

# BERICHTE

aus dem Fachbereich Geowissenschaften  
der Universität Bremen

No. 169

Lavik, G.

**NITROGEN ISOTOPES OF SINKING MATTER  
AND SEDIMENTS IN THE SOUTH ATLANTIC**

Berichte, Fachbereich Geowissenschaften, Universität Bremen, No. 169,  
140 pages, Bremen 2001



ISSN 0931-0800



**Nitrogen isotopes of sinking matter and  
sediments in the South Atlantic**

**Dissertation zur Erlangung des Doktorgrades**

**vorgelegt  
dem Fachbereich Geowissenschaften  
Universität Bremen**

**von  
Gaute Lavik  
Bremen, September 2000**

The "Berichte aus dem Fachbereich Geowissenschaften" are produced at irregular intervals by the Department of Geosciences, Bremen University.

They serve for the publication of experimental works, Ph.D.-theses and scientific contributions made by members of the department.

Reports can be ordered from:

Gisela Boelen

Sonderforschungsbereich 261

Universität Bremen

Postfach 330 440

**D 28334 BREMEN**

Phone: (49) 421 218-4124

Fax: (49) 421 218-3116

e-mail: [boelen@uni-bremen.de](mailto:boelen@uni-bremen.de)

Citation:

Lavik, G.

Nitrogen isotopes of sinking matter and sediments in the South Atlantic.

Berichte, Fachbereich Geowissenschaften, Universität Bremen, No. 169, 140 pages, Bremen, 2001.

## Table of contents

Acknowledgments.....	3
<b>1 Summary .....</b>	<b>5</b>
<b>2 Introduction .....</b>	<b>9</b>
<b>3 Nitrogen cycle and <math>\delta^{15}\text{N}</math> dynamics .....</b>	<b>10</b>
3.1 Assimilation of dissolved nitrogen (DN) .....	10
3.2 Nitrogen fixation .....	12
3.3 Nitrification .....	13
3.4 Denitrification .....	13
3.5 Oxidic decomposition (Respiration) .....	14
3.6 Anoxic decomposition (Ammonification) .....	14
3.7 Inorganic processes .....	15
<b>4 An approach to <math>\delta^{15}\text{N}</math> as a paleoceanographic tool.....</b>	<b>16</b>
4.1 Sinking matter vs. sediments.....	16
4.2 Terrigenous input .....	17
4.3 $\delta^{15}\text{N}$ and upwelling .....	18
4.4 Paleo variations .....	19
<b>5 Materials and methods.....</b>	<b>21</b>
5.1 Trap material .....	21
5.2 Sediments .....	21
5.3 Dust .....	24
5.4 Mass spectrometer.....	26
<b>6 Objectives and data presentation.....</b>	<b>28</b>

<b>7 Manuscripts 1 - 4.....</b>	<b>30</b>
7.1 Manuscript 1: $\delta^{15}\text{N}$ values on sinking matter and surface sediments in the eastern equatorial Atlantic: Evidence of a northward lateral particle transport <i>G. Lavik, G. Fischer, R. R. Schneider and G. Wefer</i> .....	30
7.2 Manuscript 2: Various impact from atmospheric dust on the marine record along the African west coast: Reflection climate and vegetation <i>G. Lavik, J.-B. Stuut, L. Dupont, P. Helmke, R. R. Schneider and G. Wefer</i> .....	55
7.3 Manuscript 3: Seasonal variability of $\delta^{15}\text{N}$ in sinking particles in the Benguela upwelling region <i>M. E. Holmes, G. Lavik, G. Fischer, M. Segl, G. Ruhland and G. Wefer</i> .....	70
7.4 Manuscript 4: Nitrogen isotopes in the Benguela Upwelling system: Sea level related offshore migration in the upwelling cell and variable impact of denitrification <i>G. Lavik, C. Eichner, G. Mollenhauer, P. J. Müller, R. R. Schneider, U. Struck and G. Wefer</i> .....	97
<b>8 Conclusion .....</b>	<b>132</b>
<b>9 References .....</b>	<b>134</b>
<b>10 Appendix.....</b>	<b>141</b>
10.1 Table 1 .....	141
10.2 Table 2.....	142
10.3 Table 3 .....	145
10.4 Table 4 .....	146
10.5 Table 5 .....	147

## Acknowledgements

I would like to express my gratitude to Prof. Dr. Gerold Wefer for giving me the possibility to do this dissertation, and for his advice and support throughout the work.

Discussions with and advice from Dr. Ralph Schneider, Dr. Gerhard Fischer and Dr. Peter Müller have increased my insight and been of great help during the progression of this work.

Thanks to Maren Voß, who also critically read through and commented on this thesis, and the working group in Warnemünde (IOW) who provided me with insight and information about both methods and interpretations during two visits at their lab. Monika Segl and Wolfgang Bevern deserve my gratitude for their assistance with the mass spectrometer.

Special thanks to Laurence Vidal, Lydie Dupont, Gesine Mollenhauer, Albert Benthien and my former office mate Oscar Romero for comments, support and numerous scientific, - and not so scientific discussions. I am indebted to Emma Eades who corrected the English language in this dissertation. Mrs. Gisela Boelen, Carmen Muerken and Adelheid Grimm-Geils, I would like to thank for guiding me through the bureaucracy. To all other colleagues at the FB Geowissenschaften I am grateful for a good and productive working atmosphere.

Stefanie Meier is hereby recognised for a lot but most of all for her patience.

Finally, thanks to Prof. Dr. Bo Baker Jørgensen for finding the time to read and evaluate this work. This study was funded by the Deutsche Forschungsgemeinschaft (Sonderforschungsberich 261).



## 1 Summary

The  $^{14}\text{N}/^{15}\text{N}$  ratio (expressed as  $\delta^{15}\text{N}$  in ‰ vs. air) were measured on sinking matter, atmospheric dust and sediments in the equatorial and eastern South Atlantic. To determine the main controls on the nitrogen composition of the marine sediment in this region for the present situation, sediment traps and surface sediments were analysed and compared to other parameters and independent oceanographic and climatic data. Additionally, to better estimate the possible impact from the terrigenous input on the deep sea sediments, shipboard collected dust samples were analysed for their isotopic composition. For reconstructions of past changes in the high production zone in the Benguela upwelling regime, a core transect off Namibia, South West Africa, were analysed for downcore variations in the  $\delta^{15}\text{N}$  signal.

In the equatorial eastern Atlantic Ocean the upwelling and advection of cold nutrient rich subsurface waters to the surface occurs during boreal summer and the rest of the year warm oligotrophic surface water condition reign. In despite of this, high fluxes with relatively light isotopic composition during the warm spring season occurred all along the studied N-S ( $3^{\circ}\text{N}$ - $6^{\circ}\text{S}$ ) sediment trap transect at  $10^{\circ}\text{W}$ . Moreover, due to low fluxes during the cold summer season at and south of the Equator, the fluxes during spring dominate the sedimentation in the equatorial and the southern Guinea Basin. Low  $\delta^{15}\text{N}$  values in the sinking matter during spring, suggest nitrogen fixation related to Fe supply through dust and precipitation of nutrients within the ITCZ (Inter Tropical Convergence Zone) as important nitrate sources for new production. High summer fluxes in the northern Guinea Basin are the major difference in the sedimentation of organic matter compared to the equatorial and southern Guinea Basin. Low  $\delta^{15}\text{N}$  values combined with high fluxes suggest an origin close to the source of new nitrate occurring along the equatorial divergence. The only mechanism to explain this is a substantial lateral northward transport, within the upper part of the water column, of the organic particles produced during the equatorial upwelling. The annual fluxes and  $\delta^{15}\text{N}$  values from the sediment trap transect correlate well to the underlying sediments and indicates that the findings in this study have important paleoceanographic implications.

Input of atmospheric dust from the continent to the ocean do not only influence the marine sediments isotopic composition through stimulation of the nitrogen fixation and thus productivity. The dust also contains carbon and nitrogen from terrestrial organic matter and inorganic nitrogen with isotopic compositions varying with vegetation and climate. Along the African west coast 7‰ change in the bulk  $\delta^{13}\text{C}$  values were found and mainly ascribed to the relative amounts of C3 and C4 plant remains contributing to the OM (organic

matter). This reflects a variation in the contribution from C4 plants from >50% of the OM in the dust between 10°N and 20°N to less than 5% between 0 and 5°S. Most of the registered change in the C/N ratios (12-29) is ascribed to the relative proportions of plant litter and charcoal (high C/N-ratio) compared to inorganic nitrogen absorbed by clay minerals (reducing the C/N-ratio). The ~5‰ (3-8‰) variation in the nitrogen isotopic composition of the dust (organic and inorganic nitrogen) is suggested to reflect the aridity of the source area, with increasing  $\delta^{15}\text{N}$  value with decreasing precipitation.

Different from the Equatorial upwelling area, the  $\delta^{15}\text{N}$  signal of sinking particles collected with sediment traps in the Benguela upwelling regime off southwest Africa mirrored variations in the input of inorganic nitrogen to the surface water. Light  $\delta^{15}\text{N}$  signal (2.5‰) corresponded to lowered sea surface temperatures two times a year (austral spring and late autumn/early winter) indicating reduced relative nitrate utilisation during increased nutrient supply by recently upwelled water. High organic fluxes coincide with the low  $\delta^{15}\text{N}$  values and sea surface temperatures, reflecting increased productivity fuelled by the upwelled nutrients. High  $\delta^{15}\text{N}$  values (up to 13.5‰) coincided with high sea surface temperatures and low particle flux rates. The pattern in the  $\delta^{15}\text{N}$  signal does not appear to have been caused by variations in the biological composition and thus, allowing reconstructions of relative utilisation of the upwelled nitrate based on  $\delta^{15}\text{N}$  of the sinking matter. During late summer/early fall and mid-winter 70-90% of the nitrate in the originally upwelled waters were used whereas the relative utilisation was only 30-50% during the intense spring blooms.

In this sediment trap sited 400km offshore, no indications of denitrification were found. Above the continental shelf a bit further south, off Namibia, evidence of water-column denitrification were found within the zone of perennial upwelling by increasing  $\delta^{15}\text{N}$  values in surface sediments from the outer shelf towards the shore. In the past, the offshore extent of the zone influenced by denitrification increased with intensified upwelling to also influenced the  $\delta^{15}\text{N}$  records from the upper slope (GeoB1712 and GeoB1711). The maximum in the upwelling intensity and denitrification occurred during marine isotope stage 3. High organic content and low sea surface temperatures also indicate a change towards a perennial upwelling during isotope stage 3. The  $\delta^{15}\text{N}$  record from the lower slope (GeoB1710) seems to be uninterrupted by denitrification and generally reflects the relative nitrate utilisation and the nutrient conditions. In this core (GeoB1710) two exceptional peaks, with high organic content and the the records lowest  $\delta^{15}\text{N}$  values, are found during late isotope stage 3 and early isotope stage 6. These two peaks coincide with similar features in the Angola Basin further north.

Abrupt changes characterised by a ~1‰ shift in the  $\delta^{15}\text{N}$  records from all three cores, are probably caused by sea-level related migrations in the upwelling cell. Only during full

---

interglacial conditions (marine isotope stage 1 and 5.5) were the sea-level stand high enough to allow the upwelled intermediate water to reach the coast before emerging at the surface. After marine isotope stage 5.5 (at 111k) the upwelling of subsurface waters shifted away from the shore and emerged at the mid shelf break about 80km off the modern coastline. Another effect of sea-level change is seen for the lowest sea-level stands during the LGM, when erosion of the exposed shelf areas might have released large amounts of nutrients and fuelled the surface and intermediate waters.



