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

Raja S. Ganeshram,<sup>1,2</sup> Thomas F. Pedersen,<sup>3</sup> Stephen E. Calvert,<sup>3</sup> Gavin W. McNeill,<sup>4</sup> and Michel R. Fontugne<sup>5</sup>

**Abstract.** The late Quaternary history of water-column denitrification of the eastern Pacific margins and the Arabian Sea is reconstructed using sedimentary  $\delta^{15}\text{N}$  measurements. The  $\delta^{15}\text{N}$  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  $\text{CO}_2$  may therefore have been modulated on glacial-interglacial timescales by variations in the oceanic  $\text{NO}_3^-$  content.

### 1. Introduction

The biological pump has been identified as being a key governor in the modulation of atmospheric  $p\text{CO}_2$  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  $\text{CO}_2$  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  $\text{O}_2$ , 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 denitrification ( $\text{N}_2\text{O}$  and  $\text{N}_2$ ) 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  $\text{Tg N yr}^{-1}$  [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, denitrification 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  $\text{NO}_3^-$  heavy. Isotopic fractionation associated with denitrification discriminates against  $^{15}\text{NO}_3^-$  (isotopic fractionation is estimated to be 22-30 ‰), and as a result  $^{14}\text{NO}_3^-$  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 becomes progressively enriched in  $^{15}\text{NO}_3^-$ . Nitrate highly enriched in  $^{15}\text{N}$  ( $\delta^{15}\text{N}$  values as high as +18‰; see Cline and Kaplan [1975] and Brandes *et al.*, [1998]) is found in the subsurface waters of all three regions discussed here, particularly near the highly productive continental margin where denitrification 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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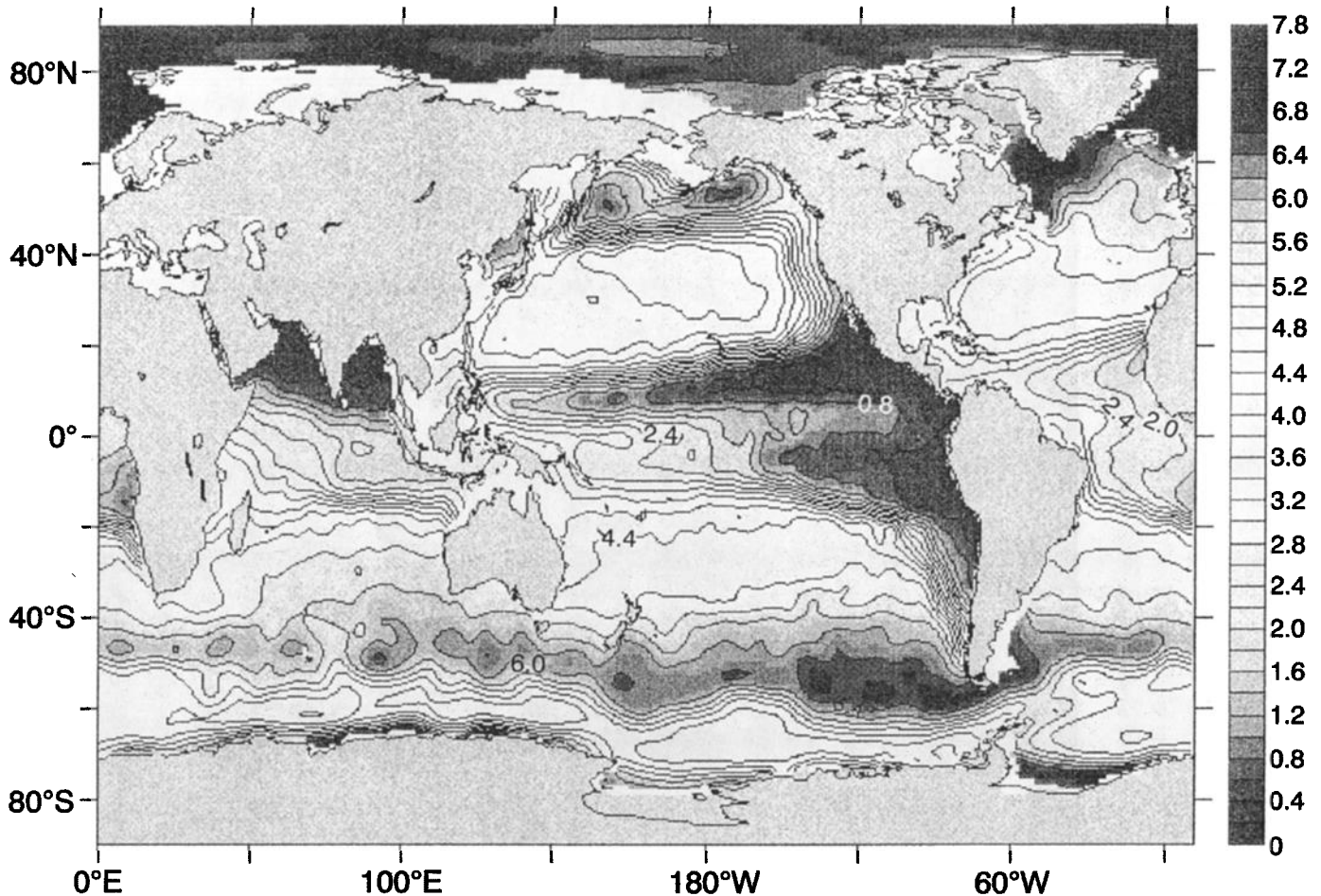


Figure 1. Oxygen concentrations in  $\text{mL L}^{-1}$  at 300 m water depth. Large subsurface water masses with oxygen concentration  $< 1 \text{ mL L}^{-1}$  occur in the eastern tropical North Pacific, the eastern tropical South Pacific, and the Arabian Sea.

