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RECONSTRUCTION OF SURFACE OCEAN NUTRIENT UTILIZATION IN THE SOUTHEAST ATLANTIC OCEAN BASED ON STABLE NITROGEN ISOTOPES

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1. SUMMARY

Stable nitrogen isotopes measured in bulk sediments and sinking particles have been used to evaluate changes in relative nutrient utilization in surface waters of the subtropical southeast Atlantic. In order to determine the dominant controls on the nitrogen isotopic composition of organic matter (OM) in this region at the present time, samples of sinking particulate matter collected with a sediment trap and surface sediments in seven sea to shore transects in the Angola and Cape Basins were analyzed. Variations in the degree of surface nitrate depletion during the Late Quaternary were also investigated based on $\delta^{15}N$ in two deep-sea cores from the Angola Basin.

The $\delta^{15}N$ signal observed in sinking particles at the Walvis Ridge over a one year period mirrored sea surface temperatures (SST) and particulate flux rates with two distinct $\delta^{15}N$ decreases of ~2‰ in austral fall and spring. Low $\delta^{15}N$ values coincided with low SST, indicating that the low temperatures were brought about by recently upwelled, nutrient-rich water, a supposition substantiated by wind stress data from the literature. The simultaneous occurrance of maxima in particle flux rates with the decreases in $\delta^{15}N$ values and SST minima provides additional evidence that the $\delta^{15}N$ signal in sinking OM in the study area records the extent to which the surface nitrate pool has been utilized as well as the productivity variations driven by euphotic zone nitrate availability.

Surface sediments showed a similar response to surface nitrate concentrations, but on a spatial scale rather than the temporal variations observed in the sinking particulate matter. $\delta^{15}N$ values in each transect increased with increasing distance from shore due to the high nearshore nutrient concentrations brought to the surface by coastal upwelling. Shelf and upper slope sediments exhibited $^{15}N/^{14}N$ ratios between 4.6 and 6.3‰. Offshore, $\delta^{15}N$ values increased to up to 11.8‰. In both the Angola and Cape Basins, bulk surface sedimentary $\delta^{15}N$ was significantly negatively correlated with historically averaged $[NO_3^-]_{surface}$. Fractionation factors (ε_u) for nitrate uptake by phytoplankton were estimated for this region from plots of sedimentary $\delta^{15}N$ versus ln $[NO_3^-]_{surface}$. These ranged from 1.0 to 5.4‰ and were used to calculate, based on Rayleigh fractionation kinetics, the amount of unutilized nitrate remaining in surface waters (f) at the time the OM in each sediment sample was produced. f values estimated from sedimentary $\delta^{15}N$ were not statistically different from those calculated from the ratio of $[NO_3^-]_{surface}$ to $[NO_3^-]$ in the original upwelled water. Using ε_u calculated from the sediments underlying the sediment trap at the Walvis Ridge, f values were estimated for the sinking particle samples as well.

No evidence for the influence of denitrification on $\delta^{15}N$ was found. The isotopic signal in neither sediments nor sinking particles was generally elevated with respect to values reported

by other investigators for typical marine-derived organic matter. Furthermore, high $\delta^{15}N$ values in sediments and sinking particulate material were accompanied by a depleted surface nitrate pool and low OM contents, the opposite of what would be expected if denitrification was the cause of the elevated isotopic values. Terrestrially-derived OM also has had little influence on the nitrogen isotopic composition of sediments in Angola and Cape Basins. Two sediment samples from the Zaire estuary revealed that the isotopic signature of terrigenous material entering the Zaire fan from the African continent is indistinguishable from that of the marine material produced in this area. Thus, the presence of this terrestrial OM does not noticably affect the marine surface-generated $\delta^{15}N$ signal.

Also addressed in this work is the effect of diagenesis on the nitrogen isotopic composition of sedimentary OM. The presence of a recognizable pattern which corresponds to upwelling events is seen in the $\delta^{15}N$ values of sinking particles, as discussed above. Furthermore, it is clear from the sedimentary $\delta^{15}N$ values, which mirror surface nitrate concentration trends, that the signal produced at the surface is transferred to the sediments, at least in a relative way. Comparison of sedimentary $\delta^{15}N$ with the $\delta^{15}N$ values which would be expected based on historically averaged $[NO_3^-]_{surface}$ indicates no recognizable offset between the isotopic signal of OM produced in the euphotic zone with respect to that measured in sediments in the Angola Basin and in the southern part of the Benguela upwelling system. In northern Benguela sediments, a diagenetic alteration of the surface-produced signal of around 1.4‰ was seen. A similar offset (1.6‰) between the nitrogen flux-weighted mean $\delta^{15}N$ of sinking particles in northern Benguela and underlying surface sediments was found.

These findings suggest that the main factor controlling $\delta^{15}N$ values in present-day sediments off the southwest coast of Africa is the degree of surface nitrate utilization and that diagenesis has had little effect on $\delta^{15}N$ in this area. Thus, $\delta^{15}N$ values in sediment samples of two gravity cores from the Angola Basin were analyzed to evaluate past changes in the biogeochemistry of the surface ocean. Sedimentary $\delta^{15}N$ values during the past 180 kyr off the Zaire River (core GeoB 1008-3) and the past 300 kyr in the middle Angola Basin (core GeoB 1016-3) are charactarized by a 23 kyr cyclicity, indicating that changes in boreal summer insolation controls nitrate availability in this region. When the earth-sun distance is greatest, monsoonal intensity decreases, leading to an increase in trade wind intensity. Trade winds, in turn, drive the coastal upwelling which brings nutrient-rich water from depth to the surface, and allows elevated northward advection of nitrate-rich waters into the Angola Basin, resulting in less extensive depletion of the available $[NO_3^-]$. This supposition is corroborated by the correspondance of low $\delta^{15}N$ values in both of the cores to low sea surface temperatures and to high organic carbon (OC) content and paleoproductivity and vice versa. During times of sedimentary ^{15}N depletion and high OC, not only was the nitrate pool in surface water less

depleted, absolute concentrations of surface nitrate must have been higher to account for the associated productivity increases.

In addition, $^{15}N/^{14}N$ ratios of sediments produced during glacial periods were significantly lower than the $\delta^{15}N$ values of interglacial sediments, indicating that the surface nitrate pool was less depleted during glacials. The lower $\delta^{15}N$ values in core GeoB 1016-3 relative to GeoB 1008-3 between 30 and 70 kyr ago indicate that nitrate levels were higher in the southern Angola Basin than off the Zaire River at this time, likely due to higher concentrations of pre-formed nutrients in the water flowing northward into the Angola Basin. No evidence was found that denitrification has occurred during the past 300 kyr in this region, refuting the idea of a global decrease in denitrification during glacials. The link between $\delta^{15}N$ in sediments, relative surface $[NO_3^-]$ utilization and paleoproductivity demonstrated in this work provide evidence for the usefulness of bulk sedimentary $\delta^{15}N$ as a proxy for past changes in nutrient dynamics in surface waters.

2. INTRODUCTION

2.1 Background

The use of nitrogen isotopes in marine sediments is a relatively new tool in the study of paleoceanography. The usefulness of this proxy lies in its recording of changes in nutrient dynamics in the water column. Such information is relevant to our understanding of paleoproductivity variations. This dissertation work was undertaken with the goal of clarifying the main controls on the sedimentary $\delta^{15}N$ signal in the southeast subtropical Atlantic and investigating past changes in the biogeochemistry of the upper ocean in this area.

Nitrogen exists as two stable isotopes: ^{14}N (99.64%) and ^{15}N (0.36%). The largest reservoir of nitrogen is the atmosphere where it occurs primarily as N_2. Nitrogen is also present on the earth as nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), oxides (NO_2, NO and N_2O) and in amino acids (FAURE, 1986). Variations in the isotopic compositions of nitrogen-containing substances result because more kinetic energy is required to break bonds formed with the heavy isotope (^{15}N) than those involving ^{14}N. The $^{15}N/^{14}N$ ratio of a substance is commonly expressed in terms of $\delta^{15}N$, which is equal to:

$$[(^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{standard}) - 1] \times 10^3$$

The standard is conventionally atmospheric nitrogen, which is assigned an arbitrary $\delta^{15}N$ value of 0‰. The $\delta^{15}N$ signal measured in sediments is ultimately the result of the fractionation of nitrogen isotopes during many biological reactions which occur in the ocean and on land. This parameter can therefore yield valuable information about the environment in which the organic matter in the sediments was produced. The most important processes known to date which affect $^{15}N/^{14}N$ ratios in marine environments are discussed below.

The isotopic signature of the nitrate available for phytoplankton uptake is key in determining the isotopic composition of organic matter. LIU & KAPLAN (1989) reported a mean $\delta^{15}N$ value for nitrate from oxygenated water in the deep sea of around 6‰, but various processes can alter the $\delta^{15}N$ of nitrate. Under oxygen-depleted conditions, denitrification can alter the isotopic signature of the nitrate pool because nitrate-reducing bacteria are able to use nitrate as the electron acceptor in place of O_2 (CLINE & KAPLAN; 1975). This process leads to enrichment of the residual nitrate in ^{15}N relative to the mean deep-sea value.

Uptake of dissolved inorganic nitrogen (primarily as nitrate in the eastern subtropical Atlantic; CHAPMAN & SHANNON, 1985) during photosynthesis in the photic zone results in fractionation of nitrogen isotopes between the inorganic source nitrogen and the organic matter which is produced. Because nitrate containing the lighter isotope is prefentially taken

up by phytoplankton, phytoplankton is typically depleted in ^{15}N relative to the nitrate substrate used for growth and the remaining nitrate pool becomes progressively enriched in ^{15}N according to Rayleigh fractionation kinetics (CIFUENTES et al., 1988; WADA, 1980). Thus, one of the most important controls on the $\delta^{15}N$ of organic matter is the concentration of nitrate in the photic zone and, more specifically, the degree to which this reservoir is utilized (MARIOTTI et al., 1982). The ensuing transfer of nitrogen through trophic levels is characterized by a systematic increase in $\delta^{15}N$, with each trophic step resulting in an enrichment of 3.5‰ (DENIRO & EPSTEIN, 1981; MINAGAWA & WADA, 1984). This effect, however, should be negligible in bulk sedimentary $\delta^{15}N$ values because of mass balance considerations (ALTABET 1988). Additionally, where surface water nitrate concentrations are high, food chains are relatively short (BIGGS, 1989).

Additionally, the fixation of dinitrogen into organic matter is charactarized by the near absence of isotopic fractionation, causing the nitrate thus produced to exhibit $\delta^{15}N$ values near 0‰ (HOERING & FORD, 1960). This process may be important in oligotrophic waters, but does not likely influence the isotopic composition of nitrate in most regions of the ocean to a significant extent (CARPENTER, 1983).

A topic of much concern regarding the use of bulk $\delta^{15}N$ in paleoceanographic investigations is the retention of the signal produced in the euphotic zone during sinking of particles to the sediments and their subsequent burial. Remineralization has been surmised to cause a constant offset of about 5‰ between surface-produced organic material and sediments in the Southern Ocean, but in the equatorial Pacific, little diagenetic alteration of the signal produced in the euphotic zone was observed (ALTABET & FRANCOIS, 1994). More recently, FRANCOIS et al. (1996) suggested applying a correction of 3 to 4‰ to sediments to compensate for the alteration due to bacterial degradation. In any case, the findings of these authors suggest that where differences between the surface-generated signal and sediments exist, the offset appears to be relatively constant within geographic regions.

The proportion of terrestrially-derived organic matter present in the sediments may significantly affect its $\delta^{15}N$ signal. $^{15}N/^{14}N$ ratios in sediments have been used to trace the origin of sedimentary nitrogen in areas where the isotopic composition of the terrigenous material was substantially depleted in ^{15}N relative to marine-derived matter (SWEENEY & KAPLAN, 1980; WADA et al., 1987). Clear evidence for the mixing of a marine with a terrestrial $\delta^{15}N$ end member is not always the case, however, due either to the masking of such a trend by processes occurring in the water column (OWENS, 1985) or to the wide range of $\delta^{15}N$ values measured in terrestrial systems (SWEENEY, et al., 1978).

Because so many factors may potentially influence the $\delta^{15}N$ signal of bulk sedimentary matter, it is important to determine the main processes governing the isotopic composition of particles sinking to the deep sea in a given area. One goal of this work was, therefore, to investigate the nitrogen dynamics in the Angola and Cape Basins and evaluate the origin of the isotopic signal measured in sinking particles and surface sediments. The first manuscript of the dissertation (section 3.1) deals with temporal variations in $\delta^{15}N$ values of sinking particles. The second two papers (sections 3.2 and 3.3) address spatial changes in surface sedimentary isotopic values and how these relate to euphotic zone processes. Another question which is addressed in the first three manuscripts (sections 3.1 - 3.3) is how remineralization affects the $\delta^{15}N$ of sediments in this area. The third main aim of this dissertation was to evaluate past changes in the biogeochemistry of the upper ocean in this paleoceanographically significant region. The final manuscript (section 3.4) concerns itself with interpretation of Late Quaternary $\delta^{15}N$ variations with regard to this last objective.

2.2 Materials and Methods

In order to achieve the first two goals mentioned above, $\delta^{15}N$ values of sinking particles and surface sediments were measured and compared with several other previously measured parameters of the same samples as well as with surface ocean nitrate concentrations. Samples of sinking particles were collected during a sediment trap experiment (WR-2) at the Walvis Ridge (20°06'S, 09°11'E) approximately 400 km offshore. The water depth was 2196 m and the trap mooring was located 599 m below the water surface. The cone-shaped sediment trap consisted of 20 cup collectors and a collection area, with a grid fitted to the top, of 0.5 m^2 (SMT 230; Salzgitter Electronics, Kiel) and was deployed from 18 March 1989 to 13 March 1990. Samples were preserved with a 1 ml saturated solution of $HgCl_2$ in 100 ml seawater (FISCHER & WEFER, 1991). NaCl was also added to the cups to increase the salinity by 3‰ relative to the surrounding seawater. After recovery of the trap samples, 0.5 ml of concentrated $HgCl_2$ solution was added per 100 ml trap solution. Surface sediment samples from the Angola Basin were obtained during "METEOR" cruise 6/6 (WEFER et al., 1988). Cape Basin surface sediments were retrieved during "METEOR" cruises 6/6 and 20/2 (WEFER et al., 1988; WEFER et al., 1992). All surface sediments were collected using a box corer (50 x 50 cm surface area) and subsamples were taken immediately after core retrieval using plastic syringes which were sealed with electrical tape and stored at 4°C until further processing. Surface sediments were taken in a total of seven transects - three in the Angola Basin (6°S, 12°S and 17°S) and four in the Cape Basin (19°S - 23°S, ~ 23°S, ~ 26°S - 28°S and around 29°S - 30°S). Samples were freeze-dried and homogenized in an agate mortar in a shore-based laboratory, then stored in plastic containers until nitrogen isotope analysis.

To address the third goal of investigating changes in the biogeochemical processes occurring in the surface ocean during the Late Quaternary, $\delta^{15}N$ in two gravity cores from the Angola Basin were measured. These cores (GeoB 1008-3 and GeoB 1016-3) were retrieved during "METEOR" cruise 6/6 (WEFER et al., 1988). GeoB 1008-3 was located at 6°35'S, 10°19'E at 3124 m water depth and GeoB 1016-3 at 11°46'S, 11°41'E and 3411 m water depth. Subsamples were taken every 5 cm and otherwise treated as described for surface sediment samples.

For nitrogen isotopic analyses, fractions of sediment trap samples (see FISCHER & WEFER, 1991 for details regarding splitting procedures) were filtered onto precombusted GF/F filters. After filtration, the samples were dried in a drying oven at 50°C overnight. The dried filters were folded into tin boats and analyzed using the following procedures described for sediment samples.

In preparation for simultaneous measurement of $\delta^{13}C$ and $\delta^{15}N$, sediment samples were decalcified with 1M HCl prior to isotopic analysis. To determine whether the decalcification process had any effect on the measured nitrogen isotopic signal of sediments, $\delta^{15}N$ in sediment samples from a tidal flat in the North Sea (WST 2) with varying amounts of $CaCO_3$ added were analyzed. No isotopic difference could be detected between samples which were decalcified and those which were not. Decalcified sediment samples (25-150 mg) were reground with copper oxide (50% of the sample weight) to facilitate combustion. The sediment/CuO mixture was placed into tin boats and pressed into small cylinders (7 x 4 mm).

A Finnigan MAT 252 mass spectrometer equipped with a trapping box was used to measure $\delta^{15}N$ in sediment and sediment trap samples. This automated system was described by FRY et al. (1992). Samples are dropped from a carousel into the combustion tube of a Hereaus oven. The combustion tube is filled with Ce-IV-oxide and maintained at 1050°C. Helium is used as the carrier gas and is doped with O_2 during sample combustion, resulting in flash combustion of the sample at around 1800°C. The gases thus produced flow through a second column filled with copper wire, kept at 600°C. Nitrogen oxides are reduced to N_2 and excess O_2 is scavenged by reaction with the elemental copper, forming CuO. In the necks of both the combustion and reduction tubes, silver wool was placed to scavenge halides. After reduction, the gases pass through a tube containing Sicapent and $MgCl_2$ in order to remove water. The stream of helium then sweeps the remaining gases into the trapping box, which consists of three liquid nitrogen traps maintained at different temperatures - the first two for collecting H_2O and CO_2 and the third, filled with Alltech 5-Å zeolite, to trap N_2. The purified N_2 gas is then measured manometrically and transferred to a small-volume cold finger and the isotopic composition relative to a standard gas (99.996% pure tank N_2) is measured.

Because a nitrogen blank (< 0.65 µmol N) was always present in the N_2 gas produced after sample combustion, reduction and purification, the isotopic value for each sample was corrected for this blank. Samples were corrected according to the following formula presented by FRY et al. (1992):

$$\delta_T = (\delta_S * m_S - \delta_B * m_B) / (m_S - m_B)$$

where δ_T is the blank-corrected true value of the sample, δ_S and δ_B are the isotopic compositions of samples and blanks, respectively, and m_S and m_B are the masses measured manometrically with the trapping box of samples and blanks. The isotopic composition of the blank could be determined from the slope of a line and the Y intercept (= to δ_T) obtained by plotting observed isotope values of a sample versus the inverse of the measured sample size. This slope is equal to $(\delta_B - \delta_T)m_B$.

Several different standards were measured to control the qualitiy of the isotopic measurements. The laboratory working standards were WST (Watt Standard) 1, 2 and 3 from a North Sea tidal flat. At least one WST standard was measured per five samples. The WST standards had the following $\delta^{15}N$ values: WST 1: 7.93 ± 0.3‰; WST 2: 6.67 ± 0.2‰ and WST 3: 7.90 ± 0.2‰. Additionally, IAEA N-1 and IAEA N-2 standards from the International Atomic Energy Agency (Vienna, Austria) were measured frequently. IAEA N-3 was not used as a reference standard due to the relatively high isotopic variability (3.81 ± 0.5‰) observed during the present work and the large range reported in NIST (1993) of +2 to +5‰. Values given in the literature for IAEA N-1 are +0.35 to +0.45‰ and for IAEA N-2 values of +20.18 to +20.35‰ have been reported (BÖHLKE et al., 1993; GONFIANTINI, 1984; KENDALL and GRIM, 1990). The mean value for IAEA N-1 measured in this study was 0.44 ± 0.3‰ and for IAEA N-2 was +20.42 ± 0.2‰. Peptone (Merck chemicals) was also used as an isotopic standard and had a $\delta^{15}N$ value of 5.72 ± 0.2‰.

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3.1

SEASONAL VARIABILITY OF $\delta^{15}N$ IN SINKING PARTICLES IN THE SOUTHEAST ATLANTIC OCEAN

(submitted to Deep-Sea Research)

Seasonal Variability of $\delta^{15}N$ in Sinking Particles in the Southeast Atlantic Ocean

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ABSTRACT

Results from a sediment trap study in the Benguela upwelling regime off southwest Africa indicate that temporal changes in $\delta^{15}N$ values of sinking particles collected with a sediment trap reflect variations in the input of inorganic nitrogen to the surface water. $\delta^{15}N$ was correlated with sea surface temperatures derived from U^{k}_{37} index. Decreases in $\delta^{15}N$ (to as low as 2.9‰) corresponded to low SST during austral spring and late autumn/early winter, indicating increased nitrate availability due to the presence of recently upwelled water. High particulate organic carbon fluxes accompanied the low $\delta^{15}N$ and SST values, reflecting increased productivity fueled by the upwelled nutrients. The observed $\delta^{15}N$ pattern does not appear to have been caused by variations in the species composition of the phytoplankton assemblage. Changes in the degree of nitrate utilization in surface water were calculated from $\delta^{15}N$ of the sinking particulate nitrogen. The surface nitrate pool was relatively more depleted during late summer and early fall (when ~ 80% of the original nitrate may have been utilized) and much less depleted during the spring bloom, when only 40% of the original nitrate was taken up. The average absolute nitrate concentration in surface water during the one year sample collection period was estimated to have been 3.4 µM from sinking particulate $\delta^{15}N$ and the relationship between surface sediment $\delta^{15}N$ and surface $[NO_3^-]$. This value compares well with the historically averaged surface nitrate concentration for this area of 3.7 µM.

INTRODUCTION

The degree of nutrient utilization in surface waters of the ocean has important implications for primary productivity and CO_2 dynamics in the euphotic zone. Better understanding of seasonal changes in nutrient utilization in productive regions of the ocean will be helpful in evaluating the contribution of such areas to the global carbon inventory. The $\delta^{15}N$ signal of particles sinking out of the euphotic zone can be useful in assessing such variations in nutrient utilization because fractionation of stable nitrogen isotopes during photosynthesis depends largely on the availability of dissolved inorganic nitrogen (DIN) (WADA, 1980; ALTABET ET AL., 1991). Nitrate is believed to be the limiting nutrient for phytoplankton growth in the Benguela region (CHAPMAN & SHANNON, 1985 and references therein). Nitrate upwelled from oxygenated waters of the deep sea has a nitrogen isotopic signature of around 5 - 6‰ (WADA ET AL., 1975). When nitrate in the euphotic zone is abundant, the $\delta^{15}N$ of the plankton is low relative to the $\delta^{15}N$ of the nitrate due to the preferential uptake of nitrate containing ^{14}N (WADA & HATTORI, 1978). As nitrate is consumed, the residual nitrate becomes progressively enriched in ^{15}N. Phytoplankton $\delta^{15}N$ also increases as it takes up this residual nitrate. It has been shown that the $\delta^{15}N$ composition of particulate organic matter (POM) mirrors nitrate concentrations in surface water over the course of a phytoplankton bloom with high nitrate concentrations corresponding to low $\delta^{15}N_{POM}$ and vice versa (NAKATSUKA, ET AL., 1992). ALTABET & MCCARTHY (1985) and VOß ET AL. (in press) also noted an inverse relationship between photic zone nutrient concentrations and $\delta^{15}N$ of suspended and sinking particles.

The purpose of the present paper is to show that the $\delta^{15}N$ signal of particles sinking out of the euphotic zone in the Benguela region is controlled by changes in surface water nitrate levels and is correlated with productivity variations. We will also present evidence that $\delta^{15}N$ in sinking particles may be useful in estimating the degree of utilization of nitrate in the euphotic zone.

STUDY AREA

The Benguela region is so named after the Benguela Current (BC), the eastern boundary current of the South Atlantic subtropical gyre which flows in a northwesterly direction off the southwest coast of Africa (Fig. 1). The BC diverges at near 28°S and the main branch, the Benguela Oceanic Current (BOC), continues to the northwest (PETERSON & STRAMMA, 1991). Part of the BC flows northward along the coast as the Benguela Coastal Current (BCC). The Benguela area is bounded in the north by the Walvis Ridge and extends southward to Cape Point at 34°S (NELSON & HUTCHINGS, 1983). Like most eastern boundary

systems, the Benguela is characterized by intense coastal upwelling. Southeasterly trade winds force surface water seaward (LUTJEHARMS & MEEUWIS, 1987) and relatively nutrient-rich (10 - 18 µM NO_3^-) South Atlantic Central Water (SACW) from 150-250 m depth comes to the surface off the coast (CALVERT & PRICE, 1971; JONES, 1971). This upwelling supports rates of productivity between 125 and 180 g C m^2 yr^{-1} (SHANNON ET AL., 1987). The true coastal upwelling area is 150-200 km wide, but a filamentous mixing zone extends further offshore, with filaments sometimes exceeding 1000 kilometers in length (LUTJEHARMS & MEEUWIS, 1987; LUTJEHARMS ET AL., 1991). Because seasonally variable winds are the driving force behind the upwelling in the Benguela, upwelling intensity and the offshore extension of upwelling filaments change seasonally. North of 31°S upwelling is perennial (SHANNON, 1985), but is most intense during austral spring and filaments extend farthest offshore during austral winter/spring (SCHELL, 1970; LUTJEHARMS & MEEUWIS, 1987).

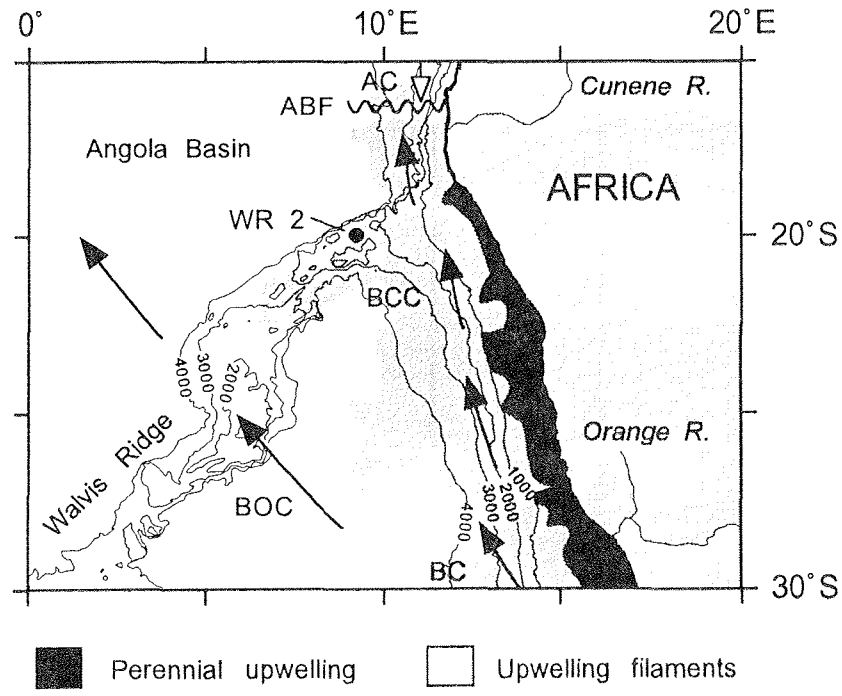

Fig. 1: Map of the study area off the southwest coast of Africa. The sediment trap mooring WR 2 is denoted by the filled circle. The location of perennial upwelling is shown by the darkly shaded area and the filamentous mixing zone is indicated by the lightly shaded region. The position of the upwelling filaments was redrawn from an infra-red satellite image (METEOSAT) taken in August 1984 and presented in LUTJEHARMS & STOCKTON (1987). Black arrows represent cool surface currents and white arrows indicate warm surface currents. Abbreviations are as follows: ABF: Angola-Benguela Front; AC: Angola Current; BC: Benguela Current; BCC: Benguela Coastal Current; BOC: Benguela Oceanic Current.

At the northern boundary of the Benguela system, the Angola-Benguela Front (ABF) separates warm, southward-flowing tropical water (Angola Current) from the cold BCC. The ABF extends 150-200 km offshore and down to 200 m water depth (SHANNON ET AL., 1987). The front migrates seasonally and interanually between 15°S and 17°S, depending on the wind field and the displacement of the Intertropical Convergence Zone (SHANNON, 1985; SHANNON ET AL., 1986, 1987; MEEUWIS & LUTJEHARMS, 1990). The ABF breaks down in the late summer, allowing warm, saline Angolan water to penetrate south as far as 20°S (BOYD ET AL., 1987).

METHODS

Twenty sediment trap samples (each representing 18 day intervals) were collected over a one year period from 18 March 1989 to 13 March 1990. The sediment trap mooring (WR 2) was located 400 km offshore over the Walvis Ridge at 20°02.8'S, 9°09.3'E (Fig. 1) where the water depth was 2196 m (WEFER & FISCHER, 1993). The cone-shaped trap (SMT 230; Salzgitter Electronics, Kiel) had a 0.5 m^2 collecting area and was attached to a moored array 599 m below the surface. The procedures for sample poisoning and processing were described by FISCHER & WEFER (1991). For $\delta^{15}N$ measurements, fractions of trap samples were filtered onto precombusted GF/F filters and dried in a drying oven at 50°C overnight. The dried filters were then placed in tin boats and combusted at 1050°C in a Hereaus Elemental Analyzer. $^{15}N/^{14}N$ ratios of the N_2 gas thus formed was measured using a Finnigan MAT 252 mass spectrometer with trapping box (FRY ET AL., 1992).

Isotopic data are presented in permil (‰) in terms of δ notation:

$$\delta^{15}N = [(^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{standard}) - 1] \times 10^3,$$

δ values are reported relative to atmospheric air. 99.996% pure tank N_2 was used as a laboratory working standard gas. The tank N_2 was calibrated against nitrogen in air and IAEA standards N-1 and N-2. The analytical precision for $\delta^{15}N$ measurements was $\leq$ 0.4‰.

WEFER & FISCHER (1993) and FISCHER & WEFER (in press) reported the fluxes of total particulate, organic carbon, carbonate, biogenic opal and lithogenic components of the WR 2 samples. Diatom and silicoflagellate fluxes were presented by TREPPKE ET AL. (in press). Based on concentrations of di- and tri-unsaturated C_{37} alkenones (U^k_{37} index; BRASSEL ET AL. 1986), sea surface temperatures were calculated from WR 2 samples (TREPPKE ET AL., in press) using the calibration derived by PRAHL ET AL. (1988).

RESULTS AND DISCUSSION

Flux rate variations

$\delta^{15}N$ values are listed in Table 1 along with C/N ratios and fluxes of total particulate, organic carbon, carbonate, biogenic opal and lithogenic components. The total particulate flux ranged from 12 to 384 mg m^{-2} day^{-1} and consisted mostly of biogenic components, especially carbonate (which was 63.3% of the total flux for the year). According to ČEPEK ET AL. (1994), most of the carbonate material derived from coccolithophorids. Organic carbon was the second most predominant component, contributing 10.4% to the total flux. Marine diatoms were the main contributors of opal (TREPPKE ET AL., in press), which was 8.3% of the total flux during the study period. Lithogenic material was present only in minor amounts and was 7.8% of the total flux.

Table 1: $\delta^{15}N$ (± 0.4), total particle, organic carbon, opal, $CaCO_3$ and lithogenic material fluxes and C/N ratios in samples from sediment trap WR-2 at 599 m depth over the Walvis Ridge. Flux data and C/N ratios are from WEFER & FISCHER (1993) and FISCHER & WEFER (in press).

Sample no.	Collection Time	$\delta^{15}N$ (‰)	C/N atom	Fluxes (mg $m^{-2}day^{-1}$)				
				Total	C_{org}	$CaCO_3$	Opal	Lithogenic
1	18.03.89-05.04.89	7.17	9.7	79.1	12.1	37.5	6.8	10.6
2	05.04.89-23.04.89	8.24	8.2	54.2	6.1	35.6	1.7	4.7
3	23.04.89-11.05.89	8.13	7.7	68.7	5.4	56.9	3.6	0.0
4	11.05.89-29.05.89	5.96	9.0	145.8	18.8	76.7	12.8	18.8
5	29.05.89-16.06.89	6.49	8.3	384.4	47.7	205.1	46.9	36.9
6	16.06.89-04.07.89	5.98	9.2	220.0	21.6	123.6	23.4	30.3
7	04.07.89-22.07.89	7.15	6.7	51.3	4.0	38.6	1.4	3.3
8	22.07.89-09.08.89	6.12	6.7	38.9	3.0	30.2	1.0	1.8
9	09.08.89-27.08.89	5.90	6.5	54.9	5.1	38.7	2.5	3.5
10	27.08.89-14.09.89	6.31	6.8	108.0	9.8	78.9	5.4	4.1
11	14.09.89-02.10.89	4.53	6.8	99.8	7.4	80.2	7.3	0.0
12	02.10.89-20.10.89	4.87	7.4	245.1	21.6	159.2	30.0	12.7
13	20.10.89-07.11.89	5.09	7.5	312.0	38.5	180.9	36.7	17.5
14	07.11.89-25.11.89	3.59	8.1	284.2	30.2	162.0	21.9	40.0
15	25.11.89-13.12.89	2.86	6.9	184.4	14.5	140.2	9.6	5.6
16	13.12.89-31.12.89	3.66	6.9	105.6	9.1	78.2	4.9	4.3
17	31.12.89-18.01.90	5.05	7.1	63.1	5.2	48.0	1.7	3.0
18	18.01.90-05.02.90	6.03	8.1	100.7	8.8	75.8	2.6	4.7
19	05.02.90-23.02.90	7.46	8.6	60.4	7.2	38.1	1.7	6.2
20	23.02.90-13.03.90	8.07	6.5	12.0	1.5	8.6	0.2	0.1

In Figure 2, total flux rates and a 15-year average of the monthly meridional wind stress off Namibia (SERVAIN ET AL., 1985) are shown. Flux maxima were observed in late austral fall (June) and spring (October - November) and were preceded by wind stress maxima by several

weeks. The total flux maxima coincided with peaks in organic carbon, carbonate, opal and lithogenic fluxes (Table 1).

