Biogeochemical changes within the Benguela Current upwelling system during the Matuyama Diatom Maximum: Nitrogen isotope evidence from Ocean Drilling Program Sites 1082 and 1084

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[1] The Matuyama Diatom Maximum (MDM) is a time of peak opal accumulation from 2.6 to ~2.0 Ma within the Benguela Current upwelling system that was initiated by increased influence of Southern Ocean water on the eastern South Atlantic. We measured opal, total organic carbon (TOC), and $CaCO_3$ fluxes and C and N stable isotopes in sediments deposited from 2.4 to 1.95 Ma at Sites 1082 and 1084 to explore the biogeochemical dynamics within the Benguela region. The infusion of Southern Ocean water delivered dissolved nutrients and Southern Ocean flora and fauna, resulting in local opal accumulation increasing up to 8 g/cm^{2}ky and the production of diatom mats. Some $\delta^{15}N$ measurements of diatom-bound organic matter indicate that the mats grew within the Benguela region. The bulk sediment $\delta^{15}N$ records are taken to reflect changes in the $\delta^{15}N$ of nitrate in the incoming water, where lower values at 2.4 Ma reflect less nitrate utilization in the Antarctic. A long-term increase in relative nitrate uptake in the Southern Ocean is evidenced by the gradual increase in $\delta^{15}N$ toward 1.9 Ma. *INDEX TERMS:* 4267 Oceanography: General: Paleoceanography; 4279 Oceanography: General: Upwelling and convergences; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4845 Oceanography: Biological and Chemical: Nutrients and nutrient cycling; *KEYWORDS:* Benguela Current, late Pliocene, diatoms, d15N, diatom-bound d15N

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1. Introduction

[2] ODP Leg 175 drilled a series of sites under the Benguela Current with the aim to reconstruct the history of the upwelling system. One of the important results from Leg 175 is a detailed record of a major increase in production of biogenic opal in the late Pliocene, named the Matuyama diatom maxima (MDM) [*Lange et al.*, 1999; *Shipboard Scientific Party*, 1998]. The MDM is expressed as an increase in diatom abundance in sediments beginning at 3.1 Ma that is centered between 2.6–2.1 Ma. Opal concentrations during the MDM range from 20–60%. The increase in opal is thought to reflect an influx of silica-rich water carrying Antarctic and sub-Antarctic flora and fauna resulting from a northward shift of the polar front zone and subtropical convergence zone [*Lange et al.*, 1999; *Abelmann et al.*, 1990]. The goal of this paper is to discuss the nitrogen isotope records of bulk sedimentary organic matter and diatom-bound organic matter during this unique time and to evaluate changes to the biogeochemical system related to the influx of Southern Ocean water and the massive deposition of opal.

1.1. Sedimentary $\delta^{15}N$

[3] The nitrogen isotopic composition of sedimentary organic matter, expressed as $\delta^{15}N$, is a useful but complicated tool for reconstructing biogeochemical processes in past water columns. The nitrogen isotope signal is a composite of local uptake and bacterial oxidation effects combined with basin-scale processes of denitrification and nitrogen fixation. Discrimination during nutrient uptake by phytoplankton relates the $\delta^{15}N$ value to the degree of nitrate utilization [*Altabet and Francois*, 1994; *Francois et al.*, 1992]. This premise is the basis for using $\delta^{15}N$ records to reconstruct changes in nitrate availability in the past. Used in conjunction with TOC and accumulation rates of other biogenic components, $\delta^{15}N$ may provide evidence for paleoproductivity changes in settings where nitrate is not completely utilized in the surface waters. This restricts the use of $\delta^{15}N$ as a nitrate utilization indicator to high nutrient, low chlorophyll (HNLC) regions of the ocean where nitrate remains in excess in the surface waters year-round.

[4] Diagenetic alteration of organic matter through bacterial oxidation during sinking and sedimentation may increase the $\delta^{15}N$ values by ~2–5‰ in deep-sea settings [*Altabet and Francois*, 1994; *Francois et al.*, 1992; *Sigman et al.*, 1999]. There is little or no alteration of the signal in

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continental margin settings [*Altabet et al.*, 1999b; *Ganeshram et al.*, 1999]. Postburial alteration of sedimentary $\delta^{15}N$ signals has not been investigated in detail. Early burial diagenesis appears to increase the $\delta^{15}N$ of the organic N fraction and release isotopically light $\delta^{15}N$ as NH_4^+. If the NH_4^+ is incorporated in the lattices of clay minerals, then this too can influence the bulk $\delta^{15}N$. Results from *Freudenthal et al.* [2001] show both these phenomena occurring in relatively short-term burial diagenetic processes, so that overall the bulk $\delta^{15}N$ value shows little or no change. There has been little work on long-term burial diagenesis, but there is some evidence for a lowering of the $\delta^{15}N$ over time with no good explanation [*Altabet*, 2001]. The lower values may result from an increase in the relative proportion of inorganic N as organic N is lost due to bacterial degradation or perhaps to a greater proportion of mineral-bound (and thus protected) nitrogen in organic-poor sediment.

