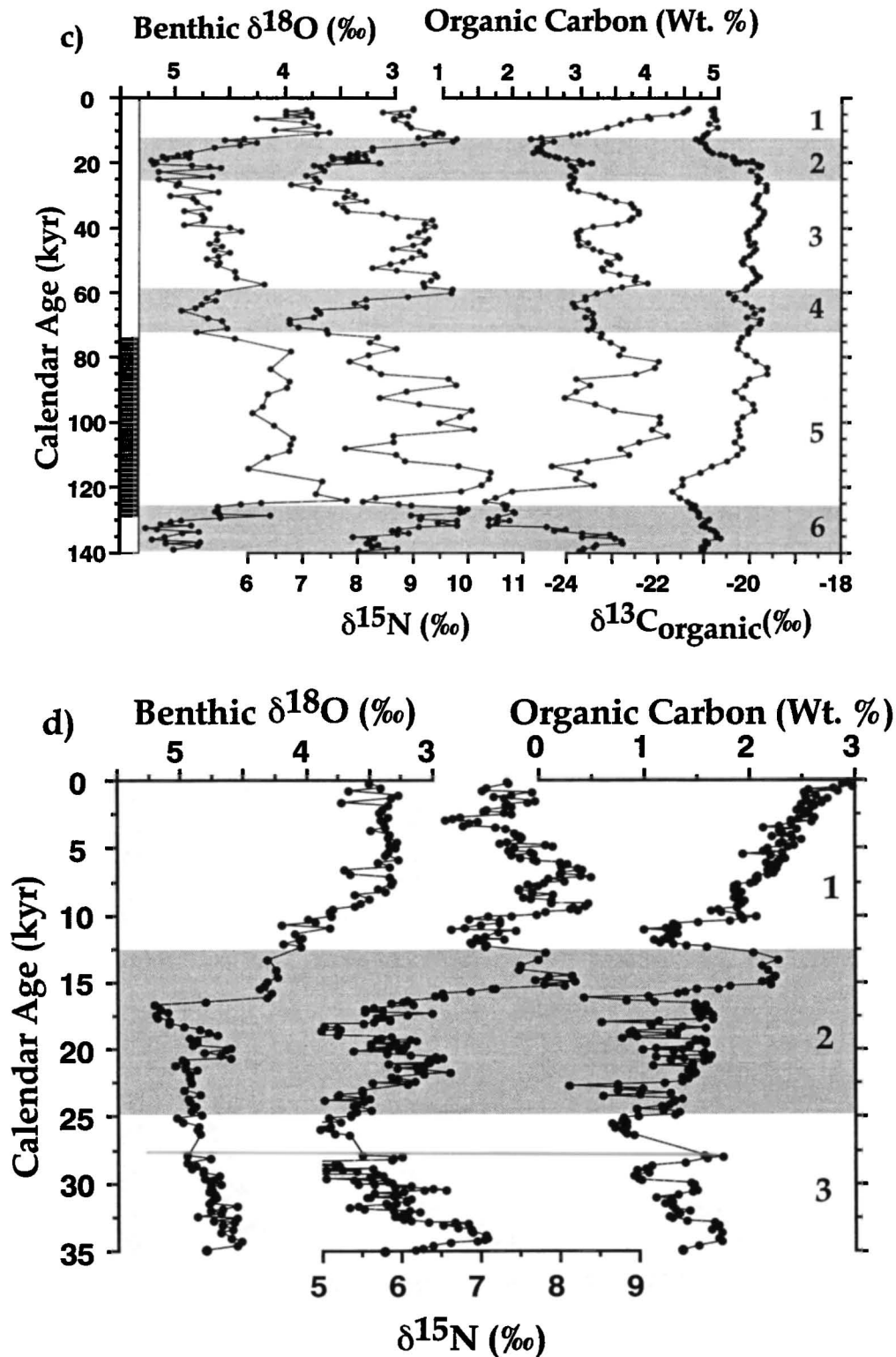
Figure 3. (continued)

1978]). The possibility that significant admixture of terrestrial organic matter affected the $\delta^{15}N$ results reported here in all areas simultaneously can be evaluated by examining the relationship between $\delta^{15}N$ and $\delta^{13}C_{org}$ (Figure 4). The carbon isotopic composition of land-derived organic matter originat-ing from C_3 plants is significantly lighter (-26 to -28‰ PDB [*Jasper and Gagosian*, 1990]) than mid-latitude and tropical marine organic matter (-18 to -22‰ PDB [*Rau et al.*, 1989]). Consequently, the presence of varying proportions of terrestrial organic material will produce a mixing line on a $\delta^{13}C_{org}$
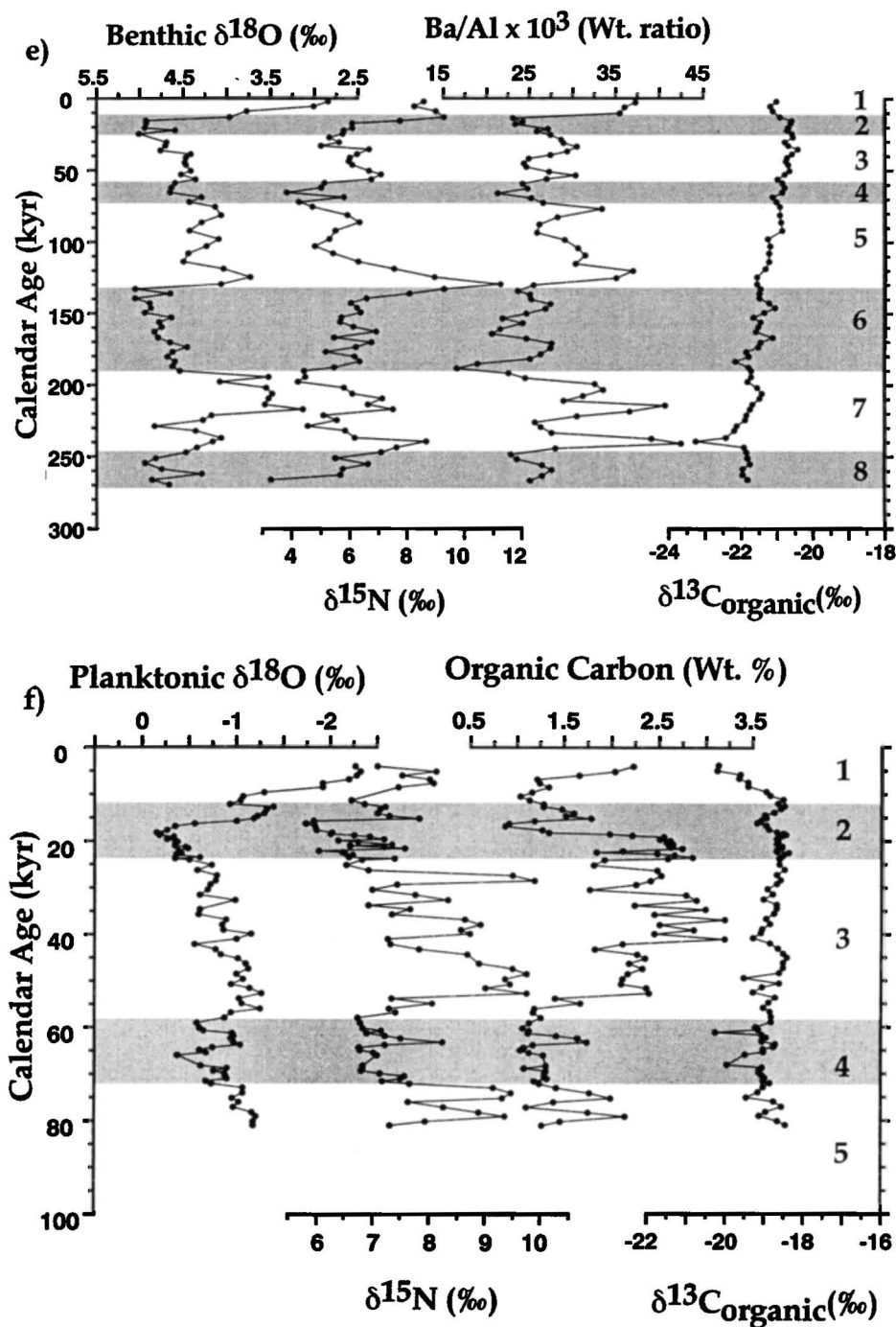
Figure 3. (continued)