## 2 Introduction

Almost half of the earth's total photosynthetic production takes place in the ocean according to new estimates ( $51 \times 10^{15} \text{ g C yr}^{-1}$ , Knauer, 1993;  $37\text{-}46 \times 10^{15} \text{ g C yr}^{-1}$ , Antoine et al., 1996(2)) of which 99,9% is produced by marine phytoplankton (Walsh, 1984). About 15 % ( $7 \times 10^{15} \text{ g C yr}^{-1}$ , Knauer, 1993) of the net primary production (NPP) in the ocean is exported out of the photic zone and considered as new production. This, which is the new production in the ocean through one year, makes up 1% of the total atmospheric carbon pool ( $750 \times 10^{15} \text{ g C yr}^{-1}$ , Schimel, 1995). Considering that this primary production is mainly limited by nutrients and the main limiting nutrients in the surface ocean is available nitrogen (Howarth, 1988; Codispoti, 1989; Vitousek and Howarth, 1991), the importance of the marine nitrogen cycle (Fig. 1) for the production in world oceans and consequently the Earth's climate is indicated.

Nitrate is the most important available nitrogen species (Codispoti, 1989) and a number of field and laboratory studies have demonstrated a close link between the utilisation of nitrate and the isotopic composition of the particulate nitrogen (Wada and Hattori, 1978; Wada, 1980; Altabet and McCarthy, 1985; Altabet et al., 1991; Francois et al., 1992; Nakatsuka et al., 1992; Wilkerson and Dugdale 1992; Altabet and Francois, 1994a; Farrell et al., 1995; Montoya and McCarthy, 1995; Pennock et al., 1996; Wu et al., 1997; Waser et al., 1998; Holmes et al., 1999). Numerous recent studies have applied nitrogen isotopic ratio ( $^{15}\text{N}/^{14}\text{N}$  reported as  $\delta^{15}\text{N}$  in ‰ relative to atm. air) of sinking matter and sediments to understand and reconstruct changes in the marine nitrogen cycle and in the oceans primary productivity (Karl et al., 1997; Francois et al., 1997; Holmes et al., 1997; 1998; Sigman et al., 1997; 1999; Brandes et al., 1998; Haug et al., 1998; Altabet et al., 1999a; 1999b; Pride et al., 1999; Bertrand et al., 2000; Eichner, 2000 and references to older studies therein). Although these studies have shown the usefulness of the  $\delta^{15}\text{N}$  measurements on sediments and particulate matter, the interpretation of these data are connected with some complexity. A number of potential processes are influential on the nitrogen cycle and alterations of the  $\delta^{15}\text{N}$  signal in sediments and water column (Fig. 1) have to be kept in mind during evaluation of  $\delta^{15}\text{N}$  values to come to the right conclusions about i.e. nutrient conditions. To ease the understanding of the following discussions about the impacts on the nitrogen cycle and the  $\delta^{15}\text{N}$  values for readers not specialised in the nitrogen isotope biogeochemistry, I will in the following chapter mention and describe the starting processes and their importance (see also Fig. 1).

### 3 Nitrogen cycle and $\delta^{15}\text{N}$ dynamics

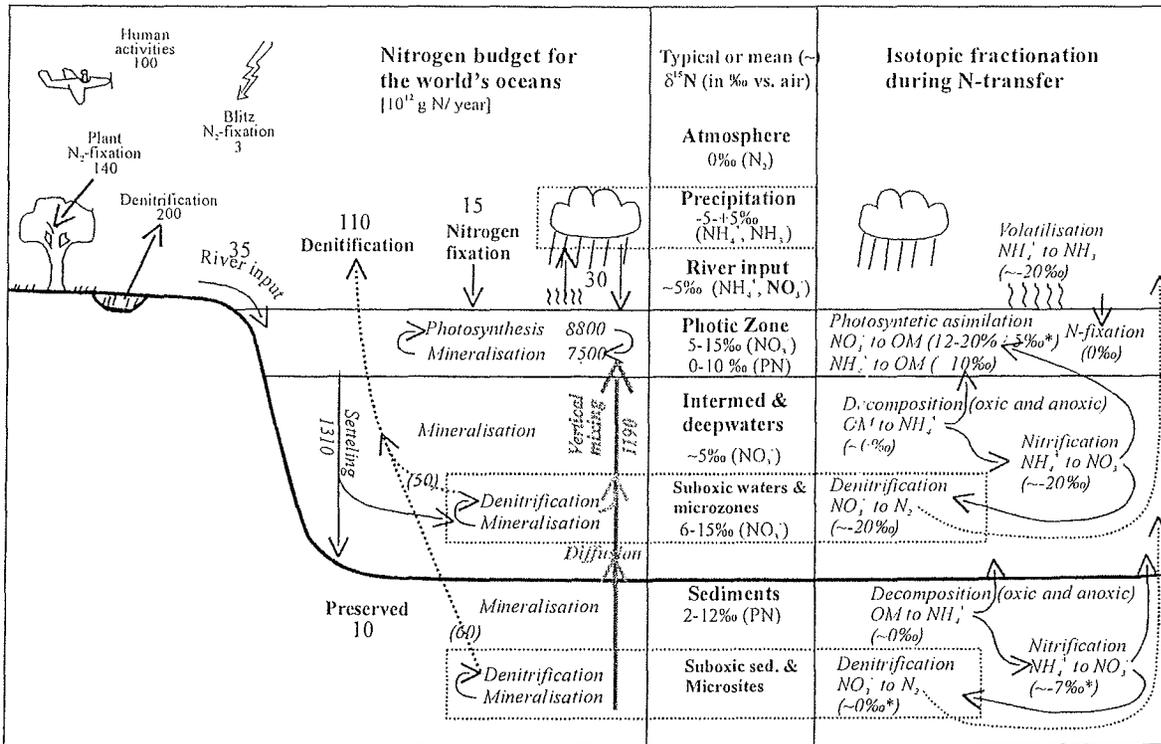
The largest reservoir of free nitrogen (97.76% is located in rocks) on Earth is the atmosphere (2.01%) where it mainly occurs as  $\text{N}_2$ -gas, but the more important nitrogen species for the marine nitrogen cycle are the dissolved nitrogen (DIN); nitrate ( $\text{NO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), and ammonium ( $\text{NH}_4^+$ )(Fig. 1). Because ammonium both are of organic and inorganic origin, the term dissolved nitrogen (DN) would hereafter be used. Additionally free nitrogen exists as oxides ( $\text{NO}_2$ ,  $\text{NO}$ , and  $\text{N}_2\text{O}$ ) and as dissolved organic nitrogen (DON) like ammonia ( $\text{NH}_3$ ) and amino acids ( $-\text{NH}_2$ ). There are two stable nitrogen isotopes,  $^{14}\text{N}$  (99.64%) and  $^{15}\text{N}$  (0.36%), and the ratio ( $^{15}\text{N}/^{14}\text{N}$ ) between them is commonly expressed as  $\delta^{15}\text{N}$ , which equals:

$$[(^{15}\text{N}/^{14}\text{N}_{\text{sample}}/^{15}\text{N}/^{14}\text{N}_{\text{standard}})-1]* 10^3 \quad (1.1)$$

The values are reported in ‰ vs. atmospheric air which is given the arbitrary value 0 (zero). The variation in the  $\delta^{15}\text{N}$  signals, measurable in sediments and sinking matter of the ocean, is due to the higher kinetic energy required to break bonds formed with the heavier isotope ( $^{15}\text{N}$ ). Thus, molecules containing the lighter  $^{14}\text{N}$ -isotope are more reactive and a discrimination against molecules containing the heavier  $^{15}\text{N}$ -isotope occurs. This causes a discrimination against the heavier isotope during most biochemical reactions which occur and produce an offset in isotope signal between the produced substance and the N-source. Consequently, the source will get relatively enriched in the heavier  $^{15}\text{N}$ -isotope (rising  $\delta^{15}\text{N}$ -values) due to the successive depletion of the lighter  $^{14}\text{N}$ -isotope. The main processes influencing the marine nitrogen budget and  $\delta^{15}\text{N}$ -signal are described and evaluated in the following section and in figure 1. In figure 1, observant readers might note that the marine nitrogen cycle described is not in balance, as more nitrogen exit than enters the system. This is, however, the current state of the knowledge.

#### 3.1 Assimilation of dissolved nitrogen (DN)

The assimilation of nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ) and nitrite ( $\text{NO}_2^-$ ) are the main processes where nitrogen is obtained during primary production (importance in respective order). The assimilation of ammonium is related to a confined isotopic fractionation compared to nitrate assimilation (Collister and Hayes, 1991).



**Figure 1** The marine nitrogen cycle (right side) and the transitional effects on the δ<sup>15</sup>N during its governing processes (left side). The basis for the mean or typical range of δ<sup>15</sup>N values (center) are collected from a large number of publications both cited in the text and others. Most numbers on the marine nitrogen cycle are collected from Schlesinger (1996) and references therein, and the isotopical fractionation is mainly taken from Collister and Hayes (1991). The (\*) numbers are estimates from natural environments from various authors (see text).

The nitrogen isotopic composition of the organic matter is reflecting the δ<sup>15</sup>N of the inorganic nutrient source (mainly NO<sub>3</sub><sup>-</sup>) taken up during photosynthesis and the Rayleigh fractionation effect (Mariotti et al., 1981). This is the base of estimating the degree of relative nitrate utilisation in surface water, where the δ<sup>15</sup>N at a given time (δ<sup>15</sup>NO<sub>3</sub><sup>-</sup>) is expressed by:

$$\delta^{15}\text{NO}_3^-(f) = \delta^{15}\text{NO}_3^-(f=1) - \epsilon * \ln f \quad (1.2)$$

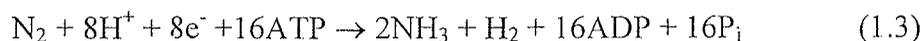
where δ<sup>15</sup>NO<sub>3</sub><sup>-</sup>(f=1) is the δ<sup>15</sup>N value of the source prior to any nitrate consumption, ε is the fractionation factor associated with nitrate assimilation (Fig. 2.1) and f is the remaining amount of nitrate relative to the original source (unutilised nitrate). Although precaution about regional and local variation have to be taken, the mean values for δ<sup>15</sup>NO<sub>3</sub><sup>-</sup>(f=1) is ~5‰ (Wada et al., 1975, Sigman et al., 1997) and for ε ~5‰ (Holmes et al., 1998; Sigman et al., 1999; Holmes et al., this study). These estimates from natural environments reveal

considerably lower fractionation rates than the 10-20‰ reported by Collister and Hayes (1991). This might be due to rapid internal recirculation of nutrients with several processes involved in a natural environment, but as long as it is applied on a natural environment the local estimated  $\epsilon$ -values should be used for estimations.

The ensuing transfer of nitrogen through trophic levels is opposite in  $\delta^{15}\text{N}$ -fractionation compared to the photosynthetic assimilation of DN and characterised by a systematic increase of  $\sim 3.5\%$  per trophic step (DeNiro and Epstein, 1981; Minagawa, and Wada, 1984). However, Altabet (1988) argued that this effect could be neglected by evaluation of bulk sedimentary  $\delta^{15}\text{N}$ -values because of mass balance considerations.