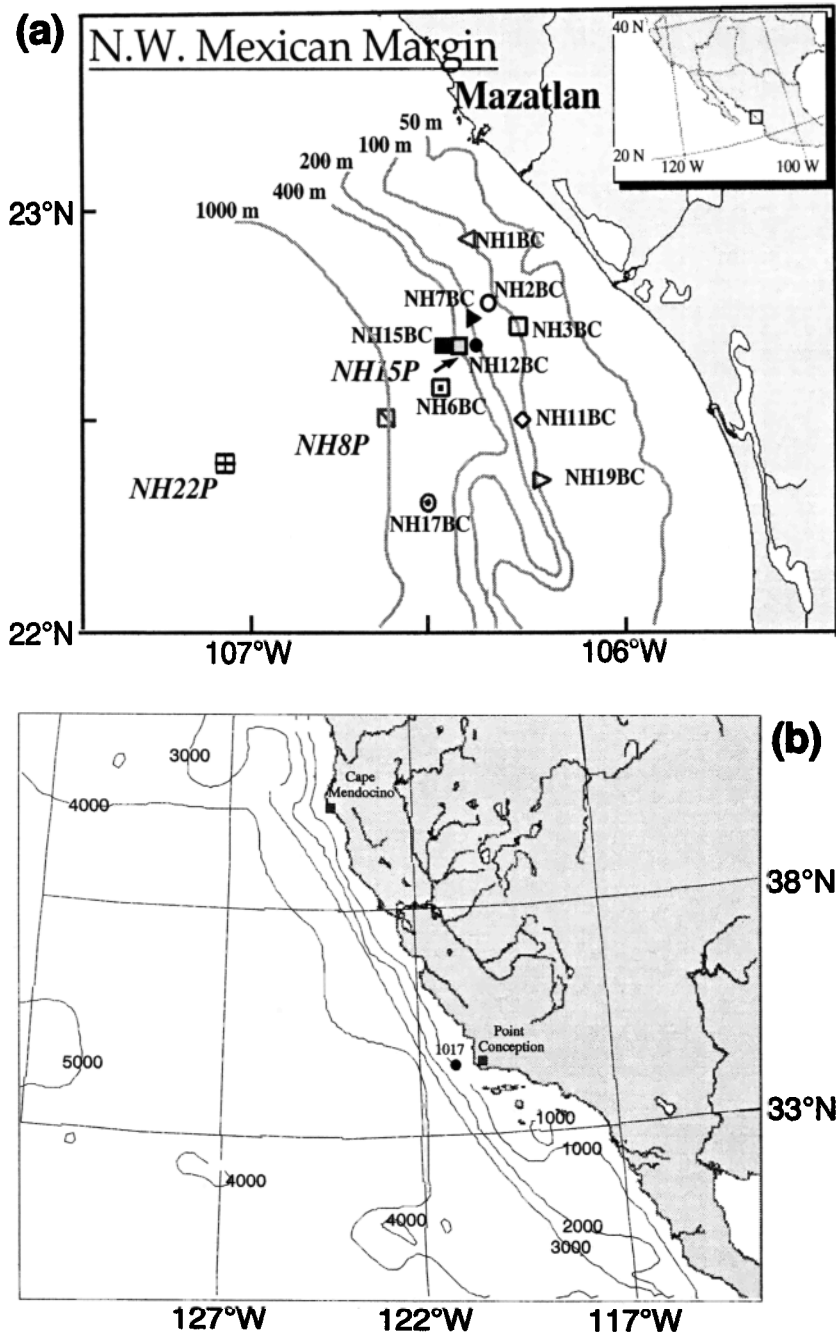
is supplied to the surface waters by upwelling and is utilized by biota, resulting in unusual  $\delta^{15}\text{N}$  enrichments (8–10‰) in particulate organic material and the underlying modern sediments [Saino and Hattori, 1987; Libes and Deuser, 1988; Shafer and Ittekkot, 1993; Altabet et al., 1999a]. 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  $\delta^{15}\text{N}$  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  $\delta^{13}\text{C}_{\text{org}}$  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  $1\sigma$  relative standard deviation (RSD) of these measurements was 1.25%. Carbonate carbon was determined by coulometry after acid evolution of  $\text{CO}_2$  with a precision of 3% ( $1\sigma$  RSD), and organic carbon (OC) was estimated by difference (total minus carbonate C) with a combined precision of 3.3% ( $1\sigma$  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% ( $1\sigma$  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‰ ( $1\sigma$ ). Both  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}_{\text{org}}$  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‰ ( $1\sigma$ ). The  $\delta^{15}\text{N}$  values are reported relative to air. The oxygen isotope stratigraphy and  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{15}\text{N}$ , the  $\delta^{18}\text{O}$  of benthic foraminifera,  $\delta^{13}\text{C}_{\text{org}}$ , and OC concentrations (Figure 3a-3c) are presented in three piston cores comprising a shore-normal 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