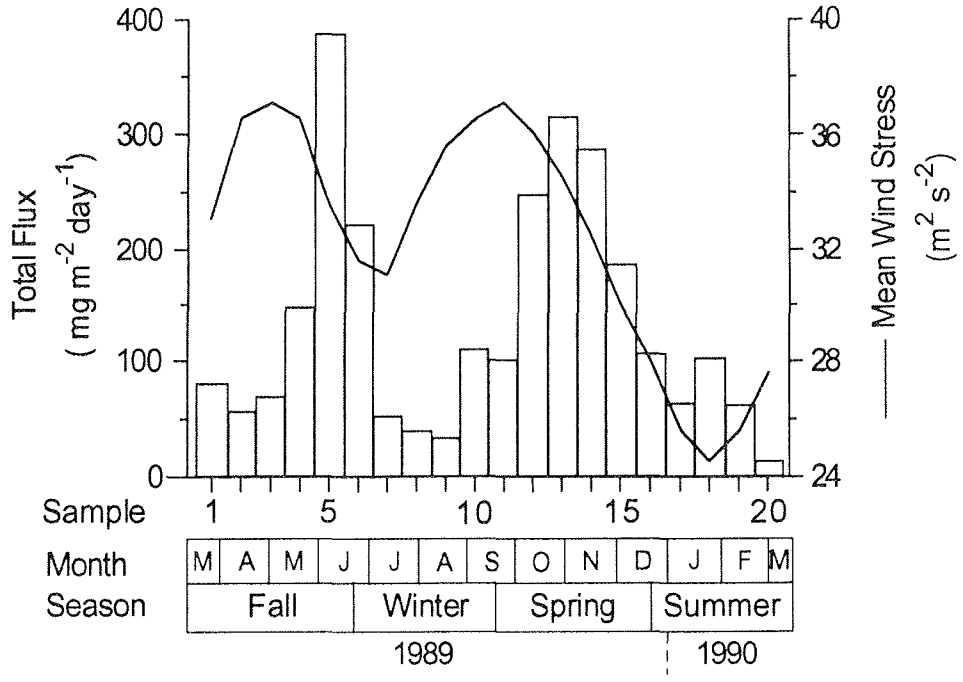

Fig. 2: Total flux in mg m^{-2} day^{-1} (WEFER & FISCHER, 1993; FISCHER & WEFER, in press) from March 1989 to February 1990 at site WR 2 at 599 m water depth. The line shows a 15-year average of the monthly meridional wind stress off Namibia (SERVAIN ET AL., 1985).

Seasonal changes in $\delta^{15}N$ and SST

Figure 3 shows the variations in the $\delta^{15}N$ signal of the sinking particulate matter along with SST calculated from concentrations of C_{37} alkenones. $\delta^{15}N$ ranged from 2.9 to 8.2‰. Highest values occurred in April and May at the same time that maximal SST (23.6°C) occurred. The high temperatures at this time and again during winter (July/August) indicate that recently upwelled water was not in the region near the trap, implying that dissolved inorganic nitrogen (DIN) concentrations in the euphotic zone were low. Therefore, the nitrate was quickly depleted and phytoplankton were forced to take up nitrate which was relatively enriched in ^{15}N, resulting in high $\delta^{15}N$ from March to April/May and low productivity as indicated by low flux rates. The 2‰ $\delta^{15}N$ decrease in late fall was accompanied by a temperature drop to values estimated to be as low as 17.3 to 17.7°C. Another SST decrease was observed during the major upwelling period in spring, when the lowest observed values (14.6 - 14.9°C) occurred. During approximately the same period, $\delta^{15}N$ decreased to its lowest measured value of 2.9‰. As seen in Figures 2 and 3, upwelling-favorable winds

peaked in fall and again in late winter/early spring, resulting in the seaward extension of upwelling filaments to the waters over the sediment trap mooring, as seen by the drops in SST which lagged the maxima in wind stress by a few weeks. The low temperatures in surface water indicate that cold, nutrient-rich water was upwelled to the surface and at these times, incorporation of the light isotope (^{14}N) was facilitated and the $\delta^{15}N$ of the particluate matter decreased with a concomitant increase in flux (late fall and spring). These peaks in flux show that the nutrient-rich water supported increased levels of primary productivity. Warm temperatures (20.8 - 21.9°C) and relatively stable $\delta^{15}N$ values (~6 to 7‰) characterized the winter months and during late spring and throughout the summer (December - March), $\delta^{15}N$ increased by 5.2‰ and temperatures rose to 21.3°C.

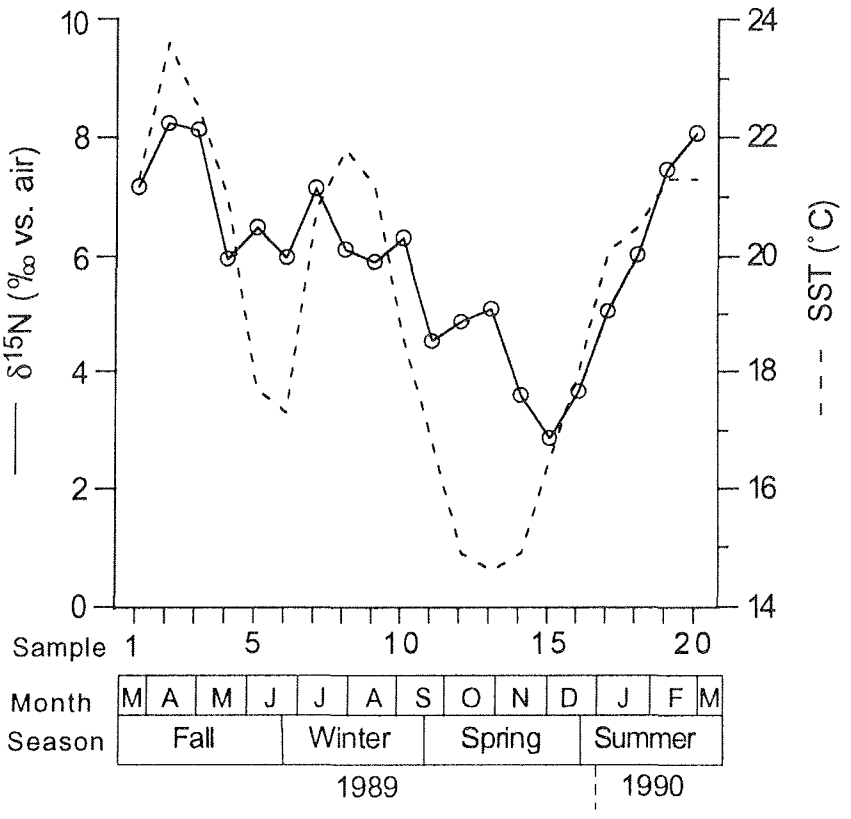

Fig. 3: $\delta^{15}N$ (‰) values (solid line) of particles sinking to 599 m from March 1989 to March 1990, compared with sea surface temperatures (dashed line) calculated from the same samples. SST was calculated from the U^{k}_{37} index (TREPPKE ET AL., in press) using the calibration derived by PRAHL ET AL. (1988): SST = U^{k}_{37} - 0.039) / 0.034.

The close correlation between $\delta^{15}N$ and SST seen in Figure 3 is confirmed by the regression between these two parameters shown in Figure 4. The significant r^2 of 0.59 (n=20) demonstrates the dependence of $\delta^{15}N$ in sinking particles in this part of the Benguela region on the input of nitrate into the photic zone. Low temperatures indicate the presence of

recently upwelled water with high nitrate concentrations which lead to relatively low $\delta^{15}N$ in organic matter produced at this time and high temperatures characterize water which has been at the surface for some time and is therefore depleted in nutrients, leading to an increase in phytoplankton $\delta^{15}N$.

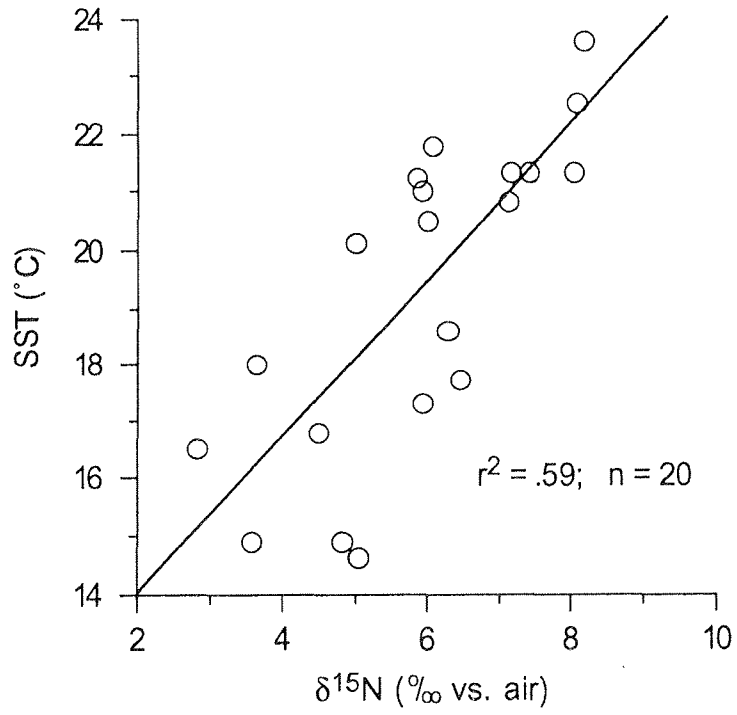

Fig. 4: $\delta^{15}N$ (‰) values of sinking particulate matter versus sea surface temperature. r^2 for the regression is .59 (n=20).

Seasonal variations in the composition of the flux

Although the correlation between $\delta^{15}N$ and SST and flux rates is strong evidence that $[NO_3^-]_{surface}$ is the most important control on $\delta^{15}N$ of sinking particles, we analyzed seasonal differences in the fluxes in order to determine whether changes in the bulk species composition of the material reaching the trap could have influenced the observed variations in $\delta^{15}N$. For example, a change in the species composition of the main phytoplankton from a carbonate producer to a siliceous species, could result in a change in the $\delta^{15}N$ of the produced organic matter because different species may fractionate nitrogen isotopes with varying efficiencies. A summary by MONTOYA (1994) of fractionation factors measured in laboratory cultures revealed, for instance, that diatoms tend to fractionate more strongly than other forms of plankton such as prymnesiophytes (e.g. coccolithophorids). In Figure 5 and Table 2, the particle flux components, divided into seasons are shown in order to compare how the relative contributions of carbonate, organic carbon, opal and lithogenic material varied during the year. Samples 1 - 5 were classified as fall, 6 - 10 as winter, 11 - 15 as spring

and 16 - 20 as summer. Subdividing the samples in this way separates high and low upwelling and productivity periods and facilitates comparison of the different production regimes. $CaCO_3$ was the dominant component of the material found in the trap samples all year (56.2% in the fall to 72.8% during summer). Organic carbon was the second most predominant constituent, ranging from 9.2% in the winter to 12.3% in the fall. Opal and lithogenic material made only minor contributions to the total flux (3.2% - 9.8% and 5.4% - 9.7%, respectively). Analysis of variance (ANOVA) detected no significant differences ($P \geq 99\%$) between seasons. For comparison, Table 2 also shows the seasonal variations of $\delta^{15}N$. An ANOVA confirmed that $\delta^{15}N$ values changed significantly from one season to another. The fact that the relative contributions of the different flux components did not change significantly from season to season, while $\delta^{15}N$ values did, is evidence that changes in the bulk composition of the particulate flux did not noticably affect $\delta^{15}N$ values of the particles.

Table 2: Seasonal variations of % fluxes ($CaCO_3$, organic carbon, opal and lithogenic matter), $\delta^{15}N$ and C/N ratios. Samples were grouped into seasons as follows: fall: samples 1 - 5; winter: samples 6 - 11; spring: samples 12-16; summer: samples 17 - 20.

Season	$CaCO_3$ (%)	C_{org} (%)	opal (%)	lithogenic matter (%)	$\delta^{15}N$ (‰)	C/N atom
fall	56.2	12.3	9.8	9.7	7.20 (± 0.9)	8.6 (± 0.8)
winter	65.5	9.2	7.1	9.1	6.29 (± 0.8)	7.1 (± 0.5)
spring	64.2	9.3	9.4	6.7	4.19 (± 0.8)	7.3 (± 0.9)
summer	72.8	9.3	3.2	5.4	6.05 (± 1.2)	7.6 (± 0.7)

Analyses of species-specific biomarkers further assumption our conclusion that changes in the bulk composition of the sinking particles were not the cause of the $\delta^{15}N$ variations. The fluxes of individual biomarkers representing three phytoplankton groups (dinoflagellates, coccolithophorids and diatoms) do not exhibit changes over the period studied which could explain the $\delta^{15}N$ fluctuations (N. Andersen, unpubl. data). Since neither the proportions of each bulk component nor the species-specific composition changed substantially, we conclude that variations in the make up of the flux did not cause the measured $\delta^{15}N$ fluctuations.

Changes in the amount of terrestrial material in particles sinking to the trap could also affect $\delta^{15}N$ of these particles. In some areas, terrestrially derived organic matter, has been shown to be depleted in ^{15}N relative to that of marine origin (SWEENEY & KAPLAN, 1980; WADA ET AL., 1987) although in other regions, terrigenous material shows no clear divergence from typical marine values (HOLMES ET AL., 1996). C/N ratios of the sinking material provide evidence that varying input of terrestrial organic material did not lead to the changes in the nitrogen isotopic composition of the samples. C/N ratios of our samples averaged 7.6 (±1.0) for the whole year and did not change much from season to season (Table 2), with samples

from winter months exhibiting the lowest values (7.2) and from fall the highest (8.6). An ANOVA detected no significant differences in C/N ratios of different seasons. Low concentrations of lithogenic material in the trap samples and low C/N ratios indicate that the organic matter was predominantly of marine origin. The relative uniformity of the proportion of lithogenic matter and C/N ratios implies that the proportion of terrestrial material reaching the trap did not change significantly for the duration of the trap deployment.

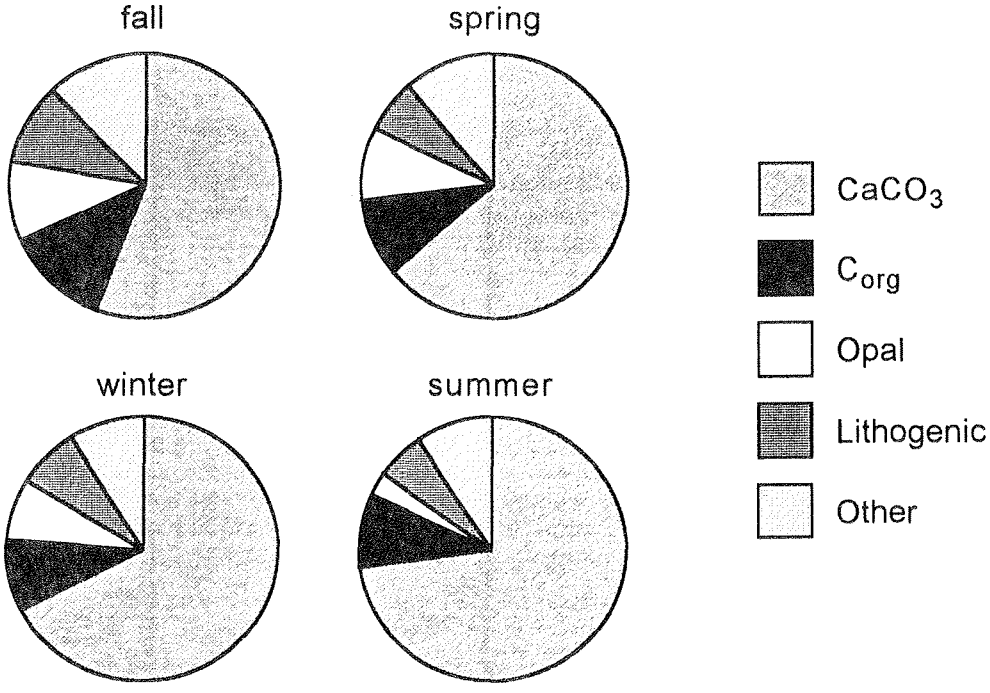

Fig. 5: % contribution of different components to the total flux. Samples were divided into seasons as follows: fall: samples 1 - 5; winter: samples 6 - 10; spring: samples 11 - 15; summer: samples 16 - 20.

Diagenetic alteration

HOLMES ET AL. (submitted manuscript) found that surface sediments underlying the sediment trap exhibited a $\delta^{15}N$ value of 7.06‰. The nitrogen flux-weighted mean $\delta^{15}N$ of the trap samples was 5.47‰, yielding a difference between sinking particles at 599 m and sediment of +1.59‰. The most likely explanation for the discrepancy between sinking particles and surface sediment $\delta^{15}N$ is bacterial remineralization of the organic material sinking to the seafloor. SAINO & HATTORI (1980) and ALTABET & MCCARTHY (1985) suggested that remineralization of organic matter in sinking particles resulted in an enrichment in ^{15}N of the residual organic matter. The difference we measured between sinking particles and surface sedimentary $\delta^{15}N$ is much smaller than the diagenetic enrichment of +5 to +7‰ in core top $\delta^{15}N$ relative to sinking particles in the southern ocean which was recognized by FRANCOIS ET

AL. (1992). ALTABET & FRANCOIS (1994) also found that sediments from south of the Polar Front in the Southern Ocean were about 5‰ more positive than the surface-generated isotopic signal. However, the latter authors also demonstrated that there was little diagenetic offset between sinking particles at 150 m and core top sediments in the equatorial Pacific and suggested that the difference in preservation of the isotopic signal between the two regions may be explained by the high opal content in the Southern Ocean sediments in which organic matrices with high $\delta^{15}N$ may be bound. The low opal content of surface sediments of the Benguela region (<6%; P.J. Müller, unpubl. data) may explain the small $\delta^{15}N$ offset between sedimentary nitrogen and particles sinking at 599 m.

Estimation of nitrate utilization in surface waters

An important use of stable nitrogen isotopic ratios is the hindcasting of the degree of nitrate utilization in surface waters at the time the organic matter was produced. The applicability of this tool in paleoceanographic studies has been shown repeatedly (CALVERT ET AL., 1992; FARRELL ET AL., 1995; GANESHRAM ET AL., 1995; NAKATSUKA ET AL., 1995). To determine seasonal changes in the fraction of unutilized nitrate in surface waters (f) at the Walvis Ridge, we used the equations of ALTABET & FRANCOIS (1994):

(1) $\delta^{15}NO_3^-{}_{(f)} = \delta^{15}NO_3^-{}_{(f=1)} - \varepsilon_u \times \ln(f)$

(2) $\delta^{15}N\text{-}PN_{(f)} = \delta^{15}NO_3^-{}_{(f)} - \varepsilon_u$ (instantaneous product)

$\delta^{15}N\text{-}PN_{(f)}$ is the measured $\delta^{15}N$ value of the particulate nitrogen, $\delta^{15}NO_3^-{}_{(f)}$ is the $\delta^{15}N$ value estimated for surface nitrate after some degree of depletion, $\delta^{15}NO_3^-{}_{(f=1)}$ is the $\delta^{15}N$ value of the original nitrate pool prior to any biological utilization and ε_u is the fractionation factor associated with nitrate uptake. ε_u was estimated as 5.42‰ for the northern part of the Benguela region by HOLMES ET AL. (submitted manuscript) from a plot of ln $[NO_3^-]$ (objectively analyzed one-degree latitude-longitude mean fields from World Ocean Atlas data set; CONKRIGHT ET AL., 1994) versus surface sediment $\delta^{15}N$ (Fig. 6). The resulting equation was:

Sedimentary $\delta^{15}N = -5.42 * \ln [NO_3^-] + 13.98$

According to ALTABET & FRANCOIS (1994), the slope of the linear regression between these two parameters is equivalent to ε_u. Since this ε_u is based on sedimentary $\delta^{15}N$ values, it represents an average fractionation factor for the past few to several hundred years.

The instantaneous product equation describes the region off the southwest coast of Africa better than the equation given by ALTABET & FRANCOIS (1994) for an accumulated product. As explained by HOLMES ET AL. (1996 and submitted manuscript), $\delta^{15}N$ of organic matter

produced in the photic zone in this region reflects spatial variations of surface nitrate concentrations, not temporal changes, since upwelled water at the coast flows seaward, becoming progressively more depleted in NO_3^-.

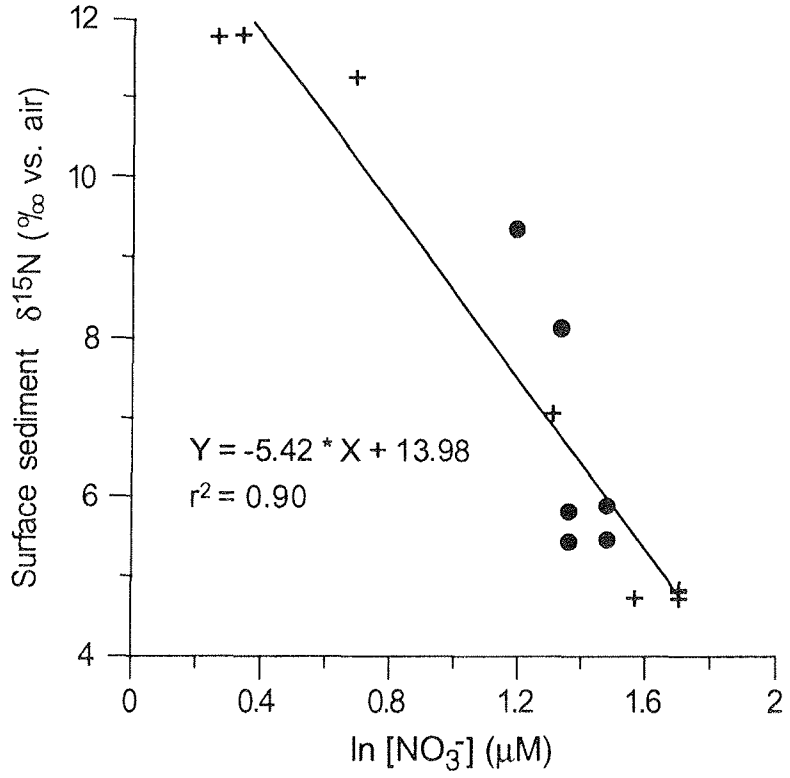

Fig. 6: $\delta^{15}N$ (‰) values of bulk surface sediments versus ln $[NO_3^-]$ (µM) from the northern part of the Benguela (19°2'S to 23°4'S) from HOLMES ET AL. (submitted manuscript). ε_u used in the present study was obtained from the slope of the regression line (5.42‰).

Table 3 shows the values for $\delta^{15}NO_3^-{}_{(f)}$ calculated from equation (2) and for f calculated from equation (1) above, with ε_u = 5.42‰ and $\delta^{15}NO_3^-{}_{(f=1)}$ = 5.5‰. f ranged from .60 to .22, indicating that between 40% and 78% of the original upwelled nitrate had been utilized. As seen in Fig. 7, f was lowest during the fall, when SST was high and input of new nitrogen to the surface water was probably low. f increased between late fall and spring, corresponding to the two upwelling events (low SST and high flux rates), and then decreased throughout the summer as SST increased and nutrients in the surface water were presumably utilized. A satellite image from LUTJEHARMS & MEEUWIS (1987) showed that upwelling filaments were not detected near the trap position during February 1984, supporting our interpretation of $\delta^{15}N$ and f variations.

Sample	$\delta^{15}NO_3^-{}_{(f)}$ (‰)	f	$[NO_3^-]$ (µM)
1	12.59	0.27	2.6
2	13.66	0.22	2.2
3	13.55	0.23	2.2
4	11.38	0.34	3.3
5	11.91	0.31	3.0
6	11.40	0.34	3.3
7	12.57	0.27	2.7
8	11.54	0.33	3.2
9	11.32	0.34	3.3
10	11.73	0.32	3.1
11	9.95	0.44	4.3
12	10.29	0.41	4.0
13	10.51	0.40	3.8
14	9.01	0.52	5.1
15	8.28	0.60	5.8
16	9.08	0.52	5.0
17	10.47	0.40	3.9
18	11.45	0.33	3.2
19	12.88	0.26	2.5
20	13.49	0.23	2.2

Table 3: $\delta^{15}NO_3^-{}_{(f)}$ and f (the fraction of unutilized nitrate remaining in surface water) calculated from equations (1) and (2) of ALTABET & FRANCOIS (1994) using $\delta^{15}N$ of sinking particles and ε_u = 5.42‰. Also shown is $[NO_3^-]$ which was estimated from the calculated f and the equation ln $[NO_3^-] = (\delta^{15}N_{PN} - 12.38) / 5.42$ (see text for explanation).

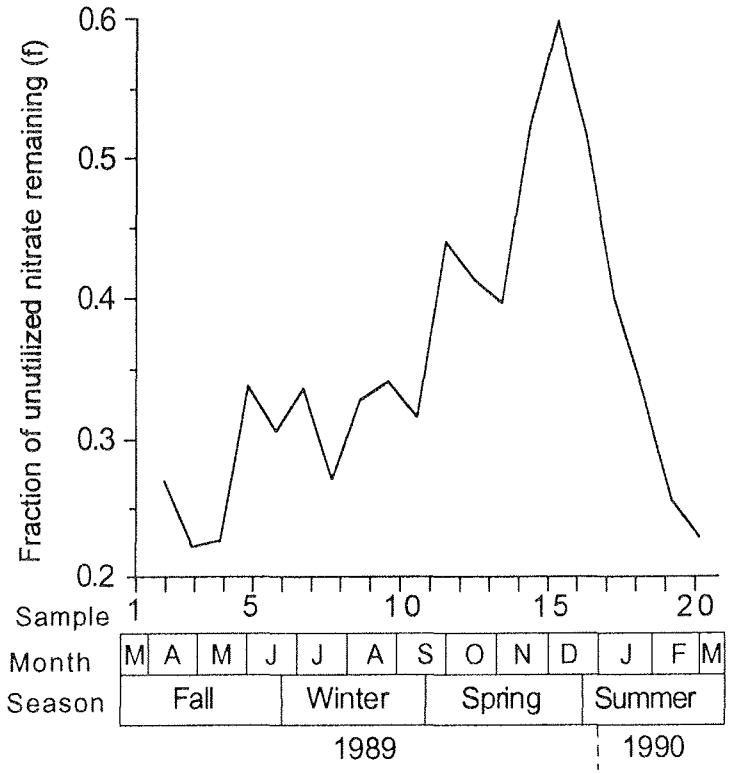

Fig. 7: f (fraction of unutilized nitrate remaining in surface water) calculated from $\delta^{15}N$ of the sinking particles using equations (1) and (2) (instantaneous product) from ALTABET & FRANCOIS (1994).

Quantitative estimation of [NO_3^-]

We attempted to estimate surface water [NO_3^-] by substituting our trap sample $\delta^{15}N$ into the equation of the linear regression of surface sediment $\delta^{15}N$ and surface water nitrate concentrations discussed above. To account for diagenetic affects on the $\delta^{15}N$ signal which may have occurred between 599 m and the sediment surface at 2196 m, we subtracted the difference between sedimentary $\delta^{15}N$ and the nitrogen flux-weighted mean $\delta^{15}N$ of the trap samples (1.59‰) from the Y intercept. Thus, the equation used to determine $[NO_3^-]_{surface}$ was:

$$\ln [NO_3^-] = (\delta^{15}N_{PN} - 12.38) / -5.42.$$

Nitrate concentrations calculated in this way are shown in Table 3. In using this equation, we assume that the amount of nitrate in the upwelled water did not change throughout the year. We have no means to verify this assumption, but the source of upwelled water in this area is South Atlantic Central Water (SACW), which contains 10 - 18 µM NO_3^- (CALVERT & PRICE, 1971; JONES, 1971) and there is no evidence that large changes in [NO_3^-] of SACW occur or that water from some other source is upwelled at different times of year. According to our estimation, $[NO_3^-]_{surface}$ ranged from 2.2 to 5.8 µM. Because the magnitude of the diagenetic alteration of the $\delta^{15}N$ signal in the water column is not known, nitrate concentrations can perhaps not reliably be estimated quantitatively as we have done here. However, the average $[NO_3^-]_{surface}$ from March 1989 to February 1990 derived from our calculations is 3.4 µM, which agrees well with the historically averaged value for $[NO_3^-]_{surface}$ at this location of 3.7 µM obtained from the World Ocean Atlas data bank of surface nitrate concentrations (CONKRIGHT ET AL., 1994). Additionally, calculation from our estimated $[NO_3^-]_{surface}$ and f of [NO_3^-] in the upwelled water yields a value of about 10 µM NO_3^-, which is within the range reported for SACW.

CONCLUSIONS

We have attempted to show that stable nitrogen isotope ratios in sinking particles at the Walvis Ridge in the Benguela system are controlled mainly by changes in nitrate concentrations in the overlying surface water. In this area, the seaward extension of upwelling filaments, which occurred twice during the year-long deployment of the sediment trap, brings nutrient-rich water to the euphotic zone and leads to elevated productivity and relatively lower $\delta^{15}N$ values of the particulate nitrogen. We calculated changes in the degree of nitrate utilization and nitrate concentrations from $\delta^{15}N$ values of the sinking particles and the latter agree well with historically averaged nitrate concentrations of surface waters in this area. Our

study demonstrates the potential of stable nitrogen isotopes as a proxy for surface nitrate utilization and attests to the usefulness of $\delta^{15}N$ for paleoceanographic studies.

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3.2

STABLE NITROGEN ISOTOPES IN ANGOLA BASIN SURFACE SEDIMENTS

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Stable Nitrogen Isotopes in Angola Basin Surface Sediments

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ABSTRACT

Sedimentary $\delta^{15}N$ contains a record of biogeochemical processes occurring in the water column. Stable nitrogen isotopes were measured in the bulk sedimentary matter of 18 surface sediment samples collected in three transects in the eastern Angola Basin, perpendicular to the coast, at 6°S, 12°S and 17°S and two samples from the Zaire estuary. Relative enrichment in ^{15}N in sediments with distance from the coast was seen in each of the three transects off northern, middle and southern Angola. Values in the Zaire Fan (northern Angola) and southern Angola increased by 1.9‰ and 1.6‰, respectively, from shallow (~100m) to deep (~4500m) water sediments and in middle Angola by 2.5‰ (water depth range 73 - 3809 m). We propose that in the Angola region the degree of fractionation of nitrogen isotopes in organic matter is a function of nutrient supply to sunlit waters. The shift towards lighter isotopic values in shallow water signifies that the larger nitrate pool is not utilized as extensively as in water farther away from the coastal upwelling centers. Southern Angola sediments were more than 1‰ lower (average $\delta^{15}N$, 5.4‰) than the middle and northern transects (average $\delta^{15}N$, 7.2‰ and 6.5‰, respectively). This difference is attributed to higher nitrate concentrations in the surface water at 17°S, for which there are two reasons. One is that these sediments are located south of the Angola/Benguela front at ~16°S which demarcates the convergence of warm equatorial water with cold, nutrient-rich Benguela Current water. The second cause is the intense Namibic coastal upwelling zone extending northward up to the front. Comparisons of bulk $\delta^{15}N$ with $\delta^{13}C_{org}$ and C/N ratios show that the observed sedimentary $\delta^{15}N$ variations with water depth are due neither to water column

diagenesis nor to mixing of terrestrial material with marine-derived organic matter. The two estuary sediment samples were mainly terrigenous in origin, based on $\delta^{13}C_{org}$ and C/N ratios. $\delta^{15}N$ values of these two samples were 7.0‰ and 7.6‰.

INTRODUCTION

Changes in the biogeochemistry of the water column have been shown to be recorded by the nitrogen isotopic composition of organic matter in marine sediments (RAU ET AL., 1987; FRANCOIS ET AL., 1992; ALTABET & FRANCOIS, 1994). The $\delta^{15}N$ signal contained in organic matter in the sediments is produced in the surface water during primary production when phytoplankton takes up dissolved inorganic nitrogen (DIN). In a process equivalent to fractional distillation, nitrate (or ammonium) containing the lighter isotope is preferentially taken up by phytoplankton and the remaining DIN pool becomes progressively enriched in the heavy isotope as photosynthesis continues. Thus, one of the most important controls on the $\delta^{15}N$ of suspended organic matter is the concentration of DIN in the photic zone and the degree to which this reservoir is utilized (MARIOTTI ET AL., 1982; VOß ET AL., in press). Several researchers have demonstrated an inverse relationship between $\delta^{15}N$ of suspended and sinking particles and photic zone nutrient concentrations (ALTABET & MCCARTHY, 1985; MONTOYA ET AL., 1991; VOß, 1991). The isotopic composition of the inorganic source material for photosynthesis (nitrate or ammonium) also influences the $\delta^{15}N$ of the organic material which sinks to the sea floor. The $\delta^{15}N$ of nitrate from oxygenated water in the deep sea is around 5 - 6‰ (WADA ET AL., 1975). However, denitrification can locally alter the $\delta^{15}N$ of residual nitrate by several parts permil. In the Eastern Tropical North Pacific Ocean, for instance, CLINE & KAPLAN (1975) measured nitrate in a denitrification zone with values of up to +18.8‰, showing that denitrifiying bacteria preferentially utilize the lighter isotope.

We investigated surface sediment $\delta^{15}N$ in the eastern Angola Basin, comparing results to variations in surface nutrient concentrations. The aim of the study was to elucidate the major influences on sedimentary $\delta^{15}N$ in the Angola Basin and use $\delta^{15}N$ in sediments to gauge spatial variations in surface water nutrient utilization. An important application of $\delta^{15}N$ is the hindcasting of surface nitrate concentrations from bulk marine sediment. ALTABET & FRANCOIS (1994) presented equations for doing this. We applied these equations to our surface sediment $\delta^{15}N$ to determine how well they hindcast surface $[NO_3^-]$ in the Angola Basin. We also evaluated the relative importance of denitrification, degradation of sedimented organic matter and terrigenous input. By demonstrating the link between water column conditions and sedimentary $\delta^{15}N$, we show that this parameter can be useful in interpreting paleoenvironmental changes from sediment cores in this area.