### 3.2 Nitrogen fixation

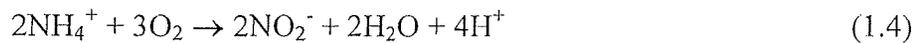
The assimilation of  $\text{N}_2$  is called nitrogen fixation and is the principal entry route for atmospheric nitrogen ( $\text{N}_2$ ) into the biological cycle. In the world ocean this process is mainly confined to some blue-green algae (cyanobacteria). Due to the high energy required to break the triple bonding between the two N-molecules, nitrogen fixation is a metabolically expensive process and where easily assimilated DN are adequate these would be preferred as nitrate source. Therefore, nitrogen fixation mainly occurs in the large oligotrophic areas of the ocean where it supplies a major part of the biologically bound nitrogen (Capone and Carpenter, 1982; Walsh et al., 1988; Michaels et al., 1994; Capone et al., 1997; Gruber and Sarmiento, 1997; Karl et al., 1997). The N-fixers do not fractionate isotopically so the  $\delta^{15}\text{N}$  of newly fixed nitrogen is about the same as air (0‰) (Minagawa and Wada 1986; Carpenter et al., 1997). The reaction from  $\text{N}_2$  to  $\text{NH}_3$  is:



and requires strict local anaerobe conditions and the enzyme complex called nitrogenase. This enzyme which consists of two proteins incorporating iron (Fe) and molybdenum (Mo) (Georgiadis et al., 1992; Kim and Rees, 1992). Thus, iron, phosphate and molybden have to be present to allow nitrogen fixation in the ocean. Other factors like sulphate ( $\text{SO}_4$ ) concentrations (Howarth and Cole, 1985), the availability of the cobalt containing vitamin  $\text{B}_{12}$  (Palit et al., 1994) and the presence of carbohydrates (Paulsen et al., 1991), is also of importance to the efficiency of the nitrogen fixation. However, on a global basis this mechanism adds about  $10\text{-}15 \cdot 10^{12}$  g N to the ocean each year (Capone and Carpenter, 1982; Walsh et al., 1988).

### 3.3 Nitrification

Nitrification is the oxidation of ammonium to nitrate or nitrite by the bacteria *Nitrosomonas* and *nitrobacter*, and is a very important process for the biological nitrogen cycle. The reactions:



and



require oxic conditions and the produced nitrate is highly soluble in water. This process is related to a isotopic fractionation of about 20‰ (which is approximately the same as nitrate assimilation, Collister and Hayes, 1991). Nitrate is the most important nitrogen species for the primary production in my main study area (Chapman and Shannon, 1985).

### 3.4 Denitrification

Denitrification is the reduction of nitrate ( $\text{NO}_3^-$ ) to  $\text{N}_2$ -gas when bacteria use  $\text{NO}_3^-$  as electron acceptor by respiration instead of  $\text{O}_2$ -gas. This process requires anoxic or suboxic conditions and can take place both in the sediments and in the water column when the respirational needs of the decaying organic matter exceeds the oxygen supply. The denitrification reaction is:



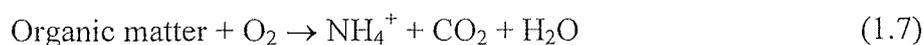
and requires external nitrate ( $\text{NO}_3^-$ ) supply in an anoxic environment where no nitrification takes place. Important to note is that many of the denitrifying bacteria species have the ability to instantly switch to aerobic respiration when oxygen is available so that they will also be present and active in an oxic environment. This makes it possible for an efficient denitrification in micro-zones in the oxic or suboxic water column (Alldredge and Cohen, 1987) and sediments (Brandes and Devol, 1997). Although denitrification could occur locally and cause a loss of isotopically light nitrate within an oxic water column, it is first becoming efficient at oxygen levels of  $0.2 \text{ ml O}_2 \cdot \text{l}^{-1}$  (or  $\sim 10 \mu\text{M}$ ) (Packard et al., 1983). Like in other biochemical reactions the molecules containing the lighter  $^{14}\text{N}$  is preferred during anoxic respiration causing a loss of light isotopes from the nitrate reservoir in the water-column. Although denitrification is the same process in the sediment as in the water-column, the N-isotopic impacts are quite different between sedimentary denitrification and water-column denitrification. Water-column denitrification is accompanied by a large

fractionation (20-40‰) towards lighter isotopes in the released  $\text{N}_2$ -gas (Cline and Kaplan, 1975; Collister and Hayes 1991; Brandes et al., 1998), leaving the source substantially enriched in  $^{15}\text{N}$ . On the contrary, Brandes and Devol (1997) reported that there is little or no net isotopic fractionation associated with denitrification within the sediments. They ascribed this to limited diffusional supply of reactants into and within the sediment. In other words, if the nitrate within a closed system is totally depleted or all incoming nitrate is instantly utilised the net isotopic fractionation is zero.

Consequently, denitrification plays the opposite role to nitrogen fixation for the biological nitrogen cycle as the released  $\text{N}_2$ -gas is mainly lost to the atmosphere. On an annual basis denitrification causes the loss of more than  $100 \cdot 10^{12} \text{ g N} \cdot \text{y}^{-1}$  from the ocean. Sediment,- and water column denitrification are estimated to be of about the same magnitude in amount nitrogen loss (Schlesinger, 1997) but not in the matter of net  $\delta^{15}\text{N}$  fractionation (Brandes and Devol, 1997).

### ***3.5 Oxidic decomposition (Respiration)***

Oxidic decomposition is the main mineralisation of dead organic matter. Under warm water conditions the bulk decomposition is performed by bacteria, whereas in colder waters more of the NPP are passed on to higher trophic levels (Pommeroy and Deibel, 1986). The reaction is in principal:



and this process is related to a very low isotopic fractionation ( $\sim 1\%$ , Collister and Hayes, 1991).

### ***3.6 Anoxic decomposition (Ammonification)***

Like denitrification, ammonification requires anoxic conditions. It occurs by bacterial decay of organic matter as organically bound nitrogen is reduced to  $\text{NH}_3$  or  $\text{NH}_4^+$ . Ammonification is the most important process to mineralise organic matter in the sediments or in the water column under anoxic or suboxic conditions. Ammonium is the main N-containing product of bacterial decomposition in anoxic sediments. As during oxidic decomposition, no large isotopic fractionation occurs.

### 3.7 Inorganic processes

Dissolution of N<sub>2</sub>-gas in water is maybe the most important inorganic process for the marine nitrogen cycle as it makes the atmospheric N<sub>2</sub> available for nitrogen fixing algae. According to Tyrell (1999) dissolved N<sub>2</sub> might be the largest N-reservoir in the world ocean.

Ammonia volatilisation represents a loss of nitrogen ( $\text{NH}_4^+_{(\text{aqu})} \rightarrow \text{NH}_3_{(\text{gas})}$ ) from the ocean to the atmosphere but most of this also precipitates over the ocean as ammonium (Schlesinger and Hartley, 1992). Therefore, the large kinetic fractionation (~34‰) during this process is of less importance to the global cycle. However, it would be of local or regional importance to the nutrient budget and the  $\delta^{15}\text{N}$  values if isotopically light nutrients are systematically moved from one region to another by this mechanism. This could account for a total amount of  $30 \cdot 10^{12} \text{ g N} \cdot \text{y}^{-1}$  (Cornell et al., 1995).

A small but subsidiary process for nitrogen fixation is normal atmospheric lightning ( $\text{N}_2 \rightarrow \text{NO}_3^*$ ) and some of the  $3 \cdot 10^{12} \text{ g N} \cdot \text{y}^{-1}$  produced nitrate (Kumar et al., 1995, Ridley et al., 1996) enters the ocean with precipitation.

Another inorganic process with some importance for the nitrogen budget is the absorption of ammonium by clay particles. There is a inorganic export or loss of ammonium from the water column to the sediments due to this process. In oligotrophic regions the inorganic N-content can exceed 20% of the total sedimentary Nitrogen (Müller, 1977) and can therefore be a notable factor by bulk  $\delta^{15}\text{N}$  measurements in areas with very low organic fluxes.

## 4 An approach to $\delta^{15}\text{N}$ as a paleoceanographic tool

Since the discovery that phytoplankton discriminate against the heavier isotope ( $^{15}\text{N}$ ) during photosynthetic assimilation of nitrate (Miyake and Wada, 1971, Wada and Hattori, 1978), the measurement of  $\delta^{15}\text{N}$  in particulate nitrogen (PN) has developed into a powerful tool for reconstructions of the marine nutrient budget. Nevertheless, there are still a number of unsolved problems by interpreting the bulk sedimentary  $\delta^{15}\text{N}$  signal like the biological differences, external input, spatial variations in the nitrate pool, and the transfer of the isotopic signal to the sediments. Although the isotope signal measured on isolated components of the sediment (i.e. diatoms) might be easier to interpret the advantage of using the bulk signal is that it would reflect the total output of the system. This is of main interest in paleoceanographic studies and the impact on the marine nitrogen cycle.

### 4.1 *Sinking matter vs. sediments*

To evaluate a proxy as paleo-tool for surface water conditions, it is essential to find out if the sediments reflect the surface water conditions above the site and to assess the main influences on the export production. In most marine systems the annual cycle is of major importance and thus the sum of an average year's export production should be reflected in the sediments. By studying sediment trap material it is possible to explore which surface water conditions through an annual cycle causes the highest export production. Furthermore, by comparing the annual product from the sediment trap to the surface sediments below we can detect the sum of the diagenetic alteration in the water column and in the sediment-water interface. However, to know if this diagenetic effect is a constant factor or if it depends on environmental and physiographic settings, several sediment traps are required. This is also what we did in Manuscript 1 for the eastern equatorial Atlantic where the north-south transect of sediment traps also enabled us to trace lateral displacement of particles in the upper part of the water column.

Although our results support earlier findings that there seems to be a more or less constant offset of  $+4\pm 1\%$  between sediment trap material and surface sediments (Altabet and Francois, 1994; Francois et al., 1997), a slight tendency towards less offset connected to higher organic content is present. This might support new results by Altabet et al. (1999b) that higher burial rates related to higher particle flux in high productivity areas reduces the diagenetic alteration of the  $\delta^{15}\text{N}$  signal in the sediments. This is further confirmed by our findings in Manuscript 3 from the upwelling filaments at Walvis Ridge with minor to no difference between sediment trap and surface sediment  $\delta^{15}\text{N}$ .

The nature of isotopic fractionation in sediments is not fully understood because nitrogen cycling in marine sediments is a complex system including a sink, denitrification, and a source, nitrification within the sediments. However, Brandes and Devol (1997) found that on continental shelves and upper slopes where the nitrate flux into the sediment and nitrification, balance the denitrification (Devol and Christensen, 1993) and thus, the  $\delta^{15}\text{N}$  value of the nitrogen lost would be close to the  $\delta^{15}\text{N}$  in the sea water. In pelagic sediments, however, the nitrification exceeds the denitrification (Berelson et al., 1990) and thus a net loss of isotopically light nitrate from the sediment to the water is possible. Another factor which could be of importance for the total diagenetic effect is the biological composition of the sediments. Sigman et al. (1999) found that nitrogen bound to diatom micro-fossils are physically protected and resistant against early diagenetic alterations and thus 0-4‰ lighter than the bulk sedimentary  $\delta^{15}\text{N}$ .

Most of the particles produced in the photic zone are decomposed and remineralised within the photic zone or the water column (Fig. 1), but because decomposition (oxic or anoxic) does not fractionate much isotopically, the diagenetic alteration of the particulate  $\delta^{15}\text{N}$  in the water column is less than in pelagic sediments. However, a tendency towards lighter  $\delta^{15}\text{N}$  values ( $\sim$ -1‰) in deeper hanging sediment traps compared to traps directly above, is found. In a detailed study on sinking particles Nakatsuka et al. (1997) suggested that this initial diagenetic effect is caused by the rapid loss (remineralisation) of proteins known to have a heavy N-isotopic composition.

## 4.2 Terrigenous input

To keep track on the terrigenous input and its possible isotopic impact is, of course, essential when measurements from bulk material are interpreted in the sense of marine processes. The main terrigenous N source to the ocean is the fluvial input which mainly affects coastal areas where the marine production is generally higher than in the open ocean. Moreover, the fluvial N-input mainly constituted by DN, is not necessarily isotopically different from the marine DN and so the fluvial N-input could be an important nutrient supply without an essential isotopic impact. This is confirmed in the South Atlantic region by Holmes et al. (1996; 1998). Nevertheless, especially by studying modern sediments, potentially large variation in the  $\delta^{15}\text{N}$  of fluvial N-input could be expected due to human activities (sewage and animal waste have high  $\delta^{15}\text{N}$  values, and anthropogenic fertilisers low  $\delta^{15}\text{N}$  values, Kendall, 1998 and references therein).