and $\delta^{15}N$ plot, with lighter $\delta^{13}C_{org}$ corresponding with lighter $\delta^{15}N$ [*Sweeney and Kaplan*, 1980]. None of the cores considered here (with the exception of the record from Site 1017, for which $\delta^{13}C_{org}$ data are unavailable) exhibits such a trend (Figure 4). Indeed, the $\delta^{13}C_{org}$ values shown in Figure 4 fall within the narrow range (-22 to -19‰) typical of marine organic matter produced in low latitude to mid latitude regions [*Rau et al.*, 1989]. Furthermore, there is no systematic glacial-interglacial change. Thus the lighter $\delta^{15}N$ values in the glacial-age intervals in all four regions cannot be explained by addition of terrestrial organic material.

4.1.2 Organic matter alterations in water column and sediments. Remineralization of organic matter while settling and during burial diagenesis could have produced variations in the sedimentary $\delta^{15}N$ signal. A uniform ~4‰ shift to heavier $\delta^{15}N$ values between settling material and near-surface sediments has been reported in the deep waters of the Southern Ocean and the equatorial Pacific [*Altabet and François*, 1994]. However, because this shift is constant with time, it will not influence variations in $\delta^{15}N$ downcore [*Sigman et al.*, 1999]. In contrast to the deep sea, comparisons in nitrogen isotopic composition between sediment trap material
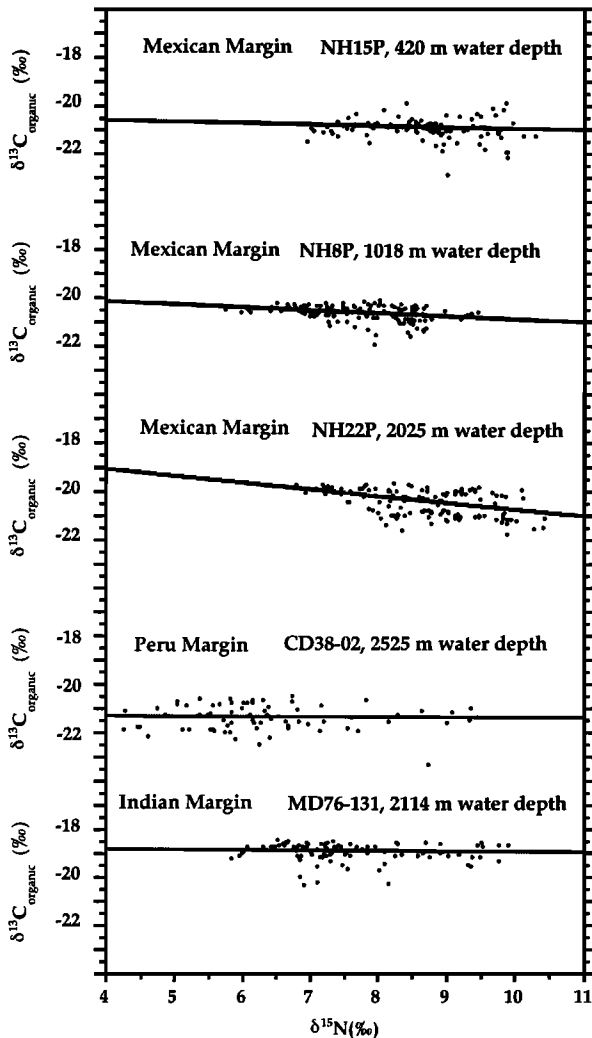
Figure 4. The relationship between $\delta^{15}N$ and $\delta^{13}C_{org}$ in piston cores.

and superficial sediments have not revealed significant isotopic shifts in productive continental margin settings where the sediments contain moderate to high organic carbon contents [Altabet et al., 1999a; Pride et al., 1999; Altabet et al., 1999b]. Rather than organic matter alterations, the nitrogen isotope composition of modern sediments that underlie zones of intense water-column denitrification seems to reflect largely the $\delta^{15}N$ of the nitrate in near-surface waters in such regions. For instance, the 9-10‰ range in $\delta^{15}N$ of superficial sediments in the ETNP and AS mirror the isotopic composition of dissolved nitrate in surface waters in these regions [Brandes et al., 1998].

Although isotopic changes may not occur during settling, $\delta^{15}N$ shifts may occur during progressive burial of organic matter. This is evaluated here using a set of 10 short box cores collected on a shore-normal transect across the outermost shelf and slope off NW Mexico (Figure 2a; Table 1). While Corg/N ratios (Figure 5a) generally show a secular increase with sediment depth, the $\delta^{15}N$ profiles are invariant, with values between 9 and 10 ‰, over the same depth intervals (Figure 5b). Thus the preferential release of nitrogen during degradation of organic matter implied by the increase in

Corg/N with depth does not cause significant isotopic fractionation. This conclusion is robust, because the 10 box cores span a broad spectrum of depositional conditions on the margin, including contrasting bottom water oxygen concentrations and a range of organic carbon contents and variable sedimentation rates [Ganeshram et al., 1999]. Thus, unlike in the deep ocean, early diagenesis in relatively organic-rich continental margin sediments does not seem to produce a significant shift in $\delta^{15}N$ toward heavier values, and it cannot be invoked to explain the lighter values seen in the glacial intervals of the cores studied here.

4.1.3. Incomplete nitrate utilization. The third possible factor affecting sedimentary N isotope variation is incomplete utilization of nitrate by phytoplankton in near-surface waters. It has been observed in continuous culture experiments that $\delta^{15}N$ of the photosynthate follows the integrated product equation of first-order Rayleigh fractionation kinetics owing to the preferential uptake of $^{14}NO_3^-$ by phytoplankton [Montoya, 1994; Waser et al., 1998]. Such fractionation coupled with lateral advection of a residual nitrate pool with variable $\delta^{15}N$ could produce a spatial pattern in sedimentary $\delta^{15}N$ values. Spatial variation in sedimentary $\delta^{15}N$ in the modern ocean owing to this process is well documented in the equatorial Pacific and the Southern Ocean, where the residence time of upwelled nitrate is long owing to Fe limitation [Altabet and François, 1994; Farrell et al., 1995; Sigman et al., 1999]. Should such a pattern vary in time, it could produce downcore changes in $\delta^{15}N$.

Incomplete nitrate utilization is a phenomenon that largely affects $\delta^{15}N$ in deep-sea settings where Fe limitation inhibits rapid uptake of nitrate. In contrast to the deep sea, however, upwelled nutrients are rapidly and completely utilized over continental margins. Therefore the mean isotopic composition of particulate organic nitrogen and surface sediments matches that of the nitrate that wells up to the euphotic zone. Thus the isotopic composition of source nitrate determines sedimentary $\delta^{15}N$. This is apparent in the box-core transect across the Mexican margin (Figure 5b), where the $\delta^{15}N$ values are relatively uniform and lack a spatial trend. Furthermore, given the higher dustiness of the glacials, it is even less likely that incomplete nitrate utilization consequent upon iron limitation was responsible for the lighter $\delta^{15}N$ values seen in the glacial intervals of our cores.