[5] Basin scale processes such as denitrification and N-fixation are revealed in records where nitrate uptake is complete and thus the $\delta^{15}N$ of nitrate ($\delta^{15}NO_3^-$) is equal to that of sedimentary $\delta^{15}N$, ignoring alteration. On average, the global deep-water $\delta^{15}NO_3$ value is 4.8‰ [*Sigman et al.*, 2000]. It is thought that the deep-water value has been relatively constant through time, being maintained as a balance between denitrification and nitrogen fixation [*Liu et al.*, 1996]. Denitrification occurs in suboxic water columns where ^{14}N is preferentially released as N_2 thus enriching the NO_3 pool in ^{15}N [*Altabet et al.*, 1995, 1999a, 2002; *Ganeshram et al.*, 2000, 1995; *Liu and Kaplan*, 1989]. $\delta^{15}N$ of organic matter produced from an enriched $^{15}NO_3^-$ pool retains this enriched signature with average values of 7–9‰. Conversely, microbial nitrogen fixers use N_2 with a $\delta^{15}N$ value of ~0‰ and make organic matter with a $\delta^{15}N$ averaging 0.9‰ in oligotrophic locales where nitrate availability is low or zero [*Haug et al.*, 1998; *Liu et al.*, 1996; *Saino and Hattori*, 1980; *Wada and Hattori*, 1976]. Remineralization of this organic N is a source of isotopically light NO_3^- to the oceans. While deep-water nitrate is relatively isotopically homogeneous, surface and subsurface water masses can have distinctive $\delta^{15}NO_3^-$ values as a result of denitrification and N-fixation influencing these pools. Thus, this isotopic signature has utility as a water mass tracer [*Brandes et al.*, 1998]. Because of these multiple processes, the N-isotopic composition of sedimentary organic matter potentially bears information about the biogeochemical histories of the water masses in the Benguela region as well as local biological productivity and microbial oxidation of organic matter.

1.2. Oceanographic Setting

[6] The Benguela Current is one of the four major Eastern Boundary Current upwelling systems. It flows northward along southwest Africa (Figure 1). The current splits into two segments at 28°S: the Benguela Ocean Current (BOC) and Benguela Coastal Current (BCC). The BOC flows northwest as a sluggish eastern boundary current while the BCC flows within 180 km of the coastline. The BCC is associated with the coastal upwelling regime. The intense upwelling brings cold nutrient-rich water from 150–250 m depth to the surface. The upwelled water is made up of South Atlantic common water (SACW), a mixture of subtropical and sub-Antarctic waters that sinks at the subtropical convergence and spreads northward [*Shannon*, 1985] and subtropical subsurface waters of the poleward flowing undercurrent [*Gordon et al.*, 1995]. The poleward undercurrent flows from the Angola Gyre in the north extending at least to 30°S [*Gordon et al.*, 1995] (Figure 1). Coastal upwelling is confined to within 200 km of the shore with filaments of nutrient-rich water extending seaward, broadening the width of the upwelling's influence and thus the high productivity zone. A longshore series of thermal fronts marks the seaward extent of the upwelling water. In addition, there is an offshore divergence responsible for offshore upwelling north of 28°S [*Shannon*, 1985]. The area of perennial upwelling is the Luderitz cell, centered at ~25°S. Seasonal upwelling cells extend to the north (Figure 1). Diatom blooms are generally confined to the core of the coastal upwelling, whereas coccolithophores live throughout the upwelling and dominate in the high productivity regions offshore [*Giraudeau and Bailey*, 1995; *Summerhayes et al.*, 1995]. The predominance of $CaCO_3$ over opal producing organisms is a result of the Si:N ratio of the surface waters [*Ragueneau et al.*, 2000]. The increase in opal productivity during the MDM suggests a former influx of water with a higher Si:N ratio than is delivered at present. The Southern Ocean is the most proximal source of high Si:N water in the South Atlantic Ocean [*Ragueneau et al.*, 2000].

2. Sampling Strategy and Methods

[7] Samples from Sites 1082 and 1084 were taken at ~3 ky intervals, at core intervals of approximately 30 and 50 cm respectively, between 2.4 and 1.95 Ma. Site 1084 is adjacent to the Luderitz upwelling cell at 25°31′ S, 13°1′ *E* while 1082 lies to the north at 21°5′ S, 11°49′ E (Figure 1).

[8] All samples were freeze-dried and powdered. Carbonate content was determined by carbonate bomb method using 3 N HCl, and the resulting residue was rinsed three times with centrifugation and then dried in an oven at 60°C. The carbonate-free residue was used for measuring total organic carbon (TOC) and total nitrogen (TN) concentrations in a Carlo Erba 1108 EA. Relative precision for carbon is ± 2% while N is ± 3%. Opal concentrations were measured according to the methods of *Mortlock and Frolich* [1989] using 0.5 M NaOH instead of $NaCO_3$ to ensure complete digestion. $^{15}N/^{14}N$ expressed as $\delta^{15}N$ (vs. air) and $^{13}C/^{12}C$ as $\delta^{13}C_{org}$ (vs. PDB), were measured from the carbonate-free residues by CE 2400 coupled to the Finnegan Delta plus mass spectrometer with Conflo II interface in the laboratory of D. Zak at the University of Michigan School of Natural Resources and the Environment. Precision was ± 0.2‰ for $\delta^{13}C$ and ± 0.3‰ for $\delta^{15}N$. The diatom fraction was extracted from bulk sediment following the procedure of *Sigman et al.* [1999]. Bulk organic matter was removed using 30% H_2O_2 at 70°C prior to the heavy liquid separation of opal. The opal fraction was cleaned in concentrated perchloric acid in a 70°C water bath overnight. The cleaned opal was rinsed and dried for isotope analyses. Precision for the $\delta^{15}N$ of diatom-bound organic matter was ± 0.7‰.