Study Area

The Angola Basin is a highly productive region, with carbon fixation rates of 90 to 125 g C m^{-2} yr^{-1} north of 8°S and 125 to 180 g C m^{-2} yr^{-1} from 8°S to 18° S (BERGER ET AL., 1987; BERGER, 1989). Figure 1 shows the hydrography of the basin. The northward flowing surficial Benguela Current (BC) splits into two parts at around 20°S, with the northwest flowing current being referred to as the Benguela Oceanic Current (BOC). The water flowing northward along the coast is known as the Benguela Coastal Current (BCC). South and southeast Trade Winds cause cold, nutrient-rich water from around 200 m depth to be brought to the surface, resulting in high nearshore nutrient concentrations. This water is entrained into the BCC between 34°S and 15°S (HART & CURRIE, 1960; CALVERT & PRICE, 1971). The South Equatorial Counter-Current (SECC) carries warm water from the north at subsurface depths to around 10°S where the SECC reaches the surface and splits into the southward flowing Angola Current (AC) and a northward branch which mixes with the BCC. This water then combines with water from the Zaire River and continues northwestward as the South Equatorial Current (SEC). The Equatorial Undercurrent also introduces warm water to the Angola Basin in the form of subsurface (50-100m), eastward flowing water which splits into northward and southward branches at the coast. In addition to the coastal upwelling between 15° and 20°S, seasonal upwelling occurs around the Zaire River mouth (VAN BENNEKOM & BERGER, 1984), which also leads to higher nutrient concentrations nearshore relative to farther offshore.

A convergence zone marks the boundary between the southward flowing, tropical/equatorial water of the Angola Current and the northward flowing, high latitude water of the Benguela Current. HART & CURRIE (1960) measured a sea surface temperature decrease of 7.5°C going from north to south over the front, which is known as the Angola/Benguela Front (ABF). This frontal system extends to 150 - 200 km offshore and down to 200 m water depth and is particularly well defined in the upper 50 m (SHANNON ET AL., 1987). These authors also noted weaker stratification and a deeper mixed layer south of 16°S relative to north of the front. The location of the ABF shifts between about 15°S during austral spring and 17°S in austral autumn (MEEUWIS & LUTJEHARMS, 1990).

River runoff, with its associated nutrients and suspended matter, is an important feature of the Angola Basin. JANSEN ET AL. (1984) found evidence that the Zaire river plume extends as far out to sea as 800 km from the river mouth. Average discharge from the Zaire River is 1450 x 10^9 m^3 yr^{-1}, making it the world's second largest river. Discharge from the Cunene River is erratic and mean run-off is estimated by CHAPMAN & SHANNON (1985) at 5.2 x 10^9 m^3 yr^{-1}.

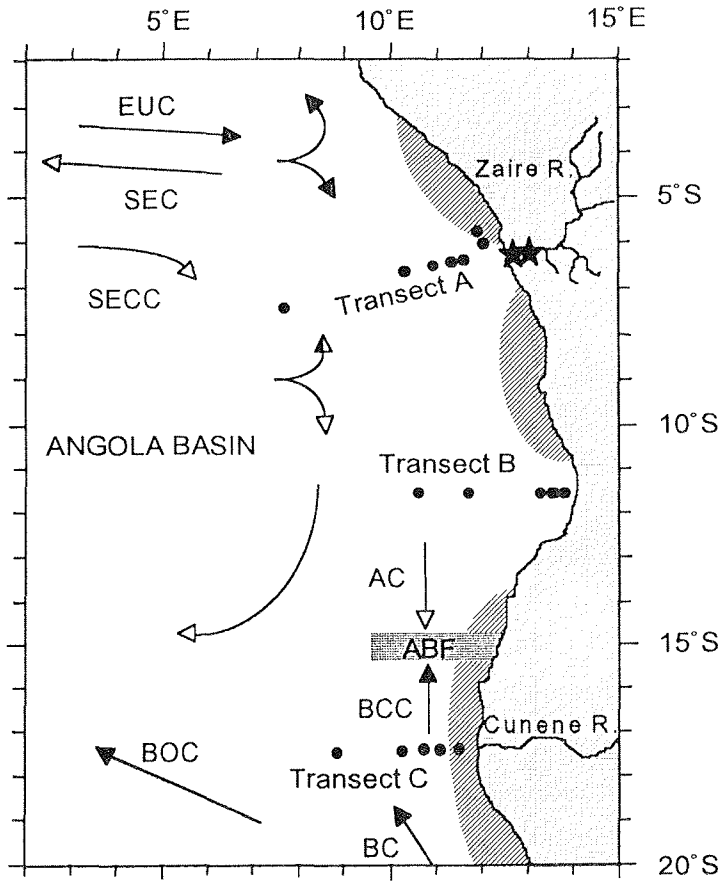

Figure 1. Map of the study area in the Angola Basin (modified from VAN BENNEKOM & BERGER, 1984; SCHNEIDER, 1991). Surface sediment transects are denoted by filled circles (Transect A - Zaire Fan: ~ 6°S; Transect B - Middle Angola: ~ 12°S; Transect C - Southern Angola: ~ 17°S). Stars represent Zaire estuary surface sediment samples. black arrows: cool surface currents; white arrows: warm surface currents; gray arrows: subsurface currents; AC: Angola Current; BC: Benguela Current; BCC: Benguela Coastal Current; BOC: Benguela Oceanic Current; EUC: Equatorial Undercurrent; SEC; South Equatorial Current; SECC: South Equatorial Counter-Current; A/B Front: Angola/Benguela Front.

$\delta^{13}C_{org}$, C/N ratios and organic carbon content of the same samples for which we present $\delta^{15}N$ data here were taken from MÜLLER ET AL. (1994). Based on $\delta^{13}C_{org}$, these authors showed a high percentage of terrestrially-derived material on the Zaire shelf (Transect A), decreasing with distance from the river mouth down the fan. C/N ratios corroborate this, with high ratios in shallow water corresponding to nitrogen-poor terrestrial matter and low ratios (in deep water) to marine organic material, which is richer in nitrogen (Table 1). The data indicate the presence of very little terrestrial matter in the sediments of Transects B (Middle Angola) and C (Southern Angola). The varied hydrography and productivity zones in the Angola Basin make it an intriguing place to investigate changes in input of terrestrial material, nutrient availability and productivity based on isotopic changes.

METHODS

The sediment samples were obtained from the eastern Angola Basin during the 1988 RV "Meteor" cruise 6/6 (WEFER ET AL., 1988). Figure 1 shows the study area and core locations. Box corers (50 x 50 cm surface area) were used to recover Holocene sediments in three transects (perpendicular to the coast) at around 6°S, 12°S and 17°S. Subsamples were removed from the core-surfaces on board immediately after collection using 10 cm^3 plastic syringes, sealed with electrical tape and kept at 4°C until being freeze-dried and ground in an agate mortar.

For the stable nitrogen isotope analyses of the bulk sediment, samples were decalcified in 1M HCl for 1 hour at 50°C then filtered, dried overnight at 50°C in a drying oven and re-ground with copper oxide to facilitate combustion. 50 - 100 mg of the sample was placed in tin boats and pressed into small (~7 x 4 mm) cylinders prior to combustion at 1050° in a Heraeus Elemental Analyzer. $\delta^{15}N$ of the N_2 gas thus formed was measured using a Finnigan Mat 252 mass spectrometer with trapping box as described by FRY ET AL. (1992).

The isotopic data are presented in permil (‰) in terms of δ notation:

$$\delta^{15}N = [(^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{standard}) - 1] \times 10^3$$

The δ values are reported relative to air. The laboratory nitrogen working standard gas (99.996% pure tank N_2) was calibrated against atmospheric air and IAEA standards N-1 and N-2. MARIOTTI (1983) demonstrated that pure tank N_2 remains isotopically stable for several years and may be used as a laboratory standard. Atmospheric air was prepared for analysis using the method described by MINAGAWA ET AL. (1984) and VOß (1991). Corrections for blanks were performed using a modified version of that proposed by FRY ET AL. (1992) and blank size was < 0.65 µmol of N, (between 4% and 9% of sample size). Analytical precision for $\delta^{15}N$ measurements was ± 0.2‰, based on repeated measurement of reference sediment standards.

RESULTS AND DISCUSSION

Table 1 gives the positions, water depths and $\delta^{15}N$ values for the Angola Basin sediment samples as well as $\delta^{13}C_{org}$ values, C/N ratios, organic carbon and total nitrogen content for Transects A, B and C (MÜLLER ET AL., 1994). We also measured $\delta^{15}N$ and $\delta^{13}C_{org}$ values, C/N ratios, organic carbon and total nitrogen content in two surface sediment samples from the Zaire estuary and these data are also shown in Table 1. $^{15}N/^{14}N$ ratios in each of the three surface sediment transects increased with water depth and distance from the coast (Fig. 2).

Table 1. Latitude, longitude, water depth, $\delta^{15}N$, surface water $[NO_3^-]$ (denoted by $[NO_3^-]_S$) (for Transects A, B and C from CONKRIGHT ET AL., 1994; for Zaire estuary from VAN BENNEKOM ET AL., 1978), upwelled $[NO_3^-]$ (denoted by $[NO_3^-]_u$) (from VAN BENNEKOM ET AL., 1978; JONES, 1971), f (fraction of unutilized nitrate in surface water: $[NO_3^-]_S/[NO_3^-]_u$), C_{org}, $\delta^{13}C_{org}$ and bulk C/N ratios of surface sediment samples. $\delta^{15}N$ in the two Zaire estuary samples was measured by H. Siegmund (Inst. für Ostseeforschung, Warnemünde). C_{org}, $\delta^{13}C$ and C/N ratios for all samples except those from the Zaire estuary are from MÜLLER ET AL. (1994).

Sample	Latitude	Longitude	Water Depth (m)	$\delta^{15}N$ (‰)	$[NO_3^-]_S$ ($\mu M\ l^{-1}$)	$[NO_3^-]_u$ ($\mu M\ l^{-1}$)	f	N_{tot} (%)	C_{org} (%)	$\delta^{13}C_{org}$ (‰)	C/N wt. Ratios
Zaire Estuary											
*24	06°02'S	12°34'E	< 6	7.04	7.3			0.23	2.76	-26.43	11.8
*26	06°04'S	12°29'E	6	7.62	7.3			0.13	1.44	-23.75	11.3
Transect A Zaire Fan											
GeoB 1001-2	05°52'S	11°58'E	45	5.87	1.06	12	.09	0.27	3.34	-25.51	12.5
GeoB 1000-1	05°42'S	11°43'E	106	5.69	0.92	12	.08	0.29	3.43	-24.58	11.7
GeoB 1005-2	06°14'S	11°30'E	237	5.89	0.78	12	.07	0.28	2.84	-23.03	10.3
GeoB 1006-2	06°17'S	11°18'E	682	5.86	0.78	12	.07	0.48	4.51	-22.73	9.5
GeoB 1007-2	06°24'S	10°56'E	1533	6.64	0.71	12	.06	0.35	3.22	-21.83	9.3
GeoB 1008-6	06°36'S	10°19'E	3100	6.87	0.71	12	.06	0.28	2.31	-21.80	8.2
GeoB 1009-3	06°55'S	09°00'E	4074					0.16	1.25	-20.55	7.8
GeoB 1010-3	07°26'S	07°26'E	4474	7.65	0.52	12	.04	0.15	0.96	-20.46	6.4
Transect B Middle Angola											
GeoB 1011-2	11°48'S	13°40'E	73	6.33	2.16	14	.15	0.10	0.95	-21.19	9.5
GeoB 1012-1	11°49'S	13°35'E	99	6.30	2.16	14	.15	0.09	0.86	-20.95	9.7
GeoB 1013-2	11°48'S	13°27'E	250	5.82	2.16	14	.15	0.20	1.83	-21.04	9.3
GeoB 1014-2	11°47'S	13°18'E	701	5.93	2.16	14	.15	0.55	5.16	-20.78	9.4
GeoB 1016-3	11°46'S	11°41'E	3410	7.80	1.74	14	.12	0.20	1.56	-20.47	7.7
GeoB 1017-3	11°44'S	10°33'E	3809	8.81	1.42	14	.10	0.14	1.06	-19.56	7.5
Transect C South Angola											
GeoB 1020-1	17°10'S	11°33'E	110	4.55	6.16	14	.44	0.24	1.99	-21.12	8.4
GeoB 1023-2	17°10'S	11°01'E	1965	5.43	6.16	14	.44	0.54	4.27	-20.11	8.0
GeoB 1024-3	17°10'S	10°41'E	2802	4.98	5.02	14	.36	0.56	4.32	-19.99	7.7
GeoB 1025-2	17°10'S	10°15'E	3565	5.48	5.02	14	.36	0.45	3.18	-19.98	7.1
GeoB 1026-3	17°10'S	08°54'E	4601	6.16	3.47	14	.25	0.15	0.94	-20.03	6.4

* Samples provided by J.H.F. Jansen and D. Eisma (NISR, Texel, The Netherlands)

Transect A, in the Zaire fan, and Transect B, off middle Angola, exhibited $\delta^{15}N$ values of 5.7 to 6.3‰ in shelf sediments at water depths less than 700 m, increasing to 7.7 and 8.8‰, respectively, in the sediments from deep water. The difference between lightest and heaviest sedimentary $\delta^{15}N$ ($\Delta\delta^{15}N$) in Transect A was 2.0‰ and in Transect B was 3.0‰. In the southern Angola Basin, represented by Transect C, a similar enrichment in ^{15}N with increasing depth was observed ($\Delta\delta^{15}N$ = 1.6‰), but the overall $\delta^{15}N$ values were lighter (4.6 - 6.2‰) by approximately 1.5‰ than in the other two transects. The surface sediments from the Zaire estuary had $\delta^{15}N$ values of 7.04‰ (station 24) and 7.62‰ (station 26). $\delta^{13}C_{org}$ values were -26.43‰ and -23.75‰ for stations 24 and 26, respectively. Station 24 was located approximately 6 sea miles upstream from station 26.

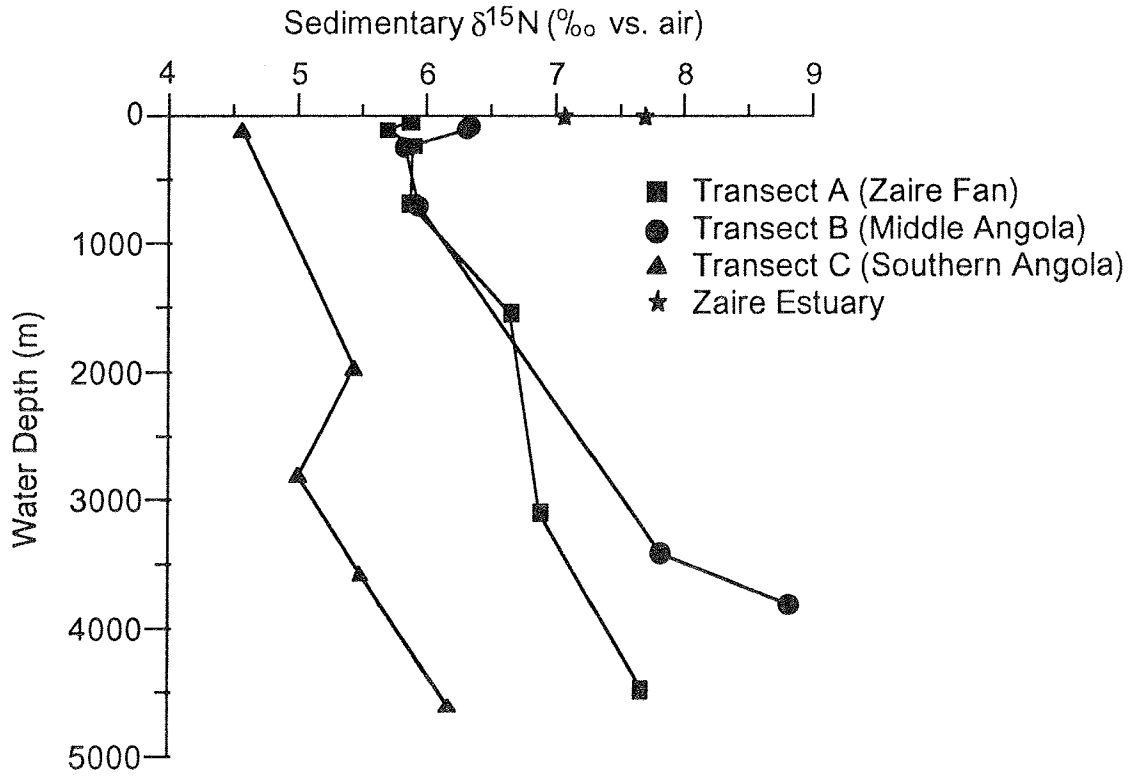

Fig. 2: $\delta^{15}N$ (‰) values measured on bulk nitrogen in surface sediments of Transects A, B and C and the Zaire estuary versus water depth in meters.

Effects of Nutrient Concentrations/Utilization

Nutrient levels are high in coastal water due to input by the Zaire River and to upwelling of deep offshore water. Nutrient enrichment of coastal water occurs when there is a deep water source of nutrients at the edge of a continental shelf (RILEY, 1967). According to HART & CURRIE (1960) and CALVERT & PRICE (1971) such a scenario exists off the southwest coast of Africa. Under the influence of steady winds between 10°S and 28°S which blow toward the

west and northwest along the coast (EMERY ET AL., 1973), surface water is advected seaward and deeper, nutrient-rich water moves shoreward. Upwelled water provides a large pool of nitrate which is available for uptake during photosynthesis, leading to lower planktonic $\delta^{15}N$ than when nitrate is more limiting. When this phytoplankton dies and sinks to the sea floor, the sediments, in turn, reflect the light $\delta^{15}N$ values originally produced at the surface. Furthermore, increased productivity, ensuing from upwelled nutrients, has been found to correlate with low $\delta^{15}N$ in both sinking organic matter and sediments (SCHÄFER & ITTEKKOT, 1993; ALTABET & FRANCOIS, 1994). In a sediment trap study, SCHÄFER & ITTEKKOT (1993) linked high organic carbon fluxes with low $\delta^{15}N$. Similarly, CALVERT ET AL. (1992) found that high $\delta^{15}N$ in sediment cores corresponded to low biogenic fluxes.

Nutrients off the southwest coast of Africa decrease from high values adjacent to the coast (up to 27.7 µM nitrate was measured in surface water over the Angolan shelf at around 18°S during the SNEC II (1986) cruise), to non-detectable levels with distance from land. To determine whether nutrient gradients are reflected in the nitrogen isotope ratios of the sediments, we obtained surface nitrate concentrations for water overlying Transects A, B and C from the World Ocean Atlas (CONKRIGHT ET AL., 1994). These values, shown in Table 1, represent an average of $[NO_3^-]_{surface}$ measurements made during different seasons over several years. No historically averaged $[NO_3^-]_{surface}$ data is available for stations 24 and 26 in the Zaire River, but a surface concentration of 7.3 µM nitrate was reported by VAN BENNEKOM ET AL. (1978).

$\delta^{15}N$ in organic material is not directly related to nitrate concentration per se, but rather to the degree of nitrate utilization. In Fig. 3, the fraction of unutilized nitrate (f) is plotted against $\delta^{15}N$. f was determined from the ratio of $[NO_3^-]$ in the surface water over each sample location to $[NO_3^-]$ at the depth where upwelled water originates. Near the mouth of the Zaire River (Transect A) upwelled water comes from 25 - 50 m depth and has an approximate nitrate concentration of 12 µM (VAN BENNEKOM ET AL., 1978). South Atlantic Central Water (SACW), which is found at around 200 m water depth, is believed to be the source of coastally upwelled water in the Benguela region (JONES, 1971). For upwelled water at Transects B and C, $[NO_3^-]$ of 14 µM was assumed because this is in the middle of the values given by JONES (1971) for SACW (10 - 18 µM). Because the estuary sediments are presumably composed mainly of terrestrial matter, their isotopic composition relative to nutrient concentrations is different from the marine sediments. Therefore, we did not attempt to calculate a value for f for these two estuary samples.

r^2 for the logarithmic regression shown in Fig. 3 is 0.57 (n=14), confirming that a significant portion of the variance in $\delta^{15}N$ is accounted for by changes in $[NO_3^-]$ ($P \leq .005$). The four shallowest sediment samples from the Zaire shelf (open symbols) were not included in the

regression calculation because the $\delta^{15}N$ of these sediments may be significantly influenced by large proportions of terrestrial material (see *Evaluation of Mixing between Marine and Terrestrial Organic Material* section).

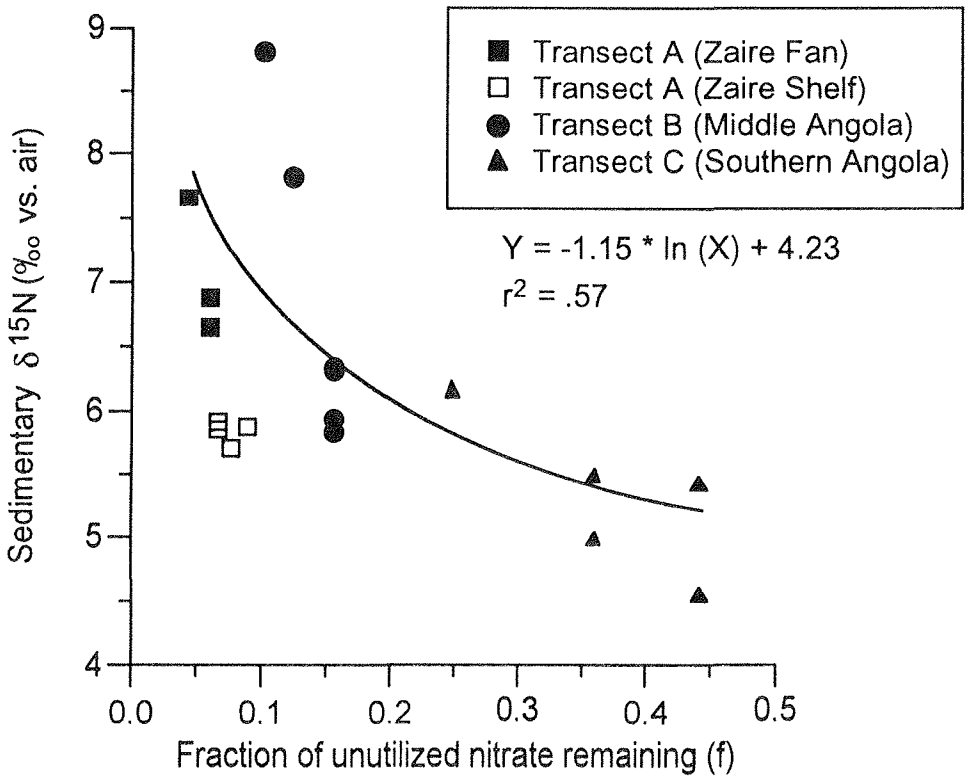

Fig. 3: $\delta^{15}N$ (‰) values of bulk surface sediments versus the fraction of unutilized nitrate remaining in surface water (f). f was estimated from the ratio of $[NO_3^-]_{surface}$ to $[NO_3^-]$ at the depth of the upwelled water. Open squares are sediments from the Zaire shelf (shallowest four samples of Transect A), which were omitted from the regression calculation because they contain high proportions of terrestrial material. The two estuary sediment samples are not plotted.

Application of hindcasting equations

We used equations (1 and 2) presented by ALTABET & FRANCOIS (1994) to test their reliability in hindcasting the degree of surface nitrate depletion levels in the Angola Basin from sediment $\delta^{15}N$.

(1) $\delta^{15}NO_3^-{}_{(f)} = \delta^{15}NO_3^-{}_{(f=1)} - \varepsilon_u \times \ln(f)$

(2) $\delta^{15}N\text{-}PN_{(f)} = \delta^{15}NO_3^-{}_{(f)} - \varepsilon_u$ (instantaneous product)

f is the fraction of unutilized NO_3^- remaining, ε_u is the fractionation factor associated with NO_3^- uptake. We used the instantaneous product equation rather than that given by ALTABET & FRANCOIS (1994) for an accumulated product. Nutrient-enriched water comes to the surface at the coast and flows westward toward the open ocean, becoming progressively more depleted in NO_3^- along the way. Sedimentary organic matter reflects the $\delta^{15}N$ of organic matter produced during utilization of increasingly ^{15}N-rich nitrate in the euphotic zone as it moves away from the coast. The sediments in such regions thus reflect spatial variations of surface nitrate concentrations, not temporal changes.

The success of these equations in determining surface nitrate values is dependent on the estimation of the fractionation factor (ε_u) exhibited by phytoplankton during photosynthesis. ε_u may be obtained from the slope of the regression line of a plot of sedimentary $\delta^{15}N$ and ln $[NO_3^-]_{surface}$ (ALTABET & FRANCOIS, 1994). ε_u thus obtained for the Angola region is 1.04‰ (Fig. 4). The two estuarine and the four shallow Zaire shelf sediments samples are not shown and were omitted from the regression calculation. This value for ε_u is within the range of previously published values (0.3 to 23‰) (from MONTOYA, 1994).

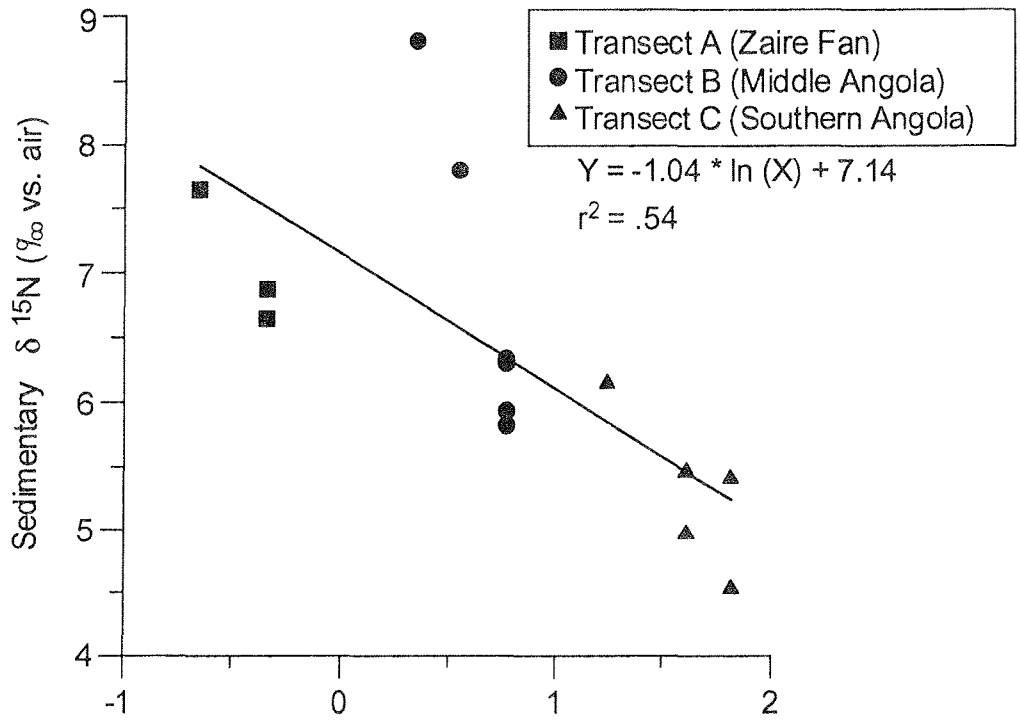

Fig. 4: $\delta^{15}N$ (‰) values of bulk surface sediments versus ln $[NO_3^-]$ (µM). The four shallowest Zaire shelf sediment samples and two estuary sediment samples are not plotted and were not included in regression calculations because of their high terrestrial matter contents. The slope of the regression line gives ε_u, the fractionation factor.

Assuming $\delta^{15}N$ of the original upwelled nitrate was 5.5‰ (which was the mean $\delta^{15}NO_3^-{}_{(f=1)}$ calculated by substituting ε_u = 1.04‰, $\delta^{15}N_{measured\ PN}$ and ln f from Table 1 into equations 1 and 2), we determined the theoretical fraction of unutilized NO_3^- remaining in the surface water (f) for our sample sites based on the measured sedimentary $\delta^{15}N$ and compared this with f calculated from water column $[NO_3^-]$ (Fig. 5). ln f was plotted instead of f so that the

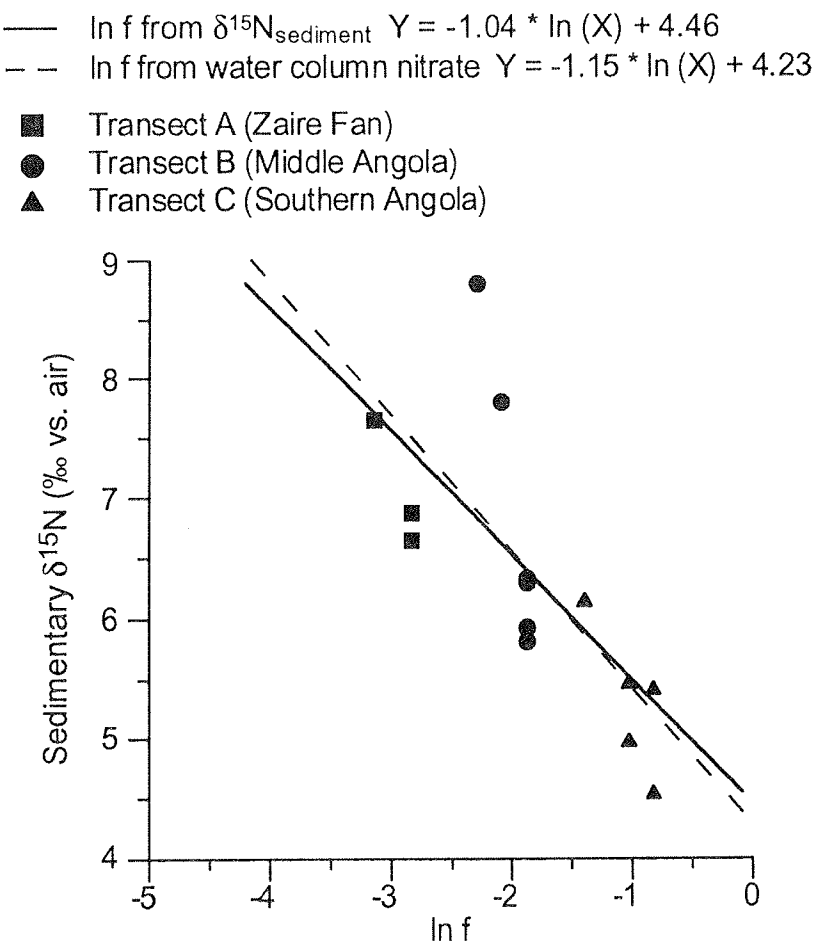

Fig. 5: $\delta^{15}N$ (‰) values of bulk surface sediments versus ln f estimated from $[NO_3^-]$ in the water column (filled symbols and dashed line) and for ln f predicted from sedimentary $\delta^{15}N$ (solid line). Equations (1) and (2) (instantaneous product) from ALTABET & FRANCOIS (1994) were used to determine ln f from sedimentary $\delta^{15}N$. The four shallowest Zaire shelf and the two estuary samples are not plotted and were excluded from the calculations.

two regression lines can be more easily compared. The slope of the ln f line estimated from sedimentary $\delta^{15}N$ was -1.04 and for ln f predicted from $[NO_3^-]$ in the water column was -1.15. The y intercept for the ln f line predicted from sedimentary $\delta^{15}N$ was 4.46‰ and for ln f estimated from $[NO_3^-]$ in the water column was 4.23‰. No significant differences were detected between either the slopes or the intercepts of the two lines based on an analysis of

covariance ($n = 14$, $P < .005$). Thus, it seems that the equations do a reasonably good job of hindcasting the degree of nitrate depletion in the surface water.

Denitrification

Denitrification in the water column plays a significant role in the nitrogen cycle in sub-oxic conditions. During denitrification, the nitrate left over after denitrifying organisms preferentially reduce ^{14}N-containing nitrate is enriched in ^{15}N relative to nitrate from oxygenated water from the deep sea (CLINE & KAPLAN, 1975). This ^{15}N-enriched nitrate is made available for primary production during upwelling events and particulate organic matter in denitrifying regions exhibits higher $^{15}N/^{14}N$ ratios than plankton from areas where denitrification does not occur (SAINO & HATTORI, 1987). Sedimentary $\delta^{15}N$ has also been shown to reflect the enrichment in ^{15}N caused by water column denitrification (ALTABET ET AL., 1995; GANESHRAM ET AL., 1995). The Angola Basin region is somewhat oxygen-depleted and an oxygen minimum zone exists between 300 and 600 m (BUBNOV, 1972). However, nitrate reduction is inhibited above concentrations of 0.2 ml O_2 l^{-1} (PACKARD ET AL., 1983) and O_2 concentrations measured by BUBNOV (1972) in the OMZ were around 1 ml l^{-1}, not low enough to promote denitrification. The $\delta^{15}N$ values we measured in sediments of the Angola Basin are similar to those reported for typical marine organic matter (6 - 10‰) elsewhere (SAINO & HATTORI, 1980; WADA ET AL., 1987) and do not exhibit a general elevation which would indicate the occurrence of denitrification. Additionally, most of the measured $\delta^{15}N$ values conform to expected values based on nitrate concentrations (see Fig. 5). Two samples which are enriched in ^{15}N relative to that expected from water column $[NO_3^-]$ are GeoB 1016-3 and GeoB 1017-3. It is possible that denitrification occurs at times in these waters and is partly responsible for the elevated $\delta^{15}N$ of GeoB 1016-3 and GeoB 1017-3 sediments. However, as ALTABET & FRANCOIS (1994) state, at the low nitrate concentrations measured in the surface water over these two samples, lateral transport of suspended particulate nitrogen and local vertical transport of $[NO_3^-]$ can be as high in magnitude as the lateral advection of $[NO_3^-]$ to the near-surface layer. This can cause the linear relationship between $\ln [NO_3^-]_{surface}$ and sedimentary $\delta^{15}N$ to break down. This may be an important reason for the increased scatter in the data at low surface nitrate concentrations (Figs. 3, 4 and 5).