In the open ocean, where the marine production and organic fluxes to the sediments are lower it is potentially easier to alter the marine isotopic signal, the main terrigenous input is wind-borne dust. For studies of  $\delta^{15}\text{N}$  variations in meso-, and oligotrophic regions, it is

important to know the possible impacts from the dust related nitrogen input on the bulk sedimentary  $\delta^{15}\text{N}$  signal. This would be of special importance for studies attempting to reconstruct past variations in the nitrogen fixation where a positive relation between the dust input exists (Manuscript 1)

Different ways to estimate the terrigenous input of organic matter to the ocean exist (Wagner and Dupont, 1999), but the most applied is sedimentary  $\delta^{13}\text{C}$  (e.g. Westerhausen et al. 1993; DeMenocal, 1995; Verardo and Ruddiman, 1996; Wagner and Dupont, 1999) which have different signatures in marine and terrigenous organic matter (e.g. O'Leary, 1988; Sackett, 1989, Meyers, 1994). However, several complications/ questions arise when this approach is going to be transformed from the impact on the organic carbon isotopes to the possible impacts on the nitrogen isotopes: 1) First of all, the estimates of terrigenous input by using  $\delta^{13}\text{C}$  measurements are not straight forward as the relative mixture of C3,- and C4-plants and thus the  $\delta^{13}\text{C}$  impact are not constant (see Manuscript 2).

2) Although no systematic differences occur in the  $\delta^{15}\text{N}$  due to photosynthetic pathway, a large span in  $\delta^{15}\text{N}$  values in terrestrial environments and OM exists (Sweeny et al., 1975; Kendall, 1998).

3) The C/N-ratio is higher in terrestrial OM (>20) than in marine OM (<10) and thus the terrestrial impact would be less on the  $\delta^{15}\text{N}$  than on the  $\delta^{13}\text{C}$ .

4) On the contrary, inorganic nitrogen absorbed by clay particles may reduce the bulk C/N ratio (Müller, 1977) and increase the terrestrial impact on the bulk  $\delta^{15}\text{N}$  value.

Especially concerning the N-isotopes, very little is known about the potential impact through dust and in Manuscript 2 we focus on and suggest some answers to these problems.

### **4.3 $\delta^{15}\text{N}$ and upwelling**

In a coastal upwelling area the overall dominant nutrient source is defined and if the close connection between particulate  $\delta^{15}\text{N}$ , upwelling intensity and primary productivity exists, this should be reflected in sinking matter within the upwelling filament. In Manuscript 3 we tested this and found a good correlation between upwelling related sea surface temperature drops, increasing productivity/ fluxes and lighter  $\delta^{15}\text{N}$  values due to decreasing relative nitrate utilisation with increasing wind-driven upwelling. This is different to what we found at the Equatorial upwelling in the eastern Atlantic (Manuscript 1). There, alternative sources like nitrogen fixation and nutrient supply by precipitation were as important DN sources for the export production on an annual basis as upwelling of water-masses from below.

Consequently, partly different considerations have to be made when interpreting the sedimentary  $\delta^{15}\text{N}$  values in these two regions. The relation between  $\delta^{15}\text{N}$  and nutrient availability/ productivity will be the same for both regions, though, only as long as denitrification does not occur. Denitrification occurs when the respirational needs of the decaying particles exceed the supply of oxygen in the water column thus increased productivity could lead to denitrification which has the opposite impact on the  $\delta^{15}\text{N}$ . In Manuscript 4 we found evidence that denitrification occurs also in the Benguela upwelling system at present and that this influenced the  $\delta^{15}\text{N}$  of the surface sediments.

#### 4.4 Paleo variations

Additional to the local or regional impacts one should keep in mind that glacial to interglacial changes in the oceans nutrient inventory and thus  $\delta^{15}\text{N}$  are not necessarily constant. Decreased denitrification during the glacial periods in the Arabian sea and in the tropical North Pacific, which are the major areas for denitrification (Altabet et al., 1995; 1999a; Ganeshram et al., 1995, respectively), might have increased the nutrient inventory and hence increased the productivity of the global ocean during the glacials. A common global glacial to interglacial connection like for the oxygen isotopes (i.e. SPECMAP) is still not found and might not exist due to the so called conveyor belt circulation. Because of this circulation pattern, nutrients are transported out of the Atlantic Ocean into the Pacific- and Indian Ocean with deeper water-masses, but in the surface water returning to the Atlantic the nutrients are depleted. This one way system rather than a conveyor for the nutrients constrains to a large degree the potential of changes in the Indian- and Pacific Oceans to influence the nutrient budget and the  $\delta^{15}\text{N}$  of the nitrate pool in the Atlantic Ocean. However, a *vice versa* impact is very well possible.

Considering this, eventual changes in the South Atlantic nutrient pool and its  $\delta^{15}\text{N}$  have to be mainly controlled by the balance between the loss, denitrification and export to the sediment (Manuscript 4), and gain, i.e. nitrogen fixation (Manuscript 1), of nutrient within the Atlantic Ocean. Broecker and Henderson (1998) suggested that increased nitrogen fixation during glacials due to higher dust input could have enhanced the primary production in the oceans. This is not supported by core data yet but our results from the eastern equatorial Atlantic supports a connection between dust and nitrogen fixation (Manuscript 1). Haug et al. (1998) also found evidence of increased nitrogen fixation during the glacial periods in the Cariaco Basin. Additionally, interactions with the southern oceans could play an essential role for the nutrient pool of the southern Atlantic.

To summarise, although there seems generally to have been more nutrients in the surface of the South Atlantic during the glacial periods (i.e. Holmes et al., 1997; Wolff et

al., 1999, Manuscript 4), more studies are needed to know the eventual glacial to interglacial variations in the total nutrient inventory of the Atlantic Ocean.

## 5 Materials and methods

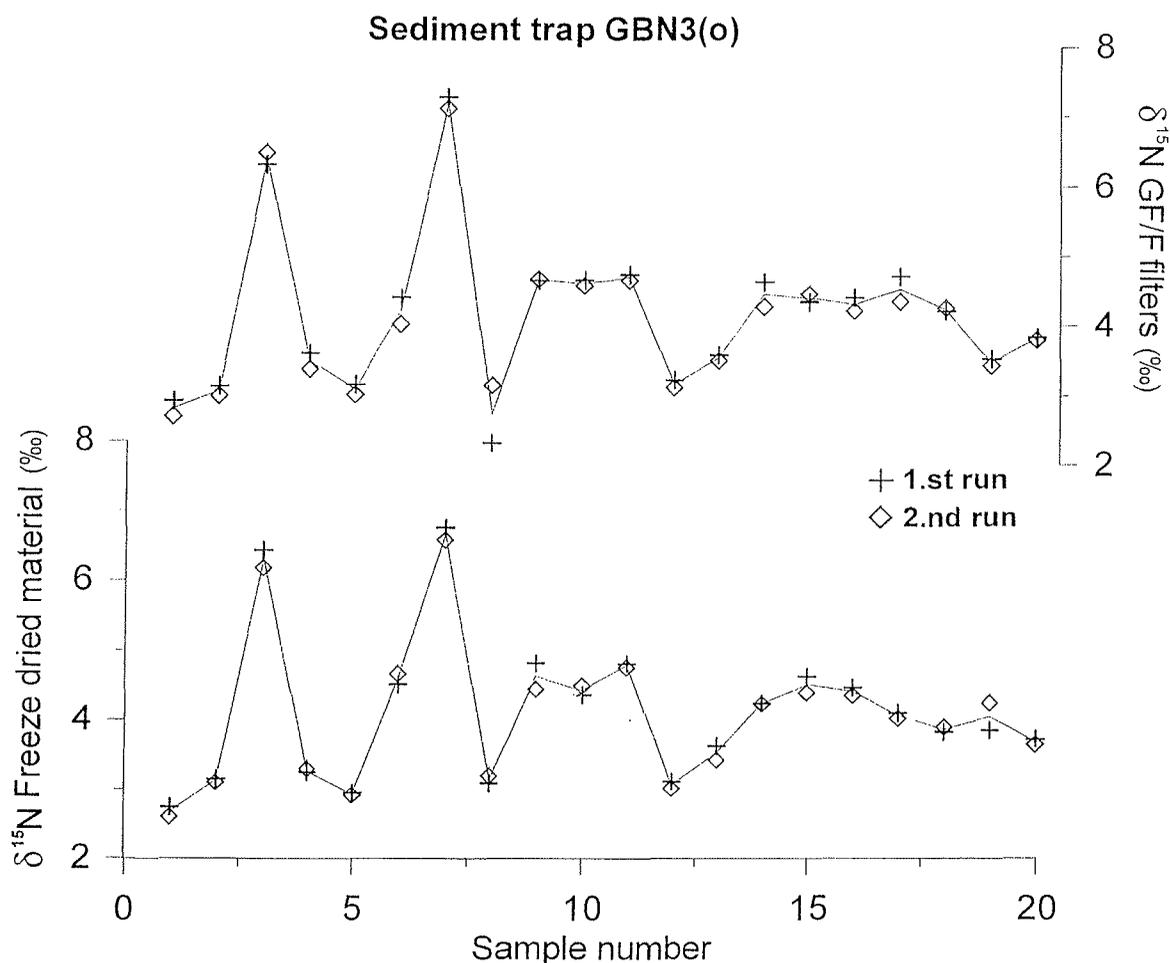
Samples from several “METEOR” cruises and one “IMAGES” cruise were analysed. For detailed information about the material, see the different manuscripts. In order of methods three different types of material were measured; sinking matter, sediments, and dust.

### 5.1 Trap material

The sediment trap material was collected with cone shaped traps with 0.5 m<sup>2</sup> opening and 20 sampling cups (Kiel SMT 230/234). Samples were preserved with a 1 ml saturated solution of HgCl<sub>2</sub> in 100 ml sea-water (Fischer and Wefer, 1991). NaCl was added to increase the salinity of the cups by 3‰ relative to the surrounding water. After recovery of the traps, 0.5 ml of concentrated HgCl<sub>2</sub> was added per 100 ml trap solution. In order to find out if the freeze dried and homogenised samples, which were in contact with freshwater, are suitable for determination of  $\delta^{15}\text{N}$  on sinking matter, we measured a split sample filtered onto a GF/F filter and the freeze dried material in one sediment trap series. No large differences or systematic effect on the  $\delta^{15}\text{N}$  value were seen but less variation by double measurements were seen in the freeze dried material (Fig. 2). This is probably due to the homogenising of these samples, and indicates an advantage for using the freeze dried sample instead of the filtered split. Additionally, HgCl<sub>2</sub> left on the filtered sample might produce highly toxic gasses by combustion and cause unnecessary corrosion within the mass spectrometer.