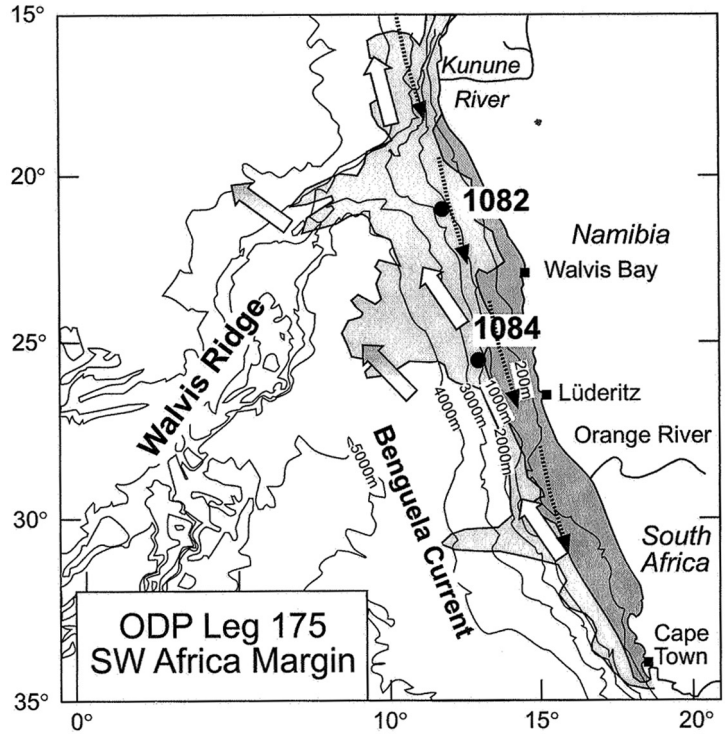

Figure 1. Location map of Benguela Current upwelling system and ODP Sites 1082 and 1084. The shaded areas highlight regions of elevated productivity that result from coastal upwelling and seaward moving filaments of nutrient-rich water that pass over the slope. The two segments of the Benguela Current, the Benguela Ocean Current (BOC) and Benguela Coastal Current (BCC), split at ~28°S. The poleward undercurrent flows from north to south along the shoreline (dashed line).

[9] In order to calculate biogenic component fluxes, we required a higher resolution age model than the biostratigraphy could provide. Using the 1.95, (*Discoaster brouweri*) and 2.70 (*Cycladophora davisiana*) biostratigraphic age ties from site 1082 and the 1.95 (*D. brouweri*) and 2.55 (*D. surculus*) ties from 1084 as pegs, shipboard color reflectance records were tuned to insolation. The resulting age depth ties were used to calculate linear sedimentation rates (LSR). The ages are anchored within one precessional cycle of biostratigraphic age ties, so the absolute ages of these intervals are dependant on the accuracy of the age ties. Within the interval, we estimate relative age to be ± 20 ky. The LSR were used to calculate bulk accumulation rates and component mass accumulation rates according to the following formula:

$$\text{LSR(cm/ky)} \; x \; \text{dry bulk density(g/cm}^3\text{)} \; x \; \text{component percentage}/100 = \text{component MAR(g/cm}^2\text{ky)}$$

[10] Shipboard dry bulk density (DBD) measures from the Leg 175 Initial Reports volume were utilized.

2.1. Results

[11] $CaCO_3$, TOC, and opal concentrations and fluxes and C and N isotope data from Sites 1082 and 1084 are shown versus age in Figures 2 and 3. Biogenic component accumulation rates show synchronous changes at the two sites. Opal accumulation peaks correlate to TOC maxima with significant peaks at 2.41 (1082 only), 2.32, 2.2, 2.1 Ma. There is a large peak at 2.04 Ma at Site 1084 that is absent at Site 1082.

[12] Patterns of change in the $\delta^{15}N$ records between the two sites correlate well (Figures 2 and 3); $\delta^{15}N$ increases toward 1.95 Ma. Positive shifts occur at 2.22 and 2.1 Ma. Diatom-bound $\delta^{15}N$ values also increase in younger sediment, showing the same trend as the bulk $\delta^{15}N$ (Figure 4). All of the diatom-bound values are larger than the bulk $\delta^{15}N$ values by ~1.6‰ (Table 1).

[13] Offsets exist in the absolute concentrations/accumulation rates of $CaCO_3$, TOC, and opal and $\delta^{13}Corg$ and $\delta^{15}N$ values between Sites 1082 and 1084 (Figures 2 and 3). In particular, there were overall higher sedimentation rates, biogenic concentrations and accumulation rates, and heavier isotope values, from both the bulk and diatom-bound organic matter at Site 1084 (Figures 2–4).

3. Discussion

[14] The region of relatively high productivity that exists today offshore of the core of the Benguela upwelling system has coccolithophores as the dominant primary producers [*Bailey*, 1991; *Giraudeau and Bailey*, 1995]. In sedimentary records from this region, past changes in carbonate accu-