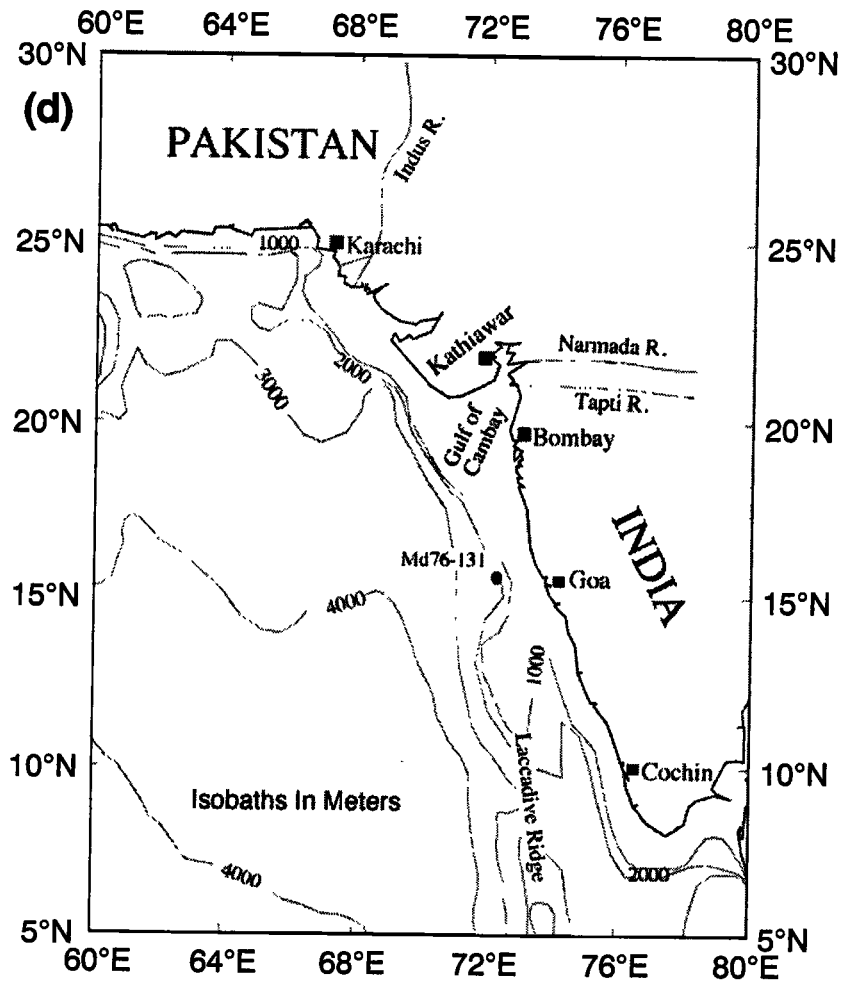
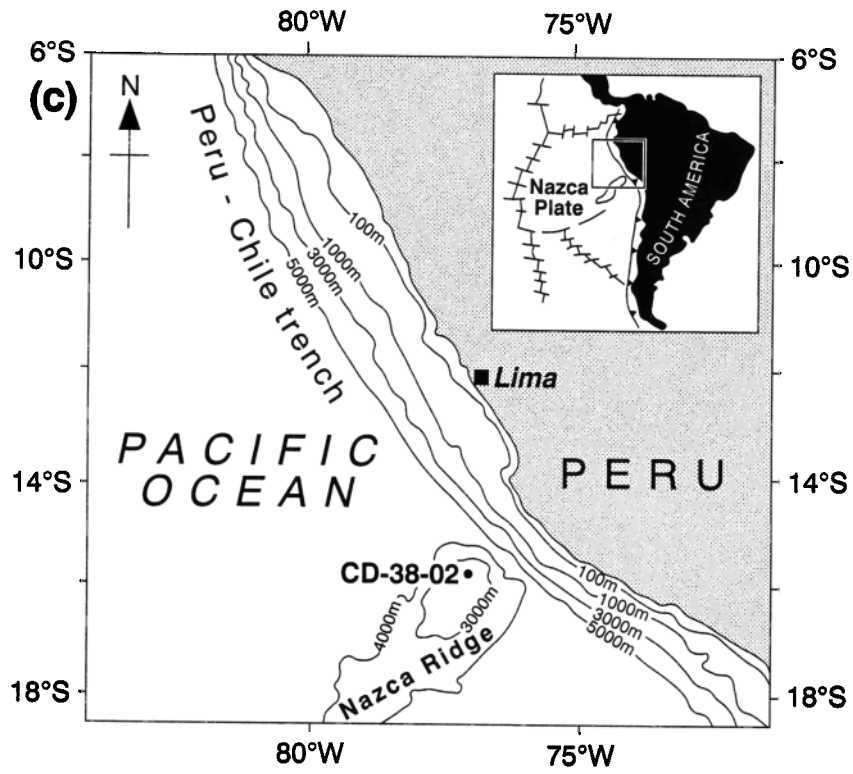


Figure 2. (continued)

**Table 1.** Locations of Cores Used in this Study

	Latitude	Longitude	Depth, m
<i>Long Cores</i>			
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
<i>Short Cores</i>			
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  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  occur almost synchronously in these cores during the last 60 kyr, indicating that the signal is regional in nature. The offsets between  $\delta^{15}\text{N}$  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  $\delta^{18}\text{O}$  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  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  and OC contents,  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  values of roughly 8‰, which persist throughout the last 15 kyr of deposition at this site. The timing and amplitudes of the shifts in  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$  of benthic foraminifera,  $\delta^{13}\text{C}_{\text{org}}$ , and Ba/Al ratios spanning 275 kyr (Figure 3e). The timescale is constructed by visual correlation with SPECMAP as described by *McNeill* [1993]. The  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  and Ba/Al ratios, the  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{15}\text{N}$ . Heavy  $\delta^{15}\text{N}$  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,  $\delta^{13}\text{C}_{\text{org}}$  values are close to -19‰ in stages 2–4, with a small decrease to ~20‰ in stage 1 (Figure 3f).