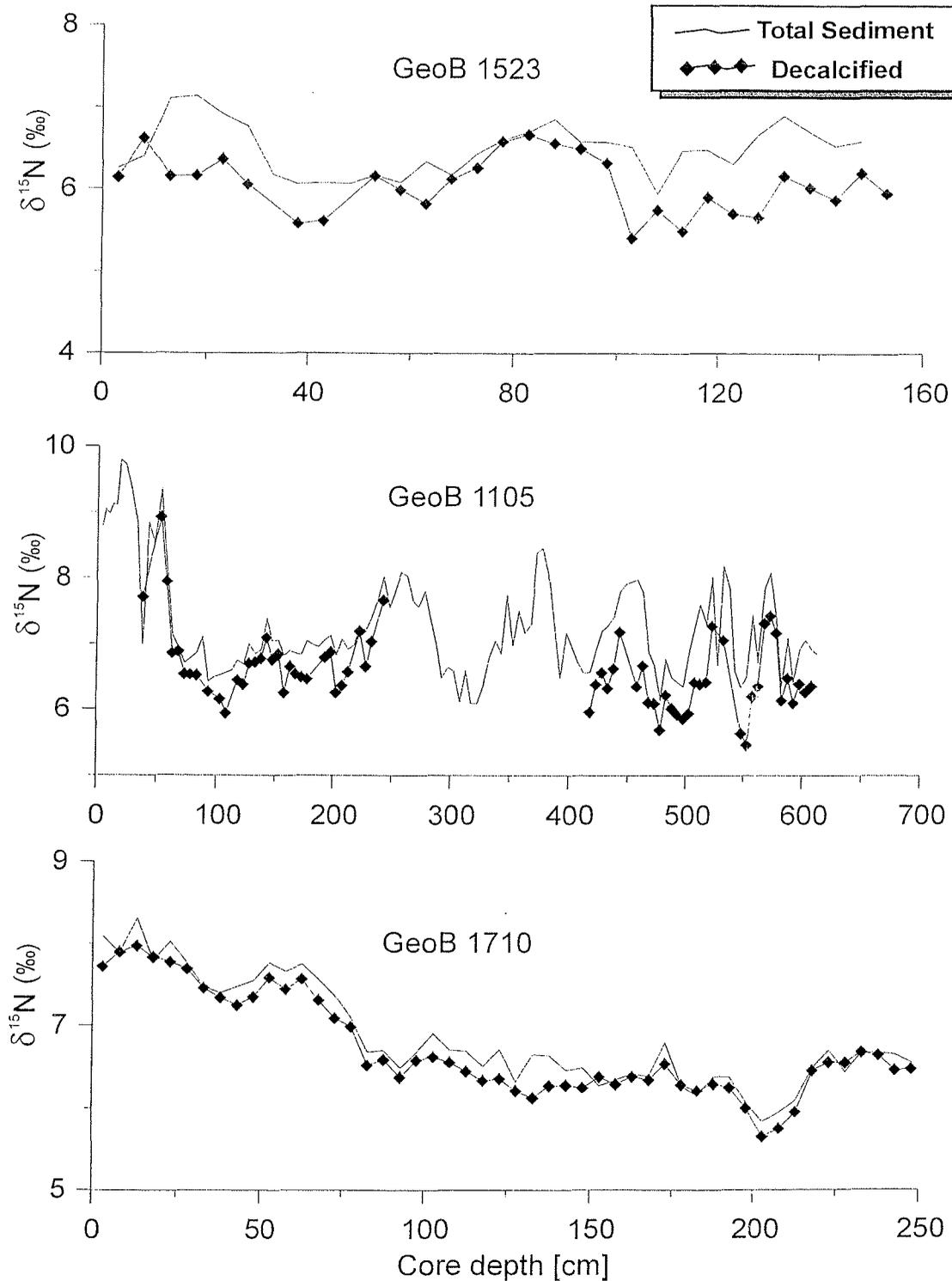
### 5.2 Sediments

The surface sediments were collected using a giant box corer (GKG) or a multiple corer (MUC) and the sediment cores using a gravity corer (SL). From the surface sediments, sub-samples were taken immediately after core retrieval using plastic syringes (GKG) or sliced in 1 cm slices (MUC) and sealed with electrical tape. Sediment cores were sub-sampled with syringes (like GKG) either onboard or in the onshore laboratory. All materials and sub-samples were stored at 4°C before being freeze-dried and ground in an agate mortar at the home laboratory. Previous studies have used both decalcified (i.e. Holmes et al., 1996) total sediment (most authors, i.e. Altabet et al., 1999a) to determine the bulk sedimentary  $\delta^{15}\text{N}$  value.



**Figure 2** Various  $\delta^{15}\text{N}$  measurements from sediment trap GBN3. Above two series measured on GF/F filters and below two series measured on freeze dried and ground (homogenised) material.

To test the effect of the decalcification on the sedimentary  $\delta^{15}\text{N}$  both decalcified,- and total sediment- $\delta^{15}\text{N}$  in sections of three different cores from different regions were measured (Fig. 3). In general a shift towards lower values occurred in the decalcified samples, but from being a relatively small and constant offset of  $\sim 0.2\%$  in GeoB 1710 the size of the offset is highly variable in the two other cores. Especially in GeoB 1523 the decalcified record has a different character than the record measured on the total sediment which would have lead to different conclusions (Fig. 3). The effect of the decalcification is not very well understood but several factors might come into account, which will have to be considered by using the decalcified samples.



**Figure 3** Parallel measurements on total sediment (black line) and decalcified sediments (line with diamonds) on three different sediment cores from the western (GeoB 1523) and eastern equatorial Atlantic (GeoB 1105) and the south-eastern Atlantic (GeoB 1710).

During the decalcification some nitrogen might be released to the atmosphere and it would be plausible that nitrogen connected to the carbonate bearing part of the sediment

(usually foraminifera and coccoliths) are the likely source of eventually released nitrogen. The  $\delta^{15}\text{N}$  of forams are known to reflect the  $\delta^{15}\text{N}$  of the surrounding waters (Altabet and Curry, 1989) and the coccoliths are known to fractionate less relative to the nutrient source than other important primary producers, i.e. the diatoms which are several ‰ lighter than the source (Montoya and McCarthy, 1995). This might offer an explanation for the preferential loss of the heavier  $^{15}\text{N}$  isotope during decalcification. However, no significant correlation is found between the carbonate content and the offset in  $\delta^{15}\text{N}$  signal in either of the cores which suggests that other factors are important.

The release of specific organic N-bearing compounds or species related difference in resistance against the acid within the organic matter could influence the isotopic effect of the decalcification process. If i.e. diatoms or terrestrial organic matter are more resistant than other organic substances, a high relative amount of one of these compounds could lower the effect of the contact with HCl. A detailed study is needed to clarify this but it should be noted that the resulting effect on the  $\delta^{15}\text{N}$  is opposite compared to natural sedimentary diagenesis (see above).

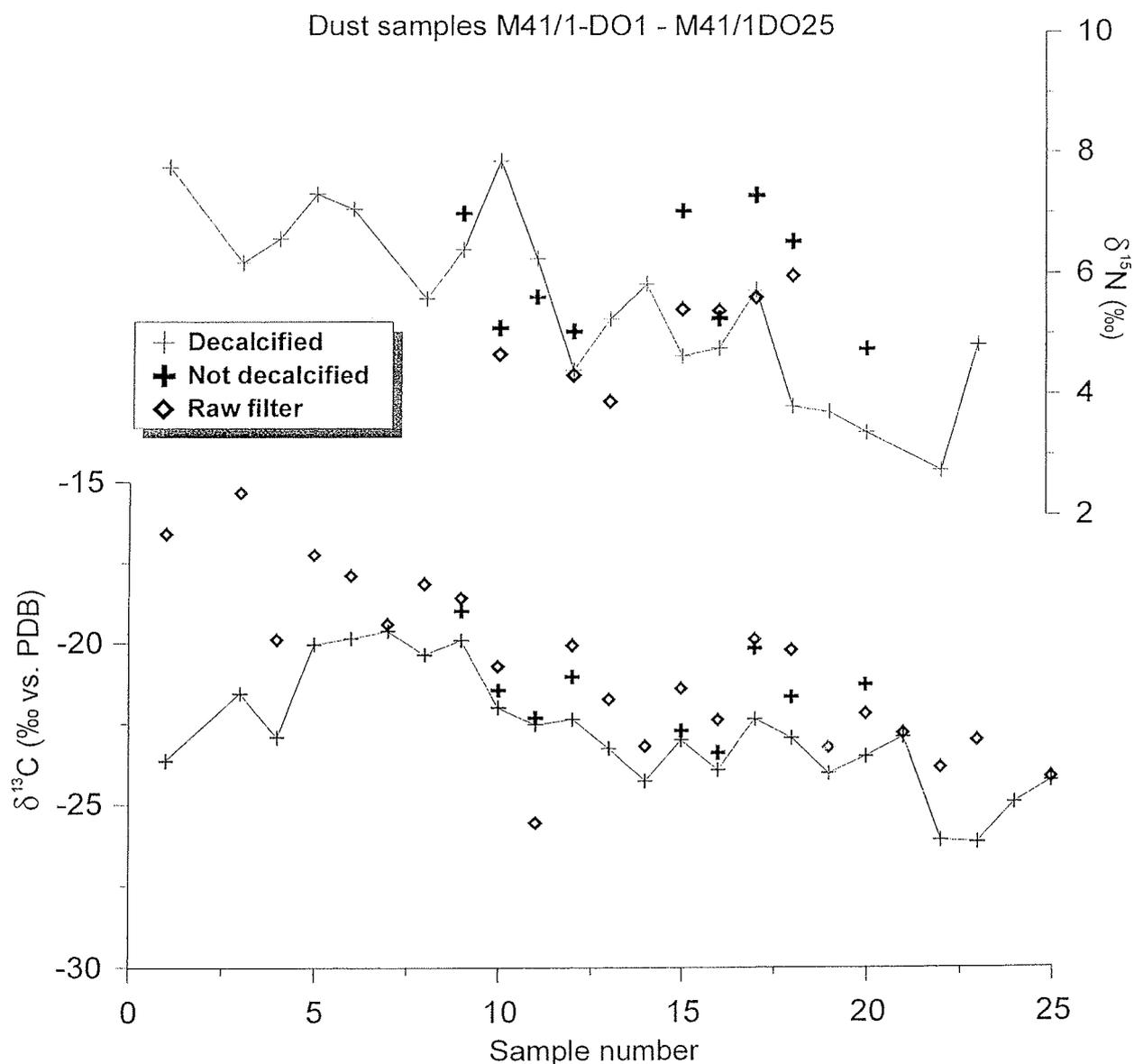
Another factor of possible importance is the inorganic clay bound nitrogen ( $\text{NH}_4^+$ ) (Müller, 1977). Although it would not change in contact with acid its relative importance for the measured  $\delta^{15}\text{N}$  increases if nitrogen from other parts of the sediment is lost. This would expectedly be more important where the amount of clay is high and possibly of variable sources. This might explain the variable downcore offset in GeoB 1523 which has possibly been influenced from the Amazonas to various degrees (Rühlemann, 1996). However, no clear correlation to the clay fraction or other parameters in the core were found.

Although the decalcified samples have the advantage of allowing combined  $\delta^{15}\text{N}/\delta^{13}\text{C}$  measurements, the total sediment have been used in this study as long as the effects of decalcification is not well understood.

### **5.3 Dust**

The dust samples for combined  $\delta^{15}\text{N}/\delta^{13}\text{C}$  measurements were recovered by a dust sampler consisting of a roofed metal house, with a vacuum cleaner engine sucking 1.2-2.0 m<sup>3</sup> air per minute onto a 200x250mm GF/F-filter. To avoid pollution from the ship-chimney sampling only occurred when the ship was moving and the net wind was coming up front. Depending on dust amount the filters were changed one to four times a day and wrapped in aluminium foil and stored at -20°C. To release the dust from the original filters these were put in an ultrasonic bath of demineralised water for 15-20 minutes and carefully flushed to release the rest material. This material was filtered onto smaller GF/F, and decalcified in

HCl vapour overnight closed from the atmosphere. For some of the larger samples, a part of these filters were not decalcified and measured, to test the effect of the decalcification on the isotope values. Additionally some of these samples were decalcified in direct contact with concentrated HCl to check if the decalcification with HCl vapour efficiently removed the  $\text{CaCO}_3$  (Fig. 4).



**Figure 4** Various  $\delta^{15}\text{N}$  (above) and  $\delta^{13}\text{C}$  (below) measurements performed on the dust samples M41/1-DO1 to M41/1-DO25.