4.1.4. Nitrogen fixation. Nitrogen fixation could have contributed a variable proportion of the $\delta^{15}N$ signal downcore. Nitrogen-fixing cyanobacteria produce photosynthate with very little fractionation from atmospheric N_2 (aproximately -1 to +1‰ [Brandes et al., 1998]). Thus, should N fixation have been enhanced during glacial stages relative to nitrate uptake, it could have contributed to the observed low $\delta^{15}N$ values by diluting the heavier $\delta^{15}N$ signature imparted on the upwelled nitrate by denitrification. Two observations argue against this effect. First, nitrogen fixation is normally significant only when nitrate concentrations in surface waters are very low. For example, in the relatively nutrient-depleted waters of the Cariaco Basin, N fixation has occurred during the last 580 kyr only during periods of enhanced sub surface denitrification [Haug et al., 1998]. It appears that N deficiency relative to P (low N/P ratios) in near surface waters triggers N fixation in this area [Walsh, 1996]. Second, in nutrient-rich
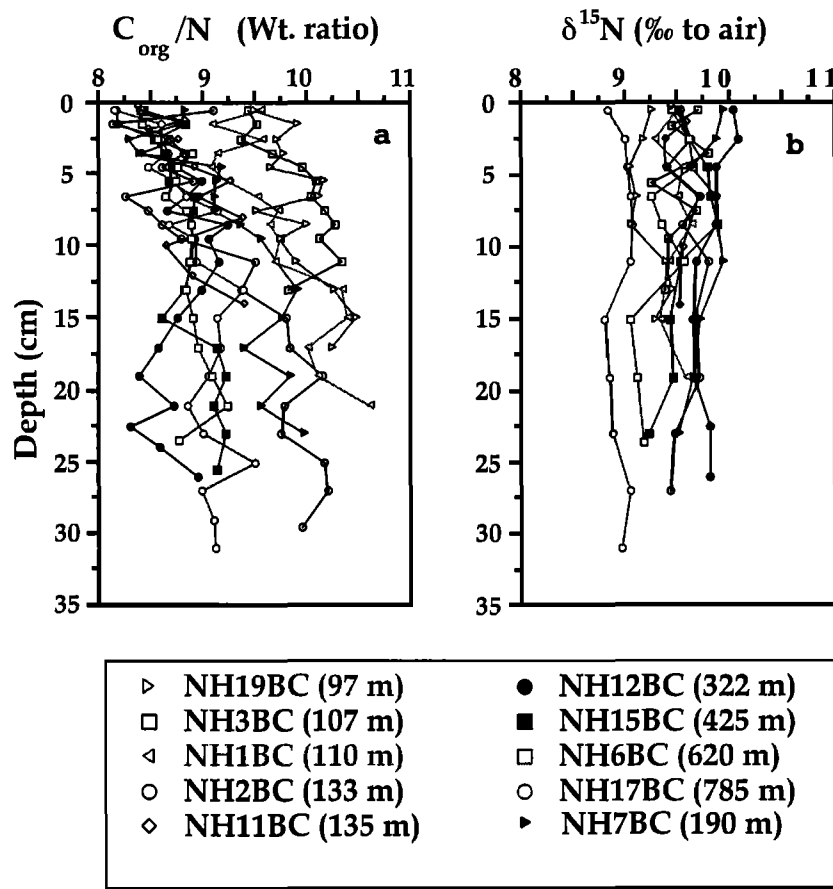
Figure 5. Downcore profiles of (a) C_{org}/N weight ratios and (b) $\delta^{15}N$ in Mexican margin box cores. The water depths for each core are shown in parentheses in the legend. C_{org}/N weight ratios are from *Ganeshram et al.* [1999]. The linear sedimentation rates and organic carbon contents in box cores range from 6 to 17 cm kyr^{-1} and 2 to 11 wt% respectively. The bottom water oxygen concentrations in core sites range from <5 to 50 μM.

coastal upwelling areas such as the AS where denitrification is prevalent, N fixation does not occur at rates high enough to affect significantly the $\delta^{15}N$ values of near surface nitrate [*Altabet et al.,* 1999a]. Thus it appears that N fixation is relatively more important in nitrate-depleted waters and only during episodes of enhanced denitrification (thus, a low oceanic N/P ratio). Thus, the absence of denitrification and the resulting higher N/P ratios during the glacials would have deminished the importance of N fixation. These observations, together with the strong body of evidence in favor of decreased glacial-age denitrification (independent of $\delta^{15}N$) discussed below, make enhanced N fixation an unlikely explanation for lighter shift $\delta^{15}N$ profiles.

4.1.5. Water-column denitrification. Finally, the heavier interglacial $\delta^{15}N$ values (9-10‰) in the trio of Mexican margin piston cores, and in cores collected off tCalifornia, Peru and western India (Figure 3), are similar to values observed in Recent sediments influenced by denitrification [*Libes and Deuser,* 1988; *Shafer and Ittekkot, 1993; Altabet et al., 1999, Pride at al., 1999; Altabet et al., 1999a; this study*]. In contrast, the lighter glacial values are common in sediments where subsurface waters are well oxygenated. For example, values of 5-7‰ (closer to the isotopic composition of

deep ocean nitrate) are commonly found in sediments underlying upwelling zones in the equatorial Pacific, the eastern Atlantic continental margins, and in the Southern Ocean [*Altabet and François,* 1994; *Farrell et al.,* 1995; *Holmes et al.,* 1997; *Sigman et al.,* 1999]. By analogy, and having ruled out varying terrestrial inputs, it appears that reduced water column denitrification is the most probable cause for the lighter $\delta^{15}N$ values observed in glacial-age sediments on the continental margins in all three marginal areas examined in this paper.

The presence of laminations in the sediment sections that have heavy $\delta^{15}N$ values in Core NH15P from the Mexican margin provides further support for increased denitrification during interglacials. This core was raised from a depth of 420 m on the upper slope, where the seafloor is in direct contact with waters that currently host denitrification. The close correspondence between lighter $\delta^{15}N$ values and the absence of laminations in the glacial intervals in this core (Figure 3a) implies that the bottom waters were well oxygenated at such times and that this allowed active bioturbation by benthic fauna. Similarly, laminated sediments are more prevalent during interglacials than during glacial periods in the oxygen minimum off California, and Peru and in the AS [*Garrison and Kastner,* 1990; *Behl and Kennett,* 1996; *Schultz et al.,* 1998].

4.2. The Cause of Diminished Denitrification During the Glacial Periods

4.2.1. Productivity changes.

Each of the three broad regions considered in this study is characterized by an upwelling regime where large settling fluxes of organic matter and their remineralization currently fuel rates of denitrification that are globally significant [*Codispoti*, 1989]. However, interannual and seasonal variations in denitrification in response to climate-induced productivity changes have been reported in such areas [*Codispoti et al.*, 1986; *Naqvi*, 1987; *Codispoti*, 1989], implying that the rates of nitrate reduction are sensitive to short-term climate fluctuations. Over longer timescales, reduced productivity during glacial stages has been previously inferred off NW Mexico and southern and northern California variously on the basis of OC, opal, and biobarium accumulation rates [*Ganeshram and Pedersen*, 1998; *Lyle et al.*, 1992; *Gardner et al.*, 1997]. Similarly, lower rates of accumulation of OC and decreases in the abundance of upwelling-related foraminifera and diatoms have been reported in glacial intervals in Peru margin sediments [*Reimers and Suess*, 1983; *Schrader and Sorknes*, 1991; *Heinze and Wefer*, 1992], while decreases in upwelling and productivity during the glacials in the AS have been inferred from OC and opal accumulation rates, Ba/Al ratios, and foraminiferal assemblages [*Clemens and Prell*, 1990; *Shimmield*, 1992; *Schultz et al.*, 1998].

In the ETNP (off Mexico and California) and ETSP (off Peru), coastal upwelling is driven by westerly winds generated by the subtropical high pressure centers in the Pacific Ocean, which are in large part sustained by the differential heating of land and ocean. One consequence of the glacial cooling on land is the weakening of such high pressure systems and the associated shore-parallel westerly winds which drive upwelling. *Ganeshram and Pedersen* [1998], for example, argued that the waxing and waning of Laurentide Ice Cap on the North American continent varied the land-sea thermal contrast and alternately strengthened and weakened upwelling-favorable winds on the western margin of North America including NW Mexico. Similarly, a slackening of upwelling winds off Peru due to a weaker subtropical high-pressure system in the South Pacific during the Last Glacial Maximum (LGM) is predicted by general circulation model simulations [*Kutzbach et al.*, 1993].