Effect of Bacterial Degradation

As particles produced in the photic zone sink to the sea floor, they are subject to isotopic modification by bacterial degradation. SAINO & HATTORI (1980) and ALTABET & MCCARTHY (1985) found ^{15}N enrichment in the residual organic matter after bacterial remineralization of sinking particles. ALTABET (1988) showed that sinking particles had higher $\delta^{15}N$ than particles suspended in the euphotic zone. Decomposition was reported by FRANCOIS ET AL.

(1992) to cause an enrichment in ^{15}N by 5 -7‰ in organic material at the sediment-water interface. In spite of the changes wrought by diagenesis, these authors showed that although it may be offset by a relatively constant value, sedimentary $\delta^{15}N$ reflects the $\delta^{15}N$ produced in the surface water. Nonetheless, relatively little is known about the isotopic effects of decomposition. Therefore, we attempted to assess the extent of diagenetic effects on the sediments in the Angola Basin. EMERY ET AL. (1973) and CHAPMAN & SHANNON (1985) measured high levels of suspended organic matter off the Angolan and Namibian coasts, with concentrations decreasing with distance from land. Furthermore, rapid sinking of organic material to the sediments was invoked by Chapman and Shannon (1987) as the reason for the low oxygen concentrations they found in nearshore water in the Angola Basin. Based on the findings of MÜLLER & SUESS (1979) who reported that preservation of organic matter improves with increasing sedimentation rates, the observed $\delta^{15}N$ variations could result from the fact that the larger amounts of sinking organic material in shallow coastal water are not as highly degraded as organic matter sinking from the euphotic zone in deep water. This process, however, should result in increasing C/N ratios with increasing degradation as the nitrogen compounds are more rapidly remineralized (ROSENFELD, 1981). C/N ratios, in fact, show the opposite trend, with higher values nearshore than offshore. This is partly due to the presence of terrestrial material in nearshore sediments, especially in Transect A, but the percentage of terrestrial matter in Transects B and C, based on $\delta^{13}C_{org}$, is very low (<15%), so this effect is probably not masking an increase in C/N ratios with distance from the coast.

Another possibility is that the C/N ratios decrease with distance from the coast because of increasing relative amounts of inorganic nitrogen in the sediments. This could result from remineralisation of organic matter in the sediments. A plot of organic carbon against total nitrogen content (the shallowest four samples from Transect A were omitted from regression due to the high amounts of terrestrial material present) reveals that at 0% organic carbon, nitrogen is also absent (Y intercept = 0.015%), indicating that most of the nitrogen in the sediments is organic in nature. The standard error of the Y intercept is also 0.015 (n=14), making it impossible to differentiate between a nitrogen concentration of 0.015% and 0.000%. Furthermore, the composition of the clay minerals in the sediments implies that fixed ammonium is not a likely cause of changing C/N ratios. Illite, in which ammonium is preferentially fixed (MÜLLER, 1977; LEW, 1981), is present at low concentrations in the sediments of the Angola Basin (< 20%) (PETSCHICK ET AL., in press). Thus, we conclude that there is no significant proportion of inorganic nitrogen in these surface sediment samples and that degradation has had little influence on the $\delta^{15}N$ trends observed in these surface sediments.

Evaluation of Mixing between Marine and Terrestrial Organic Material

Nitrogen isotopes have proved useful in some areas in recording the mixing of terrestrial organic matter with marine material. The amount of terrestrial material in the sediments may affect $\delta^{15}N$ because organic material produced on land is often isotopically different from that of marine-derived organic matter. SWEENEY & KAPLAN (1980) and WADA ET AL. (1987) used $\delta^{15}N$ as a source indicator for near-shore sedimentary organic material. These authors demonstrated that sediments became progressively more enriched in ^{15}N with increasing distance from the coast because of a decreasing admixture of an isotopically light terrestrial plant end member. Other studies, however, have been less conclusive. OWENS (1985), for example, reported that the $^{15}N/^{14}N$ variations he observed in estuarine particles did not reflect simple mixing of two end member sources and THORNTON & MCMANUS (1994) determined that the sedimentary $\delta^{15}N$ variations they observed were related to diagenesis rather than to mixing of terrigenous with marine matter.

MÜLLER ET AL. (1994) showed that the enrichment in sedimentary $\delta^{13}C_{org}$ with depth in Transect A (Fig. 6) is due to the mixing of isotopically light, nitrogen-poor terrestrial material from the Zaire River with isotopically heavy organic matter of marine origin and that Transect

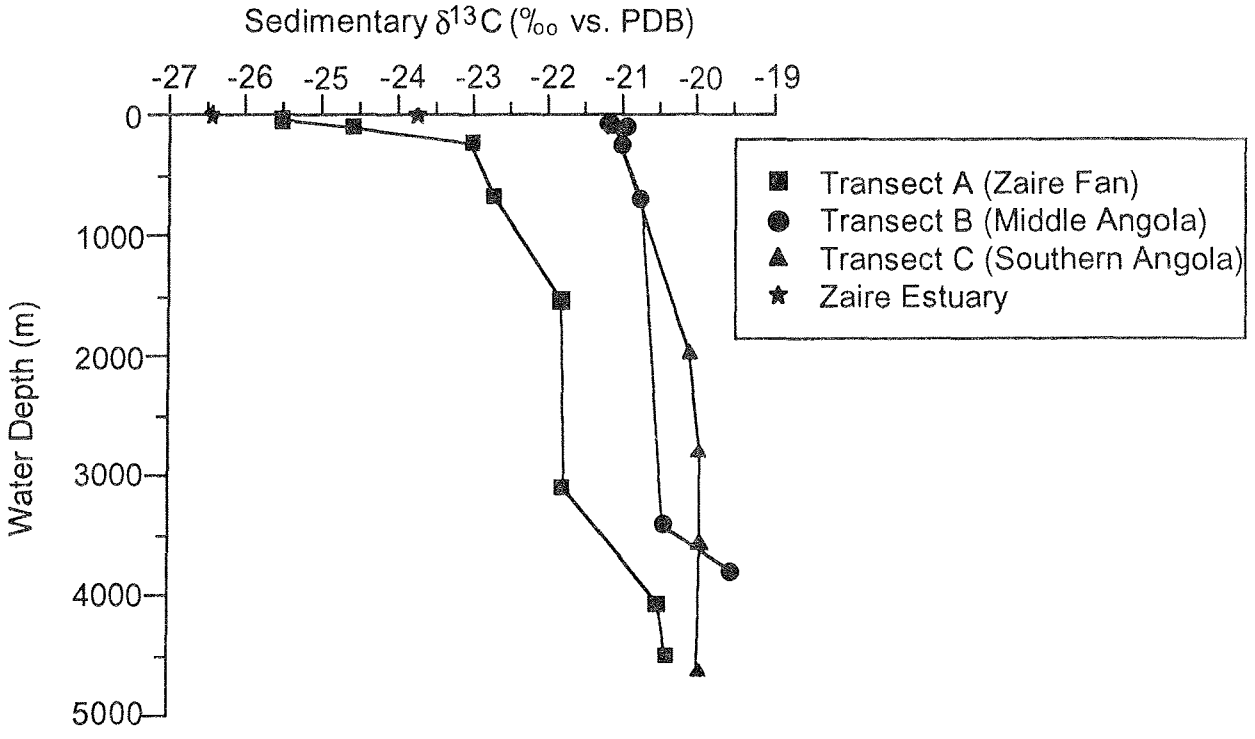

Figure 6. $\delta^{13}C_{org}$ (‰) values of surface sediments of Transects A, B and C (from MÜLLER ET AL. 1994) and the Zaire estuary versus water depth in meters.

B and C sediments show little terrestrial influence. $\delta^{13}C_{org}$ of one of the two samples (-26.43‰) within the Zaire estuary is typical for particulate organic carbon in the Zaire River and for terrestrial organic matter in general (MARIOTTI ET AL., 1991). The $\delta^{13}C_{org}$ value of the other sample (-23.75‰) is less negative than expected for a sediment composed mainly of terrigenous material and the reason for this is unknown. Nevertheless, the carbon isotopic signal of these two estuarine samples support the conclusion of MÜLLER ET AL. (1994) that the nearshore sediments of Transect A contain high proportions of terrestrial matter. Samples GeoB 1001-2, GeoB 1000-1, GeoB 1005-2 and GeoB 1006-2 were excluded from all regression calculations in this paper because they contain relatively high amounts of terrigenous matter (40 - 50% based on $\delta^{13}C_{org}$).

In contrast, the $\delta^{15}N$ signal does not clearly show the mixing of terrigenous with marine end members. The $\delta^{15}N$ values of the two samples from within the Zaire estuary were higher than expected based on the nitrate concentration in surface waters of the Zaire River (Table 1) and other studies which have reported relatively low $\delta^{15}N$ in terrestrial material (SWEENEY & KAPLAN, 1980; WADA ET AL., 1987). However, such a wide range of $\delta^{15}N$ values has been measured to date in terrestrial systems (-17 to +30‰, from SWEENEY ET AL., 1978) that it is not surprising that $\delta^{15}N$ in terrigenous matter from the Zaire River is not distinctly lower than in the marine sediments. Thus, if these isotopic values are typical of terrigenous material entering the Zaire fan from the river, then the $\delta^{15}N$ signals measured in the shallowest four samples of Transect A must be somewhat elevated due to the presence of terrestrial material than they would be if they were of purely marine origin. This would mean that in the absence of terrestrial matter $\delta^{15}N$ in these four samples would be still lower with respect to the other samples based on $[NO_3^-]_{surface}$ (Fig. 3). The reason for this discrepancy may be the sparse nutrient measurements in the northern Angola region. The available data may not provide reliable average $[NO_3^-]_{surface}$ concentrations and the $[NO_3^-]$ values obtained for this area could be underestimates. This would lead to the displacement of samples GeoB 1001-2, GeoB 1000-1, GeoB 1005-2 and GeoB 1006-2 too far below the regression line in Fig. 3.

CONCLUSIONS

$\delta^{15}N$ in sediments from the Angola Basin have been studied in order to assess changes in biogeochemical processes in the water column. $^{15}N/^{14}N$ in this region is primarily controlled by the extent of nitrate utilization. Productivity in nearshore coastal waters is less nitrate-limited relative to offshore water because of higher nutrient concentrations near the coast. Use of equations for hindcasting surface water nutrient levels yielded results which did not significantly differ from our data and indicated that the $\delta^{15}N$ of the original upwelled nitrate was around 5.5‰. Since most of the variation in $^{15}N/^{14}N$ ratios is accounted for by accompanying changes in nitrate concentration/utilization in the surface waters, denitrification

apparently does not influence sedimentary $\delta^{15}N$ to an important degree. Organic carbon and total nitrogen content as well as the clay mineral composition indicate that degradation has not occurred to a significant extent in these sediments. In contrast to the reported $^{13}C/^{12}C$ ratios, $\delta^{15}N$ did not clearly show the mixing of terrestrial material with that of marine origin in sediments from the Zaire Fan because the terrigenous signal was partly masked by the isotopic effect of varying degrees of nitrate utilization and because $\delta^{15}N$ of the terrestrial material entering the fan is similar to $\delta^{15}N$ of marine-derived organic matter. On the other hand, the $\delta^{13}C_{org}$ values do not exhibit trends relating to changes in nutrient uptake or productivity. It is clear from our results that the combined use of nitrogen and carbon isotopes in sediments allows for more reliable interpretation of the sedimentary record.

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3.3

SPATIAL VARIATIONS IN EUPHOTIC ZONE NITRATE UTILIZATION BASED ON $\delta^{15}N$ IN SURFACE SEDIMENT

(submitted to Geo-Marine Letters)

Spatial Variations in Euphotic Zone Nitrate Utilization Based on $\delta^{15}N$ in Surface Sediments

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ABSTRACT

Bulk $\delta^{15}N$ in surface sediment samples off the southwestern coast of Africa was measured in order to investigate the biogeochemical processes occurring in the water column. Our results indicate that nitrate concentrations and the degree of utilization of the nitrate pool are the predominant controls on $\delta^{15}N$ in the Benguela region. Denitrification does not appear to have had an important effect on the $\delta^{15}N$ signal of these sediments and, based on $\delta^{15}N$, $\delta^{13}C$ and C/N ratios, there was little terrestrial input.

INTRODUCTION

The use of sedimentary $^{15}N/^{14}N$ ratios is becoming increasingly accepted as a tool in the investigation of past biogeochemical processes occurring in the overlying water column. In the ocean, $\delta^{15}N$ in organic matter is a reflection of the many factors which alter the organic matter (OM) as it is produced, sinks and is buried at the sea floor. The degree of utilization of dissolved inorganic nitrogen (DIN) in surface water is one of the main controls on $\delta^{15}N$ of OM. Phytoplankton preferentially takes up DIN containing the lighter nitrogen isotope (^{14}N) during photosynthesis and thus becomes depleted in ^{15}N relative to the nitrogen substrate (WADA & HATTORI 1978). Continuing photosynthesis with no input of new nitrogen leads to increasing $\delta^{15}N$ of the residual DIN and of the phytoplankton which incorporates this ^{15}N-

enriched nitrate pool. Thus, high nitrate concentrations (and low relative utilization of this nutrient) lead to low $\delta^{15}N$ in suspended particulate organic matter (POM). An inverse relationship between photic zone nutrient concentrations and $\delta^{15}N$ of suspended and sinking particles has been clearly demonstrated by ALTABET & MCCARTHY (1985) and VOß (in press).

$\delta^{15}N$ of the inorganic nitrogen substrate taken up by plankton during photosynthesis may be altered by denitrification under sub-oxic conditions. New nitrate upwelled from oxygenated water in the deep sea has an isotopic value of 5 - 6‰ (WADA ET AL. 1975), but during nitrate reduction, nitrate containing ^{14}N is reduced preferentially by denitrifying bacteria and the residual nitrate is enriched in ^{15}N (CLINE & KAPLAN 1975). The uptake of this heavy NO_3^- results in POM (and underlying sediments) with a relatively high $\delta^{15}N$ signal (ALTABET ET AL. 1995; GANESHRAM ET AL. 1995; SAINO & HATTORI 1987).

An important consideration concerning the use of sedimentary $\delta^{15}N$ as a proxy for surface water processes is the fidelity of the transfer of the surface-produced signal to the seafloor. Sediment trap studies in the North Atlantic Ocean, the Sargasso Sea and the Greenland Sea have shown a link between surface ocean processes and $\delta^{15}N$ in particles sinking to the deep sea (ALTABET & DEUSER 1985; ALTABET ET AL., 1991; VOß ET AL., in press). CALVERT ET AL. (1992) and FRANCOIS ET AL. (1992) have extended this to sediments of the Mediterranean Sea and the southern Indian Ocean, respectively, and have shown that sedimentary $\delta^{15}N$ can be used to evaluate nutrient levels in the overlying water at the time the OM in the sediments was produced at the surface. Until now, no such $\delta^{15}N$ studies have been done in the Benguela area and it is unknown what the principal controls on $\delta^{15}N$ in this region are. The purpose of the present work was, therefore, to investigate the causes of spatial changes in sedimentary $\delta^{15}N$ in the Benguela Current region. Our data show that $\delta^{15}N$ in Benguela sediments records the degree of nitrate utilization in surface water and can be a useful proxy for paleo-oceanographic studies.

STUDY AREA

Due to its importance in the exchange of heat between the northern and southern hemispheres and as one of the major upwelling zones in the world ocean, the Benguela system has been the subject of many investigations (CHAPMAN & SHANNON 1985; SHANNON 1985; SHANNON & PILLAR 1986 compiled comprehensive reviews of the physical processes, chemistry and biology of this area). Figure 1 shows the bathymetry and hydrography of the study area, along with the sampling locations. The Walvis Ridge, a topographic high, separates the Angola Basin in the north from the Cape Basin to the south.

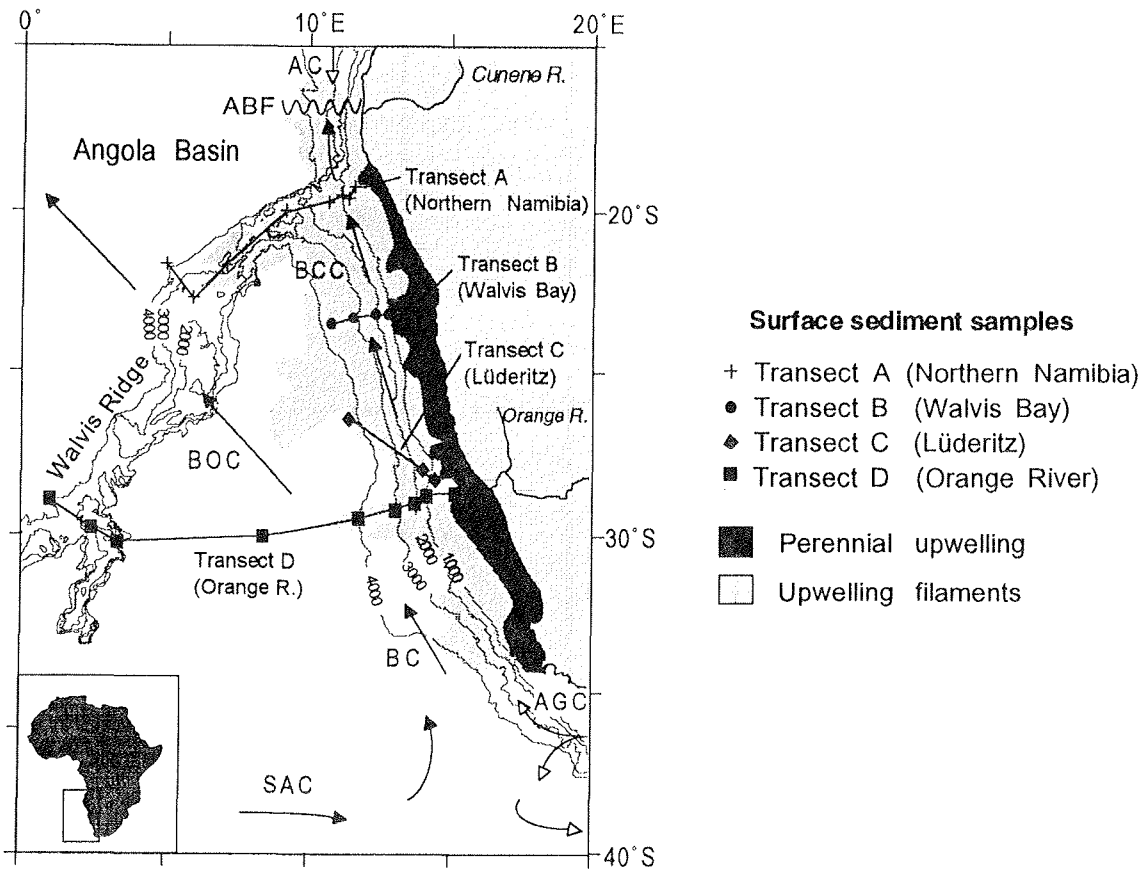

Fig. 1: Map of the study area off the southwest coast of Africa (location of upwelling redrawn from LUTJEHARMS & STOCKTON 1987). Surface sediment samples are represented by crosses (Transect A - Northern Namibia), circles (Transect B - Walvis Bay), diamonds (Transect C - Lüderitz) and squares (Transect D - Orange River). Upwelling is indicated by shaded areas. Black arrows indicate cool surface currents, white arrows are warm surface currents. The following abbreviations are used: ABF: Angola-Benguela Front; AC: Angola Current; AGC: Agulhas Current; BCC: Benguela Coastal Current; BOC: Benguela Oceanic Current; SAC: South Atlantic Current.

The Benguela upwelling system is dominated by the Benguela Current (BC), an eastern boundary current. The northwest-flowing BC diverges at around 28°S (PETERSON & STRAMMA 1989). The main part of the BC continues to the northwest as the Benguela Oceanic Current (BOC) while the Benguela Coastal Current (BCC) flows in a northerly direction within 100 nautical miles of the coast.

Intense coastal upwelling of cold, nutrient-rich water, typical of eastern boundary currents, characterizes the Benguela system. Under the influence of tradewinds which blow toward the west and northwest, surface water is advected seaward (EMERY ET AL. 1973). Nutrient-rich South Atlantic Central Water (SACW) from 150-250 m depth (CALVERT & PRICE 1971; JONES 1971) comes to the surface near the shore, replacing the advected water. SACW originates in the Subtropical Convergence Zone from subtropical and subantarctic water

which sinks and spreads northward (SHANNON 1985). The coastal upwelling area is about 150-200 km wide, but upwelling filaments may extend up to 1000 km offshore (LUTJEHARMS & STOCKTON 1987; LUTJEHARMS ET AL. 1991). The coastal upwelling regime and the filamentous mixing region in austral winter are shown in Fig. 1. Upwelling results in nitrate concentrations up to 30 µM near the coast, decreasing to undetectable levels offshore (CHAPMAN & SHANNON 1985; SNEC II 1986). Productivity rates in the Benguela region are high (125-180 g C m^2 yr^{-1}; SHANNON ET AL. 1987).

METHODS

Surface sediment samples were obtained with a box corer (50 x 50 cm surface area) during "Meteor" cruises M6/6 (WEFER ET AL. 1988) and M20/2 (WEFER ET AL. 1992). Samples were taken in four transects - off northern Namibia (19°S - 23°S), Walvis Bay at around 23°S, Lüderitz from ~26° to 28 °S and the Orange River at ~29°S - 30°S (Fig. 1). Subsamples were removed from the core-surfaces on board immediately after collection using 10 cm^3 plastic syringes. These were sealed with electrical tape and stored at 4°C until being freeze-dried and ground in an agate mortar in a shore-based laboratory.

For $\delta^{15}N$ analyses ($\delta^{15}N = [(^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{standard}) - 1] \times 10^3$), sediment samples were re-ground with copper oxide (2:1 sediment:CuO_2) to facilitate combustion. 50 - 100 mg of the sample was placed in tin boats and pressed into small cylinders prior to combustion at 1050°C in a Heraeus Elemental Analyzer. The produced N_2 gas was cryogenically purified and measured using a Finnigan MAT 252 mass spectrometer with trapping box as described by FRY ET AL. (1992). $\delta^{15}N$ values are reported relative to atmospheric nitrogen. The laboratory working standard nitrogen gas was 99.996% pure tank N_2, calibrated against atmospheric air and IAEA standards N-1 and N-2. Analytical precision for $\delta^{15}N$ measurements was ± 0.2‰, based on repeated measurement of reference sediment standards. Total organic carbon (C_{org}) and its stable isotopic composition ($\delta^{13}C_{org}$) were analyzed as described by MÜLLER ET AL. (1994.)

RESULTS

Table 1 gives the locations, water depths, distance from the coast, $\delta^{15}N$ values, $\delta^{13}C_{org}$ values and organic carbon contents for the Benguela sediment samples, surface nitrate concentrations and f (the percent of unutilized nitrate remaining in surface water). $^{15}N/^{14}N$ ratios in each of the four surface sediment transects exhibit a general relative enrichment in ^{15}N with increasing distance from shore (Fig. 2). Within 200 km of the coast, $\delta^{15}N$ off northern Namibia (Transect A) was 4.7 - 4.8‰. Sediments of the Walvis Bay and Orange

Table 1: Latitude, longitude, water depth, distance from coast, bulk $\delta^{15}N$, C_{org} and $\delta^{13}C_{org}$ of surface sediment samples, surface water $[NO_3^-]$ (from CONKRIGHT ET AL., 1994), f (calculated from the ratio of $[NO_3^-]$ in surface water to $[NO_3^-]$ in upwelled water) and f estimated based on sedimentary $\delta^{15}N$ using equations (1) and (2) from ALTABET & FRANCOIS (1994).

Sample	Latitude	Longitude	Water Depth (m)	km from coast	$\delta^{15}N$ (‰)	$[NO_3^-]$ (µM)	f	f (hind-casted)	C_{org} (%)	$\delta^{13}C$ (‰)
	Transect A	*Northern Namibia*								
1704-1	19°24'S	11°37'E	399	100	4.84	5.5	.39	.42	5.81	-19.68
1705-2	19°30'S	11°24'E	647	130	4.72	5.5	.39	.42	4.19	-19.93
1706-1	19°34'S	11°11'E	980	150	4.81	5.5	.39	.42	4.27	-20.16
1707-2	19°42'S	10°39'E	1234	200	4.73	4.8	.34	.42	3.65	-20.00
1028-4	20°06'S	9°11'E	2215	360	7.06	3.7	.26	.28	0.46	-19.71
1031-1	21°53'S	7°06'E	3103	630	11.25	2.0	.14	.13	0.15	-19.24
1032-2	22°55'S	6°01'E	2499	780	11.81	1.4	.10	.11	0.15	-19.21
1035-3	21°36'S	5°02'E	4450	810	11.78	1.3	.09	.12	0.14	-20.00
	Transect B	*Walvis Bay*								
1714-1	23°08'S	13°33'E	200	100	5.88	4.4	.31	.34	5.69	-20.04
1713-6	23°13'S	13°01'E	597	150	5.45	4.4	.31	.37	3.60	-20.07
1712-2	23°15'S	12°48'E	1007	170	5.43	3.9	.28	.37	3.71	-20.05
1711-5	23°19'S	12°23'E	1964	200	5.81	3.9	.28	.35	1.74	-20.18
1710-2	23°26'S	11°42'E	2983	280	8.13	3.8	.27	.23	0.49	-19.47
1709-3	23°35'S	10°46'E	3837	370	9.35	2.9	.21	.18	0.24	-19.16
	Transect C	*Lüderitz*								
1715-1	26°29'S	11°38'E	4097	360	9.79	1.8	.13	.04	0.34	-18.97
1716-2	27°57'S	14°00'E	1481	160	7.82	1.9	.14	.12	1.25	-20.19
1717-2	28°13'S	14°25'E	603	140	6.54	1.5	.11	.22	1.26	-19.72
	Transect D	*Orange River*								
1718-1	28°43'S	15°13'E	167	100	5.90	1.6	.11	.30	2.23	-20.39
1719-5	28°56'S	14°10'E	1024	200	6.22	1.5	.11	.26	2.41	-19.59
1720-4	29°00'S	13°50'E	2011	260	7.98	1.4	.10	.11	0.81	-19.50
1721-4	29°11'S	13°05'E	3079	340	9.37	1.3	.09	.05	0.38	-18.97
1722-3	29°27'S	11°45'E	3971	490	8.23	0.9	.06	.09	0.28	-19.20
1724-4	29°58'S	8°03'E	5086	840	9.26	0.5	.04	.06	0.51	-19.52
1726-2	30°16'S	3°16'E	1006	1250	10.46	0.3	.02	.03	0.10	-20.06
1728-3	29°50'S	2°24'E	2887	1340	10.81	0.2	.01	.03	0.19	-19.45
1729-1	28°54'S	1°00'E	4401	1450	11.64	0.2	.01	.02	0.16	-19.29

River transects (Transects B and D) were, on average, 5.7‰ and 6.1‰, respectively, within 200 km of shore. Lüderitz sediments (Transect C) were heavier with respect to $\delta^{15}N$, exhibiting a mean value of 7.2‰ within 200 km of shore. Nearshore sediments off northern Namibia were lighter by an average of 1.3‰ than nearshore sediments of the Walvis Bay, Lüderitz and Orange River transects. Between 340 and 370 km offshore in the three southern transects (Walvis Bay, Lüderitz and Orange River), sedimentary $\delta^{15}N$ was similar in each transect (9.4 - 9.8‰). Heaviest $\delta^{15}N$ values (11.8‰) were measured in northern Namibia

sediments approximately 800 km from the coast. Orange River sediments reached values almost this heavy (11.6‰) at a distance of >1000 km from the shore.

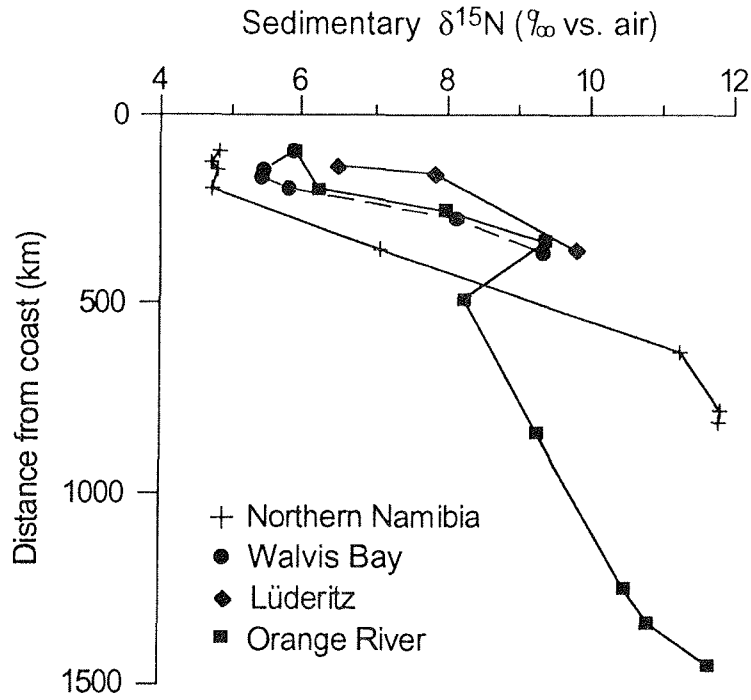

Fig. 2: $\delta^{15}N$ (‰) values measured on bulk nitrogen in surface sediments of Transects A, B, C and D versus distance from the coast in kilometers.

DISCUSSION

Nutrient Concentrations/Utilization

To evaluate how large a role surface nitrate concentrations play in determining sedimentary $\delta^{15}N$, we compared our isotope values with surface water nutrient data. These $[NO_3^-]_{surface}$ data, shown in Table 1, are from the World Ocean Atlas (CONKRIGHT ET AL. 1994) and represent mean 1° latitude-longitude $[NO_3^-]_{surface}$ values measured during different seasons and years by various investigators. Figure 3 shows the distribution of nitrate in surface waters of the Benguela system. The kriging function of the software program "Surfer" (Golden Software, Inc.) was used to create the contour plot from measurements of $[NO_3^-]_{surface}$. Surface nitrate concentrations are high in coastal waters and decrease with distance offshore. Waters off northern Namibia show the highest $[NO_3^-]_{surface}$ (6.5 µM) of the four transects. Surface waters off Walvis Bay also have high nitrate levels (5.5 µM). Nearshore Lüderitz and Orange River transect waters exhibit lower $[NO_3^-]_{surface}$ of ~1.5 µM. Surface nitrate

concentrations decrease with distance from the coast in all four transects. Lowest average $[NO_3^-]_{surface}$ are found in offshore waters of the O
range River transect (down to 0.2 µM). Highest historically averaged nitrate values in the surface water are seen just offshore of northern Namibia between 17°S and 23°S.

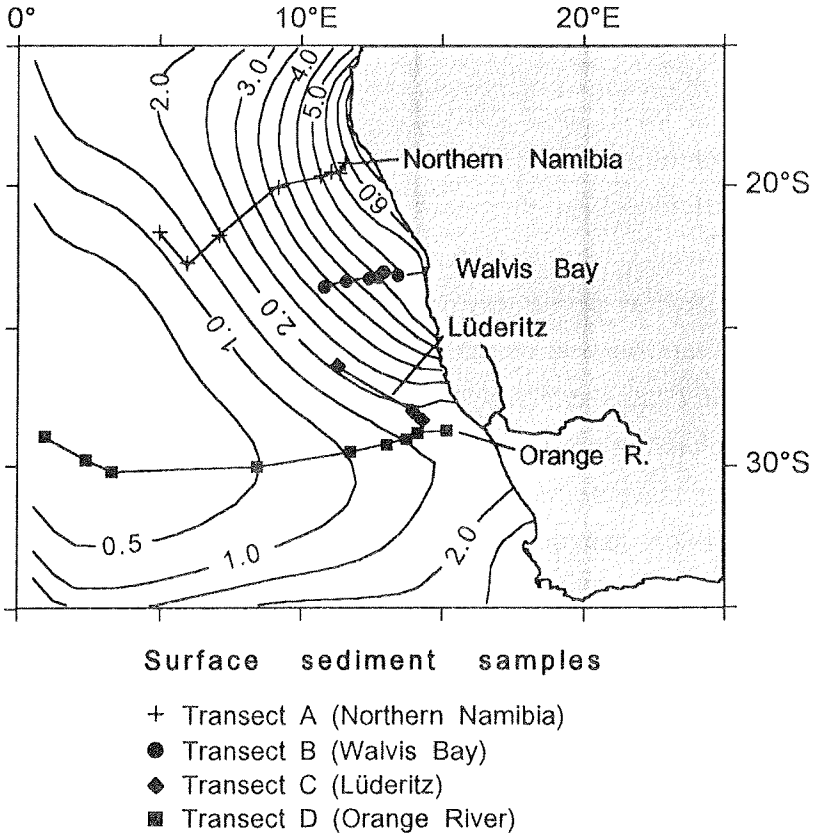

Fig. 3: Surface nitrate concentrations (µM) plotted from 1° latitude-longitude mean field values from WOA (CONKRIGHT ET AL., 1994). Contours were made with the kriging function of the Golden Software, Inc. program "Surfer". Sediment sample sites are denoted by symbols as in Fig. 1.