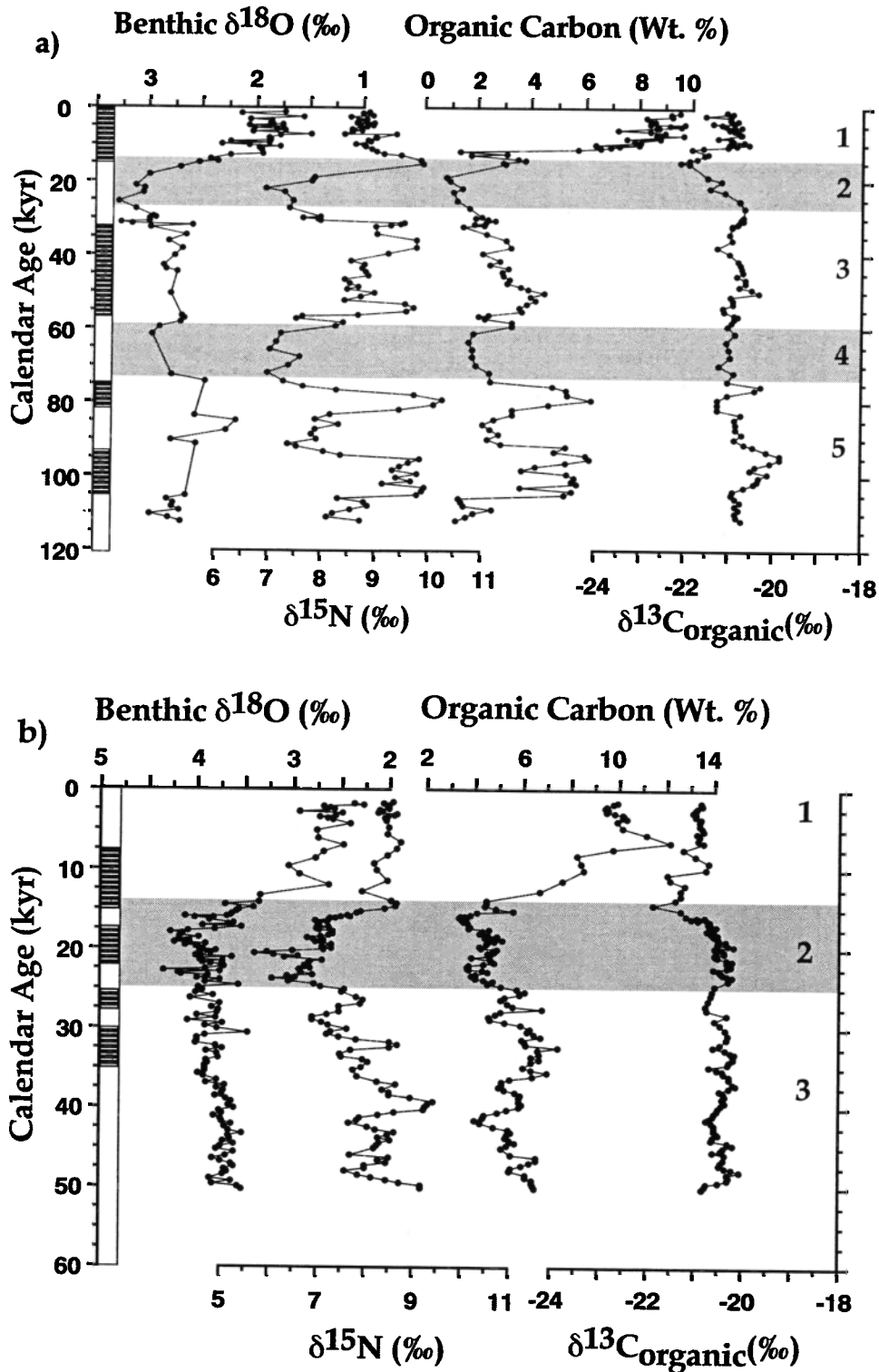
In summary, in all of the four regions reported here, there is a consistent pattern in which glacial intervals are characterized by lighter  $\delta^{15}\text{N}$  values coupled with declines in the concentrations or rates of accumulation of biogenic sedimentary components.

## 4. Discussion

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

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 (~ $\delta^{15}\text{N} = 2\text{‰}$  [*Sweeney and Kaplan*, 1980]) can produce lighter  $\delta^{15}\text{N}$  values in marine sediments [*Peters et al.*,



**Figure 3.** Records of foraminiferal  $\delta^{18}\text{O}$ , bulk sediment  $\delta^{15}\text{N}$ , weight percent organic carbon, Ba/Al weight ratios (Core MD76-131) and  $\delta^{13}\text{C}_{\text{Org}}$  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  $^{18}\text{O}/^{16}\text{O}$  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  $\delta^{18}\text{O}$  records from ODP 1017E have been reported by Kennett *et al.* [2000] and Irino and Pedersen [2000] respectively. The  $\delta^{18}\text{O}$  and Ba/Al records from Core CD38-02 were presented by McNeill [1993]. Organic carbon and  $\delta^{18}\text{O}$  records from Core MD76-131 are from Fontugne [1983].