The similarities between the Indian margin $\delta^{15}N$ record (Figure 3f) and those from the Oman [*Altabet et al.*, 1995; *Altabet et al.*, in press] and Pakistan margins [*Reichart et al.*, 1998] suggest a basin-wide decline in denitrification in the AS during the glacial periods. The OC record from the Indian margin suggests lower productivity during glacial periods in the AS. *Shimmield* [1992] came to a similar conclusion based on a glacial-age decline in biobarium and organic carbon accumulation recorded by Oman margin sediments. *Reichart et al.* [1998] found that the lowest O_2 levels in the oxygen minimum correlate with productivity maxima in sedimentary records from the Pakistan margin.

Upwelling in the Arabian Sea is driven by mosoonal winds generated by the thermal contrast between the Asian continent and the Indian Ocean. Recently, *Altabet et al.* [1999a] found strong coherence between $\delta^{15}N$ and grain-size records at the 41 and 23 Ka frequency bands, suggesting a positive relationship between higher monsoonal strength (coarser grain size of wind-borne detritus) and denitrification (heavier $\delta^{15}N$). Thus glacial decreases in productivity and denitrification in the AS

are attributed to the weakening of the summer monsoonal winds that drive seasonal upwelling and dominate mean annual export production. Thus the lower denitrification during glacial periods in the three areas (ETNP, ETSP and AS) studied here could have resulted from decreases in upwelling and the settling flux of organic material through the water column.

4.2.2. Circulation changes.

Low oxygen concentrations (<20 μM) are found at mid depths between ~150 and ~1000 m all along the continental margin in the ETNP and ETSP [*Wyrtki*, 1967]. However, maxima in nitrite and the isotopically heavy nitrate peak, both of which result from denitrification, are largely confined to depths between 150 and 500 m [*Cline and Kaplan*, 1975; *Garfield et al.*, 1983; *Brandes et al.*, 1998]. The water mass in this depth range in the ETNP and ETSP is characterized by its high salinity, indicating an equatorial origin. These high-salinity water masses, called the subtropical subsurface water off NW Mexico [*Roden*, 1972; *Warsh and Warsh*, 1973] and equatorial subsurface water off Peru [*Wyrtki*, 1967], host intense denitrification and supply isotopically heavy nitrate to surface waters during periods of upwelling. Therefore denitrification is sensitive to ventilation/circulation changes in these water masses.

The intermediate waters of the Pacific originating at high latitudes occupy a deeper stratum in the oxygen minimum (below ~600 m), beneath the intense denitrifying zone. These water masses are oxygen depleted basin-wide. The high-latitude intermediate waters in the ETNP and ETSP are Pacific Intermediate waters and Antarctic Intermediate waters, respectively. These waters are clearly distinguishable from the overlying equatorial waters by their salinity and nutrient characteristics [*Wyrtki*, 1967]. Because of their deeper position in the water column, the effect of ventilation changes in intermediate waters on dentrification should be minor in these regions.

The major source of these high-salinity waters in the ETNP and ETSP is the Equatorial Undercurrent or 13°C water [*Tsuchiya*, 1981], which flows west to east below the equatorial divergence zone. The undercurrent splits into north and south flowing arms in the eastern equatorial Pacific around the Galapagos Islands [*Lukas*, 1986]. The north flowing arm feeds the oxygen-minimum off NW Mexico and the south-flowing arm feeds that off Peru. The Equatorial Undercurrent is well oxygenated until it approaches the coast of Central America, owing to Ekman pumping related to the equatorial divergence [*Lukas*, 1986; *Toggweiller and Carson*, 1995]. This feature is seen in Figure 1 as a tongue of high-oxygen water penetrating west to east (~5°N latitudes) in the equatorial Pacific. Therefore subsurface waters of the ETNP (off NW Mexico) and ETSP (off Peru) are initially supplied with a relatively high concentration of oxygen. When compared to the underlying intermediate waters, the residence times of the subsurface water masses are thought to be relatively short (of the order of 10 years) owing to extensive upwelling in the eastern Pacific [*Wyrtki*, 1967]. Given these characteristics, the depletion of oxygen in the subsurface waters can be attributed mainly to a rate of consumption that exceeds the rate of ventilation as the waters flow beneath areas of high biological production in the eastern Pacific [*Wyrtki*, 1967]. Thus circulation at the depth of the dentrification zone in the eastern Pacific also suggests a strong coupling between local productivity and denitrification in this region.

The situation on the California margin is slightly different from those off Mexico and Peru. This area is located at the northern edge of the oxygen-deficient water mass of the ETNP (Figures 1 and 2). Off southern California, heavy nitrate occurs between 100 and 400 m depth, primarily associated with the California Undercurrent [*Liu and Kaplan*, 1989]. Despite the presence of heavy nitrate, dentrification does not occur in significant rates within the oxygen minimum in this area [*Brandes*, 1997]. Instead, the heavy nitrogen isotopic signature of subsurface waters is an advective feature originating from the denitrifying zone farther south and carried northwards via the California Undercurrent [*Liu and Kaplan*, 1989; *Brandes*, 1997]. Here, the lack of a denitrification signal in glacial sediments could be attributed simply to the absence of denitrification on the NW Mexican continental margin during glacial periods.

In the Arabian Sea, Persian Gulf and Red Sea waters occupy the upper part of the oxygen minimum (depths shallower than ~500 m), corresponding with the core of the denitrifying zone [*Brandes et al.*, 1998]. These local warm salty water masses are underlain by intermediate waters of high-latitude origin at depths greater than ~500 m [*Olson et al.*, 1989]. Thus the situation here is somewhat similar to the Pacific in that the denitrification rates are sensitive to changes in local circulation and productivity. In addition to a productivity decrease, *Altabet et al.* [1995, 1999a] also considered the lack of formation of Persian Gulf and Red Sea waters as contributing to lower glacial denitrification rates in the Arabian Sea. Because this mechanism relies on large changes in sea level, it cannot in isolation explain the full range of oscillations (e.g., sub-Milankovitch frequencies) in denitrification and in the intensity of the oxygen minimum reported in other Arabian Sea records [*Schulz et al.*, 1998; *Reichart, et al.*, 1998]. In addition, the timing of the resumption of denitrification precedes major changes in sea level during Termination I [*Altabet et al.*, 1999a]. Since the denitrification zone in the Arabian Sea resides within local water masses, its oxygenation is most likely to be sensitive to local changes in productivity.

In conclusion, in all of the three broad regions discussed in this paper there is evidence that glacial-interglacial variations in denitrification are forced largely by changes in upwelling-induced productivity, although broader upper ocean circulation changes in subsurface water masses may have played a secondary role.

4.2.3. Timing of the onset of denitrification during Termination I.
The transition to heavy $\delta^{15}N$ values during the last deglaciation (Termination I) seems to have occurred simultaneously at ~16 ka on the NW Mexican and southern California margins (Figure 6). The California margin core has a very high average sedimentation rate, and Mexican margin sediments are laminated during the deglacial. As a result, the influence of bioturbational mixing is not severe in these records, allowing accurate evaluation of the absolute timing of the intensification of denitrification. Age scales for these cores are independent of oxygen isotope stratigraphy near Termination I and are based exclusively on radiocarbon dates. The increases in $\delta^{15}N$ and OC occur simultaneously at the end of the last glacial and precede major changes in sea level, as recorded by benthic $\delta^{18}O$. The coeval changes in inferred productivity (increase in OC, opal, and Ba/Al ratios) and

$\delta^{15}N$ suggest that the onset of denitrification was induced just prior to the end of the last glacial period by strengthened upwelling-favorble winds [*Ganeshram and Pedersen*, 1998]. On the basis of the relative timing of all variables, such implied changes in atmospheric circulation preceded major changes in sea level and appear to have been coincident with the increases in atmospheric temperature and CO_2 recorded in ice cores [*Broecker and Henderson*, 1998; *Petit et al.*, 1999].