Figure 4 depicts a plot of sedimentary $\delta^{15}N$ versus ln $[NO_3^-]_{surface}$. ln $[NO_3^-]$ is plotted rather than $[NO_3^-]$ for better visualization of the trends and because the slope of the regression line for $\delta^{15}N$ and ln $[NO_3^-]$ represents ε_u, the fractionation factor associated with NO_3^- uptake during photosynthesis. The data indicate that ε_u in the northern part of the Benguela region is different from ε_u in the south. The value derived for ε_u from the slope of the regression line fitted to the data of Transects A and B (Northern Namibia and Walvis Bay) is 5.4‰. Based on the slope of the regression line for Orange River (Transect D) sedimentary $\delta^{15}N$ and $[NO_3^-]_{surface}$, ε_u in the southern part of the study area is lower (2.0‰). r^2 for both of these regressions is highly significant (.90 for Transects A and B and 0.79 for Transect D). Values for ε_u reported in the literature range from 0.3 to 23‰ (MONTOYA, 1994). According to

ALTABET & FRANCOIS (1994) ε_u in the equatorial Pacific was 2.5‰, based on historically averaged $[NO_3^-]_{surface}$ and $\delta^{15}N$ in sinking PN and sediments. In the Angola Basin, to the north of the Benguela area, a value for ε_u of 1.0‰ was calculated (HOLMES ET AL., 1996). Therefore, our estimates of ε_u (2.0 - 5.4‰) seem reasonable. No regression was performed on the data of the Lüderitz transect because it does not conform to the expected relationship between $\delta^{15}N$ and $[NO_3^-]$. The reason for this is unkown, however, it is possible that the surface nitrate concentrations obtained for this area are not representative of the true average $[NO_3^-]$.

To explain the different ε_u for Transects A and B and Transect D, we looked for documentation of differences in the main primary producers between the two regions. Diatoms are the dominant phytoplankton in the Benguela system in both the north and the south according to a review by SHANNON & PILLAR (1986). These authors also state that dinoflagellates have been found to be relatively more important in northern than central and southern Benguela. No data is available on the fractionation factor of dinoflagellates, but the abundance of these plankton are quite low, even in the northern part of the system where diatoms dominate dinoflagellate in number by 1 to 2 orders of magnitude (HART & CURRIE, 1960). Thus, it is unlikely that the presence in these small numbers of dinoflagellates, no matter what their ε_u, is the cause of the ε_u differences we observed. The only other clear floral difference between the south and the north discussed in the review by SHANNON & PILLAR (1986) is the presence of the diatom species *Skeletonema costatum* in southern Benguela and its absence from samples taken in the north. This phenomenon does not serve to explain the lower ε_u estimated for the southern part of the Benguela since the mean ε_u given by MONTOYA (1994) for *S. costatum* is 9.0 - 9.8‰. This value is higher than that measured for the most common phytoplankton species (*Chaetoceros* sp.) generally encountered in the Benguela (both south and north) (SHANNON AND PILLAR, 1986), which exhibits ε_u of 0.9 - 4.5‰ (WADA & HATTORI, 1978). Although we found no obvious explanation for the observed change in ε_u from north to south, much remains unclear about how different environmental and physiological conditions affect the fractionation of nitrogen isotopes during the photosynthetic uptake of NO_3^- and some unknown mechanism apparently causes ε_u in the north to be larger than in the south. Regardless of the differences between the transects, the significant correlation between $\delta^{15}N$ and $[NO_3^-]$ of Transects A, B and D suggests that sedimentary $\delta^{15}N$ in the Benguela system is primarily controlled by the amount of nitrate in the surface water, where low nitrogen isotope ratios in surface sediments reflect the high nitrate concentrations of upwelled water nearshore and higher ratios the increasing depletion of nutrients as the surface water is advected seaward.

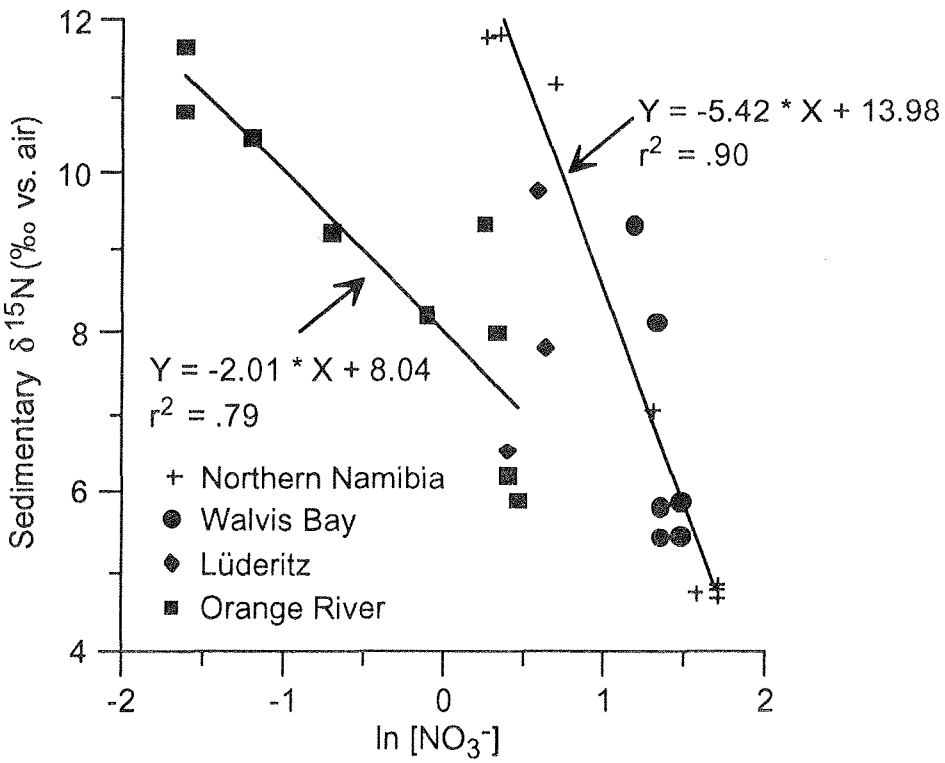

Fig. 4: $\delta^{15}N$ (‰) values of bulk surface sediments versus ln $[NO_3^-]$ (µM). The slopes of the regression lines give ε_u, the fractionation factor. The lines represent the regressions calculated for Transects A and B (crosses and circles) and for Transect D (squares). No regression was performed for Transect C.

In spite of the apparent correlation between sedimentary $\delta^{15}N$ and surface $[NO_3^-]$, $\delta^{15}N$ in organic material is not directly related to nitrate concentration per se, but rather to the degree of nitrate utilization. The fraction of nitrate utilized (f) may be determined from the ratio of $[NO_3^-]$ in the surface water over each sample location to $[NO_3^-]$ of the upwelled water (Table 1). For all four transects the concentration of nitrate in the upwelled water was assumed to be 10 µM because this is the value indicated by data from a sediment trap study at the Walvis Ridge (HOLMES, submitted manuscript) for the $[NO_3^-]$ of original upwelled water in this area. Also, JONES (1971) reported that SACW (the source of upwelled water in the Benguela region) exhibits nitrate concentrations of 10 - 18 µM. Since we presume that $[NO_3^-]_{upwelled}$ is the same throughout the study area, the relationship between sedimentary $\delta^{15}N$ and ln f (Figure 5) is identical to that shown in Figure 4 of $\delta^{15}N$ and ln $[NO_3^-]_{surface}$, except the values for ln f are more negative than for ln $[NO_3^-]_{surface}$ and thus the Y intercepts are different.

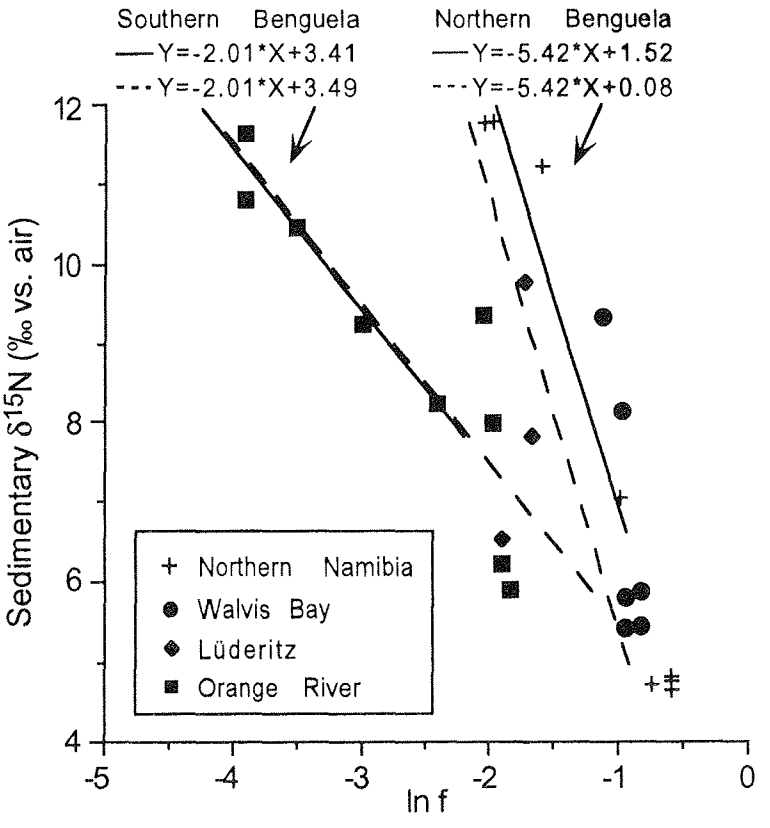

Fig. 5: $\delta^{15}N$ (‰) values of bulk surface sediments versus ln f (fraction of unutilized nitrate remaining in surface water) estimated from $[NO_3^-]$ in the water column (filled symbols and solid lines) and for ln f predicted from sedimentary $\delta^{15}N$ (dashed lines). Equations (1) and (2) (instantaneous product) from ALTABET & FRANCOIS (1994) were used to determine ln f from sedimentary $\delta^{15}N$.

The hindcasting of surface nitrate utilization is one important application of bulk sedimentary $\delta^{15}N$ in paleoceanographic research. We applied equations (1) and (2) of ALTABET & FRANCOIS (1994) to the sedimentary $\delta^{15}N$ we measured to determine how accurately these predicted the degree of surface nitrate utilization in the Benguela region.

(1) $\delta^{15}NO_3^-{}_{(f)} = \delta^{15}NO_3^-{}_{(f=1)} - \varepsilon_u \times \ln(f)$

(2) $\delta^{15}N\text{-}PN_{(f)} = \delta^{15}NO_3^-{}_{(f)} - \varepsilon_u$ (instantaneous product)

f is the fraction of unutilized NO_3^- remaining and ε_u is the fractionation factor associated with NO_3^- uptake. Equation (2) allows the estimation of $\delta^{15}NO_3^-{}_{(f)}$ based on $\delta^{15}N$ of instantaneously produced PN. $\delta^{15}NO_3^-{}_{(f)}$ thus calculated can then be inserted into equation (1) to obtain ln f. This instantaneous product equation should provide a better prediction of f in our study area than a formula for an accumulated product because upwelled water moves seaward over the sediments, becoming more and more depleted in NO_3^- with distance from

the site of upwelling. $\delta^{15}NO_3^-{}_{(f=1)}$ was assumed to be 5.5‰. ln f for Transects A and B was estimated using ε_u = 5.4‰ and for Transects C and D, ε_u = 2.0‰ was used. The dashed lines in Fig. 5 represent ln f which was predicted from sedimentary $\delta^{15}N$. The slopes of the lines based on ln f predicted from measured sedimentary $\delta^{15}N$ and the regression lines of sedimentary $\delta^{15}N$ and ln f are identical for both the two northern transects (A and B) and Transect D. The Y intercepts are different, but analysis of covariance revealed that no significant differences exist between the line derived from the equations and the regression line of Transects A and B and of Transect D ($P < .01$). A similar result was obtained from sediments of the Angola Basin, using ε_u = 1.0‰ (HOLMES ET AL., 1996). It is apparent, however, that the accurate estimation of ε_u is important in hindcasting f from sedimentary $\delta^{15}N$.

Productivity

Bulk sedimentary $\delta^{15}N$ values are correlated not only with surface nutrient concentrations, but also with sedimentary organic carbon content (C_{org}). Fig. 6 shows the exponential relationship between these two parameters. The regression is highly significant ($r^2 = .90$). Assuming that the amount of organic carbon in the sediments is indicative of euphotic zone productivity, the coincidence of low $\delta^{15}N$ with high C_{org} and vice versa underscores the dependence of primary productivity on the availability of nitrate in surface waters. The close relationship seen in Fig. 6 between sedimentary $\delta^{15}N$ and surface productivity shows that $\delta^{15}N$ in sediment cores can be a useful tool in the study of paleoproductivity.

Diagenesis

Much is unknown about the effect of degradation on nitrogen isotope ratios. $\delta^{15}N$ has been found to be elevated in residual organic matter due to the preferential uptake of ^{14}N by bacteria during remineralization of sinking particles (SAINO & HATTORI, 1980; ALTABET, 1988). FRANCOIS ET AL. (1992) reported that in the Southern Ocean, sediments at the sediment-water interface were enriched by 5 - 7‰ relative to sinking particles and argued that although the $\delta^{15}N$ signal produced at the surface may be offset to a degree in the sediments, this signal is probably not obscured by diagenesis. ALTABET & FRANCOIS (1994) found a smaller difference between sediments and sinking particles in the equatorial Pacific and proposed that the difference in preservation of the isotopic signal may be due to the high amounts of opal in the southern ocean sediments. In a recent report, FRANCOIS ET AL. (1996) suggest a constant offset of 3 - 4‰ from sinking particles to sediments. A sediment trap experiment at the Walvis Ridge revealed an isotopic enrichment of 1.6‰ between particles sinking at 599 m and the sediment surface (HOLMES, submitted manuscript). Additionally, the difference between the Y intercepts of the dashed and solid lines in Fig. 5 should approximate the diagenetic offset between particles produced at the surface and sedimentary nitrogen.

Thus, diagenesis in northern Benguela has resulted in an enrichment in sedimentary $\delta^{15}N$ of ~ 1.4‰, while in southern Benguela remineralization has had no noticable effect on sedimentary $\delta^{15}N$.

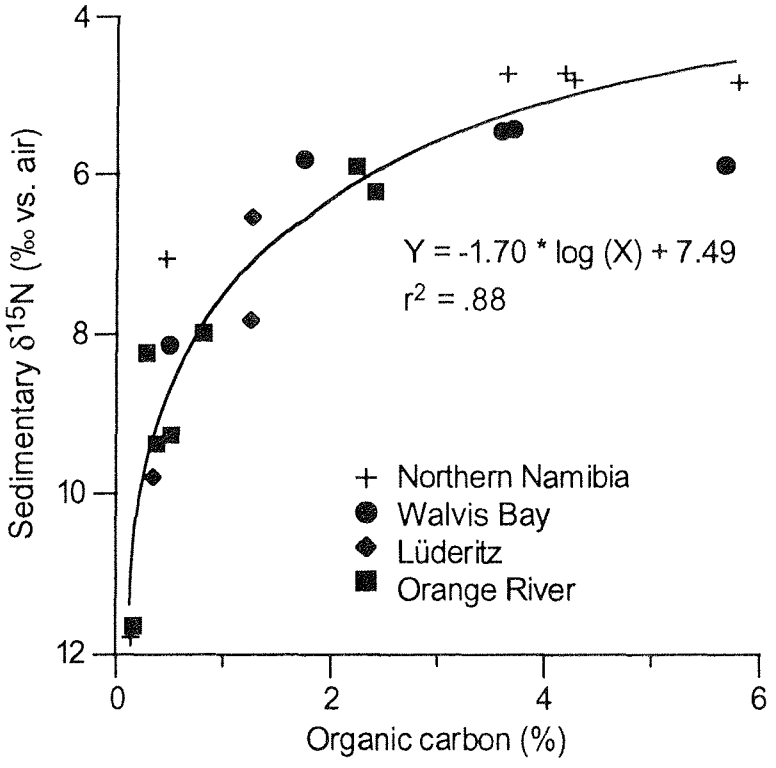

Fig. 6: $\delta^{15}N$ (‰) values of bulk surface sediments versus organic carbon content (%) of Transects A, B, C and D.

Denitrification

The Benguela current system is known to be oxygen-depleted (HART & CURRIE 1960), especially in coastal waters. Nitrate reduction in the water column is not apparent in the $\delta^{15}N$ of the sediments we measured, however, since the measured $\delta^{15}N$ is not higher than expected from the concentration of nitrate in the overlying surface water (Fig. 5). The absence of a denitrification signal in the sediments we sampled may be because most of the sediments we investigated were seaward of the shelf break. It is farther shoreward, over the shelf, where observations of sulfide production and fish kills due to anoxia have been made (BOULEGUE 1983; HART & CURRIE 1960). The two samples which were located on the shelf were GeoB 1714-1 in Transect B and GeoB 1718-1 in Transect D. The $\delta^{15}N$ of these sediments is not very different from that measured in other sediments when the surface nitrate concentration is taken into account, implying that denitrification is not observable in the $\delta^{15}N$ of these sediments.

A general elevation of Benguela sedimentary $\delta^{15}N$ due to water column denitrification in the oxygen depleted water off the shelf also does not seem to occur, since the $\delta^{15}N$ values measured are typical for that of marine systems and conform to expected values based on surface nitrate concentrations. O_2 profiles from STANDER (1964), BUBNOV (1972) and SNEC II (1986) indicate that the oxygen minimum zone (OMZ) encompasses the depth from which upwelled water originates, but the O_2 concentrations are not low enough to promote denitrification. Reduction of nitrate occurs below 0.2 ml O_2 l^{-1} (PACKARD ET AL. 1983) and concentrations this low were rarely observed off of the shelf and were instead generally 1 - 2 ml l^{-1}. Furthermore, intensification of the subsurface OMZ (believed to originate from the anoxic water which forms over the shelf off Namibia due to high productivity) should occur after upwelling events, not before. This means that even if denitrification occurs after upwelling, most of the production of OM would have taken place prior to the formation of ^{15}N-enriched nitrate and this nitrate would not be detectable in the sediments of the region.

Evaluation of Terrestrial Input

It has been shown that in some areas, terrigenous-derived OM is depleted in ^{15}N relative to OM of marine origin. SWEENEY & KAPLAN (1980) demonstrated the potential of using $\delta^{15}N$ as a tracer of the source of near-shore sedimentary organic material. These authors showed that sediments were isotopically light near the coast and became more enriched in ^{15}N with increasing distance from the coast, due to mixing of an isotopically light terrestrial plant end member with isotopically heavier marine plankton material. This is, however, not a universal phenonmenon. HOLMES ET AL. (1996) measured $\delta^{15}N$ of 7.0 - 7.6‰ in sediments of the Zaire River, which was within the range, but at the high end of Angola Basin marine sedimentary $\delta^{15}N$ (4.6 - 8.8‰). Furthermore, OWENS (1985) and THORNTON & MCMANUS (1994) reported that the $^{15}N/^{14}N$ variations they observed in nearshore particles and sediments did not reflect simple hydrodynamic mixing of two end member sources.

Terrestrial input to the Benguela Current system is substantially lower than in the Angola Basin due in part to the absence of a major river like the Zaire. Also important is that the land through which the Orange River (the only major river in the area) flows, is arid or semi-arid. EMERY ET AL. (1973) reported very low percentages of yellow color in the water off the mouth of the Orange River (measured by SCHOTT 1912) relative to the rest of the southwestern African coast, indicating that there is little material entering the sea from the river and what does arrive is probably not highly organic in nature. In order to determine whether the $^{15}N/^{14}N$ ratios in our Benguela sediment samples reflect the presence of terrigenous material, we examined $\delta^{13}C_{org}$ values and C/N ratios of the same sediments. The $\delta^{13}C_{org}$ values reveal that very little terrestrial material is present in the sediments. Except for the sample nearest the coast in the Orange River transect, nearshore sediments exhibit

$\delta^{13}C_{org}$ between -19.5 and -20.2‰. Sediments with $\delta^{13}C_{org}$ values of around 19 - 20 ‰ are considered to be of marine origin (SACKETT, 1989).

C/N ratios also do not indicate the presence of terrigenous matter in our samples. Marine sediments are typically nitrogen-rich relative to terrestrial matter, which generally has C/N ratios >15 (MEYERS, 1994). C/N ratios of Benguela sediments are between 7 and 8.5 in nearshore sediments and decrease to around 6 in sediments further away from land (P.J. Müller, unpublished data). Thus, we conclude that the influence of terrestrial material on the composition of the sediments we investigated was negligible. The only exception was the Orange River shelf sample. The $\delta^{13}C_{org}$ of this sediment was lighter by 0.2 ‰ than the other nearshore samples. The location of this sediment sample corresponds approximately to the position of a mud belt described by SHANNON (1985) of mainly terrigenous origin on the shelf off the Orange River.

Lateral Advection

A consideration to be made when using sediment proxies is whether the material being analyzed in the sediment comes from overlying water nearby or whether it is advected from elsewhere. BISHOP ET AL. (1978) investigated the vertical flux of particulate matter in the Cape Basin and found that particulater organic carbon below 200 m reflected surface productivity. Since the highest current speeds (average 17 m s^{-1}; SHANNON, 1985 and references therein) in the water column have been measured in the upper 200 m of the water column in the Benguela area, whatever advection takes place should occur near the surface and not to a great extent below 200 m. Furthermore, in a sediment trap study, TREPPKE ET AL. (in press) reported that particle fluxes at 20°03'S, 09°09'E were directly related to wind stress variations and that the diatom taxa in the trap at 599 m and at 1648 m were identical, although there was some flux enrichment in the deeper trap due to particle advection into this trap by resuspension and downslope movement. Thus, it is likely that in this area, sedimentary $\delta^{15}N$ does reflect processes occurring in the nearby overlying water.

CONCLUSIONS

Measurement of water column parameters and using these to draw conclusions about the oceanography in a given area is limiting in that one can seldom be certain whether the observed parameters are generally representative or whether they were a sporadic occurence. In addition, seasonal bias is unavoidable during single time point sampling. The use of sediments as proxies for processes in the overlying water can be helpful in that they integrate over longer time scales and eliminate seasonal effects. Since surface water nitrate concentrations and the degree of utilization of this pool appear to be the main controls on

sedimentary $\delta^{15}N$ in this region, based on Fig. 2, we conclude that nutrient input to the surface water over the past several decades which these surface sediments represent, has occured most intensely at around 20°S (off northern Namibia), since the nearshore sediments there were depleted in ^{15}N relative to the other transects. This is in agreement with the report by SHANNON (1985) of a region of winds highly favourable for upwelling at Cape Frio (at 19°S).

Our study demonstrates that the surface-generated stable nitrogen isotope signal is reliably transferred to the sediments and that sedimentary $\delta^{15}N$ is a useful proxy for processes occuring in the overlying water. In the Benguela upwelling system, $\delta^{15}N$ seems to primarily reflect surface nitrate concentrations and the extent to which the pool of upwelled nutrients in the surface water has been utilized. In spite of the agreement between sedimentary $\delta^{15}N$ and surface water processes apparent in the present work and in various other studies, one of the major uncertainties involving sedimentary $\delta^{15}N$ is the effect of bacterial remineralization and early diagenesis and more work is needed in this regard.

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RECONSTRUCTION OF PAST NUTRIENT UTILIZATION IN THE EASTERN ANGOLA BASIN BASED ON SEDIMENTARY $^{15}N/^{14}N$ RATIOS

(submitted to Paleoceanography)

Reconstruction of Past Nutrient Utilization in the Eastern Angola Basin based on Sedimentary $^{15}N/^{14}N$ Ratios

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ABSTRACT

Stable nitrogen isotope ratios in Holocene and Late Quaternary sediments from the eastern Angola Basin have been used to investigate changes in past nutrient utilization in the surface waters of this highly productive, low-latitude region. $\delta^{15}N$ values in two cores from deep (>3000 m) sites, one in the Zaire fan, at around 6°S (GeoB 1008-3) and one in the middle Angola Basin, near 12°S (GeoB 1016-3), were measured. Bulk $\delta^{15}N$ in these sediments ranges from 5.0 to 9.5‰. Core GeoB 1008-3 extends back to 180 kyr b.p. and the oldest sediments of GeoB 1016-3 are from 302 kyr b.p. Terrestrial organic matter content of core GeoB 1008-3 was found to be around 25% throughout the core and is negligible in core GeoB 1016-3. Terrestrial material entering the Zaire fan from the Zaire River has a similar $\delta^{15}N$ signature at the present time as marine-derived organic matter and does not appear to have noticably altered the $\delta^{15}N$ of the sediments at site GeoB 1008-3 over the past 180 kyr. Low $\delta^{15}N$ values in the two cores correspond to low sea surface temperatures and high sedimentary organic content. Past changes in the degree of surface water nitrate utilization were calculated from sedimentary $\delta^{15}N$ and were found to correlate with estimated paleoproductivity variations. The surface nitrate pool was less extensively depleted and paleoproductivity was elevated during oxygen isotope stages 2, 5.2, 5.4 and 6.6. Glacial $\delta^{15}N$ was lower by 0.5 - 0.7‰ than during interglacial periods at both locations, indicating about 10% lower relative nitrate utilization during glacials than in interglacials. Spectral analyses

reveal the presence of 41 kyr periodicity in the nitrogen isotope ratios, further evidence for increased nitrate concentrations during glacials. More pronounced than the glacial/interglacial variations in $\delta^{15}N$ values of both cores are precession-related (23 kyr) fluctuations. These show cyclic variations which lag minima in boreal summer insolation by 6.1 - 7.7 kyr, indicating that changes in trade wind-driven upwelling intensity and in the advection of cold, nutrient-rich water from the south drive nutrient availability and productivity off the southwest coast of Africa. During stages 3 and 4, the Benguela Current penetrated into the Angola Basin, resulting in higher $[NO_3^-]$ and lower relative nitrate utilization in GeoB 1016-3 relative to GeoB 1008-3. No strong evidence was found from sedimentary $\delta^{15}N$ values and organic carbon content for denitrification in the water column during the past 180 kyr.

INTRODUCTION

Recent studies have demonstrated the usefulness of sedimentary nitrogen isotope ratios in the reconstruction of relative surface water nitrate utilization (FRANCOIS ET AL., 1992; ALTABET & FRANCOIS, 1994; FARRELL ET AL., 1995). The nitrogen isotopic ratio of organic matter (OM) produced in the photic zone depends on the amount of nitrate present, its isotopic signal and the degree to which this inorganic nitrogen pool has been utilized (MARIOTTI ET AL., 1982; VOß ET AL., in press). Under elevated nitrate conditions, $\delta^{15}N_{OM}$ is lower than the $\delta^{15}N$ of the original nitrate due to preferential uptake by phytoplankton of $^{14}NO_3^-$. When surface nitrate has been extensively depleted, $\delta^{15}N_{OM}$ becomes relatively high (WADA & HATTORI, 1978).

The $\delta^{15}N$ of the inorganic nitrogen available for uptake by phytoplankton also affects the $\delta^{15}N$ of the produced OM. Nitrate from oxygenated water in the deep sea is around 5 - 6‰ (WADA ET AL., 1975), which is also the value of the original source nitrogen for primary production under normal upwelling conditions. However, denitrification may alter the $\delta^{15}N$ of nitrate in oxygen-depleted waters. When oxygen is in short supply, denitrifying bacteria are able to use nitrate as an electron acceptor during respiration. In doing so, these organisms preferentially utilize $^{14}NO_3^-$ and the residual nitrate becomes enriched in ^{15}N (MARIOTTI, ET AL., 1981). For instance, CLINE & KAPLAN (1975) reported that the nitrate within a denitrification zone in the Eastern Tropical North Pacific Ocean exhibited $\delta^{15}N$ values of up to 18.8‰.

The preservation of the isotopic surface-water signal in the sediments allows hindcasting of variations in productivity and hydrography. However, diagenesis may significantly alter the $\delta^{15}N$ of particles before they are buried at the sea floor. SAINO & HATTORI (1980) and ALTABET & MCCARTHY (1985) suggested that bacterial remineralization of sinking particles

resulted in ^{15}N enrichment of the residual OM. FRANCOIS ET AL. (1992) measured a ^{15}N enrichment of 5 - 7‰ in OM at the sediment-water interface relative to OM suspended in the photic zone in the Southern Ocean, but showed that the observed offset between photic zone and sedimentary OM was relatively constant and that latitudinal gradients in sedimentary $\delta^{15}N$ reflected the nutrient gradients observed in the surface water. On the other hand, in the equatorial Pacific, ALTABET & FRANCOIS (1994) detected little diagenetic offset between sinking particles at 50 m and surface sediments. These authors suggested that the difference in the observed diagenetic alteration between the two areas could be the high opal content of the Southern Ocean sediments in which organic matrices with elevated $\delta^{15}N$ could be bound.

$\delta^{15}N$ in Late Quaternary sediments has been reported for various regions of the world's oceans. In some regions (Arabian Sea and Eastern Tropical North Pacific), denitrification appears to have been the main control on $\delta^{15}N$ in OM (ALTABET ET AL., 1995; GANESHRAM ET AL., 1995). Another study showed that low $\delta^{15}N$ in sediments resulted from nitrate uptake under nutrient-replete conditions (CALVERT ET AL., 1992). In the present paper, we introduce results of $\delta^{15}N$ analyses of two cores from the continental margin off southwest Africa and compare these with other productivity proxies. Paleoproductivity changes in the Angola Basin have been estimated previously based on changes in diatom assemblages, organic carbon content and biogenic barium (JANSEN & VAN IPEREN, 1991; SCHNEIDER, 1991; RUTSCH ET AL., 1995; SCHNEIDER ET AL., submitted manuscript). These studies demonstrated higher productivity during glacials relative to interglacials. SCHNEIDER ET AL. (1994, in press, submitted manuscript) reported that in addition to glacial/interglacial changes, productivity in this region varies with a 23 kyr, precession-forced periodicity. Additionally, various authors have proposed different scenarios for the temporal and spatial variability of the currents in the South Atlantic (MCINTYRE ET AL., 1989; SCHNEIDER ET AL., 1995; JANSEN ET AL., in press). $\delta^{15}N$ fluctuations may provide clues as to how and when the portions of nutrient-poor equatorial warm water and nutrient-rich cold upwelled water changed in the Late Quaternary. Furthermore, because the Angola Basin is highly productive and tends to be somewhat oxygen-depleted at the present time, this area may have been an important site of nitrate reduction in the past. This could have implications for the availability of nutrients for photosynthesis because of loss of nitrate to the atmosphere due to denitrification. Until now there have been few studies done in this area on the changes in nutrient utilization which drive productivity variations (STRUCK ET AL., 1993). With this study, we hope to add to the existing information on the Angola Basin and South Atlantic to improve our understanding of past processes which occurred in this region.

ANGOLA BASIN HYDROGRAPHY

Figure 1 shows the study area and core locations. Also shown in Figure 1 are the locations of three surface sediment transects in which $\delta^{15}N$ and other parameters have been previously presented and which are discussed in the present study. The Angola Basin is predominantly influenced by two current systems: the Angola Current (AC) and the Benguela Current (BC). The AC, a warm surface current, flows over both samples sites. The AC is an extension of the South Equatorial Counter Current (SECC), which brings warm equatorial water into the Angola Basin. The BC splits into two parts at around 28° S (STRAMMA & PETERSON, 1989). The main part of the BC is deflected to the northwest, becoming the Benguela Oceanic Current (BOC). The cold Benguela Coastal Current (BCC) flows northward, meeting the AC at the Angola-Benguela Front (ABF). The ABF separates the oceanic upwelling area north of the front from the coastal upwelling region off Namibia and is presently located between 15° and 17°S (MEEUWIS & LUTJEHARMS, 1990). HART & CURRIE (1960) noted a sea surface temperature difference of 7.5°C between the warm waters north of the front and the cold Benguela waters. The ABF extends down to 200 m water depth and 150 - 200 km offshore (SHANNON ET AL., 1987). The BCC continues to flow north of the ABF as a subsurface current, at 20 - 40 m depth, to between 5°S and 10°S (HAGEN ET AL., 1981; VAN BENNEKOM & BERGER, 1984).

The area between about 5°S and nearly 20°S and westward to about 0° has been described as a high productivity region by VAN BENNEKOM & BERGER (1984). Offshore primary productivity rates in the Angola Basin are high, ranging from 90 to 125 g C m^{-2} yr^{-1} north of 8°S and 125 to 180 g C m^{-2} yr^{-1} from 8°S to 18°S (BERGER ET AL., 1987; BERGER, 1989). Runoff from the Zaire and the gyres and fronts formed by the various currents cause this high productivity. South of 15°S, coastal upwelling is induced by zonally directed trade winds, while north of 10°S, geostrophic coastal upwelling of the subsurface EUC occurs (VOITURIEZ & HERBLAND, 1982). The high productivity leads to oxygen depletion in some areas of the Angola Basin. The main oxygen minimum zone (OMZ) in the southeast Atlantic is between 300 and 600 m, with O_2 concentrations of around 1 ml l^{-1} (BUBNOV, 1972; CHAPMAN & SHANNON, 1987).