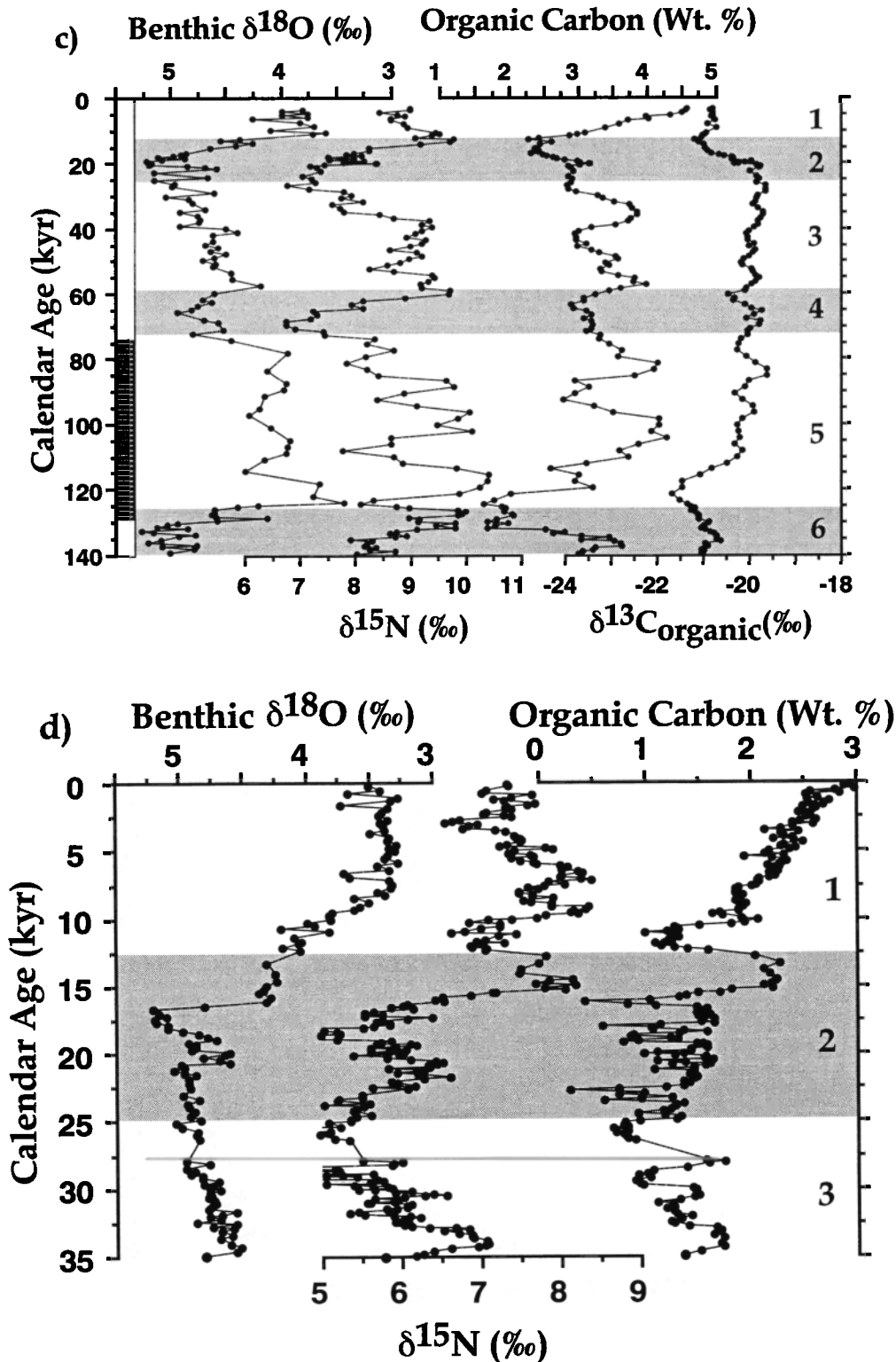


Figure 3. (continued)

1978]). The possibility that significant admixture of terrestrial organic matter affected the  $\delta^{15}\text{N}$  results reported here in all areas simultaneously can be evaluated by examining the relationship between  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{org}}$  (Figure 4). The carbon isotopic composition of land-derived organic matter originat-

ing from  $\text{C}_3$  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  $\delta^{13}\text{C}_{\text{org}}$