4.3. Implications for the Oceanic-Nitrate Inventory and pCO_2 During Glacial Periods

The widespread diminished glacial-age denitrification implied by our results has profound global ramifications. Fixed N is supplied to the ocean by rivers, *in situ* N fixation by cyanobacteria, and atmospheric fallout. Of these, N fixation is by far the largest source [*Capone et al.*, 1997]. The major sinks are denitrification in oxygen-deficient waters and in shelf sediments and the burial of organic nitrogen in sediments [*Codispoti and Christensen*, 1985]. Previous investigations have suggested that the fixed-N budget of the ocean is unbalanced, with the supply being ~90 Tg N yr^{-1} and the total loss amounting to some 200 Tg N yr^{-1}. As a result, the ocean until very recently was thought to be losing fixed nitrogen at a rate faster than it is being supplied [*Devol*, 1991; *McElroy*, 1983; *Ganeshram et al.*, 1995, *Codispoti*, 1995]. However, recent studies suggest that N fixation rates in the modern ocean may have been underestimated and that the budget could be in near balance [*Gruber and Sarmiento*, 1997]. Other studies contend that denitrification rates have also been underestimated [*Codispoti*, 1995; *Middelburg et al.*, 1998]. Despite these uncertainties, it is clear that the balance between N fixation and denitrification controls the oceanic N inventory on glacial-interglacial timescales.

Several studies have raised the possibility that the oceanic N content increased during the glacial stages. *Christensen et al.* [1987] asserted that the sink for nitrogen increases during interglacials owing to an increase in the area of the submerged continental shelf that hosts sedimentary denitrification. Assuming that the decrease in denitrification is proportional to the shelf area, reducing the shelf area by 75%, as during the LGM [*Hay and Southam*, 1977], would decrease modern shelf denitrification rates from 100 [*Devol*, 1991] to 25 Tg N yr^{-1}. *Falkowski* [1997] speculated that higher dust deposition during glacials should enhance N fixation, which is thought to be limited by the availability of Fe in the modern ocean. Evidence from sedimentary records for enhanced glacial N fixation has so far been limited to localized areas such as the Cariaco Basin and Caribbean Sea [*Haug et al.*, 1998; M. Altabet, personal communication, 1999]. The declines in water-column denitrification in the ETNP, the ETSP and the AS, which account for almost all of the ~100 Tg N yr^{-1} lost to water-column denitrification in the present ocean, imply that global denitrification must have been greatly diminished during glacial periods. The combination of N supply due to increased nitrogen fixation combined with reduced N loss from denitrification should have led to an increase in glacial N inventory.

Primary production in the modern ocean is thought to be nitrogen-limited [*Codispoti*, 1989; *Fanning*, 1992] although in some areas production may be constrained by a dearth of micronutrients such as iron [*Martin*, 1990; *Kolber et al.*, 1994].
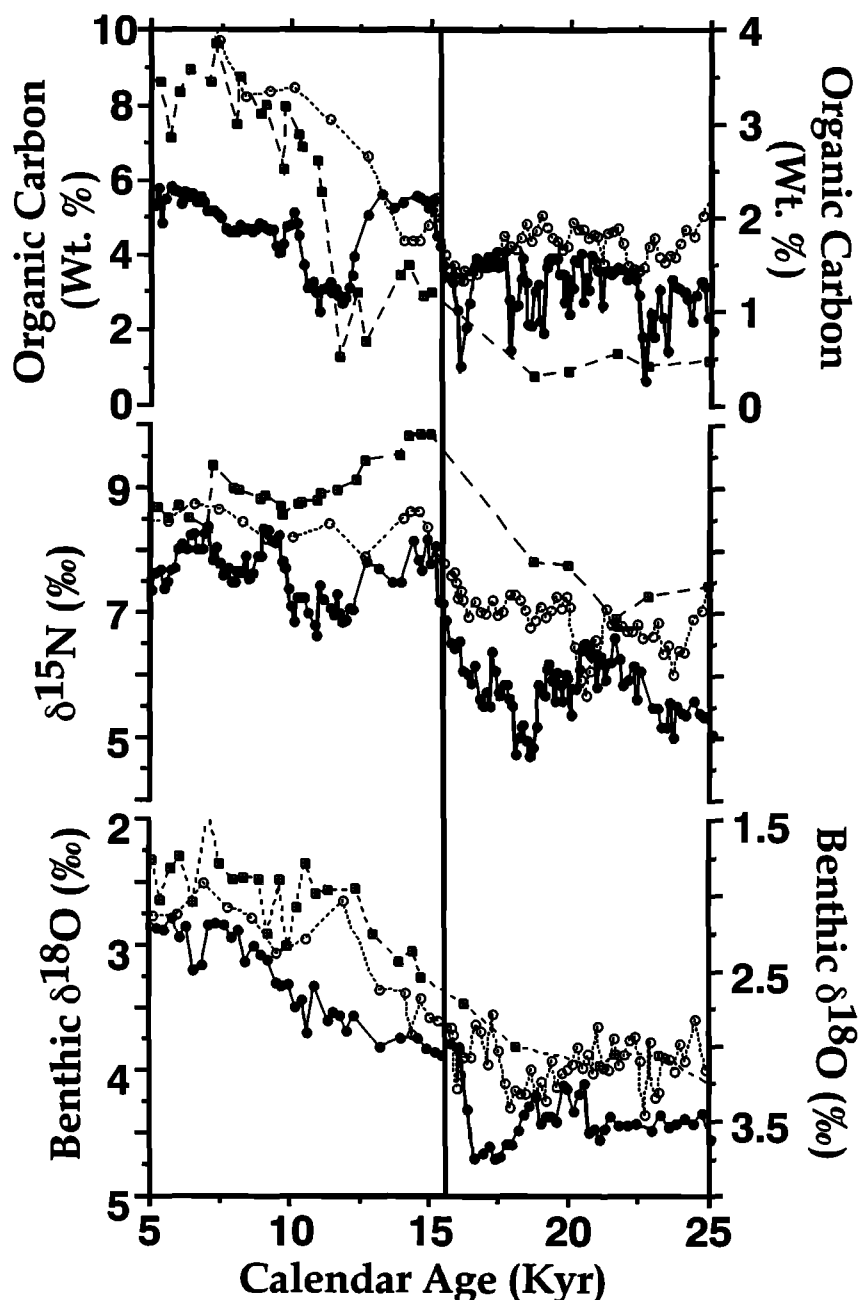
Figure 6. The timing of the change in $\delta^{18}O$, $\delta^{15}N$, and percent organic carbon near Termination I in radiocarbon dated cores from the Mexican (NH15P, open squares; NH8P, open circle) and southern California margin (1017E, solid circles). (bottom) Cores NH8P and 1017E are plotted on the right axis and NH15P is plotted on the left axis. (top) Cores NH8P and NH15P are plotted on the right axis, and 1017E is plotted on the left axis. Heavy $\delta^{15}N$ values indicating the onset of denitrification (indicated by the vertical line) appear simultaneously in all the three cores between 15 and 16 Ka. The increase in $\delta^{15}N$ is accompanied by increase in weight percent organic carbon and opal (not shown) and precedes major increase in sea level recorded by $\delta^{18}O$. In Core NH15P, the first appearance of heavy $\delta^{15}N$ is also matched by the presence of laminations (see Figure 2a).

Indeed, the molar N:P ratios in shallow waters in large areas of the Pacific and Indian Oceans where denitrification occurs are much lower than the Redfield ratio [Codispoti, 1989; Fanning, 1992; Gruber and Sarmiento, 1997]. Given the observed relative N deficiency in the modern ocean, the higher glacial N contents could have enhanced oceanic productivity in areas that are today considered to be oligotrophic. A significant increase in the glacial NO_3^- budget (~25%), via this mechanism,

could theoretically account for all of the observed pCO_2 (80 ppmv) decline seen in the ice-core records [Berger and Keir, 1984; Shaffer, 1989, Altabet and Curry, 1989].