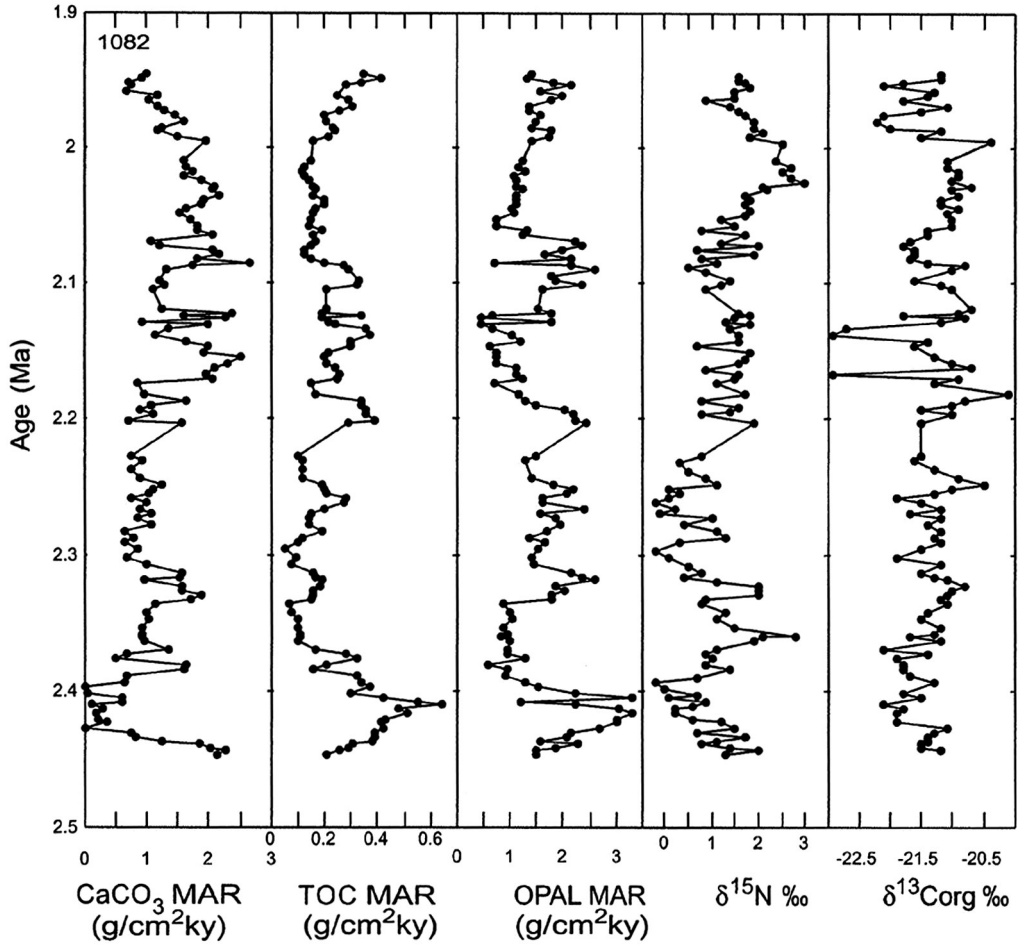

Figure 2. Profiles of $CaCO_3$, TOC and opal mass accumulation rates and $\delta^{15}N$ and $\delta^{13}Corg$ at Site 1082. TOC and opal MAR records agree well. There is a long-term increase in of ~2‰ in the $\delta^{15}N$ record.

mulation rates result from dissolution processes rather than coccolith productivity [*Diester-Haass et al.*, 1992, 1986; *Gardner et al.*, 1984; *Robinson et al.*, 2002]. During the MDM, $CaCO_3$ accumulation rates vary negatively with TOC ($r^2 = 0.40$), indicating that carbonate concentrations are responding at least in part to organic matter oxidation. However, distinct peaks in $CaCO_3$ concentrations that are not limited to minima in TOC suggest that changes in productivity also played a role in the $CaCO_3$ accumulation record.

[15] TOC delivery to the seafloor in the Benguela region has been high and at times has varied considerably over short time spans [*Brüchert et al.*, 2000; *Meyers et al.*, 1983; *Robinson et al.*, 2002]. During the MDM TOC concentrations fluctuate moderately between 3–10% (half the range found during the Pleistocene). The $\delta^{13}Corg$ values, averaging ~21‰, indicate that the variability in the TOC concentrations and fluxes cannot be attributed to the input of land-derived organic matter and instead must be due to variations in production and delivery of marine organic matter. The strongest maxima in the TOC MAR records correspond to peaks in opal accumulation rate. The correspondence could be the result of increased organic matter delivery to the seafloor via diatom mats and/or enhanced local production of both opal and TOC.

3.1. The $\delta^{15}N$ Evidence of Nonlocal Processes

[16] Three sources of water contribute to the surface waters of the Benguela Current upwelling system: 1) subtropical water and 2) sub-Antarctic mode water (SAMW), which combine at the subtropical convergence to form South Atlantic common water (SACW), and 3) Indian central water (ICW) from filaments of the Agulhas Current that leak around the Cape of Good Hope. The BCC contains SACW that enters the region through upwelling, collecting dissolved nutrients as it passes over the organic matter-rich continental shelf. In addition, the poleward flowing undercurrent contributes saline, poorly oxygenated, subtropical water from the north that is delivered to the surface during upwelling [*Gordon et al.*, 1995]. The BOC carries relatively warm water from the subtropical gyre and Agulhas leakage [*Shannon*, 1985; *Stramma and England*, 1999]. The MDM represents a long-term infusion of silicate-rich water from the Southern Ocean. *Lange et al.* [1999] assert that the Southern Ocean water is advected into the BOC. Nitrate is in excess in the surface and subsurface waters of the