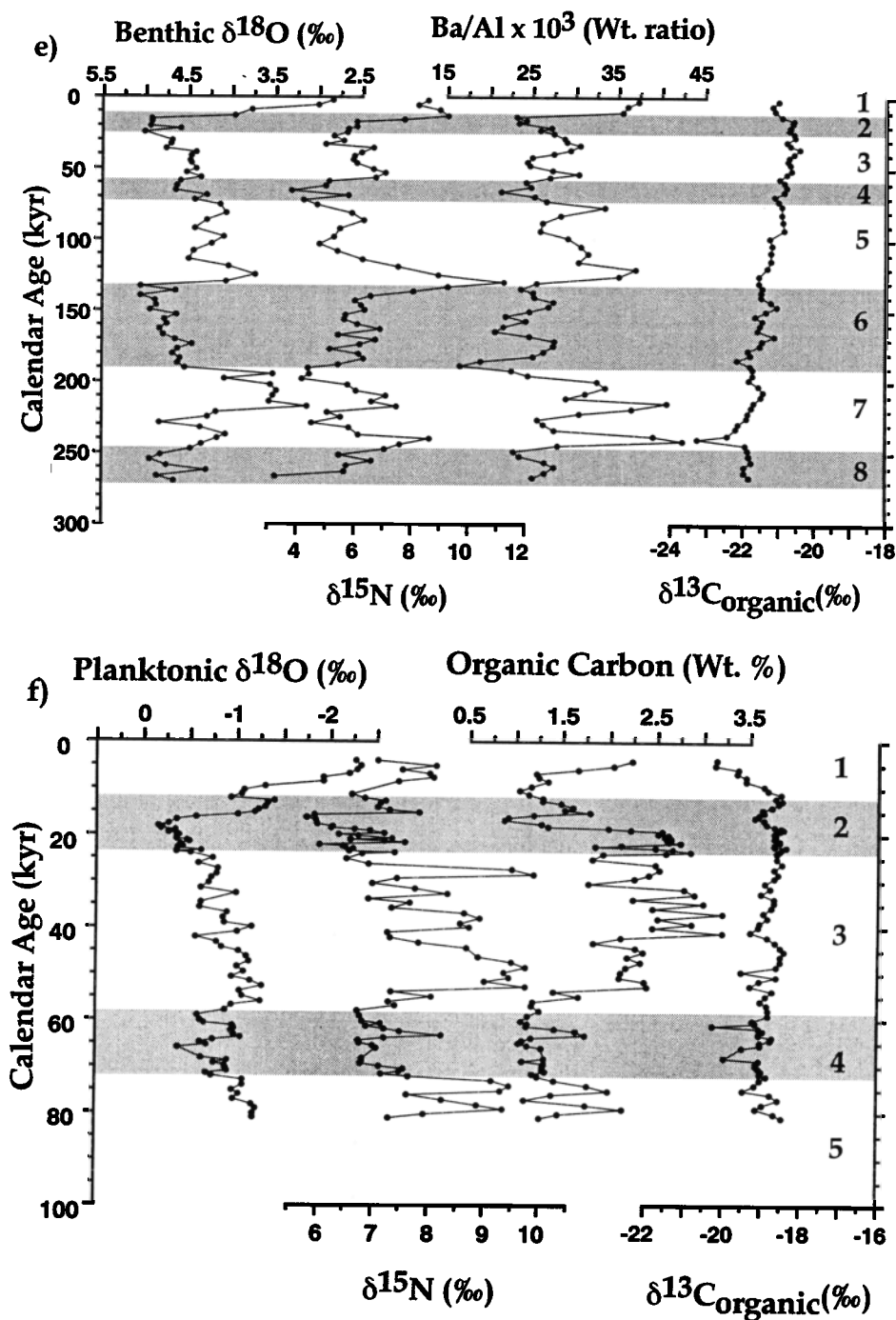


Figure 3. (continued)

and  $\delta^{15}\text{N}$  plot, with lighter  $\delta^{13}\text{C}_{\text{org}}$  corresponding with lighter  $\delta^{15}\text{N}$  [Sweeney and Kaplan, 1980]. None of the cores considered here (with the exception of the record from Site 1017, for which  $\delta^{13}\text{C}_{\text{org}}$  data are unavailable) exhibits such a trend (Figure 4). Indeed, the  $\delta^{13}\text{C}_{\text{org}}$  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  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  signal. A uniform ~4‰ shift to heavier  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  downcore [Sigman et al., 1999]. In contrast to the deep sea, comparisons in nitrogen isotopic composition between sediment trap material

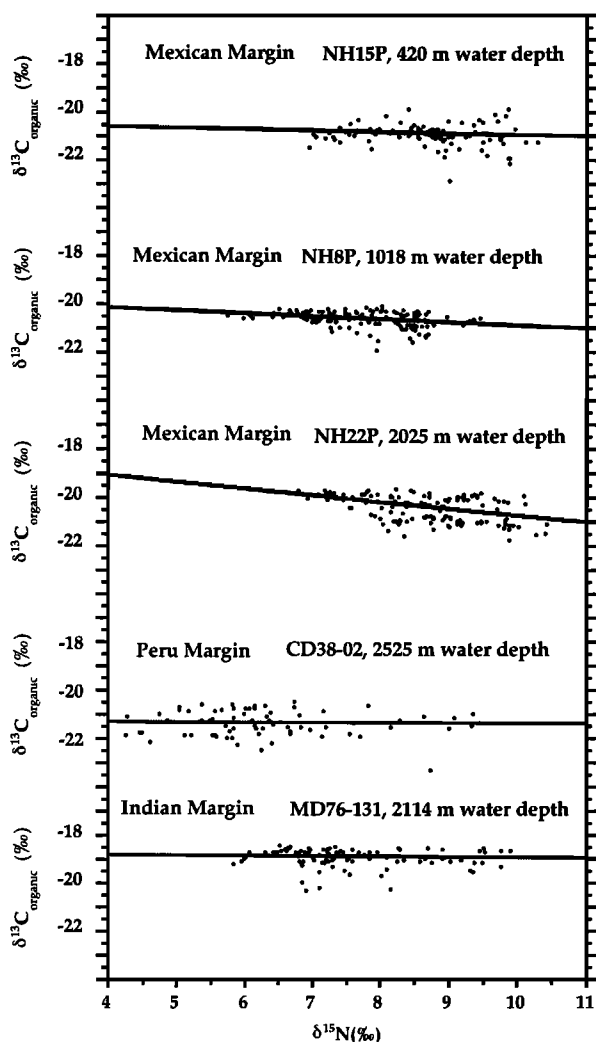


Figure 4. The relationship between  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{Org}}$  in piston cores.

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  $\delta^{15}\text{N}$  of the nitrate in near-surface waters in such regions. For instance, the 9–10‰ range in  $\delta^{15}\text{N}$  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].