No large effects were seen on the  $\delta^{13}\text{C}$  indicating that the amounts of  $\text{CaCO}_3$  either were relatively low (supported by visual inspections) or the  $\text{CaCO}_3$  had a  $\delta^{13}\text{C}$  value close

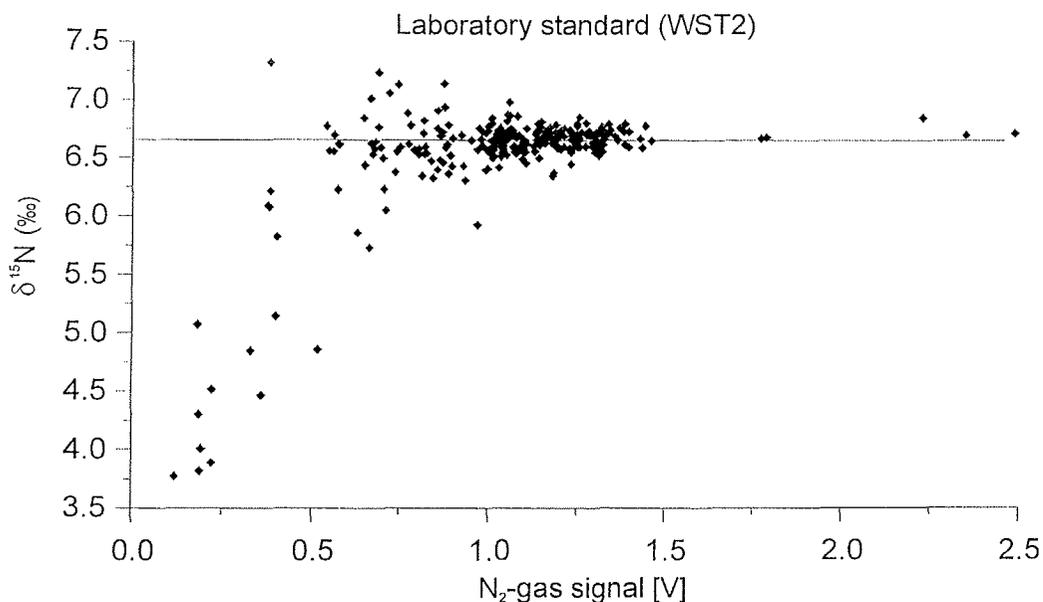
to the organic carbon. The slightly heavier  $\delta^{13}\text{C}$  values on the total material (not decalcified) implies that the  $\delta^{13}\text{C}$  of the  $\text{CaCO}_3$  was somewhat higher than the organic carbon. The same is indicated by the test measurements performed on a small piece of the rawfilter (the original exposed 200x250mm GF/F-filter) which reveal somewhat heavier  $\delta^{13}\text{C}$  signal than the decalcified sample. These rawfilter samples contained various amounts of carbon and it is not clear if the exceptionally large offset in the two first samples are correct or not. If they are correct there tends to be more  $\text{CaCO}_3$  in the northernmost samples compared to the rest.

For the  $\delta^{15}\text{N}$  values the effect of the decalcification remains uncertain due to the small sample amounts available for experimenting but the few values available do not reveal a tendency. However, also including the small rawfilter samples there tend to be some consistency in the direction of the changes (either above or below the decalcified sample), but it is too weak and variable to suggest any probable cause.

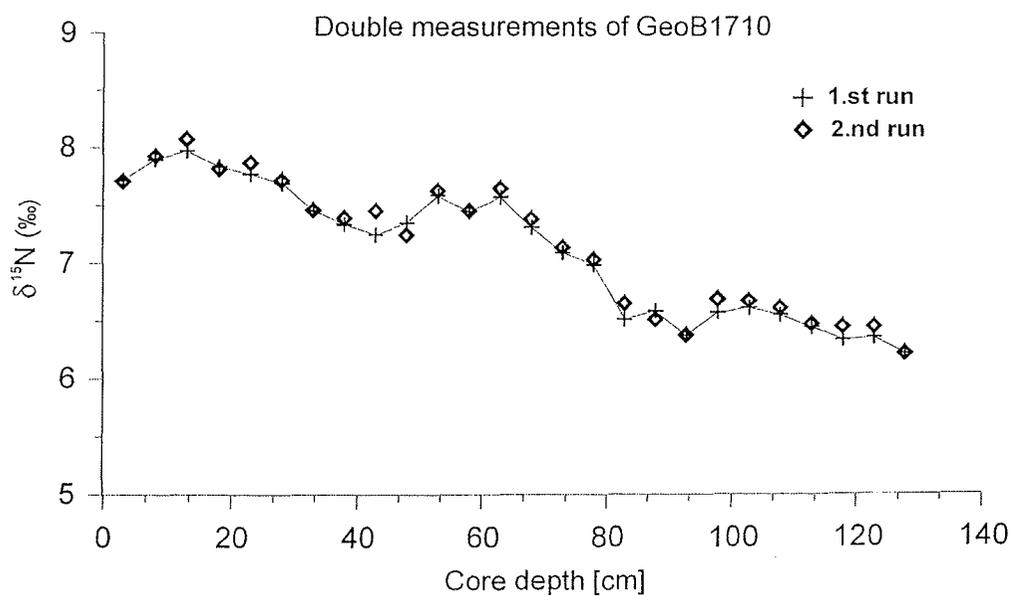
#### **5.4 Mass spectrometer**

All  $\delta^{15}\text{N}$  measurements were performed on a Finnigan Delta Plus attached via a CONFLO to a Carlo/Erba NC2500 automatic elemental analyser as preparation line. The stable isotope determination was made from  $\text{N}_2$  gas released by flash combustion in excess oxygen at 1050°C with helium in continuous flow as carrier gas. Depending on organic content, between 2-150 mg of bulk material were weighted in (for filter samples the GF/F filters were weighted before and after filtration) and measured against 99.996% pure  $\text{N}_2$  tank gas. One internal standard (WST2 6,66‰) was measured for every fifth sample and the sample values were corrected according to the mean value of the measured standards. The  $\text{N}_2$  tank gas and the WST2 house standard were calibrated against the IAEA standards N-1 and N-2. Standard deviation on replica measurements were better than 0.3‰ when the amount of  $\text{N}_2$ -gas exceeded 1.1V (Fig. 5) and samples were weighted in to produce a signal of 1.3V if the total N-content were known. To test the reliability on core material with highly variable organic content and  $\delta^{15}\text{N}$  signal, we did double measurements on the upper 150 cm of GeoB 1710 with encouraging results (Fig. 6) In samples with low organic content, the acquired amount of material to produce at least a 1.1V gas signal would exceed the sample size suitable for measurements. In the range between 1.1V and 0.6V no size related correction had to be done but due to the lower reproducibility systematic double measurements were performed. In samples with less than 0.6V signal the  $\delta^{15}\text{N}$  is getting successively lighter (Fig. 6) and more standards with variable size are needed to correct this effect which might be variable from one measurement series to the next.

Consequently, the reliability is not within 0.3‰ for measurements performed on small samples.



**Figure 5** Testing of the accuracy and stability of  $\delta^{15}\text{N}$  measurements on the laboratory standard WST2 (Decalcified) by repeated measurements and various sample size.



**Figure 6** Double measurements of core material (bulk) for the upper 133 cm of GeoB 1710.

## 6 Objectives and presentation

The main aim of this study is to increase the knowledge about the nitrogen isotopes in the South Atlantic and to further develop the assets of this proxy to apply it as an paleoceanographic tool in this region. This includes to increase the knowledge of the external inputs and impacts on the marine nitrogen cycle as well as the various internal processes influencing the  $\delta^{15}\text{N}$  in sediments and sinking matter. Four manuscripts for international publication have been prepared to cover these goals.

Manuscript 1 focuses on the seasonal and annual variations in  $\delta^{15}\text{N}$  values and the particle fluxes (mainly  $C_{\text{org}}$ ) from 8 sediment traps in comparison to the regional oceanographic and climatic conditions tropical Atlantic area. Particles produced close to the source of new nitrate will carry a different  $\delta^{15}\text{N}$  signal compared to particles produced at a location distant from the same nitrate source, and thus the  $\delta^{15}\text{N}$  should be a suitable parameter to trace eventual lateral displacement of particulate organic matter (POM). In the last part of this study we look at the  $\delta^{15}\text{N}$  signals and total organic carbon content (TOC) recorded in the surface sediments. By comparing the sediment values to the sediment trap results we intended to find out which surface conditions govern the sedimentation in this region and to detect possible differences in diagenetic effect during sedimentation.

In Manuscript 2 the focus is set on the terrigenous dust input and its possible isotopic impacts which are essential when measurements from bulk material are interpreted in the sense of marine processes. Although the main input from the continents to the ocean is riverine, this mainly influences the coastal areas where the marine production is high. In the open ocean, where the marine production and organic fluxes to the sediments are low and it is potentially easier to alter the marine isotopic signal, the main terrigenous input is wind-blown dust. Especially for studies of  $\delta^{15}\text{N}$  variations in meso,- and oligotrophic regions, it is important to know the possible impacts from the dust nitrogen contents on the bulk sediment  $\delta^{15}\text{N}$  signal. To cover a possibly large span in climatic and vegetation zones, dust samples were collected along the African West coast from 34°N to 12°S and the Equator from 10°W to 10°E.

The purpose of Manuscript 3 is to show that the  $\delta^{15}\text{N}$  signal of particles sinking out of the euphotic zone in the Benguela region is controlled by changes in surface water nitrate levels correlated with productivity variations. We also attempt to show that  $\delta^{15}\text{N}$  in sinking particles may be useful in estimating the degree of utilisation of nitrate in the euphotic zone. Four sediment trap series from three continuous years from the outer upwelling filaments on the Walvis Ridge was used in this study.

The last Manuscript (4) aims to reconstruct the changes in the Walvis Bay upwelling cell based on sedimentary  $\delta^{15}\text{N}$ . A parameter which is considered not to be directly affected by changes in temperature of the upwelled water, sea surface temperature, carbonate dissolution, and in high production areas the dependency on burial rates is limited. A three core transect is needed to reach the aim of isolating the different processes governing the sedimentary  $\delta^{15}\text{N}$  in a high production zone and to better view the changes in the offshore extent of the upwelling filament. Special focus is set on the possible impacts of sea-level change on the upwelling system and the occurrence of denitrification on the sedimentary  $\delta^{15}\text{N}$  records.

The data used in the graphics of this dissertation, which are not published elsewhere and referred to, are presented in the Appendix.