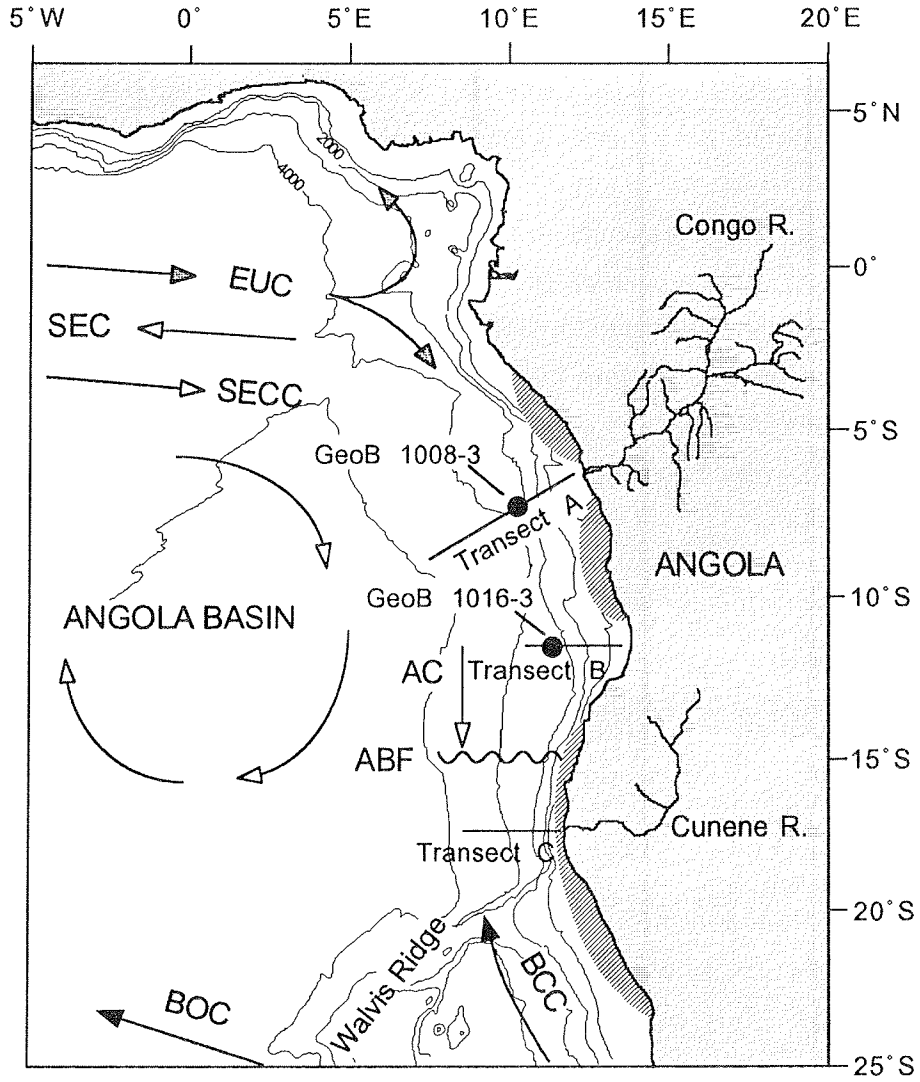

Fig. 1: Map of the study area off the southwest coast of Africa (modified from SCHNEIDER, 1991). The locations of gravity cores GeoB 1008-3 and GeoB 1016-3 are shown, along with the three surface sediment transects (A, B and C) discussed in the text. Coastal upwelling is indicated by shaded areas. Black arrows represent cool surface currents, white arrows indicate warm surface currents and gray arrows denote warm subsurface currents. The following abbreviations are used: ABF: Angola-Benguela Front; AC: Angola Current; BCC: Benguela Coastal Current; BOC: Benguela Oceanic Current; EUC: Equatorial Undercurrent; SEC: South Equatorial Current; SECC: South Equatorial Counter Current.

MATERIALS AND METHODS

Gravity cores were retrieved from 6°35'S, 10°19'E (GeoB 1008-3) and 11°46'S, 11°41'E (GeoB 1016-3) during the RV/Meteor cruise 6/6 from 23 February to 23 March 1988. GeoB 1008-3 was located at 3124 m water depth and GeoB 1016-3 at 3411 m water depth.

Procedures for core recovery have been described by WEFER ET AL. (1988). Subsamples of approximately 10 cm^3 were removed at 5 cm intervals from the cores on board immediately after recovery. The plastic syringes containing the sediment subsamples were sealed with electrical tape and stored at 4°C until further processing. The sediment was freeze-dried and homogenized in a shore-based laboratory. Sediment samples were then decalcified in 1M HCl and dried overnight in a drying oven at 50°C.

For stable nitrogen isotope analyses, 25 - 150 mg of bulk sediment was re-ground with copper oxide and placed in tin boats before being combusted in a Heraeus Elemental Analyzer at 1050°C. The resulting N_2 gas was cryogenically purified using a trapping box (FRY ET AL., 1992) and measured with a Finnigan MAT 252 mass spectrometer. Isotopic data are presented in the standard δ notation:

$$\delta^{15}N = [(^{15}N/^{14}N_{sample}/^{15}N/^{14}N_{standard}) - 1] \times 10^3$$

δ values are reported relative to air. Pure tank N_2 (99.996%) was used as the working standard gas. The tank N_2 was calibrated against atmospheric air and IAEA standards N-1 and N-2. Reproducibility of $\delta^{15}N$ measurements was ± 0.2‰ based on repeated measurement of reference sediment standards.

As described by SCHNEIDER ET AL. (1994, 1995), $\delta^{18}O$ values of the planktonic foraminifera *Globigerinoides ruber* (pink) and *Globigerina bulloides* were compared with the SPECMAP record (IMBRIE ET AL., 1984) to obtain the age models used in this study.

For time series analyses, the software program SPECTRUM (SCHULZ, 1995) was used. A modification of the test by FISCHER (1929) in which compound periodicity can be analysed (SIEGEL, 1980) was used to test for the presence of harmonic components in our data. Cross-spectral analyses were also performed with SPECTRUM. Using this program, interpolation of the data to regular time intervals is not necessary. For cross-spectral analyses, a Welch window was used and core GeoB 1008-3 was divided into two and core GeoB 1016-3 into three 50% overlapping segments.

RESULTS

Results of the stable nitrogen isotope analyses performed on cores GeoB 1008-3 and GeoB 1016-3 are shown in Appendix 1 and Fig. 2. The numbers shown at the right in Fig. 2 represent oxygen isotope climate stages. Highest $\delta^{15}N$ values in both cores were reached in the Holocene. GeoB 1008-3 $\delta^{15}N$ during this time was 7.68‰ and in GeoB 1016-3 was

9.50‰. Both cores also attained the lowest measured $\delta^{15}N$ values simultaneously, during late stage 6 (~180 kyr b.p.), with GeoB 1008-3 exhibiting $\delta^{15}N$ as low as 4.95‰ and GeoB 1016-3 down to 4.52‰. Noteworthy minima in $\delta^{15}N$ in core GeoB 1008-3 occured during stages 2 (14 - 22 kyr), 3 (42 - 54 kyr), 5.2 (83 - 87 kyr) and 5.4 (104 - 115 kyr). GeoB 1016-3 exhibited a decrease in $\delta^{15}N$ in stage 2 relative to Holocene values and minima during stages 3 (29 - 35 kyr), 4 (62 - 69 kyr), 5.2 (82 - 88 kyr), 5.4 (105 - 115 kyr), 6.6 (180 - 186 kyr), 7.2 (200 - 212 kyr), 7.4 (223 - 235 kyr), 8.2 (240 - 253 kyr) and 8.4 (271 - 284 kyr). Also presented in Appendix 1 are sediment depth, age, organic carbon content (SCHNEIDER, 1991), sea surface temperature based on alkenones (SCHNEIDER ET AL., 1995, in press), $\delta^{13}C_{org}$ (core GeoB 1016-3: from MÜLLER ET AL., 1994), paleoproductivity rates (from SCHNEIDER, 1991), $\delta^{15}NO_3^-{}_{(f)}$ and f (the fraction of unutilized nitrate remaining in surface water). $\delta^{15}NO_3^-{}_{(f)}$ and f were estimated from sedimentary $\delta^{15}N$ values (see Discussion).

DISCUSSION

Present-day surface water [NO_3^-] and $\delta^{15}N$ in surface sediments

ALTABET & FRANCOIS (1994) showed that sediments underlying nutrient-rich surface water in the equatorial Pacific and the Southern Ocean were depleted in ^{15}N relative to those from oligotrophic regions. Similarly, HOLMES ET AL. (1996) reported that nitrate-rich water upwelled off the southwest African coast led to lower $\delta^{15}N$ in surface sediments on the outer shelf and upper slope (~5‰) and that as the upwelled water moved offshore and became increasingly depleted in nitrate, the underlying sediments were progressively enriched in ^{15}N (up to ~9‰). In that study, surface sediments were collected in three east-west profiles (transects A, B and C in Fig. 1) and sedimentary $\delta^{15}N$ was found to be significantly correlated with historically averaged surface [NO_3^-] (objectively analyzed one-degree latitude-longitude mean fields from World Ocean Atlas data set; CONKRIGHT ET AL., 1994). HOLMES ET AL. (1996) also found that the sedimentary $\delta^{15}N$ did not show any clear evidence for denitrification in the water column. These results indicate that at the present time in the Angola Basin, the sedimentary nitrogen isotopic signal is controlled primarily by the degree of nutrient utilization in the surface water and that in this region, the relative isotopic signal of the OM produced in surface water is preserved during sinking and burial in the sediments.

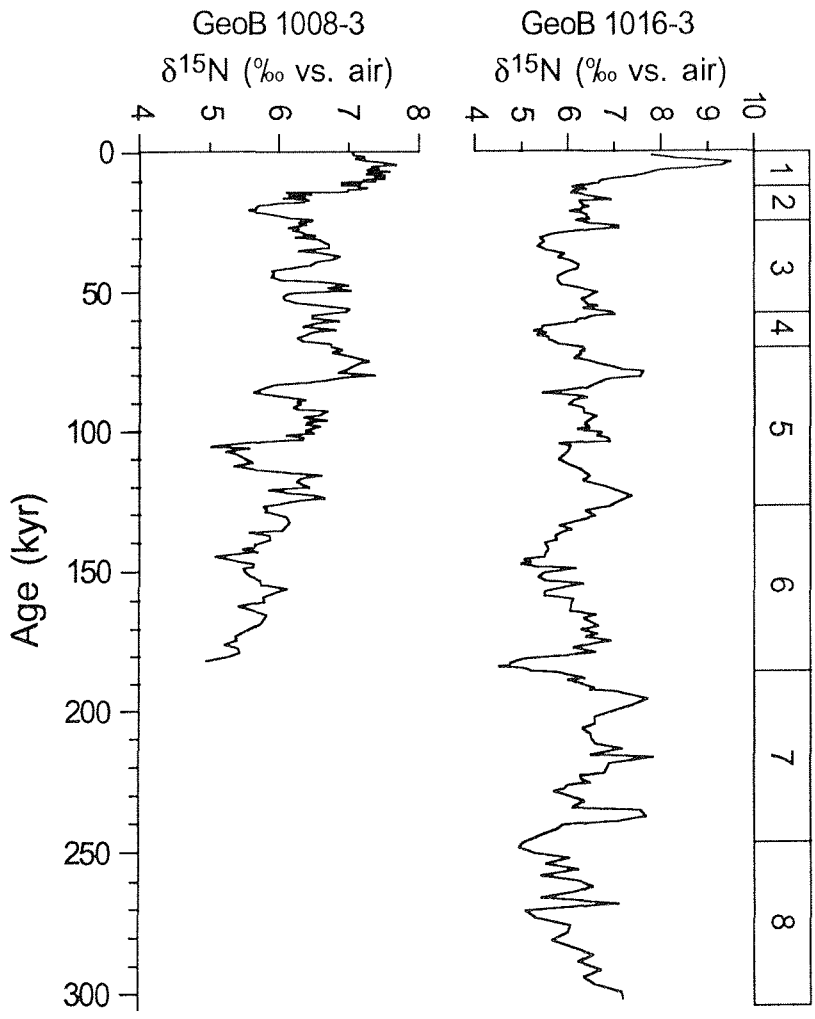

Fig. 2: Bulk sedimentary $\delta^{15}N$ values from cores GeoB 1008-3 and GeoB 1016-3. Oxygen isotope stages are also shown.

Terrestrial Input

Since core GeoB 1008-3 is located near the Zaire River, the question of the influence of terrestrial material on the $\delta^{15}N$ values of these sediments must be addressed. Sedimentary stable carbon isotope ratios clearly reflect the presence of terrestrial material. Figure 3 shows $\delta^{13}C_{org}$ of surface sediments in the Angola Basin (transects A, B and C) and of two sediment samples from the Zaire estuary. Terrestrial matter typically exhibits $\delta^{13}C_{org}$ values of about -26‰ while marine-derived organic matter is comparatively enriched in ^{13}C ($\delta^{13}C_{org}$ ~ -20‰) (SACKETT, 1989). $\delta^{13}C$ of particulate organic carbon in the Zaire River was shown by MARIOTTI ET AL. (1991) to be -26.7 ± 0.4‰ and similar values (-26.6 and -27.8‰) were measured for soils underlying C-3-type vegetation in southern Zaire (SCHWARTZ ET AL., 1986). The light isotopic values in estuary and shelf sediments seen in Figure 3 reflect the

presence of high amounts of terrestrial material in these sediments, with less negative $\delta^{13}C_{org}$ indicating the increasing importance of marine material with distance from shore and the mouth of the Zaire River. Based on $\delta^{13}C_{org}$, the organic matter of surface sediments of core GeoB 1008-3 (-22.09‰) are composed of approximately 35% terrestrial organic matter. The core top of GeoB 1016-3, on the other hand, with $\delta^{13}C_{org}$ of -20.47‰, contains very little terrigenous organic carbon.

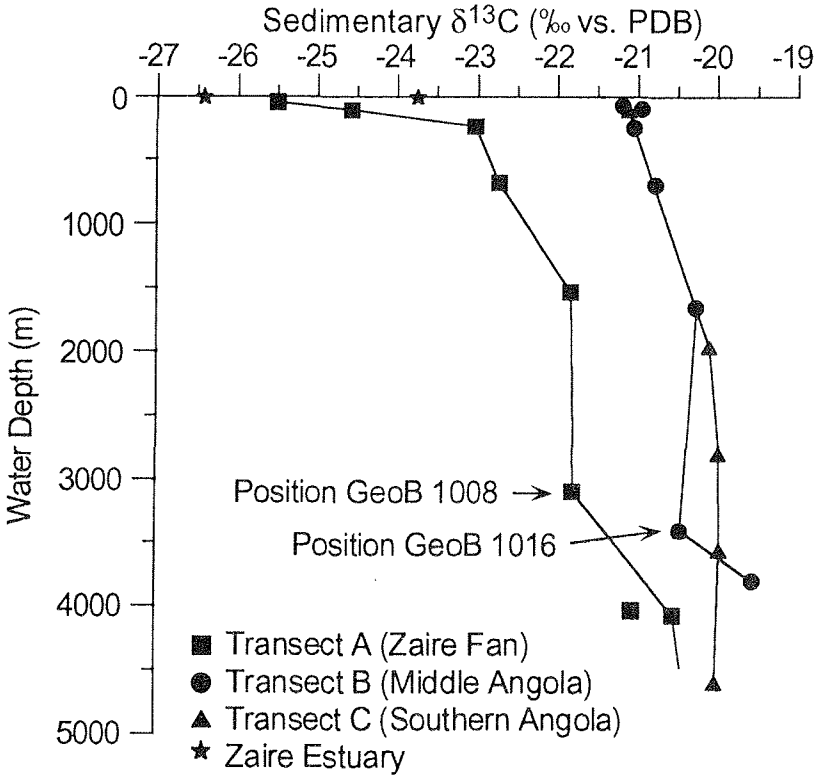

Fig. 3: $\delta^{13}C_{org}$ (‰) values of surface sediments of transects A, B and C versus water depth in meters (from MÜLLER ET AL., 1994). $\delta^{13}C_{org}$ values of estuary samples are from HOLMES ET AL. (1996).

C/N ratios are another measure of the proportion of terrigenous material contained in OM. Terrigenous material is generally poor in nitrogen compared with marine-derived matter (BORDOWSKIY, 1965; MÜLLER, 1977). MÜLLER ET AL. (1994) found that C/N ratios of the surface sediments of the Zaire fan mirror the trend observed in the carbon isotopic ratios, indicating high amounts of terrestrial material in estuary and shelf sediments (C/N ratios between 10.3 and 12.5) and decreasing C/N ratios (as low as 6.4) in sediments farther from the coast. The sediment surface of GeoB 1008-3 exhibits a C/N value of 8.6 and GeoB 1016-3 of 7.7, revealing that at the present time, GeoB 1008-3 surface sediments may contain terrigenous matter, albeit in low concentrations, while GeoB 1016-3 consists mainly of marine-derived matter.

HOLMES ET AL. (in press) reported that $\delta^{15}N$ values of terrestrial material entering the coastal area via the Zaire River are not obviously distinguishable from $\delta^{15}N$ of marine-derived particulate matter. Increases in $\delta^{15}N$ of similar magnitude with increasing distance from the shore were observed in all three transects so that no differences could be detected between the pattern of $\delta^{15}N$ distribution in transect A and that of transects B and C, although neither of the latter profiles are near a major river and both contain very little terrestrially-derived organic matter. Also, the trend toward higher $\delta^{15}N$ with increasing distance from the shore is explainable by surface water [NO_3^-] variations. The core top of GeoB 1008-3 exhibited a $\delta^{15}N$ value of 7.06‰, which is not distinguishable from the estuary samples (7.04 and 7.62‰) and the $\delta^{15}N$ of the two estuary samples is within the range of $\delta^{15}N$ values for marine sediments in the Angola Basin (5.4 - 8.8‰). Thus, it seems that at the present time, the $\delta^{15}N$ signature of terrestrial matter in the sediments is masked by the apparently more important factor of the degree of nitrate utilization.

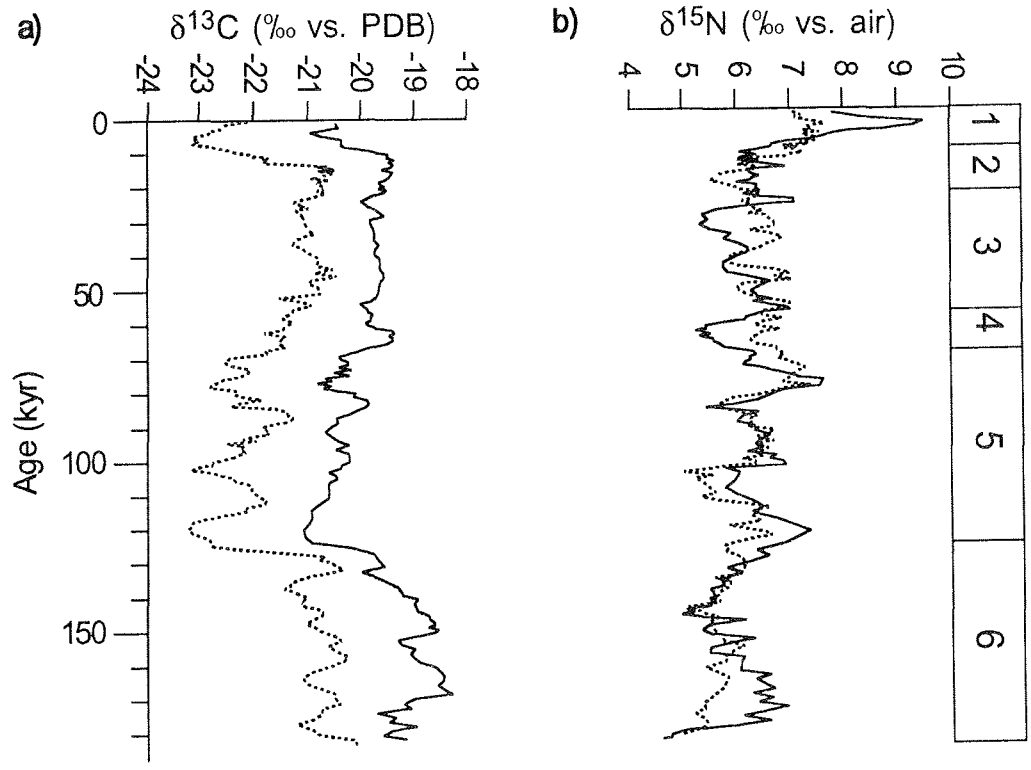

Fig. 4: a) $\delta^{13}C_{org}$ (‰) values from GeoB 1008-3 (dashed line) and GeoB 1016-3 (solid line; from MÜLLER ET AL., 1994); b) Bulk $\delta^{15}N$ (‰) values from GeoB 1008-3 (dashed line) and GeoB 1016-3 (solid line).

Figure 4a shows $\delta^{13}C_{org}$ of cores GeoB 1008-3 and 1016-3. The fairly constant downcore offset of about -1.5‰ in GeoB 1008-3 from 1016-3 is indicative of an approximate contribution of 25% terrigenous organic material. In contrast, $\delta^{15}N$ values in GeoB 1008-3 and 1016-3 show no such systematic shift (Figure 4b). We are, therefore, of the opinion that

varying concentrations of terrestrial organic matter do not exert a significant influence on the observed fluctuations of the nitrogen isotopic signal of the sediments of either core, due in part to the relatively low concentrations of terrestrially-derived OM and also because the nitrogen isotopic signature of this terrigenous matter is not significantly different from that of marine OM in this area.

Late Quaternary nutrient utilization

Organic carbon (OC) content and SST in cores GeoB 1008-3 and GeoB 1016-3 are shown in Appendix 1 and Figure 5. Based on $\delta^{13}C_{org}$, SCHNEIDER (1991) resolved the total OC in core GeoB 1008-3 into two components - marine OC and terrestrial OC (Appendix 1a). In Figure 5, only the marine portion of the OC is shown. As seen in Figure 5, low $\delta^{15}N$ corresponds to low SST and high OC and vice versa. Shaded bars highlight the correspondence of minima in $\delta^{15}N$ with SST minima and OC maxima. Low SST indicates the presence of recently upwelled, nutrient-rich water, which supported high productivity levels, as evidenced by high sedimentary OC. The low $\delta^{15}N$, which occured simultaneously, reflects the increased supply of nitrate which was not completely utilized. At times when $\delta^{15}N$ was high, on the other hand, SST was also elevated and OC generally lower, implying relatively greater depletion of surface water nitrate because of the absence of newly upwelled water and lower productivity. Similar results have been obtained for sediments of the Mediterranean (CALVERT ET AL., 1992) and for the equatorial Pacific in sediments of the Last Glacial Maximum and Holocene (FARRELL ET AL., 1995).

Estimates of the relative depletion of nitrate in surface water should be possible as long as the effects of diagenetic alteration of the $\delta^{15}N$ is similar in all the sediments under investigation (FRANCOIS ET AL., 1992). HOLMES ET AL. (1996) demonstrated, based on C/N ratios and the low amount of inorganic nitrogen in the sediments that bacterial remineralization of the organic material produced in the photic zone during sinking and at the sediment surface had little effect on the $\delta^{15}N$ composition of Angola Basin surface sediments. Furthermore, the concentration of OC in both cores is similar - mean marine OC in Zaire fan sediments is 1.78 $\pm$ 0.70% and the mean total OC in middle Angola sediments is 2.34 $\pm$ 0.78%. Therefore, we presume that if bacterial remineralization has affected the $\delta^{15}N$ of these sediments, the effect has likely been similar at both sites. Another assumption which must be made in the hindcasting of the relative utilization of surface nitrate is that $\delta^{15}N$ of nitrate in the deep sea has remained constant over time.

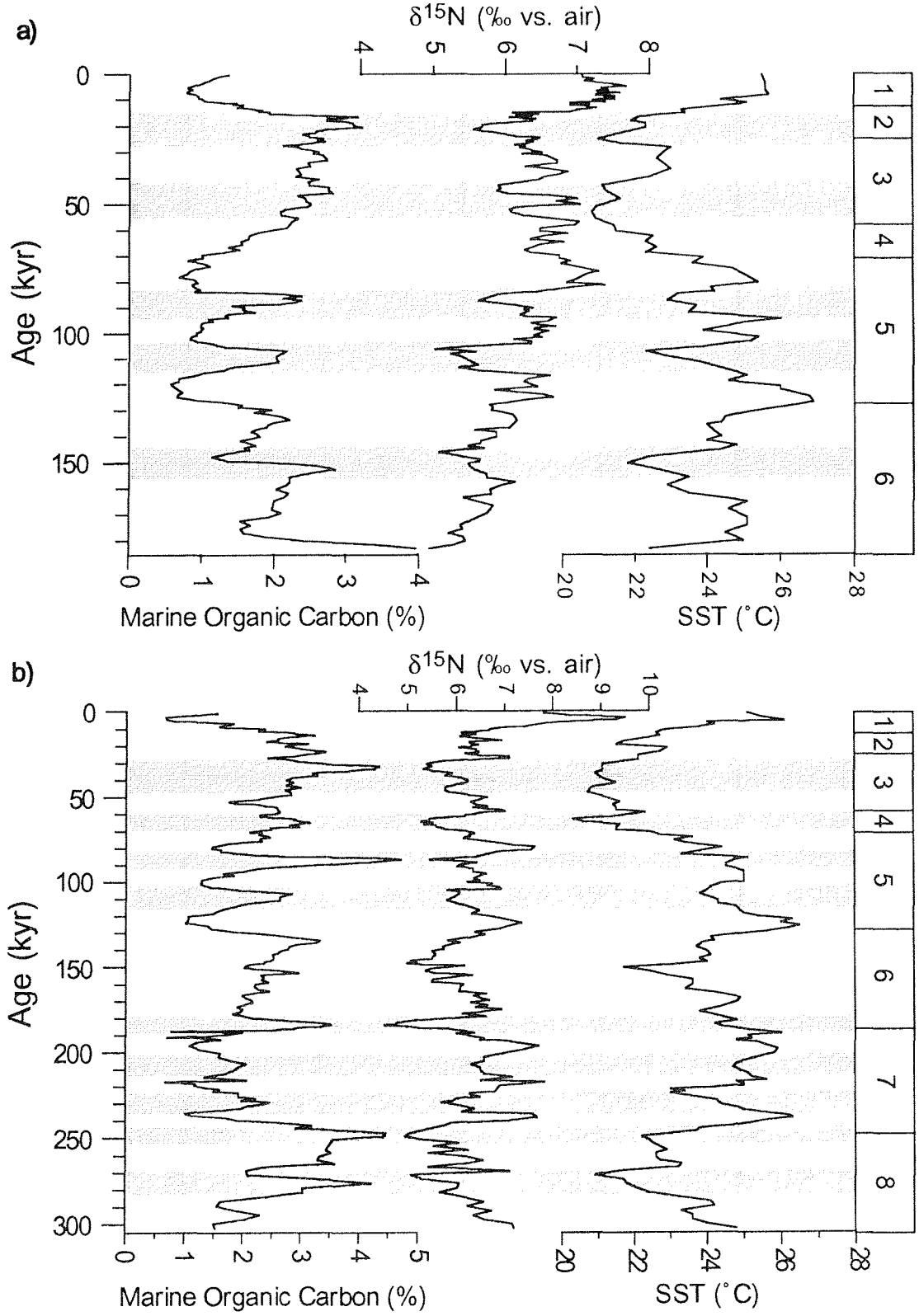

Fig. 5: Bulk $\delta^{15}N$ (‰) values, marine organic carbon content and sea surface temperature (SST) based on alkenone analysis (from SCHNEIDER ET AL., 1995, in press) of a) GeoB 1008-3 and b) GeoB 1016-3. Shaded bars indicate coincidence of low $\delta^{15}N$, low SST and high organic carbon.

ALTABET & FRANCOIS (1994) presented equations for calculating the fraction of unutilized nitrate remaining in surface water based on the $\delta^{15}N$ of particulate organic matter:

(1) $\delta^{15}NO_3^-{}_{(f)} = \delta^{15}NO_3^-{}_{(f=1)} - \varepsilon_u \times \ln(f)$

(2) $\delta^{15}N\text{-}PN_{(f)} = \delta^{15}NO_3^-{}_{(f)} - \varepsilon_u$ (instantaneous product)

$\delta^{15}NO_3^-$ and $\delta^{15}N$-PN are the isotopic ratios of nitrate in the surface water and particulate nitrogen, respectively. f is the fraction of unutilized NO_3^- remaining in surface water and ε_u is the fractionation factor associated with NO_3^- uptake during photosynthesis. HOLMES ET AL. (1996) estimated ε_u for the Angola Basin from a plot of sedimentary $\delta^{15}N$ against ln $[NO_3^-]$ in surface water. The slope of the regression line approximates ε_u (1.04‰) (ALTABET & FRANCOIS 1994). $\delta^{15}NO_3^-{}_{(f=1)}$ ($\delta^{15}N$ of the upwelled nitrate prior to any removal by biological processes) was assumed to be 5.5‰. Equation (2) allows the estimation of $\delta^{15}NO_3^-{}_{(f)}$ based on $\delta^{15}N$ of the particulate nitrogen produced in the euphotic zone at a given time. $\delta^{15}NO_3^-{}_{(f)}$ thus calculated can then be inserted into equation (1) to obtain ln (f). ALTABET & FRANCOIS (1994) also presented a formula by which one can estimate f in a system where the particulate nitrogen represents an accumulated product of nitrate utilization in surface water. The valid use of this equation to predict f requires that all the particulate nitrogen produced from a given pool of nitrate remain in one place and thus be representative of temporal changes in nitrate utilization. We used the instantaneous product equation because off the southwest coast of Africa, upwelled water moves seaward over the sediments, becoming more and more depleted in NO_3^- with increasing distance from the site of upwelling. Therefore, the sediments in our study area record spatial changes in the degree of surface water nitrate depletion. f obtained from these calculations is shown in Appendix 1 and Figure 6.

To estimate paleoproductivity variations, SCHNEIDER (1991) used the formula proposed by MÜLLER & SUESS (1979):

$$PaP = (C * DBD) / (0.003\ SR^{0.3})$$

In this formula, PaP is paleoproductivity (g C m^{-2} yr^{-1}), C is organic carbon, DBD is dry bulk density (g cm^{-3}) and SR is the bulk sedimentation rate (cm 1000^{-1} yr). Appendix 1 and Figure 6 show the results of these paleoproductivity calculations.

f ranged from .05 to .62 (95% to 38% of the upwelled nitrate had been utilized) in the Zaire fan and was between .01 to .95 (99% to 5% nitrate utilization) in middle Angola.

Paleoproductivity was as low as 43 g C m^{-2} yr^{-1} in the Zaire fan and 69 g C m^{-2} yr^{-1} in middle Angola and reached values of up to 322 g C m^{-2} yr^{-1} in the Zaire fan and 622 g C m^{-2} yr^{-1} in middle Angola. As seen in Figure 6, high f generally corresponds to periods of high paleoproductivity and vice versa. Thus, although relatively less of the available nitrate pool was utilized by the phytoplankton (high f), productivity increased, suggesting that absolute nitrate concentrations must have been elevated to support the high rates of productivity. This means that phytoplankton exploited the higher nutrient levels, but the large f which occurred at the same time implies that the plankton were unable to deplete the available nitrate pool to as large an extent as when [NO_3^-] was lower.

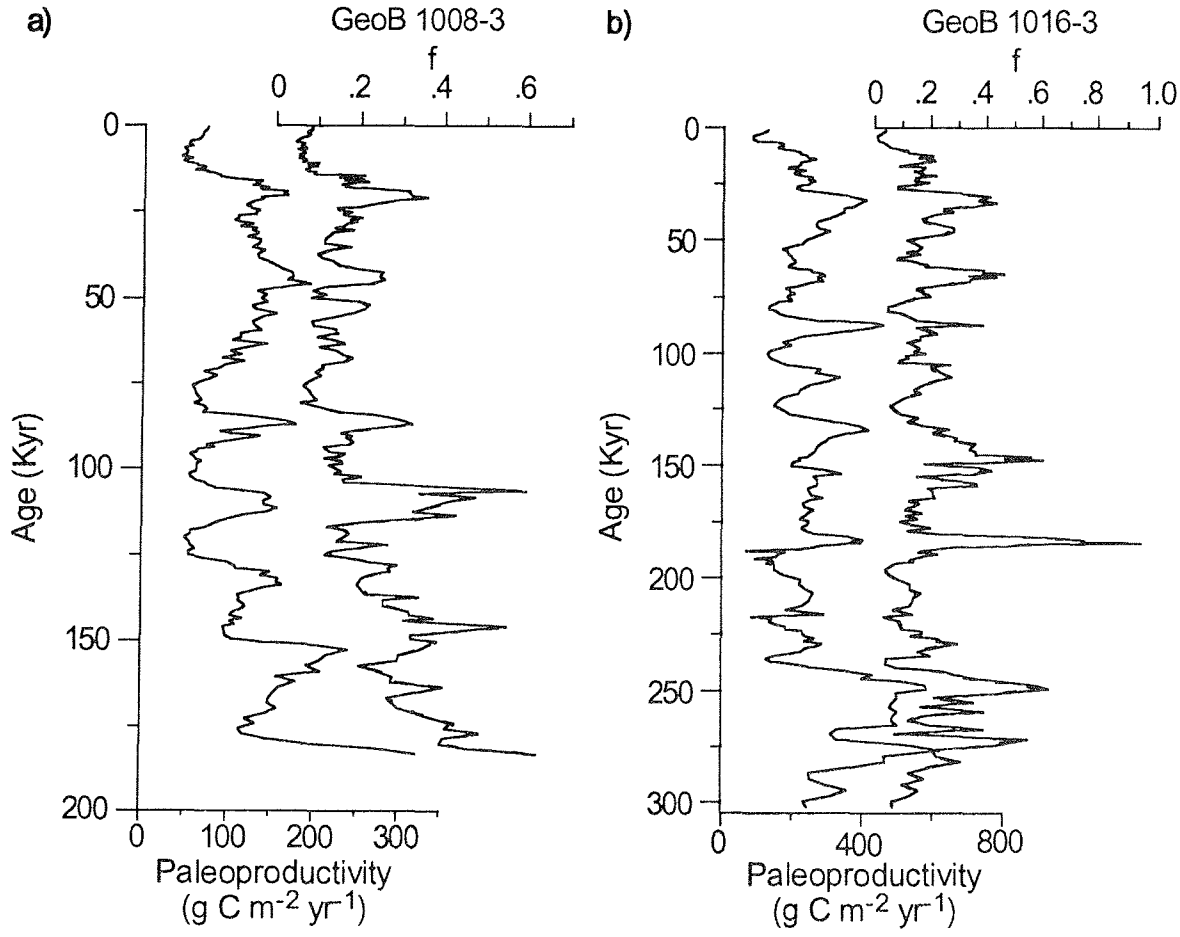

Fig. 6: Paleoproductivity variations (g C m^{-2} yr^{-1}), f (fraction of unutilized nitrate remaining in surface water) predicted from sedimentary $\delta^{15}N$ using equations (1) and (2) (instantaneous product) from ALTABET & FRANCOIS (1994).