Among the proposed mechanisms that could have produced glacial-interglacial changes in oceanic N contents, only nitrogen fixation and water column denitrification could have been causative factors in climate change. This is because variations in sediment denitrification occurring along margins

respond passively to changes in sea level. *Broecker and Henderson* [1998] recognized this in their recent evaluation of the sequence of events recorded in ice cores during Terminations I and II. The ice cores record a slow gradual increase in temperature and CO_2 over several thousand years prior to major declines in ice volume recorded by the $\delta^{18}O$ of trapped air. As noted by Broecker and Henderson, this sequence of events at both terminations is consistent with a perturbation in the N cycle that forces a glacial to interglacial transition. The ~3000 year residence time of fixed N means that resumption of denitrification, for example, would cause a gradual decline in the oceanic N content over several thousand years, leading to lower mean export productivity, commensurate increases in CO_2 and mean temperature, and the melting of Northern Hemisphere ice sheets. *Broecker and Henderson* [1998] offered a different model which has the same result: declines in dust (thus iron) input forced a decline in N fixation, leading to a diminished oceanic N content.

Is the sequence of events described above consistent with denitrification-induced deglacial warming? The $\delta^{15}N$ records in Figure 6 show that the onset of water-column denitrification occurred before 15 ka, and possibly 16 ka, and thus led the mid point of ice volume change by as much as 3 kyr. A similar conclusion holds for the Peru margin where heavy $\delta^{15}N$ values appear well before major ice volume changes, as recorded by $\delta^{18}O$ near Termination I (Figure 3e). Recently, Altabet et al. [1999a] evaluated the lead-lag relationship between $\delta^{15}N$ and $\delta^{18}O$ records from the AS and concluded that the onset of denitrification preceded sea level rise by several thousand years. Indeed, the resumption of denitrification at the end of the LGM does coincide with the start of the CO_2 and temperature increase and the demise of dust flux at Vostok [*Broecker and Henderson*, 1998; *Petit et al.*, 1999]. Thus it seems that the decline in dust flux recorded in both Vostok ice and Southern Ocean sediment cores and the increase in upwelling and export productivity over oxygen-deficient subsurface water masses in the eastern Pacific occurred at the same time near Termination I. This alludes to the interesting possibility that all of these changes are related and are part of a large-scale atmospheric reorganization that preceded the warmings and CO_2 increases recorded at terminations.

We note that through variations in N/P ratios, N fixation may have provided a negative feedback for denitrification-induced losses in oceanic nitrate. On average, productivity in the modern ocean is nitrogen limited, which partly reflects the importance of denitrification [*Codispoti*, 1989; *Fanning*, 1992; *Gruber and Sarmiento*, 1997]. However, lower denitrification during the glacials would have increased not only the N inventory but also the N/P ratios in seawater, assuming no change in P content. Thus phosphate limitation during the glacial may have inhibited N fixation, and this would have muted the effect of lower denitrification in the N mass balance. This scenario assumes that N fixation requires excess P in addition to micronutrients such as iron. The situation in the modern Cariaco Basin provides an analogy. There, *Trichodesmium* plays a compensatory role by providing fixed N to compensate for the deficit in nitrate relative to phosphate that results from denitrification [*Walsh*, 1996; *Haug et al.*, 1998 *and references therein*]. This is consistent with suggestion that N is the proximate and P is the ultimate limiting nutrient in the ocean [*Tyrell*, 1999].

Does this feedback by N fixers disqualify changes in denitrification as the mechanism that forces glacial to interglacial transitions? The onset of denitrification at the end of the last glacial should have lowered the N inventory and N/P ratios leading to conditions that are ideal for enhanced N fixation. However, this transition is also marked by a decline in dust deposition leading to Fe limitation. This should have prevented N fixers from taking full advantage of the higher N/P ratios, thereby providing a compensatory response. Thus it appears that the feedback by N fixers may not have been automatic and effective in holding the N inventory constant during glacial-interglacial transitions.

Finally, we suggest that changes in oceanic denitrification may also have modulated glacial-interglacial climate by influencing atmospheric concentrations of N_2O. N_2O is a greenhouse gas, which also plays an important role in stratospheric ozone depletion. The large oxygen-deficient water masses of the eastern Pacific and Arabian Sea are known to be an important source of N_2O to the atmosphere [*Naqvi et al.*, 1998, and references therein]. Recently, Greenland ice cores have revealed that the N_2O concentration in the atmosphere during glacial periods was 70 ppbv lower than in the Holocene [*Fluckiger et al.*, 1999]. Such declines are consistent with the ocean-wide decline in denitrification and the absence of large bodies of denitrifying water masses during the glacials identified in this study.

5. Summary and Conclusions

Nitrogen isotope measurements indicate that during the glacial periods a substantial decrease in dentrification occurred in the oxygen-deficient water masses of the ETNP, the ETSP, and the AS. Since denitrification in these regions accounts for half of the fixed nitrogen loss in the modern ocean, the oceanic N content may have been modulated on glacial-interglacial timescales by changing rates of denitrification. The decreases in $\delta^{15}N$ in glacial-age sediments that reflect declines in denitrification are matched by decreases in the accumulation of biogenic sedimentary components. This suggests that reduced denitrification may have been forced by reduced upwelling, decreased export productivity, and consequent lower oxidant demand along the continental margins bordering southern California, NW Mexico, Peru and western India. The remarkable synchroneity in the timing of the onset and cessation of denitrification in these three widely separated oceanographic regions provides strong support for the hypothesis that oceanic productivity and attendant changes in atmospheric CO_2 may have been modulated on glacial-interglacial timescales by changes in the oceanic nitrate inventory. Furthermore, the timing of the onset of denitrification and the sequence of events recorded in ice cores during Termination I are both internally consistent with denitrification-induced climatic warming.

References

Altabet, M. A., and W. B. Curry, Testing models of past ocean chemistry using foraminifera $^{15}N/^{14}N$, *Global Biogeochem. Cycles*, 3, 107-119, 1989.

Altabet, M., and R. François, The use of nitrogen isotopic ratio for reconstruction of past changes in surface-ocean nutrient utilization, in *Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change*, edited by R. Zahn et al., pp. 281-306, Springer-Verlag, New York, 1994.

Altabet, M. A., R. François, D. W. Murray, and W. L. Prell, Climate-related variations in denitrification in the Arabian Sea from $^{15}N/^{14}N$ ratios, *Nature*, 373, 506-509, 1995.

Altabet, M. A., D. W. Murray, and W. L. Prell, Climatically linked oscillations in Arabian Sea denitrification over the past 1 m.y.: Implications for the marine N Cycle, *Paleoceanography*, 14, 732-743,1999a.

Altabet, M. A., C. Pilskaln, R. Thunell, C. Pride, D. Sigman, F. Chavez, and R. Francois, The nitrogen isotope biogeochemistry of sinking particles from the margin of the Eastern North Pacific, *Deep Sea Res.,Part 1*, 46, 655-679, 1999b.

Behl, R. J., and J. P. Kennett, Brief interstadial events in the Santa Barbara Basin, NE Pacific, during the past 60 kyr, *Nature*, 379, 243-246, 1996.

Berger, W.H., and R.S. Keir, Glacial-Holocene changes in atmospheric CO_2 and the deep-sea record, in *Climate Processes and Climate Sensitivity*, edited by J. Hansen and T. Takahashi, pp. 337-351, AGU, Washington, D.C.,1984.

Berger, W. H., V. S. Smetacek, and G. Wefer, Ocean productivity and paleoproductivity: An overview, in *Productivity of the Ocean: Present and Past*, edited by W. H. Berger, V. S. Smetacek, and G. Wefer, pp. 1-34, John Wiley, New York, 1989.