## 7 Manuscripts 1 – 4

### 7.1 Manuscript 1:

*$\delta^{15}\text{N}$  values on sinking matter and surface sediments in the eastern equatorial Atlantic: Evidence of a northward lateral particle transport*

Abstract .....	31
1. Introduction.....	32
2. Oceanographic setting and atmospheric circulation .....	33
3. Materials and methods .....	35
4. Sediment trap results .....	37
5. Seasonal and annual variations .....	40
5.1. Warm seasons (Spring, fall and winter).....	42
5.2. Cold season (Summer) .....	44
6. Mean values and surface sediments .....	47
6.1. Mean values.....	47
6.2. Surface sediments.....	47
7. Paleoceanographic implications.....	48
8. Conclusions.....	49
Acknowledgements.....	49
References .....	50

---

**δ<sup>15</sup>N values on sinking matter and surface sediments  
in the eastern equatorial Atlantic: Evidence of a northward  
lateral particle transport**

Gaute Lavik, Gerhard Fischer, Ralph R. Schneider, and Gerold Wefer

*All authors at: FB Geowissenschaften, Universität Bremen, Klagenfurter Strasse, 28359 Bremen*

**Abstract**

The δ<sup>15</sup>N composition was measured on sinking matter and surface sediments along a North-South transect in the equatorial Atlantic, and compared to sea surface temperatures, nutrient availability, and primary production. Taking the whole N-S transect into consideration, the biogenic fluxes (C<sub>org</sub> and opal) during the warm spring season were the dominating fluxes towards the sediments. This makes the primary production during spring as important for the export fluxes as the production related to nutrient supply from subsurface waters at the equatorial divergence during the cold summer (upwelling) season. Light δ<sup>15</sup>N values in the sinking matter during spring, suggests nitrogen fixation related to Fe supply through dust and precipitation of nutrients within the ITCZ as important sources of nitrate for new production in the northern Guinea Basin. Beneath the high production area during summer at and south of the Equator in southern Guinea Basin, the organic fluxes were low. In the less productive northern Guinea Basin we find high organic carbon fluxes during summer combined with light δ<sup>15</sup>N values, which suggests a production area close to the source of new nitrate. This is best explained by a substantial northward transport of the sinking matter during the upwelling season. This transport is probably driven by prevailing winds from the South and surface currents from the South-East, crossing the Equator and entering the northern Guinea Basin. The North-South trends in the δ<sup>15</sup>N of sinking matter and C<sub>org</sub> fluxes are also found in the δ<sup>15</sup>N,- and TOC values in the surface sediments. This implies that the pattern seen in the sediment trap data is not exceptional for the studied years and thus, of importance for the sedimentation patterns in this region.

## 1. Introduction

The degree of nutrient utilisation in surface waters of the ocean has important implications for primary productivity in the euphotic zone. The  $\delta^{15}\text{N}$  signal of particles sinking out of the euphotic zone can be a useful tool in assessing variations in the nutrient utilisation in surface waters due to fractionation of stable nitrogen isotopes during photosynthesis. The  $^{14}\text{N}/^{15}\text{N}$  composition of particulate organic matter (POM) is largely dependent on the availability of dissolved inorganic nitrogen (mainly nitrate,  $\text{NO}_3^-$ ) (e.g. Wada, 1980; Altabet and Francois., 1994). Nitrate upwelled from oxygenated waters of the deep sea has a nitrogen isotope signature of 5-6‰ versus atmospheric air (Wada et al., 1975). Preferential uptake of nitrate containing the lighter  $^{14}\text{N}$  isotope makes the  $\delta^{15}\text{N}$  of the plankton low relative to the source, leaving the source relatively enriched in  $\delta^{15}\text{N}$  as nitrate is consumed. This results in light nitrogen isotopic composition of the POM when nitrate is abundant close to the source and increasing  $\delta^{15}\text{N}$  values with increasing degree of nitrogen utilisation.

Applying this at an open ocean divergence, the  $\delta^{15}\text{N}$  in POM values will rise (heavier isotope composition) with increasing nutrient depletion and distance from the source of new nitrate at the centre of the divergence. Wilkerson and Dugdale (1992), for instance, demonstrated the impact of equatorial upwelling on nitrate distribution and  $\delta^{15}\text{N}$  uptake in the Pacific Ocean. They found that increasing nitrate concentration supplied by equatorial upwelling was accompanied by increased nitrate uptake due to enhanced primary production. The  $\delta^{15}\text{N}$  values were increasing with the degree of nitrate utilisation to the north and south of the divergence. A relationship between the sedimentary  $\delta^{15}\text{N}$  signal and the overlying surface water nutrient conditions, with increasing  $\delta^{15}\text{N}$  values at both sides of the divergence zone, is demonstrated for the equatorial Pacific (Altabet and Francois, 1994; Farrell et al., 1995). The major difference between the equatorial upwelling regions in the Pacific Ocean and our study area in Atlantic Ocean is the proximity of a continent to the north.

Under low nitrate conditions in oligotrophic regions, nitrogen fixing cyanobacteria are thought to provide a substantial input to the marine nitrogen budget, by breaking gaseous  $\text{N}_2$  into nitrate ( $\text{NO}_3^-$ ) (Michaels et al., 1994; Capone et al., 1997; Gruber and Sarmiento, 1997; Karl et al., 1997) which eventually could be made available to other primary producers. Because this is a metabolically expensive process, the N-fixers are outcompeted by diatoms and other algae when other dissolved nitrogen sources ( $\text{NO}_2^-$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) are adequate. However, the N-fixers can be dominating if other key nutrients like phosphate and iron are available. The  $\delta^{15}\text{N}$  in newly fixed nitrogen is close to the N-isotopic composition of atmospheric  $\text{N}_2$  defined as zero (Wada and Hattori, 1976).

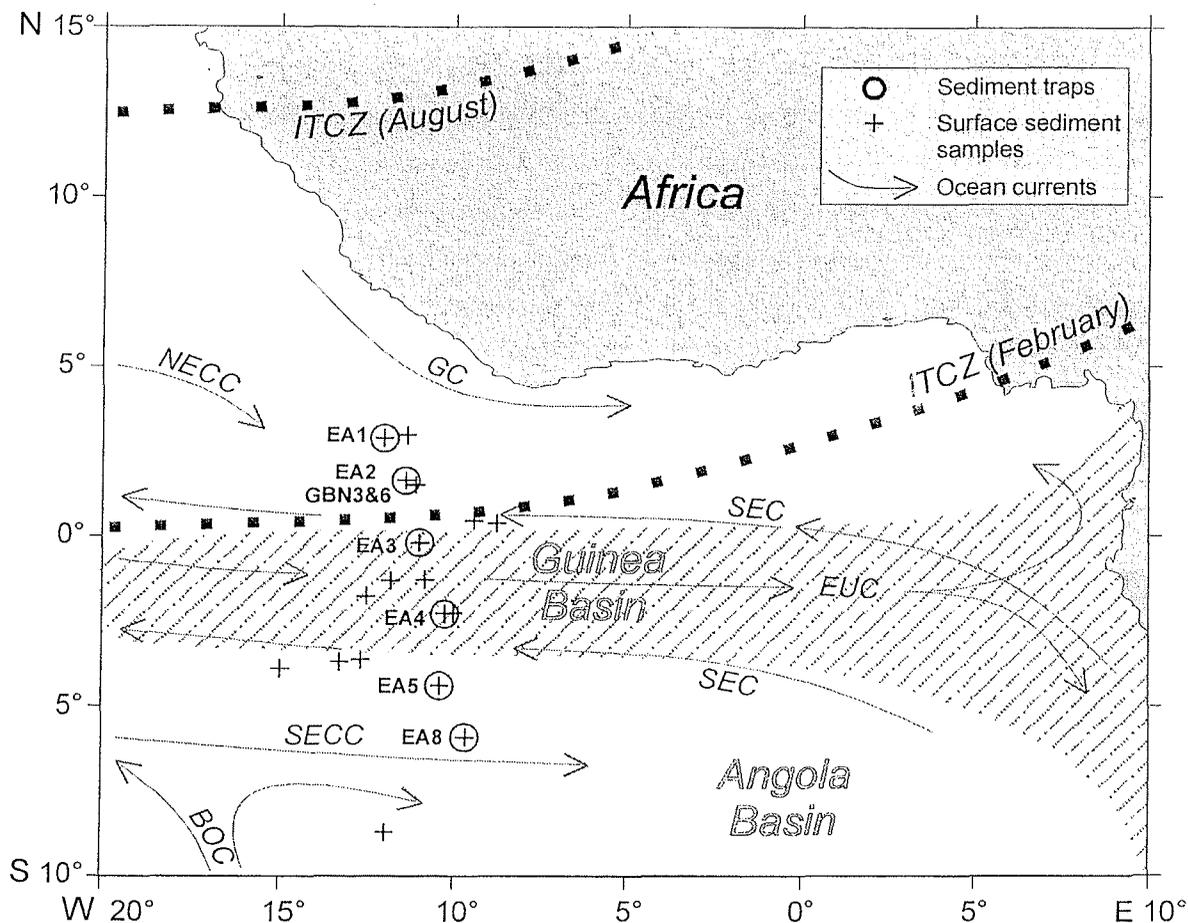
Sedimentary  $^{15}\text{N}/^{14}\text{N}$  ratios can be used as a measure of past changes in surface ocean nutrient utilisation which in turn is a function of past changes in primary productivity and nutrient input from subsurface waters (Altabet and Francois, 1994; Farrell et al., 1995; Holmes et al. 1997). Although the  $\delta^{15}\text{N}$  value measured on the bulk sediment potentially can be altered by particle decomposition (Saino and Hattori, 1980; 1987; Altabet 1988; Altabet et al., 1991; De Lange et al., 1994; Nakatsuka et al., 1997) and trophic exchange (DeNiro and Epstein, 1981; Minagawa and Wada, 1984; Fry, 1988), several studies from different geographical areas demonstrate that the surface water signal is coherently transferred to the sediments (Altabet and Francois; 1994, Farrell et al., 1995; Voss et al., 1996, Francois et al., 1997; Holmes et al., 1996; 1998; and references therein).

In this study we will focus on the seasonal and annual variations in  $\delta^{15}\text{N}$  values and the particle fluxes (mainly  $\text{C}_{\text{org}}$ ) from the presented sediment traps in comparison to the regional oceanographic and climatic conditions in the tropical Atlantic area. Because particles produced close to the source of new nitrate will carry a different  $\delta^{15}\text{N}$  signal compared to particles produced at a location distant from the same nitrate source, the  $\delta^{15}\text{N}$  should be a suitable parameter to trace eventual lateral displacement of particulate organic matter (POM). In the last part of this study we will look at the  $\delta^{15}\text{N}$  signals and total organic carbon content (TOC) recorded in the surface sediments. By comparing the sediment values to the sediment trap results we intend to find out which surface conditions that govern export fluxes to the sediments.

To avoid confusion, boreal seasons are used throughout this manuscript, also for the sites south of the Equator.