Glacial/interglacial differences

Glacial/interglacial changes in $\delta^{15}N$ and f are detectable in Angola Basin sediments. A comparison of glacial $\delta^{15}N$ and f values with interglacial periods reveals lower $\delta^{15}N$ and

higher f during glacial times (Table 1). On average, f was between 7 and 12% higher during glacials than interglacials in both cores. t-tests showed that the differences between glacial and interglacial $\delta^{15}N$ and f were significant ($t_{.05}$). $\delta^{15}N$ and f differences between both cores were small during glacials ($\Delta\delta^{15}N$ = 0.15‰ and Δf = .04, respectively) and during interglacials ($\Delta\delta^{15}N$ = 0.08‰ and Δf = .01). During the Holocene, however, $\delta^{15}N$ in core GeoB 1016-3 was up to 1.8‰ higher than in core GeoB 1008-3. The presence of 41 kyr periodicity revealed by time series analyses in sedimentary $\delta^{15}N$ in the Angola Basin provides additional evidence for glacial-interglacial changes in nitrate availability in surface water. Our results corroborate the findings of other investigations of the Angola Basin region. For example, SCHNEIDER (1991) and SCHNEIDER ET AL. (1994) calculated higher paleoproductivity rates during glacials than in the Holocene in the Zaire fan and middle Angola. BORNHOLD (1973) and POKRAS (1987) also found evidence, based on organic carbon accumulation rates and fossil diatom assemblages, for increased productivity during glacials. SCHNEIDER (1991) suggested that increased glacial productivity was caused by the northward advection of nutrient-rich Benguela waters (VAN ZIDDEREN BAKKER, 1976, 1982; JANSEN ET AL., 1984).

Table 1: Comparison of $\delta^{15}N$ and f between glacial (stages 2-4, 6 and 8) and interglacial (stages 1, 5 and 7) periods. f was calculated using equations (1) and (2) (instantaneous product) of ALTABET & FRANCOIS (1994). The $\delta^{15}N$ and f differences between glacial and interglacial periods are statistically significant ($t_{.05} \leq 2.00$) (SOKAL & ROHLF, 1981).

	Interglacial	**Glacial**	
	$\delta^{15}N$		t-test
GeoB 1008-3	6.61	6.15	5.36
GeoB 1016-3	6.69	6.00	7.69
	f		
GeoB 1008-3	.15	.22	4.66
GeoB 1016-3	.14	.26	6.05

It has been suggested that the BC flowed north through the Angola Basin during glacial periods, diverging offshore at around 2°S (DIESTER-HAASS, 1985; DIESTER-HAAS ET AL., 1988) instead of at 28°S where the BC is presently diverted to the northwest. However, SCHNEIDER ET AL. (1995) presented evidence that the ABF did not shift this far to the north during the past 180 kyr. We propose, therefore, that an increase in preformed nutrient concentrations advected northward from the Southern Ocean could have led to the observed lower glacial $\delta^{15}N$ values.

Response of $\delta^{15}N$ to orbital forcing

More obvious in both cores than the glacial/interglacial differences are $\delta^{15}N$ fluctuations with higher frequency periodicities (23 kyr). SCHNEIDER ET AL. (1994) showed that productivity in the Angola Basin during the Late Quaternary varied in response to precessional forcing and suggested that changes in upwelling and the thermocline depth (based on organic carbon and $\delta^{13}C$ differences between *Globigerina bulloides* and *Globigerinoides ruber* (pink) in core GeoB 1008-3), driven by southeasterly tradewinds, caused these productivity variations. Precessional variations in the earth-sun distance during boreal summer induces periodic 23 kyr variations in African low latitude insolation. Boreal summer insolation minima are manifested in a decrease in the intensity of African southwest-monsoons, which leads to higher zonal intensity of trade winds. Trade winds thus reach their highest intensities when the earth-sun distance in boreal summer is greatest and equatorial upwelling is enhanced at this time (MCINTYRE ET AL., 1989; MOLFINO & MCINTYRE, 1990).

Figure 7 shows the results of the analyses of harmonic components in the $\delta^{15}N$ signal. $\delta^{15}N$ in both cores shows peaks at 100 kyr, but these will not be considered further because the sediment records extend only to 304 and 183 kyr b.p. Both cores exhibit peaks at 41 and 23 kyr, the obliquity and precessional cycles, respectively. GeoB 1008-3 shows an additional strong peak at 31 kyr, which is not present in GeoB 1016-3 $\delta^{15}N$ nor in most of the other parameters which have been analyzed. Two exceptions are marine OC and SST in GeoB 1008-3, which also exhibit peaks at 31 kyr. We speculate that the peak at 31 kyr in core GeoB 1008-3 $\delta^{15}N$ is a cross product between the 23 and 41 kyr periods.

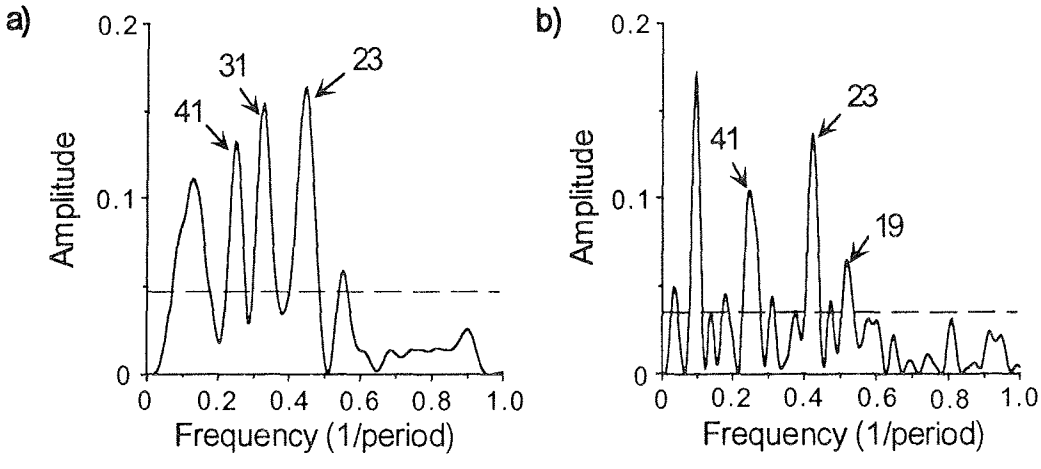

Fig. 7: Results of harmonic analyses performed on the $\delta^{15}N$ signal of a) GeoB 1008-3 and b) GeoB 1016-3 using the software program SPECTRUM (SCHULZ, 1995). A Fischer/Siegel test for compound periodicity was employed and significant peaks are labelled. The peaks at 100 kyr were significant in both cores, but due to the shortness of our records, they will not be discussed.

Cross-spectral analysis allows comparison of two time series as a function of frequency. The resulting coherency values give the degree of correlation (like a linear correlation coefficient, r^2) between the time series at a given frequency (BENDAT & PIERSOL, 1986). The same software program (SPECTRUM) was used to perform cross-spectral analyses of $\delta^{15}N$ and ETP (eccentricity, tilt and precessionary indices). These reveal significant coherency at 41 kyr and 19-23 kyr (the 6 dB bandwidth was too large to allow separation of these two frequencies) in both cores (Fig. 8). The peak amplitude at a frequency of around .03 in core GeoB 1008-3 apparently results from a combination, due to the 6 dB bandwidth, of the peaks at 41 and 31 kyr observed in the harmonic analysis of the $\delta^{15}N$ of this core. $\delta^{15}N$ minima lag minima in boreal summer insolation (June 21) by 6.1 ± 3.2 kyr and 7.7 ± 1.5 kyr in cores GeoB 1008-3 and GeoB 1016-3, respectively. $\delta^{15}N$ in both cores shows little or no difference in phase from paleoproductivity as calculated by SCHNEIDER (1991) (GeoB 1008-3: 0 ± 2.0 kyr; GeoB 1016-3: 1.2 ± 1.6 kyr) or SST from SCHNEIDER ET AL. (1995, in press) (GeoB 1008-3: 0.2 ± 2.6 kyr; GeoB 1016-3: 2.4 ± 1.2 kyr). The presence of the 23 kyr cycle in the $\delta^{15}N$ signal and its close correlation with paleoproductivity and sea surface temperature demonstrates the importance of the intensity of the trade winds and the monsoonal system in determining upwelling of nutrient-rich water and ensuing productivity. Although the intense coastal upwelling associated with the Benguela system does not extend to the north past ~15°S, during periods of high trade wind zonality, more nutrients are upwelled to the surface south of the Angola Basin and this nitrate-rich water is advected northward into the Angola Basin, resulting in the observed sensitivity of $\delta^{15}N$ to precessional forcing.

Differences in nutrient utilization between the Zaire fan and middle Angola

To obtain a clearer picture of the isotopic differences between the two cores, $\delta^{15}N$ of GeoB 1008-3 was subtracted from $\delta^{15}N$ of GeoB 1016-3 to yield $\Delta\delta^{15}N$ (solid line in Fig. 9). Also shown in Fig. 9 is the difference in SST (dashed line) and PaP (paleoproductivity: solid line on the left plot) between the two cores (ΔSST and ΔPaP). As seen in Figure 9, twice during the past 185 kyr, $\delta^{15}N$ in middle Angola was much lower (up to -1.3‰) than off Zaire (28 - 40 kyr and 60 - 75 kyr b.p.). This evidence for less extensive nitrate depletion in surface water (and higher nitrate availability) is corroborated by the corresponding lower SST in waters of the Angola margin relative to the Zaire fan at the same time. SCHNEIDER ET AL. (1995) found that at approximately the same time as the negative excursion of $\Delta\delta^{15}N$, ΔSST_{ABF} (the SST difference north and south of the ABF) was at its lowest. Additionally, Jansen et al. (1994) reported that, based on foraminiferal assemblages, the ABF was displaced northward to as far as 9°S during isotopic stages 3 and 4 at nearly the same time as the lower $\delta^{15}N$ and SST measured in core GeoB 1016-3 relative to GeoB 1008-3. Our data thus support the work of other authors which indicates that at times between ~30 and 75 kyr b.p., more nutrient-rich water was advected into the Angola Basin from the south, but that this water did not reach the

position of GeoB 1008-3 off the Zaire river mouth. This supposition is corroborated by the higher PaP at GeoB 1016-3 relative to 1008-3 at the same time.

SCHNEIDER ET AL. (submitted manuscript) proposed that productivity changes caused by fluctuations in fluvial discharge were superimposed on the productivity variations brought about by increased advection of nutrient-rich water and oceanic upwelling. This is supported by the $\Delta\delta^{15}N$ signal which suggests that relative nitrate utilization was lower (and likely nitrate concentrations higher) at approximately the same periods when river discharge (reconstructed from Aluminum/Kaolinite ratios) was high (SCHNEIDER ET AL., submitted manuscript).

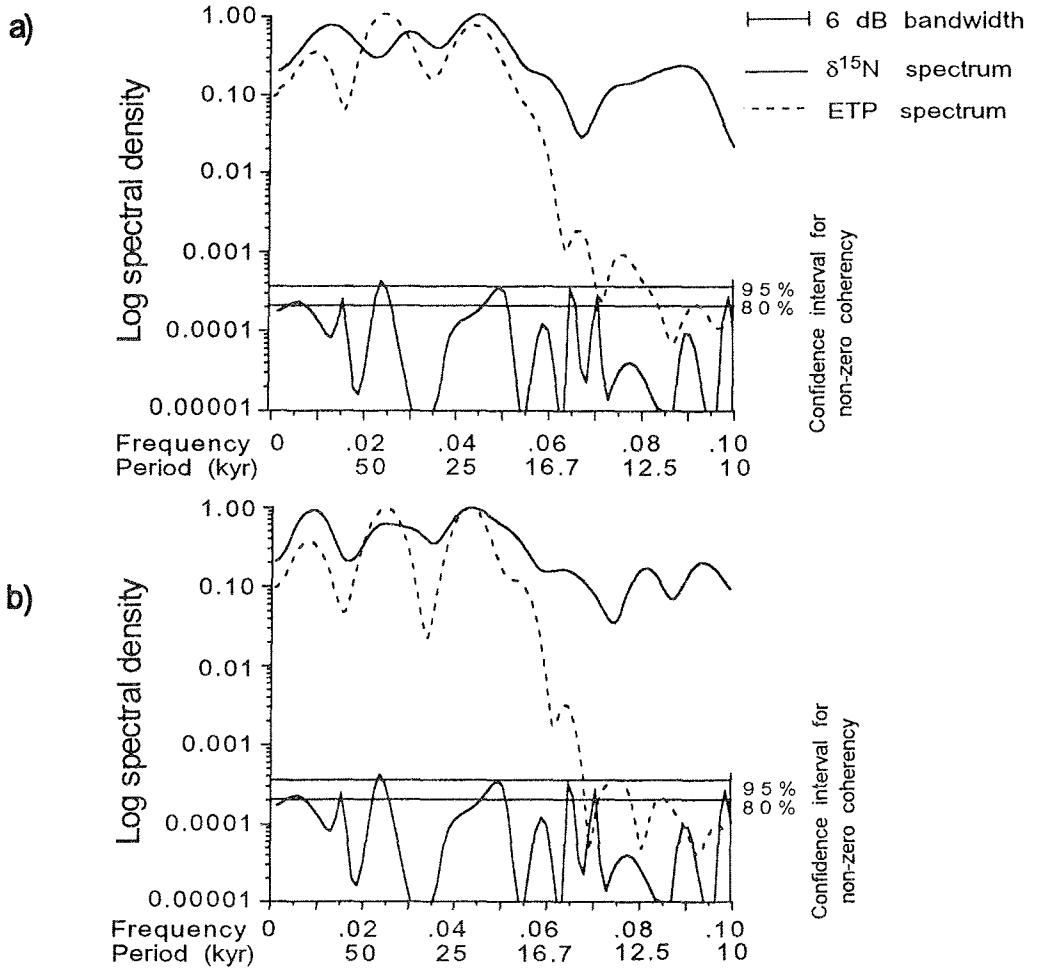

Fig. 8: Cross spectral analyses of $\delta^{15}N$ and ETP (eccentricity, tilt and precession) using SPECTRUM (SCHULZ, 1995) with the Welch window and 2 segments for core GeoB 1008-3 (a) and 3 segments for GeoB 1016-3 (b). The upper solid and dashed lines are the normalized log spectral densitiy and the lower solid line represents the coherence between $\delta^{15}N$ and ETP. Horizontal lines indicate the 80% and 95% confidence intervals for non-zero coherency. The 6 dB bandwidth was too wide to separate the frequencies at 19 and 23 kyr.

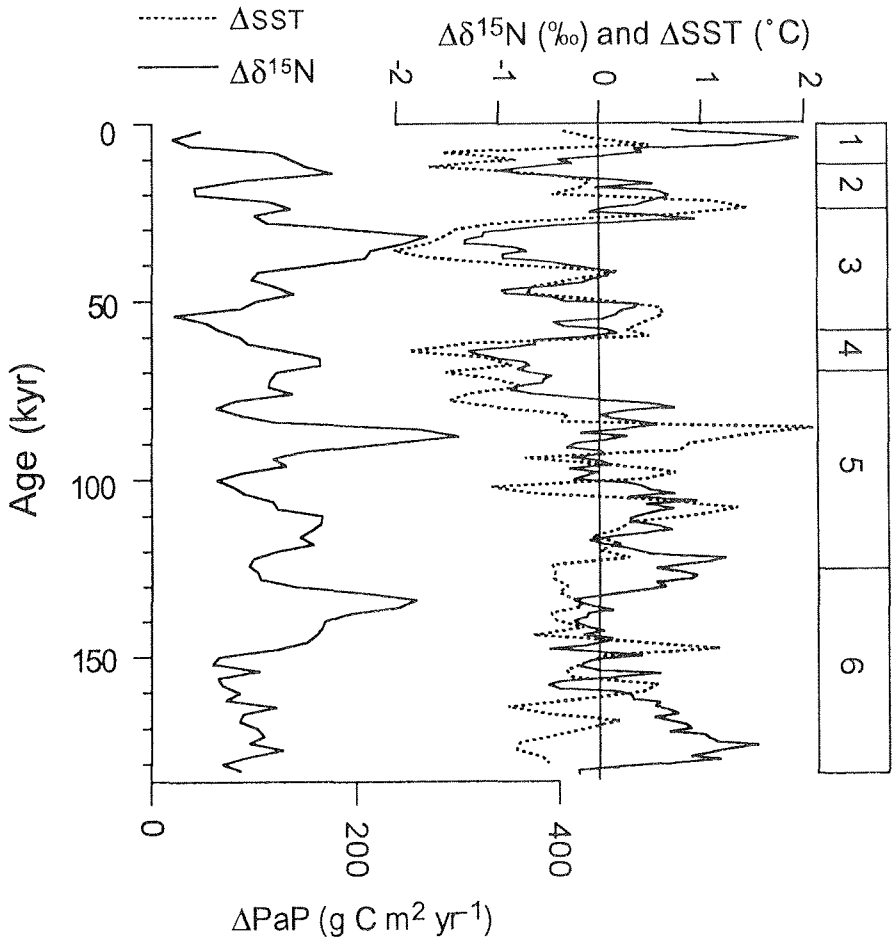

Fig. 9: $\Delta\delta^{15}N$ (solid line), ΔSST (dashed line) and ΔPaP (solid line to the left) of GeoB 1008-3 and GeoB 1016-3. $\Delta\delta^{15}N$, ΔSST and ΔPaP were calculated by subtracting GeoB 1008-3 $\delta^{15}N$, SST and PaP from GeoB 1016-3.

Denitrification

ALTABET ET AL. (1995) and GANESHRAM ET AL. (1995) reported that the $\delta^{15}N$ changes they measured in sediments from the Arabian Sea and the eastern tropical North Pacific, respectively, were predominantly caused by variations in water column denitrification. Oxygen depletion has been reported in the Angola Basin (BUBNOV, 1972; CHAPMAN AND SHANNON, 1987), with O_2 concentrations in the OMZ around 1 ml l^{-1}. According to SKERMAN & MCRAE (1959) and PACKARD ET AL. (1983), nitrate reduction is inhibited when oxygen concentrations exceed 0.15 to 0.2 ml l^{-1}. Therefore, it appears that at the present time, denitrification is not a prevalent characteristic of the Angola Basin, although it can occur locally, especially over the shelf, where measured O_2 levels may be lower than in the OMZ. During the SNEC II cruise of 1986, O_2 concentrations as low as 0.15 ml l^{-1} were measured in shelf water a few meters above the sediment surface at around 19°S. We know of no studies

which have thus far been made on the extent of denitrification in the Angola Basin water column during the past. Denitrification is commonly associated with high rates of biological productivity because the supply of oxygen cannot keep up with the respiration of the OM and NO_3^- is used as the electron acceptor instead. Thus, if denitrification were an important factor affecting the $\delta^{15}N$ in this area, high $\delta^{15}N$ should coincide with high sedimentary OM content, as argued by GANESHRAM ET AL. (1995) in a study of past denitrification in the eastern tropical North Pacific Ocean. The inverse correlation of OC content with $\delta^{15}N$ in our cores (Fig. 5) indicates that in general, denitrification has not played an important role in the water column of the Angola Basin over the past 300 kyr.

However, it is possible that nitrate reduction was locally important for limited periods of time. Because core GeoB 1016-3 is located in the center of an oxygen minimum zone (CHAPMAN & SHANNON, 1987), positive excursions in GeoB 1016-3 relative to GeoB 1008-3 (in particular, in stages 1, 5.5 and 6.5 - 6.6: see Fig. 9) could be related to periods when denitrification at 12°S was more important than today. It would be expected that at times when denitrification occurred over GeoB 1016-3, $\Delta\delta^{15}N$ would have increased with a corresponding relative increase in OC. However, in stage 1, the time of the largest $\Delta\delta^{15}N$, this was certainly not the case (OC < 1%). At the same time, SST was not significantly higher over GeoB 1016-3 (higher ΔSST might indicate that nitrate depletion caused the high $\Delta\delta^{15}N$), so it is not clear whether denitrification could have caused the much higher $\delta^{15}N$ at the Angola margin relative to the Zaire Fan during the Holocene. At no time throughout the series is elevated $\Delta\delta^{15}N$ associated with high OC, implying that denitrification in this region has not occurred to a significant extent during the past 180 kyr.

As discussed above, lower $\delta^{15}N$ during glacials than interglacials suggests that denitrification did not occur during glacials. Some models of ocean chemistry predict that increases in nutrient utilization during glacials led to decreased surface ocean and atmospheric pCO_2 (ENNEVER & MCELROY, 1985; TOGGWEILER & SARMIENTO, 1985). This would have led to extensive oceanic anoxia and presumably increased denitrification, resulting in a net loss of oceanic nitrogen. Such a condition should be reflected as a positive excursion in glacial $\delta^{15}N$ records due to an increase in $\delta^{15}NO_3^-$. However, sedimentary $\delta^{15}N$ in the Angola Basin is lower during glacials than interglacials - the opposite of what would be expected under the glacial anoxia scenario. Our results support the findings of ALTABET & CURRY (1989) who reported no decrease in $\delta^{15}N$ from foraminifera tests during the last deglaciation.

CONCLUSIONS

Stable nitrogen isotope ratios in two sediment cores from the Angola Basin spanning the past 185 and 300 kyr have been measured. $\delta^{15}N$ values of surface sediments here have been previously shown to be controlled primarily by the concentration and relative utilization of nitrate in the surface water. Variations in the paleo-$\delta^{15}N$ signal are consistent with changes in organic carbon content, sea surface temperature and estimated paleoproductivity, indicating that nitrate availability and productivity in this region have responded to precessional forcing during the Late Quaternary. $^{15}N/^{14}N$ ratios also exhibit glacial/interglacial variations, implying that relatively more nitrate was available and the surface nitrate pool was less depleted during glacial periods than interglacials. Also, the lower $\delta^{15}N$ measured in glacial sediments relative to interglacial is a sign that global denitrification did not occur during glacials. Past changes in the degree of nutrient utilization in surface waters was calculated from measured sedimentary $\delta^{15}N$ and were found to correspond to paleoproductivity variations. No strong evidence for denitrification in the water column during the last 185 kyr was found.

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Appendix 1: Analytical data for core GeoB 1008-3 (a) and GeoB 1016-3 (b). As described by Schneider et al. (1994), $\delta^{18}O$ values of *Globigerinoides ruber* and *Globigerina bulloides* were compared with the SPECMAP record (Imbrie et al., 1984) to obtain the age models used in this study.

Appendix 1a. (GeoB 1008-3)

Depth (cm)	Age (kyr)	$\delta^{15}N$ (‰)	Marine OC (%)	$\delta^{13}C$ (‰)	SST (°C)	PaP (g C m^{-2} y^{-1})	$\delta^{15}N$ $NO_3^-{}_{(f)}$	f	$[NO_3^-]$ (µM)
3	0.4	7.06	1.36	-22.09	25.5	73	8.10	0.08	1.1
8	1.1	7.07	1.21	-22.43		72	8.11	0.08	1.1
13	1.8	7.23	1.15	-22.58		68	8.27	0.07	0.9
18	2.5	7.1	1.08	-22.57		68	8.14	0.08	1.0
23	3.2	7.25	1.02	-22.80	25.6	66	8.29	0.07	0.9
28	3.9	7.51	0.97	-22.80		62	8.55	0.05	0.7
33	4.6	7.68	0.87	-23.04		53	8.72	0.05	0.6
38	5.3	7.33	0.80	-23.12		52	8.37	0.06	0.8
43	6.0	7.43	0.86	-22.98	25.6	56	8.47	0.06	0.8
48	6.5	7.27	0.81	-23.05		46	8.31	0.07	0.9
53	7.0	7.59	0.79	-23.13		47	8.63	0.05	0.7
58	7.5	7.3	0.83	-22.99		50	8.34	0.07	0.9
63	8.0	7.26	0.92	-22.74	25.7	49	8.30	0.07	0.9
68	8.5	7.52	0.95	-22.54		46	8.56	0.05	0.7
73	9.0	7.38	0.95	-22.40		43	8.42	0.06	0.8
78	9.5	7.52	1.00	-22.29		55	8.56	0.05	0.7
83	10.0	7.22	1.02	-22.12	24.4	48	8.26	0.07	0.9
88	10.3	7.23	1.05	-22.02		45	8.27	0.07	0.9
93	10.6	7.39	1.13	-22.04		50	8.43	0.06	0.8
98	10.9	6.91	1.28	-21.81	25.1	50	7.95	0.10	1.3
103	11.2	7.01	1.48	-21.70		61	8.05	0.09	1.1
108	11.5	7.17	1.42	-21.83		61	8.21	0.07	1.0
113	11.8	6.90	1.57	-21.74	24.8	67	7.94	0.10	1.3
118	12.2	7.14	1.54	-21.75		71	8.18	0.08	1.0
123	12.5	7.16	1.52	-21.81		68	8.20	0.07	1.0
128	12.8	7.27	1.48	-21.65		59	8.31	0.07	0.9
133	13.2	7.16	1.66	-21.32		74	8.20	0.07	1.0
138	13.5	6.99	1.74	-20.95	23.3	72	8.03	0.09	1.2
143	13.8	7.00	1.83	-20.63		81	8.04	0.09	1.2
148	14.2	6.92	1.78	-20.80		84	7.96	0.09	1.2
153	14.5	6.10	1.93	-20.59		89	7.14	0.21	2.7
158	14.8		1.92	-20.48	23.4	88	1.04		
163	15.2	6.46	1.93	-20.81		94	7.50	0.15	1.9
168	15.5	6.14	2.22	-20.49	22.6	105	7.18	0.20	2.6
173	15.8	6.37	2.53	-20.53		122	7.41	0.16	2.1
178	16.1	6.18	3.00	-20.60		136	7.22	0.19	2.5
183	16.5	6.05	3.16	-20.73	22.1	134	7.09	0.22	2.8
188	16.8	6.27	2.93	-20.72		128	7.31	0.18	2.3
193	17.1	6.42	2.74	-20.75		132	7.46	0.15	2.0
198	17.4	6.37	2.85	-20.94		125	7.41	0.16	2.1
203	17.7	6.37	2.74	-20.59	21.9	136	7.41	0.16	2.1
208	18.1	6.26	2.98	-20.72		144	7.30	0.18	2.3
213	18.4	6.01	3.05	-20.79		134	7.05	0.22	3.0
218	18.7	5.87	3.10	-20.83	22.3	136	6.91	0.26	3.4
223	19.2	5.68	3.10	-20.72		165	6.72	0.31	4.1
228	19.8	5.66	3.14	-20.73		161	6.70	0.31	4.1
233	20.3	5.65	3.22	-20.70	22.3	166	6.69	0.32	4.2
238	20.9	5.55	2.81	-20.83		135	6.59	0.35	4.6
243	21.4	5.66	2.67	-20.65		138	6.70	0.31	4.1

Appendix 1a. (continued)

Depth (cm)	Age (kyr)	$\delta^{15}N$ (‰)	Marine OC (%)	$\delta^{13}C$ (‰)	SST (°C)	PaP (g C m^{-2} y^{-1})	$\delta^{15}N$ NO_3^- (f)	f	$[NO_3^-]$ (µM)
248	22.0	5.81	2.59	-20.72		129	6.85	0.27	3.6
253	22.5		2.57	-20.84		124	1.04		
258	23.1		2.39	-20.97	21.4	119	1.04		
263	23.6	6.14	2.48	-21.17		123	7.18	0.20	2.6
268	24.2	6.48	2.49	-21.25		124	7.52	0.14	1.9
273	24.7	6.45	2.69	-21.13	21.0	134	7.49	0.15	2.0
278	25.3	6.28	2.60	-21.10		130	7.32	0.17	2.3
283	25.8	6.39	2.71	-20.98		130	7.43	0.16	2.1
288	26.4	6.31	2.54	-21.22	21.6	109	7.35	0.17	2.2
293	26.9	6.13	2.36	-21.08		109	7.17	0.20	2.7
298	27.5	6.28	2.12	-21.12		105	7.32	0.17	2.3
303	28.0	6.20	2.33	-21.09	23.0	112	7.24	0.19	2.5
308	28.6	6.33	2.38	-21.03		127	7.37	0.17	2.2
313	29.2	6.38	2.53	-21.09		112	7.42	0.16	2.1
318	29.8	6.51	2.62	-21.06	22.8	130	7.55	0.14	1.8
323	30.4	6.23	2.54	-21.03		126	7.27	0.18	2.4
328	31.0	6.57	2.67	-20.99		133	7.61	0.13	1.7
333	31.6		2.70	-21.01		129	1.04		
338	32.3		2.72	-21.00	22.6	121	1.04		
343	33.1	6.72	2.74	-20.87		135	7.76	0.11	1.5
348	34.2	6.72	2.47	-21.11	22.8	134	7.76	0.11	1.5
353	35.2	6.28	2.50	-21.23		125	7.32	0.17	2.3
358	36.3	6.64	2.31	-21.28	23.0	140	7.68	0.12	1.6
363	37.3	6.87	2.34	-21.12		132	7.91	0.10	1.3
368	38.4	6.76	2.37	-21.03		133	7.80	0.11	1.4
373	39.4	6.54	2.30	-20.90	22.4	144	7.58	0.14	1.8
378	40.4	6.46	2.62	-20.79		153	7.50	0.15	1.9
383	41.5	6.21	2.47	-20.80		160	7.25	0.19	2.4
388	42.5	5.90	2.49	-20.84	21.1	172	6.94	0.25	3.3
393	43.6	5.93	2.77	-20.53		173	6.97	0.24	3.2
398	44.6	5.88	2.75	-20.87	21.2	166	6.92	0.25	3.4
403	45.7	6.02	2.82	-20.46		194	7.06	0.22	2.9
408	46.7	6.71	2.33	-20.92		160	7.75	0.12	1.5
413	47.8	7.00	2.43	-20.98	21.6	132	8.04	0.09	1.1
418	48.8	6.71	2.44	-20.80		143	7.75	0.11	1.5
423	49.9	7.04	2.51	-20.76		136	8.08	0.08	1.1
428	50.9	6.16	2.46	-20.76	20.9	143	7.20	0.20	2.6
433	52.0	6.06	2.16	-21.52		126	7.10	0.22	2.8
438	53.0	6.08	2.08	-21.09	20.8	130	7.12	0.21	2.8
443	54.2	6.24	2.09	-20.91		154	7.28	0.18	2.4
448	55.4		2.33	-21.25	20.9	137	1.04		
453	56.6	7.02	2.24	-21.30		126	8.06	0.09	1.1
458	57.8	6.97	2.20	-21.46	21.4	129	8.01	0.09	1.2
463	59.0	6.48	2.17	-21.27		137	7.52	0.14	1.9
468	60.1	6.48	1.93	-21.40	21.5	112	7.52	0.14	1.9
473	61.1	6.87	1.75	-21.46		113	7.91	0.10	1.3
478	62.2	6.52	1.65	-21.79	22.5	104	7.56	0.14	1.8
483	63.2	6.35	1.64	-21.40		144	7.39	0.16	2.1
488	64.3	6.82	1.54	-21.49	22.3	119	7.86	0.10	1.4
493	65.3	6.48	1.56	-21.52		101	7.52	0.14	1.9
498	66.4	6.38	1.37	-21.40	22.6	114	7.42	0.16	2.1
503	67.4	6.27	1.52	-21.77		92	7.31	0.18	2.3
508	68.5	6.35	1.31	-21.74	22.3	117	7.39	0.16	2.1
513	69.5	6.75	1.00	-22.44		96	7.79	0.11	1.5
518	70.6	6.76	1.02	-22.53	23.9	88	7.80	0.11	1.5
523	71.6	6.91	0.81	-22.44		71	7.95	0.09	1.3
528	72.7	6.77	1.03	-22.08	23.6	86	7.81	0.11	1.4

Appendix 1a. (continued)