Brandes, J. A., Isotopic effect of denitrification in the marine enviroment, Ph. D. thesis, Univ. of Wash., Seattle, 1997.

Brandes, J. A., A. H. Devol, T. Yoshinari, D. A. Jayakumar, and S. W. A. Naqvi, Isotopic composition of nitrate in the central Arabian Sea and eastern tropical North Pacific: A tracer for mixing and nitrogen cycles, *Liminol. Oceanogr.*, 43, 1998

Broecker, W. S., and G. M. Henderson, The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial CO_2 changes, *Paleoceanography*, 13, 352-364, 1998.

Calvert, S. E., B. L. Cousens, and M. Y. S. Soon, An X-ray fluorescence spectrometric method for the determination of major and minor elements in ferromanganese nodules, *Chem. Geol.*, 51, 9-18, 1985.

Capone, D. G., J. P. Zehr, H. W. Pearl, B. Bergman, and E. J. Carpenter, *Trichodesmium*, a globally significant marine cyanobacterium, *Science*, 276, 1221-1229, 1997.

Christensen, J. J., J. W. Murray, A. H. Devol, and L. A. Codispoti, Denitrification in continental shelf sediments has major impact on the oceanic nitrogen budget, *Global Biogeochem. Cycles*, 1, 97-116, 1987.

Clemens, S. C., and W. L. Prell, Late Pleistocene variability of Arabian Sea summer monsoon winds and continental aridity: Eolian records from lithogenic components of deep-sea sediments, *Paleoceanography*, 5, 109-145, 1990.

Cline, J. D., and I. R. Kaplan, Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical north Pacific Ocean, *Mar. Chem.*, 3, 271-299, 1975.

Codispoti, L., A., Is the ocean losing nitrate?, *Nature*, 376, 724, 1995.

Codipoti, L. A., Phosphorus vs. nitrogen limitation of new and export production, in *Productivity In the Ocean: past and Present*, edited by W. H. Berger, V. S. Smetacek and G. Wefer, pp.377-394, John Wiley, New York,1989.

Codispoti, L. A., and J. P. Christensen, Nitrification, denitrification and nitrous oxide cycling in the eastern tropical South Pacific Ocean, *Mar. Chem.*, 16, 277-300, 1985.

Codispoti, L. A., and T. T. Packard, Denitrification rates in the eastern tropical South Pacific, *J. Mar. Res.*, 38, 453-477, 1980.

Codispoti, L. A., and F. A. Richards, An analysis of the horizontal regime of denitrification in the eastern tropical North Pacific, *Limnol. Oceanogr.*, 21, 379-388, 1976.

Codispoti, L. A., et al., High nitrite levels off northern Peru: A signal of instability in the marine denitrification rates, *Science*, 233, 1200-1202, 1986.

Devol, A. H., Direct measurement of nitrogen gas fluxes from continental shelf sediments, *Nature*, 349, 319-321, 1991.

Dymond, J., E. Suess, and M. Lyle, Barium in deep-sea sediment: A geochemical proxy for productivity, *Paleoceanography*, 7, 163-181, 1992.

Falkowski, P. G., Evolution of nitrogen cycle and its influence on the biological pump in the ocean, *Nature*, 342, 637-642, 1997.

Fanning, K. A., Nutrient provinces in the sea: Reaction rate ratios, concentration ratios, and ideal covariation, *J.Geophys. Res.*, 97, 5693-5712, 1992.

Farrell, J. W., T. F. Pedersen, S. E. Calvert, and B. Nielsen, Glacial-interglacial changes in nutrient utilization in the equatorial Pacific Ocean, *Nature*, 377, 514-517, 1995.

Fluckinger, J., A. Dallenbach, T. Blunier, B. Stauffer, T. F. Stocker, D. Raynaud and J. -M. Barnola, Variation in atmospheric N_2O concentration during abrupt climatic changes, *Science*, 285, 227-230, 1999.

Fontugne, M. R., Les isotopes stables du carbone organique dans l'ocean: Application à la palaeoclimatologie, doctoral thesis, Univ.of Paris, Paris, 1983.

Ganeshram, R. S.and T. F. Pedersen, Glacial-

interglacial variability in upwelling and bioproductivity off NW Mexico: Implication to Quaternary Paleoclimate, *Paleoceanography*, 13, 634-645, 1998.

Ganeshram, R. S., T. F. Pedersen, S. E. Calvert, and J. W. Murray, Large changes in oceanic nutrient inventories from glacial to interglacial periods, *Nature*, 376, 755-758, 1995.

Ganeshram, R. S., S. E. Calvert, T. F. Pedersen, and G. A. Cowie, Factors controlling the burial of organic carbon in laminated and bioturbated sediments off NW Mexico: Implications for hydrocarbon preservation, *Geochim. Cosmochim. Acta*, 63, 1723-1734, 1999.

Gardner, J. V., W. E. Dean, and P. Dartnell, Biogenic sedimentation in the California Current system for the past 30 Kyr and its paleoceanographic significance, *Paleoceanography*, 12, 207-225, 1997.

Garfield, P. C., T. T. Packard, G. E. Friederich, and L. A. Codispoti, A subsurface particle maximum layer and enhanced microbial activity in the secondary nitrite maximum of the northeastern tropical Pacific Ocean, *J. Mar. Res.*, 41, 747-768, 1983.

Garrison, R. E., and M. Kastner, Phosphatic sediments and rocks recovered from Peru margin during ODP Leg 112, *Proc. Ocean Drill. Program Sci. Results*, 112, 111-134, 1990.

Gruber, N., and J. L. Sarmiento, Global patterns of marine nitrogen fixation and denitrification, *Global Biogeochem. Cycles*, 11, 235-266, 1997.

Haug, G. H., T. F. Pedersen, D. M. Sigman, S. E. Calvert, B. Nelson, and L. C. Patterson, The Cariaco Basin: Sea level controls variations in N_2 fixation during the last 580 Ka, *Paleoceanography*, 13, 427-432,1998.

Hay, W. W., and J. R. Southam, Modulation of marine sedimentation by the continental shelves, in *The Fate of FossilFfuel CO_2 in the Oceans*, edited by N. R. Andersen and A. Malahoff, pp. 569-604, Plenum, New York, 1977.

Heinze, H-M., and G. Wefer, The history of coastal upwelling off Peru over the past 650,000 years, in *Upwelling Systems: Evolution Since the Early Miocene*, edited by C. P. Summerhayes, W. L. Prell, and K. C. Emeis, *Geol. Soc. Spec. Pub.*, 64, pp. 451-462,1992.

Holmes, M. E., R. R. Schneider, P. J. Muller, M. Segl, and G. Wefer, Reconstruction of past nutrient utilization in the eastern Angola basin based on sedimentary $^{15}N/^{14}N$ ratios, *Paleoceanography*, 12, 604-614, 1997.

Irino, T., and T. F. Pedersen, Geochemical character of glacial to interglacial sediments at Site 1017, southern Californian Margin: Minor and trace elements *Proceedings Ocean Drill.Program, Sci. Results*, in press, 2000.

Jasper, J. P., and R. B. Gagosian, The sources and deposition of organic matter in the Late Quaternary Pigmy Basin, Gulf of Mexico, *Geochim. Cosmochim. Acta*, 54, 1117-1132, 1990.

Kennett, J.P., E.B. Roark, K.G. Cannariato, B.L. Ingram, and R. Tada, Late Quaternary variations foraminiferal proxies at Site 1017, southern Californian Margin, *Proceedings Ocean Drill.Program, Sci. Results*, in press, 2000.

Kolber, Z. S., et al., Iron limitation of phytoplankton photosynthesis in the equatorial Pacific Ocean. *Nature, 371*, 145-149, 1994.

Kutzbach, J. E., P. J. Guetter, P. J. Behling, and R. Selin, Simulated climatic changes: Results of the COHMAP climate-model experiments, in *Global Climates Since the Last Glacial Maximum*, edited by H. E. Wright, et al., pp. 24-93, Univ. of Minn. press, Minnesota, 1993.