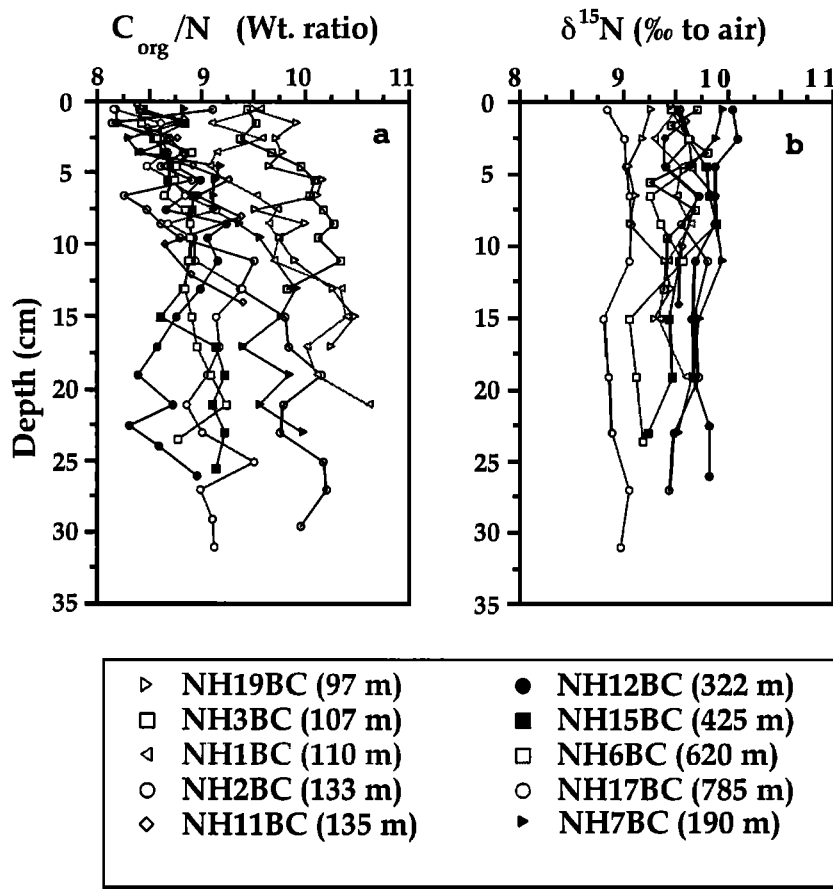
Although isotopic changes may not occur during settling,  $\delta^{15}\text{N}$  shifts may occur during progressive burial of organic matter. This is evaluated here using a set of 10 short box cores collected on a shore-normal transect across the outermost shelf and slope off NW Mexico (Figure 2a; Table 1). While Corg/N ratios (Figure 5a) generally show a secular increase with sediment depth, the  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  of the photosynthate follows the integrated product equation of first-order Rayleigh fractionation kinetics owing to the preferential uptake of  $^{14}\text{NO}_3^-$  by phytoplankton [Montoya, 1994; Waser et al., 1998]. Such fractionation coupled with lateral advection of a residual nitrate pool with variable  $\delta^{15}\text{N}$  could produce a spatial pattern in sedimentary  $\delta^{15}\text{N}$  values. Spatial variation in sedimentary  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$ .

Incomplete nitrate utilization is a phenomenon that largely affects  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$ . This is apparent in the box-core transect across the Mexican margin (Figure 5b), where the  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  values seen in the glacial intervals of our cores.

**4.1.4. Nitrogen fixation.** Nitrogen fixation could have contributed a variable proportion of the  $\delta^{15}\text{N}$  signal downcore. Nitrogen-fixing cyanobacteria produce photosynthate with very little fractionation from atmospheric  $\text{N}_2$  (approximately -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  $\delta^{15}\text{N}$  values by diluting the heavier  $\delta^{15}\text{N}$  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  $\mu M$ .

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 diminished 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 *et 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; Shimmiel, 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  $\delta^{15}\text{N}$  record (Figure 3f) and those from the Oman [Altabet *et al.*, 1995; Altabet *et al.*, in press] and Pakistan margins [Reichert *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. Shimmiel [1992] came to a similar conclusion based on a glacial-age decline in biobarium and organic carbon accumulation recorded by Oman margin sediments. Reichert *et al.* [1998] found that the lowest  $\text{O}_2$  levels in the oxygen minimum correlate with productivity maxima in sedimentary records from the Pakistan margin.

Upwelling in the Arabian Sea is driven by monsoonal winds generated by the thermal contrast between the Asian continent and the Indian Ocean. Recently, Altabet *et al.* [1999a] found strong coherence between  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$ ). 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 ( $<20 \mu\text{M}$ ) are found at mid depths between  $\sim 150$  and  $\sim 1000$  m all along the continental margin in the ETNP and ETSP [Wyrski, 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 [Rodén, 1972; Warsh and Warsh, 1973] and equatorial subsurface water off Peru [Wyrski, 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  $\sim 600$  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 [Wyrski, 1967]. Because of their deeper position in the water column, the effect of ventilation changes in intermediate waters on denitrification should be minor in these regions.