Depth (cm)	Age (kyr)	$\delta^{15}N$ (‰)	Marine OC (%)	$\delta^{13}C$ (‰)	SST (°C)	PaP (g C m^{-2} y^{-1})	$\delta^{15}N$ NO_3^-(f)	f	$[NO_3^-]$ (μM)
533	73.7		1.11	-22.08		76	1.04		
538	74.8	7.13	0.92	-22.23	24.7	65	8.17	0.08	1.0
543	75.8	7.29	0.83	-22.55		58	8.33	0.07	0.9
548	76.9	7.13	0.80	-22.70	25.0	60	8.17	0.08	1.0
553	77.9		0.69	-22.81		62	1.04		
558	79.0	6.97	0.89	-22.30		65	8.01	0.09	1.2
563	80.0	6.86	0.94	-22.35	25.4	68	7.90	0.10	1.3
568	80.9	7.38	0.86	-22.14		60	8.42	0.06	0.8
573	81.8	6.89	0.91	-21.86	24.1	72	7.93	0.10	1.3
578	82.6	6.68	0.98	-22.26		75	7.72	0.12	1.6
583	83.5	6.44	0.90	-22.41	24.2	69	7.48	0.15	2.0
588	84.4	5.93	2.04	-21.58	23.2	117	6.97	0.24	3.2
593	85.3		2.38	-21.39		146	1.04		
598	86.1	5.70	2.12	-21.38		168	6.74	0.30	4.0
603	87.0	5.63	2.37	-21.26	22.9	178	6.67	0.33	4.3
608	87.7		2.30	-21.32		142	1.04		
613	88.3		2.09	-21.46		122	1.04		
618	89.0	6.19	1.42	-21.74	23.7	91	7.23	0.19	2.5
623	89.7	6.38	1.59	-21.84		102	7.42	0.16	2.1
628	90.3	6.26	1.56	-21.75		136	7.30	0.18	2.3
633	91.0	6.32	1.62	-21.81		127	7.36	0.17	2.2
638	91.7		1.73	-21.71	23.5	107	1.04		
643	92.3	6.21	1.34	-22.03		88	7.25	0.19	2.5
648	93.0	6.27	1.32	-22.19		75	7.31	0.18	2.3
653	93.7	6.70	1.36	-21.95		84	7.74	0.12	1.5
658	94.3		1.09	-22.49	26.0	65	1.04		
663	95.0	6.58	1.15	-22.17		63	7.62	0.13	1.7
668	95.7	6.36	1.00	-22.25	25.0	56	7.40	0.16	2.1
673	96.3	6.44	0.99	-22.20		60	7.48	0.15	2.0
678	97.0	6.69	0.98	-22.13	24.6	63	7.73	0.12	1.5
683	97.7	6.41	1.02	-22.27		69	7.45	0.15	2.0
688	98.3	6.40	0.99	-22.35		63	7.44	0.16	2.1
693	99.0	6.60	0.99	-22.56	23.9	63	7.64	0.13	1.7
698	99.8		0.92	-22.76		64	1.04		
703	100.6	6.39	0.93	-22.74		62	7.43	0.16	2.1
708	101.4	6.50	0.85	-23.00	25.4	56	7.54	0.14	1.9
713	102.2	6.11	0.83	-23.15		56	7.15	0.20	2.7
718	103.0	6.36	0.92	-22.75	25.2	62	7.40	0.16	2.1
723	103.8	6.35	1.12	-22.60		73	7.39	0.16	2.1
728	104.6	5.69	1.21	-22.37		77	6.73	0.31	4.0
733	105.4		1.32	-22.34	23.9	87	1.04		
738	106.2	5.02	1.80	-22.13		117	6.06	0.58	7.7
743	107.0	5.58	2.17	-22.03	22.3	142	6.62	0.34	4.5
748	108.1	5.23	2.09	-22.04		149	6.27	0.48	6.3
753	109.1	5.38	2.02	-21.98	22.9	140	6.42	0.41	5.4
758	110.2		2.03	-21.88		141	1.04		
763	111.3		2.06	-21.76	23.8	156	1.04		
768	112.4	5.62	1.81	-21.80		144	6.66	0.33	4.3
773	113.4	5.36	1.41	-22.13		112	6.40	0.42	5.6
778	114.5	5.64	1.30	-22.08	24.6	98	6.68	0.32	4.2
783	115.6	6.15	1.02	-22.53		84	7.19	0.20	2.6
788	116.6	6.62	0.89	-22.85	25.1	75	7.66	0.13	1.7
793	117.7	6.33	0.69	-23.13		57	7.37	0.17	2.2
798	118.8	6.26	0.69	-23.13	24.6	57	7.30	0.18	2.3
803	119.9		0.58	-23.21		50	1.04		
808	120.9	6.45	0.63	-23.12	26.0	55	7.49	0.15	2.0
813	122.0	5.85	0.68	-22.95	26.0	57	6.89	0.26	3.5

Appendix 1a. (continued)

Depth (cm)	Age (kyr)	$\delta^{15}N$ (‰)	Marine OC (%)	$\delta^{13}C$ (‰)	SST (°C)	PaP (g C m^{-2} y^{-1})	$\delta^{15}N$ NO_3^-(f)	f	$[NO_3^-]$ (µM)
818	123.0	6.15	0.74	-22.78		62	7.19	0.20	2.6
823	123.9	6.55	0.67	-22.81		55	7.59	0.13	1.8
828	124.9	6.66	0.66	-22.73	26.8	55	7.70	0.12	1.6
833	125.9	6.27	0.89	-22.14		71	7.31	0.18	2.3
838	126.9	6.02	1.33	-21.47	26.9	100	7.06	0.22	2.9
843	127.8	5.77	1.56	-20.68	26.5	108	6.81	0.28	3.7
848	128.8	5.83	1.50	-20.81		110	6.87	0.27	3.5
853	129.8	5.80	1.96	-20.56		148	6.84	0.28	3.6
858	130.7	6.00	1.73	-20.50	25.1	138	7.04	0.23	3.0
863	131.7	6.11	1.99	-20.35		158	7.15	0.21	2.7
868	132.7		2.13	-20.59	24.5	156	1.04		
873	133.6	6.16	2.22	-20.97		163	7.20	0.20	2.6
878	134.6		2.00	-21.17	24.4	138	1.04		
883	135.5		1.92	-21.33	24.0	126	1.04		
888	136.4	6.05	1.89	-21.33		112	7.09	0.22	2.9
893	137.2	5.57	1.75	-21.44		114	6.61	0.34	4.5
898	138.1	5.87	1.68	-21.28	24.2	112	6.91	0.26	3.4
903	139.0		1.76	-21.17		118	1.04		
908	139.8	5.87	1.80	-21.02	24.4	120	6.91	0.26	3.4
913	140.7		1.68	-21.12		115	1.04		
918	141.5	5.65	1.53	-21.13	24.0	105	6.69	0.32	4.2
923	142.4	5.65	1.64	-21.06		103	6.69	0.32	4.2
928	143.3	5.47	1.74	-20.80	24.8	117	6.51	0.38	5.0
933	144.1	5.69	1.59	-20.71		103	6.73	0.31	4.0
938	145.0		1.66	-20.72	24.4	108	1.04		
943	145.8	5.08	1.46	-20.84		95	6.12	0.55	7.3
948	146.7		1.30	-20.95		97	1.04		
953	147.6	5.41	1.14	-21.05	22.4	96	6.45	0.40	5.3
958	148.4	5.64	1.25	-20.88		98	6.68	0.32	4.3
963	149.3	5.63	1.35	-20.81		106	6.67	0.32	4.3
968	150.1	5.48	2.07	-20.68	21.8	138	6.52	0.38	5.0
973	151.0	5.49	2.58	-20.50		198	6.53	0.37	4.9
978	152.5	5.57	2.85	-20.38	22.6	241	6.61	0.34	4.5
983	154.1	5.73	2.47	-20.62		214	6.77	0.29	3.9
988	155.6	5.74	2.21	-20.49	23.5	207	6.78	0.29	3.8
993	157.2	6.13	2.22	-20.27		192	7.17	0.20	2.7
998	158.7	5.92	2.17	-20.34	22.9	208	6.96	0.25	3.2
1003	160.2	5.78	2.03	-20.62		157	6.82	0.28	3.7
1008	161.8	5.80	2.20	-20.94	23.5	180	6.84	0.28	3.6
1013	163.3	5.41	2.14	-21.10		160	6.45	0.40	5.3
1018	164.8		2.00	-21.06	25.1	154	1.04		
1023	166.4	5.83	1.99	-20.81		149	6.87	0.27	3.5
1028	167.9		1.97	-20.52	24.6	147	1.04		
1033	169.5	5.73	2.10	-20.50		158	6.77	0.29	3.9
1038	171.0		1.93	-20.41	25.1	144	1.04		
1043	172.5		1.54	-20.74		122	1.04		
1048	174.0	5.37	1.68	-20.76	25.1	133	6.41	0.42	5.5
1053	175.5	5.40	1.54	-20.92		114	6.44	0.41	5.3
1058	177.0	5.21	1.59	-21.21	24.5	118	6.25	0.49	6.4
1063	178.5	5.41	1.88	-20.91		144	6.45	0.40	5.3
1068	180.0	5.44	2.39	-20.80	25.0	189	6.48	0.39	5.2
1073	181.5	5.28	3.47	-20.17		274	6.32	0.45	6.0
1078	183.0	4.95	3.96	-20.10	22.4	322	5.99	0.62	8.2

Appendix 1b. (GeoB 1016-3)

Depth (cm)	Age (kyr)	$\delta^{15}N$ (‰)	Total OC (%)	$\delta^{13}C$ (‰)	SST (°C)	PaP (g C m^{-2} y^{-1})	$\delta^{15}N$ NO_3^- (f)	f	$[NO_3^-]$ (µM)
6	1.3	7.81	1.56	-20.47	25.1	124	8.85	0.04	0.5
12	2.6	8.30	1.15	-20.42		106	9.34	0.02	0.3
18	9	9.50	0.67	-20.93	25.5	82	10.54	0.01	0.1
23	4.9	9.32	0.69	-20.73		80	10.36	0.01	0.1
28	6.0	8.80	0.80	-20.36	26.1	93	9.84	0.02	0.2
33	6.7	8.02	1.52	-20.36	24.0	157	9.06	0.03	0.4
38	7.5	7.79	1.83	-20.37		168	8.83	0.04	0.5
43	8.2	7.64	1.77	-20.29	24.2	169	8.68	0.05	0.6
48	9.0	7.44	1.58	-19.96		151	8.48	0.06	0.8
53	9.7	6.92	1.68	-19.69	23.8	170	7.96	0.09	1.2
58	10.4	6.69	2.37	-19.49		200	7.73	0.12	1.5
63	11.2	6.67	2.26	-19.51	22.8	216	7.71	0.12	1.6
68	11.9	6.42	2.26	-19.37		216	7.46	0.15	2.0
73	12.6	6.09	2.85	-19.48	22.6	235	7.13	0.21	2.7
78	13.4	6.39	2.90	-19.39		240	7.43	0.16	2.1
83	14.1	6.11	3.24	-19.44	22.7	262	7.15	0.20	2.7
88	14.9	6.06	2.96	-19.60		239	7.10	0.21	2.8
94	15.6		2.66	-19.40	22.4	215			
98	16.3		2.58	-19.44		218			
103	17.1	6.93	2.60	-19.47		210	7.97	0.09	1.2
108	17.8	6.24	2.40	-19.55	21.7	184	7.28	0.18	2.4
113	18.4	6.27	2.65	-19.65		182	7.31	0.18	2.3
118	19.0	6.32	3.12	-19.63		231	7.36	0.17	2.2
123	19.6	6.44	3.06	-19.56	21.5	221	7.48	0.15	2.0
128	20.2	6.30	2.80	-19.65		198	7.34	0.17	2.3
133	20.8	6.29	2.72	-19.53		206	7.33	0.17	2.3
138	21.4	6.04	2.86	-19.57	22.9	218	7.08	0.22	2.9
143	22.2	6.41	3.02	-19.76		252	7.45	0.15	2.0
148	23.1	6.38	3.24	-19.87		239	7.42	0.16	2.1
153	23.9	6.46	3.43	-19.99	22.7	260	7.50	0.15	1.9
158	24.7	6.17	3.26	-19.92		247	7.21	0.19	2.5
163	25.5	6.46	3.01	-19.86	22.1	240	7.50	0.15	1.9
168	26.4	7.08	2.90	-19.72		208	8.12	0.08	1.1
173	27.2	7.09	2.42	-19.64		207	8.13	0.08	1.1
178	28.0	6.37	2.77	-19.57	22.1	223	7.41	0.16	2.1
183	29.4	5.66	2.93	-19.84		299	6.70	0.32	4.2
188	30.8	5.38	3.44	-19.81	21.1	367	6.42	0.41	5.4
193	32.2	5.49	4.35	-19.77	21.1	405	6.53	0.37	4.9
198	33.6	5.33	4.26	-19.74		387	6.37	0.43	5.7
203	34.9	5.52	3.81	-19.76	21.1	372	6.56	0.36	4.7
208	36.3	5.91	3.21	-19.67	20.9	342	6.95	0.25	3.3
213	37.7	5.78	3.30	-19.74		345	6.82	0.28	3.7
218	39.1	6.08	2.86	-19.75	21.1	325	7.12	0.21	2.8
223	40.5	6.24	2.75	-19.65		300	7.28	0.18	2.4
228	41.9	6.20	2.88	-19.64	21.5	268	7.24	0.19	2.5
233	43.3	5.94	2.75	-19.65		262	6.98	0.24	3.2
238	44.7	5.77	3.00	-19.59	20.8	272	6.81	0.28	3.7
243	46.1	5.77	2.73	-19.57		304	6.81	0.28	3.8
248	47.4	5.85	2.82	-19.63	20.7	282	6.89	0.26	3.5
253	48.8	6.26	2.84	-19.65		258	7.30	0.18	2.3

Appendix 1b. (continued)

Depth (cm)	Age (kyr)	$\delta^{15}N$ (‰)	Total OC (%)	$\delta^{13}C$ (‰)	SST (°C)	PaP (g C m^{-2} y^{-1})	$\delta^{15}N$ NO_3^- (f)	f	$[NO_3^-]$ (µM)
258	50.2	6.64	2.51	-19.67	21.2	234	7.68	0.12	1.6
263	51.6	6.46	2.25	-19.71		225	7.50	0.15	1.9
268	53.0	6.29	1.76	-19.80	21.6	185	7.33	0.17	2.3
273	53.8	6.37	1.87	-20.01		168	7.41	0.16	2.1
278	54.6	6.41	2.27	-19.94	21.4	182	7.45	0.15	2.0
283	55.3	6.64	2.37	-19.88		181	7.68	0.12	1.6
288	56.1	6.34	2.56	-19.86	21.5	186	7.38	0.16	2.2
293	56.9	6.62	2.60	-19.78		194	7.66	0.12	1.6
298	57.7	6.93	2.59	-19.82	21.5	193	7.97	0.09	1.2
303	58.5	7.01	2.63	-19.81		201	8.05	0.09	1.1
308	59.2	6.50	2.64	-19.91	22.3	207	7.54	0.14	1.9
313	60.0	6.36	2.55	-19.86		200	7.40	0.16	2.1
318	60.8	6.19	2.30	-19.72		189	7.23	0.19	2.5
323	61.6	6.17	2.29	-19.41	21.4	184	7.21	0.19	2.6
328	62.4	5.76	2.50	-19.37		210	6.80	0.29	3.8
333	63.1	5.44	2.90	-19.48	20.3	249	6.48	0.39	5.1
338	63.9	5.45	2.88	-19.40		253	6.49	0.39	5.1
343	64.7	5.27	3.02	-19.42	20.6	282	6.31	0.46	6.1
348	65.5	5.52	3.16	-19.54		288	6.56	0.36	4.7
353	66.2	5.33	2.92	-19.75	21.6	266	6.37	0.43	5.7
358	67.0	5.57	2.80	-19.96		271	6.61	0.34	4.5
363	67.8	5.58	2.98	-20.08	21.5	283	6.62	0.34	4.5
368	68.5	5.69	2.46	-20.26		243	6.73	0.31	4.0
373	69.3	5.78	2.49	-20.42	21.5	232	6.82	0.28	3.7
378	70.1	6.07	2.31	-20.37		210	7.11	0.21	2.8
383	70.8	6.34	2.12	-20.25	22.5	177	7.38	0.16	2.2
388	71.6	6.37	2.33	-20.25		186	7.41	0.16	2.1
393	72.4	6.25	2.27	-20.42	22.7	190	7.29	0.18	2.4
398	73.1	6.28	2.41	-20.20		201	7.32	0.17	2.3
403	73.9	6.17	2.46	-20.50	23.6	187	7.21	0.19	2.6
408	74.6	6.13	2.30	-20.23		179	7.17	0.20	2.6
413	75.4	6.47	2.28	-20.67	23.1	190	7.51	0.15	1.9
418	76.2	6.62	2.33	-20.56		195	7.66	0.12	1.6
423	76.9		1.89	-20.81	23.4	154			
428	77.7	7.04	1.71	-20.57		146	8.08	0.08	1.1
433	78.5	7.16	1.58	-20.71	23.8	135	8.20	0.07	1.0
438	79.2	7.62	1.47	-20.46		128	8.66	0.05	0.6
443	80.0		1.46	-20.11	24.4	130			
448	81.0	7.55	1.62	-20.15		150	8.59	0.05	0.7
453	82.0	6.84	1.61	-19.90	23.8	159	7.88	0.10	1.3
458	83.0		1.84	-19.86		174			
463	84.0		2.18	-19.94	23.3	215			
468	85.0	6.40	2.69	-20.10		266	7.44	0.15	2.0
473	86.0	5.98	4.34	-20.24	25.1	428	7.02	0.23	3.1
478	87.0	5.44	4.72	-20.48	24.8	458	6.48	0.39	5.1
483	88.3	6.41	4.20	-20.44		424	7.45	0.15	2.0
488	89.7	6.11	3.53	-20.58	24.5	364	7.15	0.20	2.7
493	91.0	6.00	2.82	-20.68	24.5	297	7.04	0.23	3.0
498	92.3	6.33	2.26	-20.57		228	7.37	0.17	2.2
503	93.7	6.33	2.02	-20.46	25.0	199	7.37	0.17	2.2

Appendix 1b. (continued)

Depth (cm)	Age (kyr)	$\delta^{15}N$ (‰)	Total OC (%)	$\delta^{13}C$ (‰)	SST (°C)	PaP (g C m^{-2} y^{-1})	$\delta^{15}N$ $NO_3^-{}_{(f)}$	f	$[NO_3^-]$ (µM)
508	95.0	6.62	1.66	-20.24		17	7.66	0.13	1.7
513	96.3	6.46	1.84	-20.47	25.0	194	7.50	0.15	1.9
518	97.7	6.35	1.45	-20.24		159	7.39	0.16	2.1
523	99.0	6.48	1.28	-20.22	25.0	134	7.52	0.14	1.9
528	100.0	6.22	1.29	-20.22	25.0	127	7.26	0.18	2.4
533	101.0	6.73	1.26	-20.37	24.4	128	7.77	0.11	1.5
538	102.0	6.62	1.33	-20.39		136	7.66	0.12	1.6
543	103.0	6.87	1.44	-20.61	24.1	147	7.91	0.10	1.3
548	104.0	6.92	1.74	-20.49		164	7.96	0.09	1.2
553	105.0	5.81	1.93	-20.46	24.0	182	6.85	0.27	3.6
558	106.0	6.06	2.41	-20.60		227	7.10	0.22	2.8
563	107.0	6.04	2.84	-20.62	23.8	279	7.08	0.22	2.9
568	108.9	5.94	2.63	-20.61		263	6.98	0.24	3.2
573	110.8	5.80	2.64	-20.62	24.3	334	6.84	0.28	3.6
578	112.6	6.00	2.06	-20.82	24.3	301	7.04	0.23	3.0
583	114.5	6.29	1.85	-20.95	24.8	245	7.33	0.17	2.3
588	116.4	6.48	1.61	-20.92	24.9	218	7.52	0.14	1.9
593	118.3	6.32	1.48	-20.98	25.0	212	7.36	0.17	2.2
598	120.1	6.77	1.06	-21.09	25.4	166	7.81	0.11	1.4
603	122.0		1.07	-21.06	26.3	155			
608	123.8	7.36	1.02	-20.94	26.0	144	8.40	0.06	0.8
613	125.5	7.11	1.39	-20.17	26.5	173	8.15	0.08	1.0
618	127.3	6.89	1.46	-19.76	26.2	188	7.93	0.10	1.3
623	129.0	6.38	1.85	-19.69	25.6	248	7.42	0.16	2.1
628	130.8	6.59	2.43	-19.58	24.7	314	7.63	0.13	1.7
633	132.5	6.27	2.86	-19.99	24.1	390	7.31	0.18	2.3
638	134.3	5.82	3.33	-19.69	24.2	417	6.86	0.27	3.6
643	135.7	6.07	3.26	-19.49	23.9	371	7.11	0.21	2.8
648	136.9	5.84	2.90	-19.33		327	6.88	0.26	3.5
653	138.1	5.72	2.79	-19.26	23.7	302	6.76	0.30	3.9
658	139.3	5.75	2.78	-19.23		296	6.79	0.29	3.8
663	140.5	5.51	2.65	-18.95	24.0	282	6.55	0.37	4.8
668	141.7	5.55	2.60	-19.03		271	6.59	0.35	4.6
673	142.9	5.57	2.51	-18.97	24.1	267	6.61	0.34	4.5
678	144.1	5.51	2.53	-18.94		264	6.55	0.37	4.8
683	145.3	5.50	2.53	-18.74	23.8	253	6.54	0.37	4.8
688	146.3	5.06	2.48	-18.71		243	6.10	0.56	7.4
693	147.1	5.19	2.36	-18.64	24.0	216	6.23	0.49	6.5
698	147.9	4.98	2.37	-18.61		222	6.02	0.60	8.0
703	148.7	5.31	2.11	-18.73	23.1	202	6.35	0.44	5.8
708	149.4	6.16	2.06	-18.55		197	7.20	0.19	2.6
713	150.2	5.81	2.02	-18.61	21.7	197	6.85	0.27	3.6
718	151.0	5.47	2.19	-18.83		234	6.51	0.38	5.0
723	152.3	5.36	2.68	-19.32	22.4	300	6.40	0.42	5.5
728	153.7	5.53	2.97	-19.25		340	6.57	0.36	4.7
733	155.0	6.33	2.31	-19.00	22.9	259	7.37	0.17	2.2
738	156.3	5.88	2.36	-19.08		270	6.92	0.26	3.4
743	157.7	5.51	2.32	-19.01	23.6	271	6.55	0.37	4.8
748	159.0	5.49	2.44	-18.90		268	6.53	0.37	4.9
753	160.3	6.13	2.21	-18.60	23.6	243	7.17	0.20	2.6

Appendix 1b. (continued)

Depth (cm)	Age (kyr)	$\delta^{15}N$ (‰)	Total OC (%)	$\delta^{13}C$ (‰)	SST (°C)	PaP (g C m^{-2} y^{-1})	$\delta^{15}N$ NO_3^-(f)	f	$[NO_3^-]$ (µM)
758	161.7	6.07	2.20	-18.52		247	7.11	0.21	2.8
763	163.0	6.08	2.26	-18.45	23.4	253	7.12	0.21	2.8
768	164.3	6.04	2.45	-18.47		286	7.08	0.22	2.9
773	165.7	6.61	2.16	-18.56	24.3	242	7.65	0.13	1.7
778	167.0	6.35	1.99	-18.45		228	7.39	0.16	2.1
783	168.3	6.52	2.05	-18.30	24.9	234	7.56	0.14	1.8
788	169.7	6.67	2.14	-19.03		259	7.71	0.12	1.6
793	171.0	6.29	2.17	-19.21	24.8	243	7.33	0.17	2.3
798	172.3	6.64	2.02	-19.09		236	7.68	0.12	1.6
803	173.7	6.39	1.89	-19.72	24.4	220	7.43	0.16	2.1
808	175.0	6.93	2.00	-19.38		246	7.97	0.09	1.2
813	176.3	6.48	1.95	-19.50	23.8	240	7.52	0.14	1.9
818	177.7	6.12	1.82	-18.99		224	7.16	0.20	2.7
823	179.0	6.60	2.01	-19.46	24.3	243	7.64	0.13	1.7
828	180.3	6.00	2.16	-19.61		262	7.04	0.23	3.0
833	181.7	5.05	2.77	-19.08	24.8	366	6.09	0.57	7.5
838	183.0	4.76	3.30	-19.73		402	5.80	0.75	9.9
843	183.7	4.75	3.46	-19.70	24.2	369	5.79	0.76	9.9
848	184.4	4.52	3.53	-19.76		396	5.56	0.95	12.5
853	185.1	5.07	3.34	-19.92	24.4	332	6.11	0.56	7.3
858	185.8	5.20	2.93	-19.85		280	6.24	0.49	6.5
863	186.4	5.82	2.88	-20.03		259	6.86	0.27	3.6
868	187.1	5.96	2.56	-20.00	25.1	226	7.00	0.24	3.1
873	187.8		0.77	-19.48		69			
878	188.5	6.36	1.99	-19.98		179	7.40	0.16	2.1
883	189.2	5.99	1.85	-19.90	26.0	160	7.03	0.23	3.0
888	189.9	6.15	1.71	-20.00		157	7.19	0.20	2.6
893	190.6	6.29	1.44	-20.24	25.1	151	7.33	0.17	2.3
898	191.3		0.70	-20.18		93			
903	191.9	6.57	1.50	-20.06	25.2	141	7.61	0.13	1.7
908	192.6	6.47	1.63	-20.42	24.9	147	7.51	0.14	1.9
913	193.3	7.05	1.38	-20.59	24.8	127	8.09	0.08	1.1
918	194.0	7.19	1.22	-20.57	25.3	148	8.23	0.07	1.0
923	196.2	7.72	1.09	-20.56	25.6	148	8.76	0.04	0.6
928	198.4	7.39	1.27	-20.00	25.9	172	8.43	0.06	0.8
933	200.6	6.95	1.62	-20.05	25.8	224	7.99	0.09	1.2
938	202.8	6.57	1.58	-20.03	25.4	218	7.61	0.13	1.7
943	205.0	6.58	1.81	-20.23	25.0	239	7.62	0.13	1.7
948	206.8	6.30	2.06	-20.25	24.8	259	7.34	0.17	2.2
953	208.7	6.49	1.92	-20.16	24.7	251	7.53	0.14	1.9
958	210.5	6.50	1.84	-20.30	24.9	245	7.54	0.14	1.9
963	212.3	6.59	1.70	-20.22	25.1	226	7.63	0.13	1.7
968	214.2	7.16	1.34	-19.53	25.2	182	8.20	0.07	1.0
973	216.0	6.50	2.07	-19.96	25.6	291	7.54	0.14	1.9
978	217.1	7.83	0.68	-19.62	24.8	83	8.87	0.04	0.5
983	218.2	7.34	1.19	-20.23	25.0	141	8.38	0.06	0.8
988	219.3	6.89	1.17	-19.92	25.0	134	7.93	0.10	1.3
993	220.4		1.36	-19.47	24.2	150			
998	221.5		1.60	-19.62	23.0	179			
1003	222.6	6.79	1.49	-19.83	23.4	180	7.83	0.11	1.4

Appendix 1b. (continued)

Depth (cm)	Age (kyr)	$\delta^{15}N$ (‰)	Total OC (%)	$\delta^{13}C$ (‰)	SST (°C)	PaP (g C m^{-2} y^{-1})	$\delta^{15}N$ NO_3^- (t)	f	$[NO_3^-]$ (µM)
1008	223.7	6.27	1.92	-20.01	23.0	228	7.31	0.17	2.3
1013	224.8	6.29	1.93	-20.02	23.3	229	7.33	0.17	2.3
1018	225.9	6.49	1.93	-20.18	23.6	237	7.53	0.14	1.9
1023	227.0	5.99	2.22	-20.21		263	7.03	0.23	3.0
1028	228.1	5.93	1.98	-20.03	24.3	235	6.97	0.24	3.2
1033	229.2	5.70	2.46	-20.30	24.3	286	6.74	0.30	4.0
1038	230.3		2.35	-20.32	24.4	269			
1043	231.4	6.13	2.06	-20.47	24.6	235	7.17	0.20	2.6
1048	232.5	6.36	1.98	-20.49	24.9	226	7.40	0.16	2.1
1053	233.6		1.69	-20.67	25.0	197			
1058	234.7	6.11	1.19	-20.68	25.4	146	7.15	0.21	2.7
1063	235.8	7.57	1.02	-20.54	25.7	125	8.61	0.05	0.7
1068	236.9		1.11	-20.42	26.2	139			
1073	238.0	7.68	1.69	-20.41	26.3	205	8.72	0.05	0.6
1078	239.6	7.09	1.89	-20.52	25.6	249	8.13	0.08	1.1
1083	241.1	5.90	2.69	-20.42	25.2	361	6.94	0.25	3.3
1088	242.7	5.76	3.20	-20.29	24.7	430	6.80	0.29	3.8
1093	244.3	5.49	2.91	-20.02	23.8	398	6.53	0.37	4.9
1098	245.9		3.94	-20.26	23.7	520			
1103	247.4	5.03	4.47	-20.37	23.0	579	6.07	0.58	7.6
1108	249.0	4.95	4.42	-20.68	22.2	584	5.99	0.63	8.2
1113	251.0	5.29	3.56	-20.49	22.4	496	6.33	0.45	5.9
1118	253.0	6.04	3.52	-20.43	22.5	499	7.08	0.22	2.9
1123	255.0	5.53	3.48	-20.57	22.7	485	6.57	0.36	4.7
1128	257.0	6.23	3.43	-20.45	22.9	478	7.27	0.18	2.4
1133	259.0	5.43	3.53	-20.63	22.6	501	6.47	0.40	5.2
1138	261.0	6.25	3.31	-20.55	22.6	486	7.29	0.18	2.4
1143	263.0	6.54	3.29	-20.48	22.7	483	7.58	0.14	1.8
1148	265.0	6.17	3.59	-20.59	23.3	500	7.21	0.19	2.5
1153	267.0	5.43	2.36	-19.83	23.2	329	6.47	0.39	5.2
1158	269.0	7.10	2.06	-19.42	21.6	310	8.14	0.08	1.0
1163	271.6	5.08	2.10	-19.71	20.9	327	6.12	0.55	7.2
1168	274.1	5.31	3.35	-20.05	21.7	531	6.35	0.44	5.8
1173	276.7	6.06	4.22	-20.48	21.8	622	7.10	0.21	2.8
1178	279.3	6.00	3.03	-20.31	22.1	463	7.04	0.23	3.,
1183	281.9	5.66	3.05	-20.57	22.4	466	6.70	0.31	4.1
1188	284.4	6.11	2.43	-20.75	23.3	365	7.15	0.20	2.7
1193	287.0	6.56	1.62	-20.33	24.1	248	7.60	0.13	1.7
1198	289.6	6.22	1.56	-20.20	24.2	251	7.26	0.18	2.4
1203	292.1	6.73	1.86	-19.86	23.3	295	7.77	0.11	1.5
1208	294.7	6.35	2.30	-20.12	23.6	8	7.39	0.16	2.1
1213	297.3	6.58	2.04	-20.34	23.6	312	7.62	0.13	1.7
1218	299.9	7.16	1.50	-20.48	24.0	233	8.20	0.07	1.0
1223	302.4	7.19	1.54	-20.79	24.8	244	8.23	0.07	1.0

4. CONCLUSIONS

From stable nitrogen isotope analyses of sinking particulate matter, surface sediments, and Late Quaternary sediments off the southwest coast of Africa, the following conclusions about nutrient dynamics in surface waters of this region and diagenetic effects on the sedimentary $\delta^{15}N$ signal have been drawn:

1. The concentration of nitrate in surface water and the degree to which it is utilized are the predominant controls on $\delta^{15}N$ in organic matter produced in the Angola and Cape Basins. This is shown in manuscript 3.1, where $\delta^{15}N$ values in sinking particles were positively correlated with SST and mirrored particle flux rates and wind stress. The results of manuscripts 3.2 and 3.3 support this by demonstarting that surface sedimentary $\delta^{15}N$ was negatively correlated with surface water nitrate concentrations. The findings of these manuscripts indicate that neither denitrification nor the presence of terrestrial material appear to play important roles in determining the nitrogen isotopic composition of sediments in this area. Furthermore, estimates of the relative utilization of the surface nitrate pool based on measured $\delta^{15}N$ values and Raleigh fractionation principles were in close agreement with values calculated from nitrate concentrations in surface water, providing encouraging evidence for the successful hindcasting of nitrate utilization in surface water from $\delta^{15}N$ values in Late Quaternary sediments.

2. Bacterial remineralization appears to have had little or no effect on the sedimentary $\delta^{15}N$ signal. Manuscripts 3.1 and 3.3 reveal that sinking particles at 599 m in the northern Benguela region were 1.6‰ lighter than the underlying sediments. Comparison of the $\delta^{15}N$ values in the sediments of this region with sedimentary $\delta^{15}N$ predicted from nitrate concentrations in the water column corroborate the evidence from the sediment trap data, indicating a similar enrichment (~1.4‰) in sediments relative to the surface generated signal. In the Angola Basin (manuscript 3.2) and southern Cape Basin (manuscript 3.3), no significant difference was found between sedimentary $\delta^{15}N$ and $\delta^{15}N$ calculated from water column nitrate concentrations.

3. Changes in nutrient utilization in surface water over the past 300 kyr in the Angola Basin has responded primarily to changes in boreal summer insolation and trade wind intensity. The results presented in the first three manuscripts suggest that nitrogen isotope ratios in bulk sediments reflect relative nitrate utilization in surface water. Thus, in manuscript 3.4, variations in sedimentary $\delta^{15}N$ values over the past 300 kyr in the southeast Atlantic Ocean with respect to changes in euphotic zone nutrient depletion are discussed. Low $\delta^{15}N$ values in both of the cores studied corresponded to low sea surface temperatures and to high organic

carbon content and paleoproductivity and vice versa. glacial $\delta^{15}N$ values were significantly lower than the $\delta^{15}N$ of interglacial sediments, indicating less intense depletion of the surface nitrate pool during glacials due to elevated nitrate concentrations. Time series analyses revealed the presence of 23 kyr cycles in the $\delta^{15}N$ record, suggesting that nitrate availability in this region is controlled by the intensity of tradewind-driven upwelling. Differences between the two cores reveal that between 30 and 70 kyr ago, nitrate levels were higher in the southern Angola Basin than off the Zaire River, likely due to advection of nitrate-rich waters from the southern coastal upwelling region into the Angola Basin, but not as far as Zaire. Denitrification does not appear to have occurred to a significant extent during the past 300 kyr in this region and changes in terrestrial input were undectectable on the basis of $^{15}N/^{14}N$ ratios.

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