Libes, S. M., and W. G. Deuser, The isotope geochemistry of particulate nitrogen in the Peru upwelling area and the Gulf of Maine, *Deep Sea Res., Part A, 35*, 517-533, 1988.

Liu, K.-K., and I. R. Kaplan, The eastern tropical Pacific as a source of ^{15}N-enriched nitrate in seawater off southern California, *Limnol. Oceanogr., 34*, 820-830, 1989.

Lukas, R., The termination of equatorial undercurrent in the eastern Pacific, *Prog. Oceanogr., 16*, 63-90, 1986.

Lyle, M., R. Zahn, F. Prahl, J. Dymond, R. Collier, N. Pisias, and E. Suess, Paleoproductivity and carbon burial across the California Current: The multitracers transect, 42°N, *Paleoceanography, 7*, 251-272, 1992.

Martin, J., Glacial-interglacial CO_2 change: The iron hypothesis, *Paleoceanography, 5*, 1-13, 1990.

Martinson, D.G., N.G. Pisias, J.D. Hays, J. Imbrie, T.C. Moore, and N.J. Shackleton, Age dating and the orbital theory of the Ice Ages: Development of a high-resolution 0 to 300,000 year chronostratigraphy, *Quat. Res., 27*, 1-27, 1987.

McElroy, M. B., Marine biological controls on atmospheric CO_2 and climate, *Nature, 302*, 328-329, 1983.

McNeill, G. W., The geochemical paleoceanography and mineralogy of marine sediments from the Peruvian continental margin, Ph. D. thesis, Univ. of Edin., Edinburgh, 1993.

Middelburg, J. L., K. Soetaert, P. M. J. Herman, and C. H. R. Heip, Denitrification in marine sediments: A model study, *Global Biogeochem. Cycles, 10*, 661-673, 1998.

Montoya, J. P., Nitrogen isotope fractionation in the modern ocean: Implications for the sedimentary record, in *Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change*, edited by R. Zahn et al., pp. 259-279, Springer-Verlag, New York, 1994.

Mortlock, R. A. and P. N. Froelich, A simple method for the rapid determination of biogenic opal in pelagic marine sediments, *Deep Sea Res. Part A 36*, 1415-1426, 1989.

Naqvi, S. W. A., Some aspects of the oxygen-deficient conditions and denitrification in the Arabian Sea, *J. Mar. Res., 45*, 1049-1072, 1987.

Naqvi, S. W. A., T. Yoshinari, D. A. Jayakumar, M. A. Altabet, P. V. Narvekar, A. H. Devol, J. A. Brandes, and L. A. Codispoti, Budgetary and biogeochemical implications of N_2O isotope signatures in the Arabian Sea, *Nature, 394*, 462-464, 1998.

Olson, D. B., G. L. Hitchcock, R. A. Fine and B. A. Warren, Maintanence of the low-oxygen layer in the central Arabian Sea, *Deep Sea Res. Part A, 40*, 673-685, 1989.

Pedersen, T. F., B. Nielsen, and M. Pickering, The timing of Late Quaternary productivity pulses in the Panama Basin and implications for atmospheric CO_2, *Paleoceanography, 6*, 657-677, 1991.

Peters, K. E., R. E. Sweeney, and I. R. Kaplan, Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter, *Limnol. Oceanogr., 23*, 598-604, 1978.

Petit, J. R. et al., Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica, *Nature, 399*, 429-436, 1999.

Pride, C., R. Thunnell, D. Sigman, L. Keigwin, M. Altabet, and E. Tappa, Nitrogen isotope variations in the Gulf of California since the last deglaciation: Response to global climate change, *Paleoceanography, 14*, 394-409, 1999.

Rau, G. H., T. Takahashi and D. J. D. Marais, Latitudinal variations in plankton $\delta^{13}C$: Implications for CO_2 and productivity in past oceans, *Nature, 341*, 516-518, 1989.

Reichart, G. J., L. J. Lourens, and W. J. Zachariasse, Temporal variability in the northern Arabian Sea Oxygen Minimum Zone (OMZ) during the last 225,000 years, *Paleoceanography, 13*, 607-621, 1998.

Reimers, C. E., and E. Suess, Spatial and temporal patterns of organic matter accumulation on the Peru continental margin, in *Coastal Upwelling: Its Sedimentary Record, Part B*, edited by E. Suess and J. Thiede, pp. 311-346, Plenum, New York, New York, 1983.

Roden, G. I., Thermohaline structure and baroclinic flow across the Gulf of California entrance and in the Revilla Gigedo Islands region, *J. Phys. Oceanogr., 2*, 177-183, 1972.

Saino, T., and A. Hattori, Geographical variation of the water column distribution of suspended particulate organic nitrogen and its ^{15}N natural abundance in the Pacific and its marginal seas, *Deep Sea Res.Paart A, 34*, 807-827, 1987.

Schrader, H., and R. Sorknes, Peruvian Coastal Upwelling: Late Quaternary productivity changes revealed by diatoms, *Mar. Geol., 97*, 233-246, 1991.

Schultz, H., U. V. Rod and H. Erlenkeuser, Correlations between Arabian Sea and Greenland climate oscillationsof the past 110,000 years, *Nature, 393*, 54-57, 1998.

Shafer, P., and V. Ittekkot, Seasonal variability of $\delta^{15}N$ in settling particles in the Arabian Sea and its paleochemical significance, *Naturwissenschaften, 80*, 511-513, 1993.

Shaffer, G., A model of biogeochemical cycles of P, N, O and S in the ocean: One step towards global climate model, *J. Geophys. Res., 94*, 1979-2004, 1989.

Shimmield, G. B., Can sediment geochemistry record changes in coastal upwelling paleoproductivity? Evidence from NW Africa and Arabian Sea, in *Upwelling Systems: Evolution Since the Early Miocene*, edited by C. P. Summerhayes, W. L. Prell, and K. C. Emeis, *Geol. Soc. Spec. Publ. 64*, pp. 29-46, 1992.

Sigman, D. M., M. A. Altabet, R. Francois, D. C. McCorkle, and J-F. Gaillard, The isotopic composition of diatom-bound nitrogen in Southern Ocean sediments, *Paleoceanography, 14*, 118-134, 1999.

Sweeney, R. E., and I. R. Kaplan, Natural abundances of ^{15}N as a source indicator for near-shore marine sedimentary and dissolved nitrogen, *Mar. Chem., 9*, 81-94, 1980.

Toggweiler, J. R., and S. Carson, What are upwelling systems contributing to the ocean's carbon and nutrient budgets?, in *Dahlem Workshop on Upwelling in the ocean: Modern Processes and Ancient Records*, edited by C. P. Summerhayes et al., 337-360, John Wiley, New York, 1995.

Tsuchiya, M., The origin of Pacific equatorial 13°C water, *J. Phys. Oceanogr., 11*, 794-812, 1981.

Tyrrell, T., The relative influence of nitrogen and phosphorous on oceanic primary production, *Nature, 400*, 525-531, 1999.

Walsh, J. J., Nitrogen fixation within a tropical upwelling ecosystem: Evidence for a Redfield budget of carbon/nitrogen cycling by the total phytoplankton community, *J. Geophys. Res. Oceanogr. Abstr., 101*, 20, 607-616. 1996.

Warsh, C. E., and K. L. Warsh, Nutrients and water masses at the mouth of the Gulf of California, *Deep-Sea Res., 20*, 561-570, 1973.

Waser, N. A. D., P. J. Harrison, B. Nielsen, and S. E. Calvert, Nitrogen isotopic fractionation during the uptake and assimilation of nitrate, nitrite, ammonium, and urea by a marine diatom, *Oceanol. Limnol., 43*, 215-224,1998.

Wyrtki, K., Circulation and water masses in the eastern equatorial Pacific Ocean, *Int. J. Oceanol. Limnol., 1*, 117-147, 1967.

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