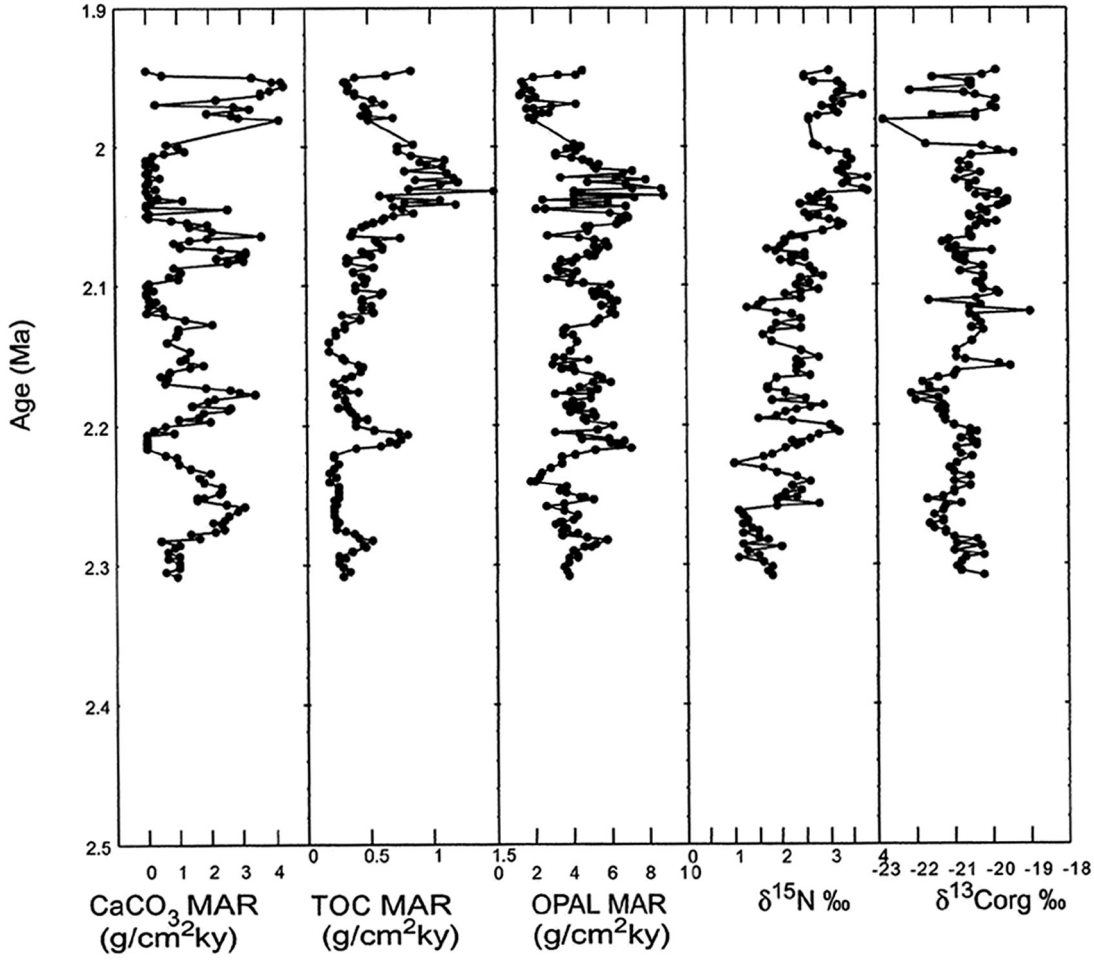

Figure 3. Profiles of $CaCO_3$, TOC and opal mass accumulation rates and $\delta^{15}N$ and $\delta^{13}Corg$ at Site 1084. The Site 1084 records share most biogenic flux maxima with Site 1082 except the large, broad peak at 2.07 Ma. The $\delta^{15}N$ record at 1084 correlates well with that from Site 1082 and includes a long-term increase in of ~2 ‰ in the $\delta^{15}N$ record.

Southern Ocean, and thus this water-type intrusion would necessarily contribute nitrate to the region. This Southern Ocean nitrate potentially has a distinctive $\delta^{15}N$ signature.

[17] There are no published measurements of the $\delta^{15}N$ of nitrate from the modern Benguela Current region. *Holmes et al.* [1996] made estimates of $\delta^{15}NO_3^-$ for the Benguela region based on calculations using the $\delta^{15}N$ of particulate organic nitrogen and an estimated ε value. They conclude the $\delta^{15}NO_3^-$ of upwelled nitrate, thus within the BCC, to be ~5.5‰. Recent measurements of the $\delta^{15}NO_3^-$ from the sub-Antarctic thermocline in the Indian and Pacific sectors of the Southern Ocean estimate the $\delta^{15}N$ in these regions to be ~ 6‰ [*Sigman et al.*, 2000]. We will assume that this value will hold true for the south Atlantic sector of the Southern Ocean as well. The thermocline water is the upper layer of SAMW, a mixture of subsurface Antarctic water and subtropical surface water entering the region from the gyre, essentially the same as SACW. The isotopic composition of the upwelled water is probably slightly lower within the upwelling system than that of the sub-Antarctic thermocline since it incorporates the $\delta^{15}N$ signal of regenerated nitrate from the seafloor.

[18] The poleward undercurrent also contributes nitrate from the subtropical region, but the $\delta^{15}N$ of this water mass is unknown. In general, Atlantic subtropical water masses bear a relatively low $\delta^{15}N$ signature because they are derived from oligotrophic locales where inputs from nitrogen fixers are important. In the poleward undercurrent, which is low in O_2, there is the possibility of water column denitrification [*Dittmar and Birkicht*, 2001], which would contribute an isotopically heavy nitrate pool. It is consequently difficult to estimate how contributions from the north would affect the $\delta^{15}N$ signal.

[19] BOC water at present is a mixture of subtropical water and Agulhas water, but Agulhas contributions are likely too small to influence isotopic composition of the water mass. If during the Pliocene it was primarily the BOC that was infused with Southern Ocean water as *Lange et al.* [1999] contend, then the $\delta^{15}N$ of nitrate in the BOC was likely more similar to SACW, a mix of subtropical and sub-