The major source of these high-salinity waters in the ETNP and ETSP is the Equatorial Undercurrent or  $13^\circ\text{C}$  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; Toggweiler and Carson, 1995]. This feature is seen in Figure 1 as a tongue of high-oxygen water penetrating west to east ( $\sim 5^\circ\text{N}$  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 [Wyrski, 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 [Wyrski, 1967]. Thus circulation at the depth of the denitrification 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, denitrification 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; Reichert, 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  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  and OC occur simultaneously at the end of the last glacial and precede major changes in sea level, as recorded by benthic  $\delta^{18}\text{O}$ . The coeval changes in inferred productivity (increase in OC, opal, and Ba/Al ratios) and

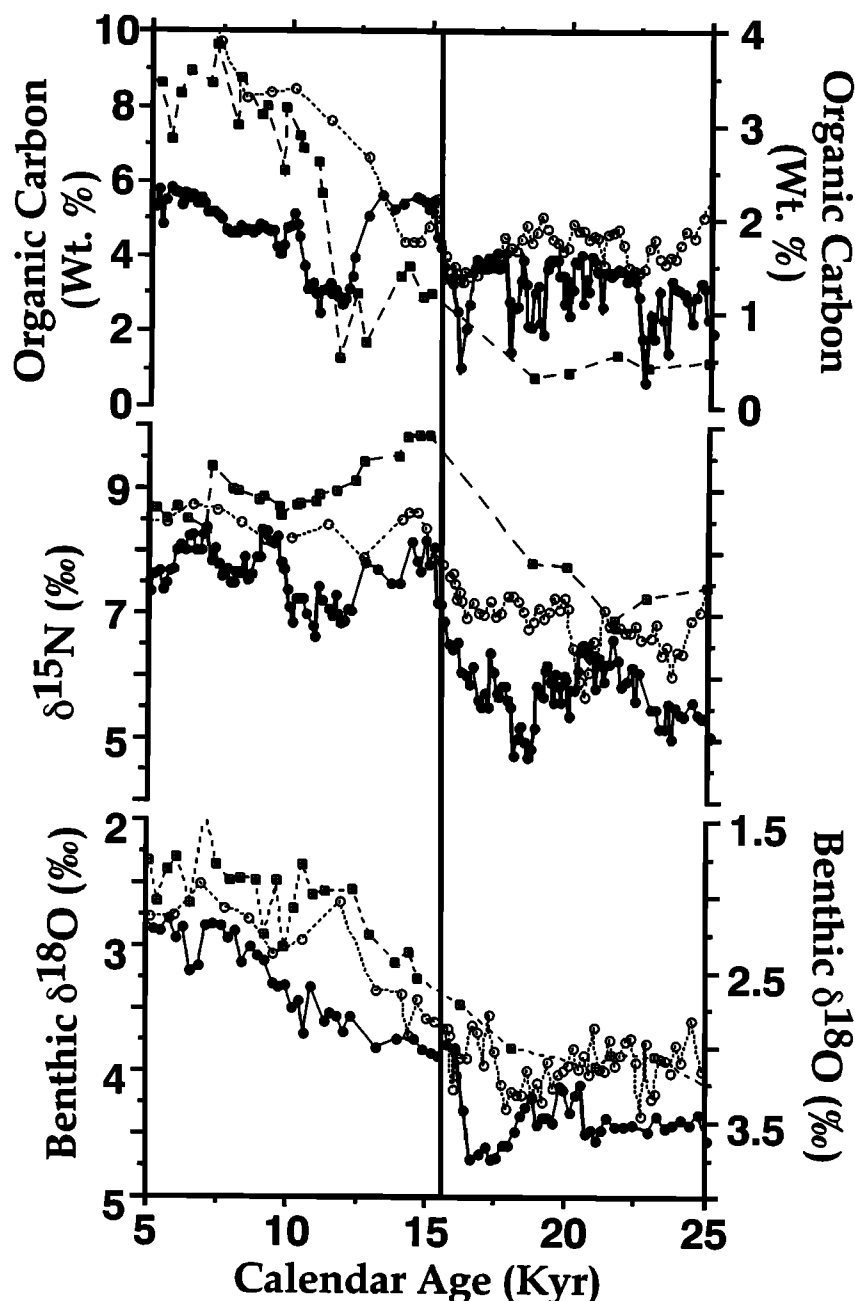
$\delta^{15}\text{N}$  suggest that the onset of denitrification was induced just prior to the end of the last glacial period by strengthened upwelling-favorable winds [Ganeshram and Pedersen, 1998]. On the basis of the relative timing of all variables, such implied changes in atmospheric circulation preceded major changes in sea level and appear to have been coincident with the increases in atmospheric temperature and  $\text{CO}_2$  recorded in ice cores [Broecker and Henderson, 1998; Petit et al., 1999].

#### 4.3. Implications for the Oceanic-Nitrate Inventory and $p\text{CO}_2$ 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<sup>-1</sup> and the total loss amounting to some 200 Tg N yr<sup>-1</sup>. 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<sup>-1</sup>. 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<sup>-1</sup> 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  $\delta^{18}\text{O}$ ,  $\delta^{15}\text{N}$ , 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  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  is accompanied by increase in weight percent organic carbon and opal (not shown) and precedes major increase in sea level recorded by  $\delta^{18}\text{O}$ . In Core NH15P, the first appearance of heavy  $\delta^{15}\text{N}$  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  $\text{NO}_3^-$  budget (~25%), via this mechanism,

could theoretically account for all of the observed  $p\text{CO}_2$  (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<sub>2</sub> over several thousand years prior to major declines in ice volume recorded by the  $\delta^{18}\text{O}$  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<sub>2</sub> 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  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  values appear well before major ice volume changes, as recorded by  $\delta^{18}\text{O}$  near Termination I (Figure 3e). Recently, *Altabet et al.* [1999a] evaluated the lead-lag relationship between  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>O. N<sub>2</sub>O 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<sub>2</sub>O to the atmosphere [*Naqvi et al.*, 1998, and references therein]. Recently, Greenland ice cores have revealed that the N<sub>2</sub>O 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 denitrification 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  $\delta^{15}\text{N}$  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 synchronicity 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<sub>2</sub> 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.

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