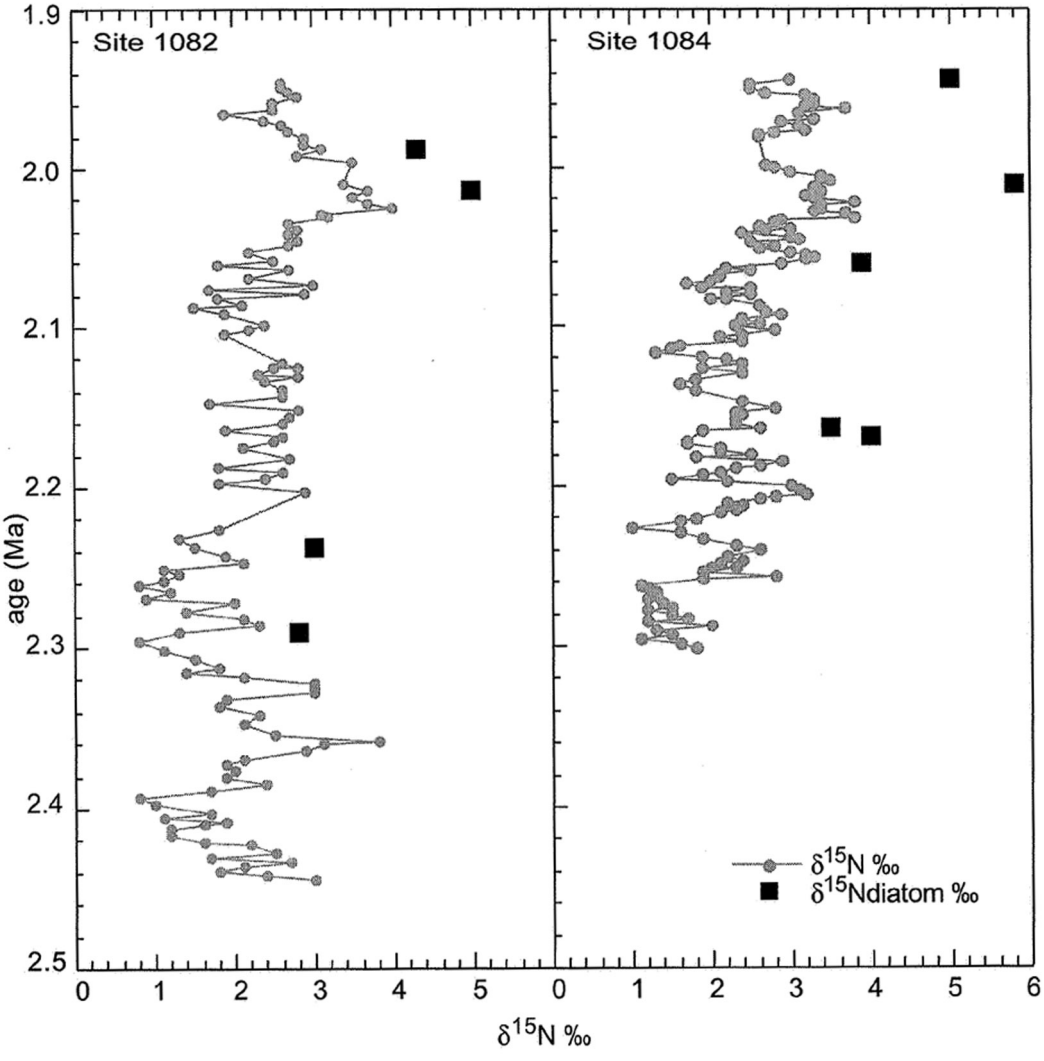

Figure 4. Profiles of $\delta^{15}N$ from Sites 1082 and 1084 and measured diatom-bound $\delta^{15}N$ values. Variations in the bulk and diatom-bound $\delta^{15}N$ values agree well. The diatom-bound $\delta^{15}N$ values are offset from the bulk values by ~1–2‰. This may indicate diagenetic alteration of the bulk isotopic composition during burial.

Antarctic water. Sub-Antarctic surface water $\delta^{15}NO_3^-$ and nitrate concentrations are determined by local productivity and therefore any changes in the exported nitrate signal likely reflect sub-Antarctic nutrient utilization. High opal deposition on the Benguela margin suggests that nutrients were not extensively utilized in Antarctic or sub-Antarctic and thus export concentrations were elevated and the $\delta^{15}NO_3^-$ was low.

3.2. Diatom-Bound $\delta^{15}N$

[20] The diatom-bound $\delta^{15}N$ values, while few in number, follow the same overall trend as the bulk values, in which diatom-bound $\delta^{15}N$ values increase toward the present and values at Site 1084 are on average about 1‰ greater than those from Site 1082 (Table 1; Figure 4). The matching patterns between bulk and diatom-bound $\delta^{15}N$ values and the consistent offset between the sites suggest that the diatoms grew within the Benguela region at both locations. This evidence of local origin would include *Thalassiothrix Antarctica*; the mat-formers that *Marlow et al.* [2000] suggest were advected into the region. These authors argue that intermingling of mats, which are formed by a predominantly sub Antarctic species, with warm water species indicates that the mat-formers must have grown in the cool of the sub-Antarctic and were subsequently carried into the Benguela region. *Thalassiothrix* mats dominate the diatom fraction throughout this interval, and although we did not isolate only *Thalassiothrix* for $\delta^{15}N$ analyses, the diatom-bound $\delta^{15}N$ signal is likely dominated by the *Thalassiothrix* as well. Diatom mats significantly enrich the opal concentrations but the diatom-bound fraction comprises only 1–2% of the total nitrogen in the sediments. Hence, the bulk

Table 1. Comparison of Diatom-Bound and Bulk Sedimentary $\delta^{15}N$ Values[a]

Sample ID	Depth, mbsf	Age, Ma	δ^{15}Nsed, ‰	δ^{15}N diatom, ‰	$\Delta\delta^{15}$N, ‰
		Site 1082[b]			
23 X 6 66 68	211.87	1.992	2.1	3.3	1.2
24 X 1 41 43	215.91	2.029	2.7	4.0	1.3
26 X 1 78 80	235.58	2.209	0.5	2.0	1.6
26 X 4 17 19	239.47	2.244	0.3	1.8	1.5
		Site 1084[c]			
36 X 1 10 12	316.40	1.956	3.0	5.0	2.0
37 X 2 125 127	328.65	2.011	3.4	5.8	2.4
38 X 3 100 102	339.60	2.061	2.9	3.9	1.0
40 X 2 120 122	357.50	2.164	2.6	3.5	0.9
40 X 3 55 57	358.35	2.169	1.8	4.0	2.2

[a] Values of $\Delta\delta^{15}$N are δ^{15}Ndiatom-δ^{15}N from bulk sediment. Diatom-bound organic matter has on average a δ^{15}N value that is 1.6‰ higher than bulk sediment.
[b] Where the mean is 1.4, and $1\sigma = 0.2$.
[c] Where the mean is 1.7, and $1\sigma = 0.7$.

δ^{15}N could not have been strongly influenced by the advective input of the mats.

[21] *Thalassiothrix* require a vertically stable water column for growth [*Kemp et al.*, 2000]. The Benguela Current upwelling system is presently a perennial upwelling region and is therefore not hospitable to mat growth. For the mats to grow within the Benguela region, upwelling and the turbulent mixing related to it must have been reduced over Sites 1082 and 1084, perhaps by contraction of the extent of the BCC. At present, the drill sites are proximal to the BCC/BOC front such that if the BCC had contracted during the Pliocene, then the oceanic regime of the BOC would dominate the surface waters over the drill sites. The ''fall dump'' model of diatom deposition outlined by *Kemp et al.* [2000] describes a sequence of terrigenous material, upwelling diatom species followed by deeper dwelling mat formers, and then upwelling species once again. *Lange et al.* [1999] describes a pattern of alternating upwelling and pelagic diatom species including the Southern Ocean types. The mat formers live in a relatively stratified water column and are either tolerant of low-light conditions and live within the nutricline where nutrient concentrations are high, or they have ability to control their buoyancy and return to the surface to proceed with photosynthesis.

[22] Relatively warm alkenone sea-surface temperatures (R. Robinson, unpublished data, 2000) and those shown by *Marlow et al.* [2000], which average ~23°C, suggest that upwelling intensity was lower during the late Pliocene. The relatively warm temperatures indicate at least seasonal (i.e., when coccolithophorids, the source of the alkenone temperature signal, thrived) warmth over the drill sites. We speculate that this warmth may have been sufficient to allow stratification of the surface waters during the summer months, providing stability necessary for the *Thassilothrix* mats to develop. This scenario could reflect the position of the BOC/BCC front where dominance of the BOC would provide an environment more hospitable to the mat forming diatoms or a more seasonal character to upwelling during the Pliocene. While we assert that the mats grew within the Benguela region, we maintain that there was an intrusion of Southern Ocean water, bringing nutrients and sub-Antarctic flora and fauna that triggered the MDM. The warm and likely stable water column appears to have been present throughout the Pliocene record presented by *Marlow et al.* [2000], but the MDM clearly stands out at the end of the period of sustained warmth.

[23] Diatom-bound N is thought to be a component of unaltered organic matter encapsulated within the mineral matrix and thus a good reflection of the original nitrate pool [*Sigman et al.*, 1999]. The higher δ^{15}N values for diatom-bound organic matter may indicate that the bulk δ^{15}N values reflect an altered external N pool, and thus the relatively low bulk δ^{15}N values should be considered a result of alteration and not a shift in the δ^{15}N of the starting nitrate. Using the $\Delta\delta^{15}$N values of 1.4 and 1.7‰ for Sites 1082 and 1084 respectively (Table 1), we can estimate an unaltered bulk δ^{15}N signal. This approximation estimates values at the younger end of the interval that approach those of modern sedimentary δ^{15}N in the region. Alternatively, assuming no diagenesis, the diatom mats, which developed in the summer after the initial spring bloom, used a diminished and thus ^{15}N enriched nitrate pool. While there may be a long-term diagenetic signal in the bulk δ^{15}N, the excellent intersite agreement indicates that the variability in δ^{15}N within the interval reflects paleoceanographic changes and not diagenesis.

3.3. Local Processes

[24] If nitrate is not completely utilized, relative changes in nitrate utilization mask changes in δ^{15}N related to source water variations. The offset in δ^{15}N values between Sites 1082 and 1084 has been attributed to regional differences in the relative draw on the nitrate pool [*Holmes et al.*, 1998]. This offset is visible in modern nitrate and δ^{15}N data from transects that approximate the drill site locations, and these authors suggest that more available nitrate in the surface waters over 1082 than 1084 causes the lower δ^{15}N values for underlying surface sediment [*Holmes et al.*, 1998]. Alternatively, these data can be interpreted as a difference in the δ^{15}N of source nitrate, probably related to the increased influence of the poleward undercurrent at Site 1082 and a stronger influence by SACW in the south and thus near Site 1084. This interpretation assumes complete nitrate uptake over the annual cycle. The Benguela is not an HNLC region of the ocean and nitrate is thought to be limiting [Chapman and *Shannon*, 1985]. Complete nitrate

consumption is documented for other coastal upwelling systems such as the California and Arabian Sea [*Altabet et al.*, 2002, 1999a].

[25] Assuming incomplete uptake, relative utilization of nitrate can be estimated using sediment $\delta^{15}N$ values from Sites 1082 and 1084 and the integrated product form of the Rayleigh fractionation equation [*Altabet and Francois*, 1994]:

$$\delta^{15}N_{sed} = \delta^{15}NO_{3\ initial}^{-} + f/(1-f)\ x\ \varepsilon\ x\ \ln(f)$$

in which f is the fraction of the initial nitrate pool remaining. Using average $\delta^{15}N_{sed}$ values from sites 1082 and 1084, 1.3‰ and 2.4‰ respectively, $\delta^{15}NO_{3\ initial}^{-} = 5.5‰$, and $\varepsilon = 5‰$ [*Holmes et al.*, 1998], values for f of ~0.7 or ~0.4 are derived, suggesting that 70% and 40% percent of the respective nitrate pools were unutilized. Using values adjusted for potential long-term alteration of the $\delta^{15}N$ signal (the average plus 1.4 or 1.7‰ ($\Delta\delta^{15}N$ values) for 1082 and 1084 respectively, values of 0.35 (35%) and 0.11 (11%) are estimated. Use of the unadjusted values gives unreasonably low levels of nitrate utilization. The estimates made from the adjusted values are more realistic but still low. It should be stated that initial $\delta^{15}NO_3^-$ is an estimate and may have been different and/or variable during the Pliocene. The magnitude of fractionation (ε) can vary with species and environmental conditions, so assuming a constant ε value may also contribute to the low estimates of utilization. The second estimates of utilization can be taken to indicate the presence of an extremely large nitrate pool, perhaps due to the combined inputs from the upwelling and the Southern Ocean, and thus nitrate was not limiting as it is today. Even with the infusion of Southern Ocean water it remains unlikely that 35% of the nitrate pool remained at Site 1082 during the late Pliocene, given the modern condition of nitrate limitation. If nitrate uptake was incomplete, then one might infer that the limiting nutrient was not being supplied at the same rate as nitrate [e.g., *Altabet*, 2001]. If this is true, then we can infer that the shift in $\delta^{15}N$ toward higher values in younger sediment is related to an increase in supply of this nutrient, perhaps related to the intensification in upwelling around this time [*Marlow et al.*, 2000].

[26] Both the records presented here and background knowledge about other upwelling systems suggest that the $\delta^{15}N$ record reflects source changes and not the relative uptake of nitrate. There is excellent intersite agreement between the $\delta^{15}N$ records, yet there are significant differences in the biogenic component records (Figures 2 and 3); $\delta^{15}N$ and biogenic accumulation rates do not consistently covary (Figures 2 and 3). For example, at Site 1084, $\delta^{15}N$ abruptly shifts to lower values at 2.07 and 2.12 and 2.23 Ma despite high accumulation rates. Similar shifts occur at 2.24 and 2.40 Ma at Site 1082. If $\delta^{15}N$ and the biogenic component records were recording the same process (paleoproductivity), then they should agree.

3.4. Biogeochemical Reorganization During the MDM

[27] The MDM represents the transition between the warm middle Pliocene and the upwelling-dominated Pleistocene. Sea surface temperature estimates suggest that upwelling was substantially reduced compared to present conditions while nutrients, carried in by the Southern Ocean water and intruding due to cooling on Antarctica and the northward migration of the polar front and subtropical convergence zones [*Abelmann et al.*, 1990], allowed for moderate levels of productivity and the massive deposition of opal. Diatoms, enjoying the relatively stable water column conditions and abundant silicate, were the dominant primary producers instead of coccolithophorids. While diatom production and opal accumulation was relatively high, TOC burial was moderate relative to Pleistocene accumulation rates, suggesting that despite the diatoms' success and the availability of nutrients, export productivity was limited by the weak upwelling conditions.

[28] $CaCO_3$ and TOC MARs do not show variation from their normally cyclic patterns but the opal MAR and nitrogen isotope values are strikingly different from other records from the region; opal fluxes are high and $\delta^{15}N$ values are low. The opal enrichment strongly suggests an increased supply of silica and likely nitrate to the region, and the variations within the MDM probably reflect episodic inputs of nutrients. The opal and $\delta^{15}N$ records do not covary. This can be easily explained when considering that silicate is used by only opal-producing organisms while nitrate is utilized by all groups of primary producers.

[29] The variability in the $\delta^{15}N$ values likely reflects changes in the $\delta^{15}N$ of source waters. Local differences in the relative source contributions, i.e., from the undercurrent versus the SACW, were probably not a significant factor, given the relatively consistent offset between the two sites and overall excellent agreement in the $\delta^{15}N$ records. Rather, the variability in $\delta^{15}N$ was likely due to a regional change in the $\delta^{15}N$ of nitrate. Because of the high opal deposition at this time, we will assert that it was due to Southern Ocean nitrate contributions. Relatively high nitrate concentrations in sub-Antarctic water would necessarily mean the $\delta^{15}NO_3^-$ would reflect this water mass rather than subtropical water masses where nitrate concentrations are likely lower.

[30] $\delta^{15}N$ values are lowest during the peak of the MDM and increase as the record approaches the termination. There is change in the isotopic composition of the source water through time. The massive export of nutrients from the Southern Ocean implied by the MDM also implies that nutrient utilization in the sub-Antarctic was relatively low. Reduced draw on the nitrate pool increases nutrient concentrations and lowers the isotopic composition of the nitrate. The overall increase in the sedimentary $\delta^{15}N$ records across this 400 ky record can be taken as an increase in nitrate consumption and concomitant $\delta^{15}NO_3^-$ increase in the sub-Antarctic. Why there is not a similarly gradual decrease in opal is not clear. The increase could also signal an increase in contributions by an isotopically heavy water mass such as the poleward undercurrent. However, the poleward undercurrent is an unlikely source of ^{15}N-enriched nitrate given the 1‰ intersite offset of $\delta^{15}N$, where lower values lie to the north. If the poleward undercurrent were contributing isotopically heavy water, higher values should appear at Site 1082, not Site 1084.

[31] *Dowsett and Willard* [1996] present a general model for glacial-interglacial changes in nutrient utilization in the

Southern Ocean, where during glacial times, ice cover limits the extent of phytoplankton uptake of nutrients, thus allowing for increased nutrient export out of the Antarctic into the SE Atlantic. During interglacials, nutrient export is diminished because of local uptake [*Dowsett and Willard*, 1996]. The late Pliocene interval here is regarded as a time of cooling and ice expansion in Antarctica with a contraction and northward shift in the zone of silica deposition [*Abelmann et al.*, 1990]. This decrease in silica deposition may indeed have left more nutrients to export during the late Pliocene. Global cooling may have triggered the onset of the MDM, coupling the nutrient cycles of the Southern Ocean and Benguela Current region for an extended period of time, but why did the MDM end? It may be related to the onset of relatively strong upwelling within the Benguela system [*Marlow et al.*, 2000] and an associated subsurface circulation change that cut off the import of Southern Ocean water. On the other end, there may have been a change in the sub-Antarctic that essentially shut off the enhanced supply to the southeast Atlantic, either due to increased uptake or perhaps a shift in the locations of thermal fronts such as the subtropical convergence and the polar front. Either way, it appears that this strong coupling ended sometime after 1.9 Ma.

[32] Our adjustment of the $\delta^{15}N$ values, which are based on the diatom-bound $\delta^{15}N$ measurements, introduces questions of a broader scale. If the offset is not due to diagenetic alteration, the extremely low $\delta^{15}N$ values measured during the late Pliocene may be indicative of a major change in the isotopic composition of nitrate, either within the South Atlantic or in the global ocean, perhaps due to diminished rates of denitrification. The effects of long-term burial diagenesis must be investigated before paleoceanographers will be able to make more confident interpretations of long-term changes in the nitrogen cycle.

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