## 2. Oceanographic setting and atmospheric circulation

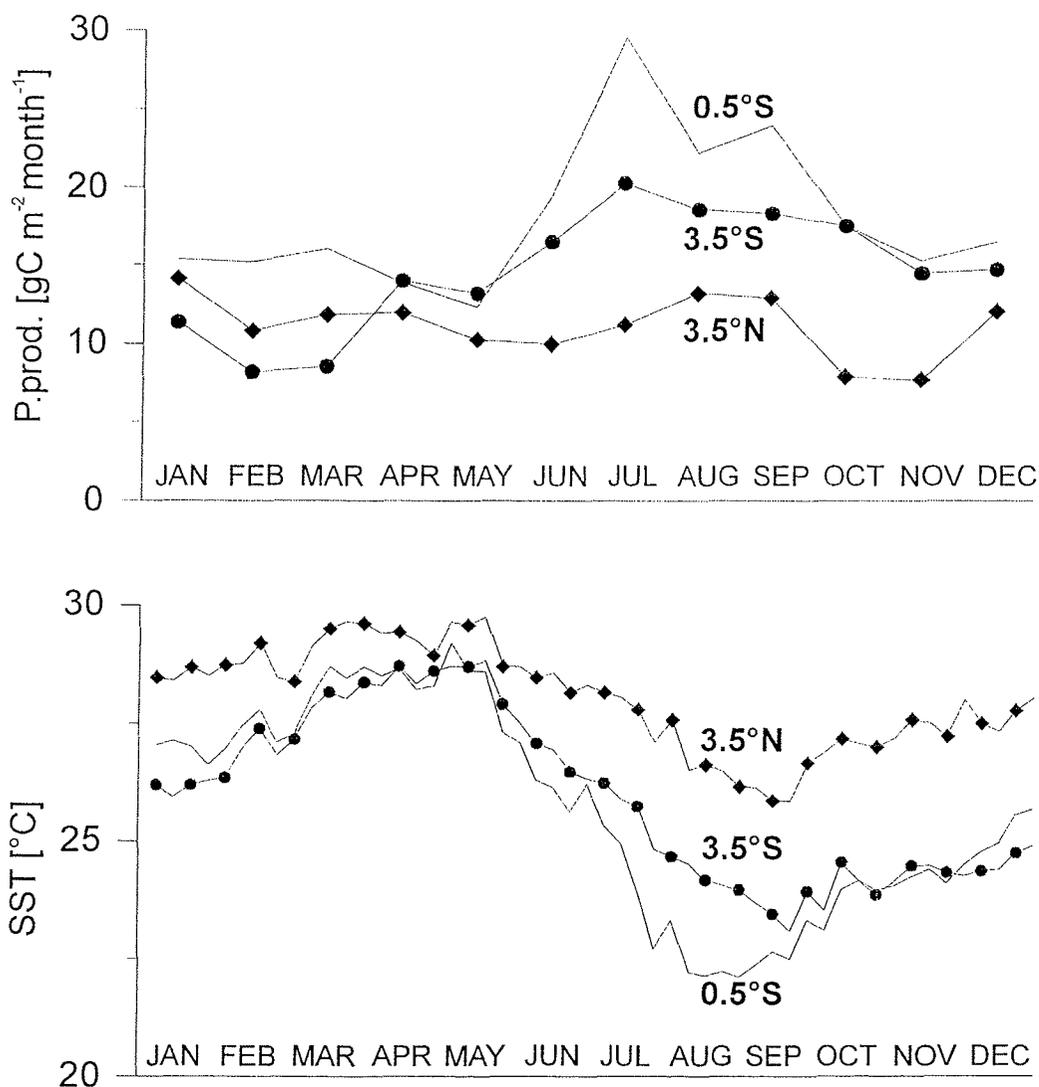
The system of upper-level ocean circulation in the eastern Equatorial Atlantic comprises a complex array of surface and subsurface currents. The most important are the westward flowing South Equatorial Current (SEC) and eastward flowing countercurrents, like North Equatorial Counter-current (NECC), South Equatorial Countercurrent (SECC) and the Equatorial Undercurrent (EUC) (Fig. 1) (Peterson and Stramma, 1991). The average surface water velocities for the central part of the study area (8-12°W and 6°S-5°N) are 15-40 cm/sec in a western to north-western direction, with the higher surface current velocities during spring and summer (Richardson and Walsh, 1986). The Guinea Current (GC) (Fig. 1) is a coastal current following the African coast.



**Figure 1** Overview map of the study area showing the sites of the sediment traps and surface sediment samples. The most important surface and subsurface currents and the high production area (shaded area) are indicated on the map. The following abbreviations are used; SEC: South Equatorial Current; SECC: South Equatorial Counter Current; EUC: Equatorial Under Current; NECC: North Equatorial Counter Current; BOC: Benguela Ocean Current; GC: Guinea Current; ITCZ: Inter Tropical Convergence Zone.

Strong SE (South Eastern) trade winds during boreal summer lead the maximum development of the SEC within this period (Peterson and Stramma, 1991). This intensified wind stress causes an uplift of the thermocline and the nutricline in the eastern Equatorial Atlantic (Longhurst, 1993) supplying nutrients to the surface waters resulting in enhanced primary production during summer between 0° and 4°S (Fig. 1 and 2a) (Longhurst, 1995; Antoine, 1996). The upwelling of colder nutrient-rich subsurface water masses also occurs due to Ekman drift directly at the Equator during summer. This is shown by clearly lower sea surface temperatures (SST) at the Equator compared to the North and South during summer (Fig. 2). The maintained low temperatures after the upwelling period in the southern Guinea Basin (Fig. 2) is probably caused by the maximum extension of the cold Benguela Ocean Current during fall (Peterson and Stramma, 1991). During winter the atmospheric circulation reverses and the ITCZ (Inter-tropical Convergence Zone) migrate

from more than  $10^{\circ}N$ , southwards to the Equator. The northern Guinea Basin is then directly influenced by the NE (North Eastern) trades.



**Figure 2** Sea-surface temperatures (SST) and primary production (P.prod) from the northern (EA1), central (EA3) and southern part (EA5) of our study area. The SST data are taken from IGOS weekly Sea Surface Measurements (Reynolds and Smith, 1994) and cover the sampling period of sediment trap transect EA1-EA5 (1991). The P.prod data are taken from Antoine et al. (1996).

### 3. Materials and Methods

In this study we present data from 8 different sediment trap series (Fig. 1, Table 1) and 19 surface sediment samples (Fig. 1, Table 2) from the Guinea Basin between  $5^{\circ}N$  and  $9^{\circ}S$  at about  $10^{\circ}W$ . The sediment trap material was collected with normal cone shaped traps with  $0.5\ m^2$  opening and 20 sampling cups (Kiel SMT 230/234).

**Table 1** The sediment trap data used in this study as seasonal mean values and total (annual) mean values.  $\delta^{15}\text{N}$  values (‰ vs. air) are weighted against the total amount of nitrogen in each measured subsample.

Site	Trap Position Trap/ Water depth	Season (boreal)	Sampling period	Fluxes (mg/ m <sup>2</sup> / day)					C/N $\delta^{15}\text{N}$	
				Total	Opal	C <sub>org</sub>	CaCO <sub>3</sub>	Lithog.		
<b>Northern Guinea Basin</b>										
EA1	03°09.9'N/ 11°9.9'W 984 m/ 4524 m	Spring	13.04.91 - 21.06.91	125.9	14.4	11.5	37.3	51.1	7.6	2.7
		Summer	21.06.91 - 21.09.91	100.4	7.4	10.8	50.8	20.7	7.1	3.9
		Fall	21.09.91 - 29.11.91	66.1	6.7	7.7	27.5	14.2	7.4	3.7
		Mean	13.04.91 - 29.11.91	97.8		10.1			7.3	3.4
EA2	01°46.9'N/ 11°15.2'W 953 m/ 4399 m	Spring	13.04.91 - 21.06.91	114.7	10.0	11.0	49.6	33.1	7.2	3.2
		Summer	21.06.91 - 21.09.91	127.3	14.3	15.1	54.6	28.3	7.0	5.0
		Fall	21.09.91 - 29.11.91	64.2	3.4	4.7	47.3	7.1	6.3	3.5
		Mean	13.04.91 - 29.11.91	105.4		10.7			7.0	4.3
GBN3	01°47.5'N/ 11°07.6'W 853 m/ 4481 m	Spring	20.03.89 - 23.06.89	74.8	8.8	8.5	35.9	13.0	8.9	4.3
		Summer	23.06.89 - 26.09.89	101.4	9.7	11.6	63.0	7.0	7.9	4.5
		Fall	26.09.89 - 30.12.89	50.3	5.9	5.3	27.7	6.0	7.3	3.9
		Winter	30.12.89 - 16.03.90	52.1	6.5	5.4	25.7	9.1	7.5	3.8
		Mean	20.03.89 - 16.03.90	81.0		7.8			8.0	4.2
GBN6	01°47.3'N/ 11°08.3'W 859 m/ 4522 m	Spring	04.04.90 - 15.06.90	74.1	3.6	4.9	50.8	9.9	6.3	4.5
		**	15.06.90 - 07.04.91	86.2	10.5	8.8	43.5	14.5	7.5	4.7
		Mean	04.04.90 - 07.04.91	83.8		8.1			7.4	4.6
<b>Equatorial Guinea Basin</b>										
EA3	00°04.5'S/ 10°46.1'W 1097 m/ 4141 m	Spring	13.04.91 - 21.06.91	81.7	4.9	5.3	54.0	12.1	6.6	4.7
		Summer	21.06.91 - 21.09.91	36.3	1.4	2.1	22.9	3.9	5.9	6.4
			*(With sub-sample No. 12)	43.7*	2.1*	5.6*	24.3*	3.4*	6.8*	8.2*
		Fall	21.09.91 - 29.11.91	25.2	1.0	1.2	17.5	4.4	6.9	4.8
Mean	13.04.91 - 29.11.91	49.6		4.2			6.4	5.2		
<b>Southern Guinea Basin</b>										
EA4	02°11.4'S/ 10°05.5'W 1068 m/ 3906 m	Spring	13.04.91 - 21.06.91	94.7	6.8	10.6	57.8	9.0	8.0	5.9
		Summer	21.06.91 - 21.09.91	47.3	1.9	2.5	35.3	3.5	6.9	5.1
		Fall	21.09.91 - 29.11.91	1.6	n.d	n.d	n.d	n.d	n.d	n.d
		Mean	13.04.91 - 29.11.91	47.8		4.2			7.7	5.7
EA5	04°11.4'S/ 10°15.8'W 948 m/ 3490 m	Spring	13.04.91 - 21.06.91	100.8	5.3	6.8	69.4	13.2	7.0	4.9
		Summer	21.06.91 - 21.09.91	23.4	1.8	1.3	14.1	2.7	6.3	5.6
		Fall	21.09.91 - 29.11.91	40.8	3.7	3.0	25.1	4.6	6.8	6.5
		Mean	13.04.91 - 29.11.91	51.8		3.5			6.8	5.4
EA8a	05°47.1'S/ 09°25.5'W 598 m/ 3450 m	Winter	15.12.91 - 20.03.92	59.9	3.9	6.4	35.2	8.1	6.7	6.5
		Spring	20.03.92 - 20.06.92	101.1	4.2	10.7	66.9	8.5	6.8	5.0
		Summer	20.06.92 - 21.09.92	59.8	4.0	5.4	41.0	4.0	5.4	6.7
		Mean	15.12.91 - 21.09.92	73.5		7.5			6.4	6.1

\* The summer data for EA3 presented with the contaminated subsample number 12, see text for explanation.

\*\*A malfunction in this trap led to that all the material sampled between 15.06.90 and 07.04.91 was collected in one sampling cup. was overflowed and there was probably a loss of material and the fluxes have to be considered as minimum values.

Procedures for poisoning and processing of the sediment trap samples are described in Fischer and Wefer (1991). The surface sediments were collected using a giant box corer (GKG) or a multiple corer (MUC) during several R/V Meteor cruises (Table 2). All sediment samples were stored at 4°C before being freeze-dried and ground in an agate mortar at the home laboratory.

For the determination of total organic carbon (TOC) and nitrogen in the sediment trap material and surface sediments, sub-samples from the freeze-dried and homogenised material were decalcified using 6M HCl in silverboats and dried at 60°C. The samples were combusted at 1050°C in excess oxygen using a commercial Hereaus CHN analyser (Fischer and Wefer 1990; Müller et al., 1994).

$\delta^{15}\text{N}$  measurements were performed on a Finnigan Delta Plus attached to a Carlo/Erba NC2500 automatic elemental analyser as preparation line. The stable isotope determination was made from  $\text{N}_2$  gas released by flash combustion in excess oxygen at 1050°C. Depending on organic content, between 2-90 mg of bulk material (freeze-dried and homogenised) was weighted in and measured against 99.996% pure  $\text{N}_2$  tank gas. One internal standard (WST2 6,66‰) was measured for every fifth sample. The  $\text{N}_2$  tank gas and the WST2 house standard were calibrated against the IAEA standards N-1 and N-2. Standard deviation on replica measurements were better than 0.2‰.

#### 4. Sediment trap results

Fig. 3 shows the  $\delta^{15}\text{N}$  values and the  $\text{C}_{\text{org}}$  fluxes from the sediment traps (EA1- EA5, EA8, GBN3 and GBN6). We have chosen to present the  $\text{C}_{\text{org}}$  instead of the total nitrogen (TN) fluxes which is the actual source for the measured nitrogen gas. The  $\text{C}_{\text{org}}$  and TN fluxes correlate closely, but we prefer the  $\text{C}_{\text{org}}$  flux because productivity is usually calculated in amounts of organic carbon. Additionally, the  $\text{C}_{\text{org}}$  fluxes are closer connected to sedimentary total organic carbon content (TOC).

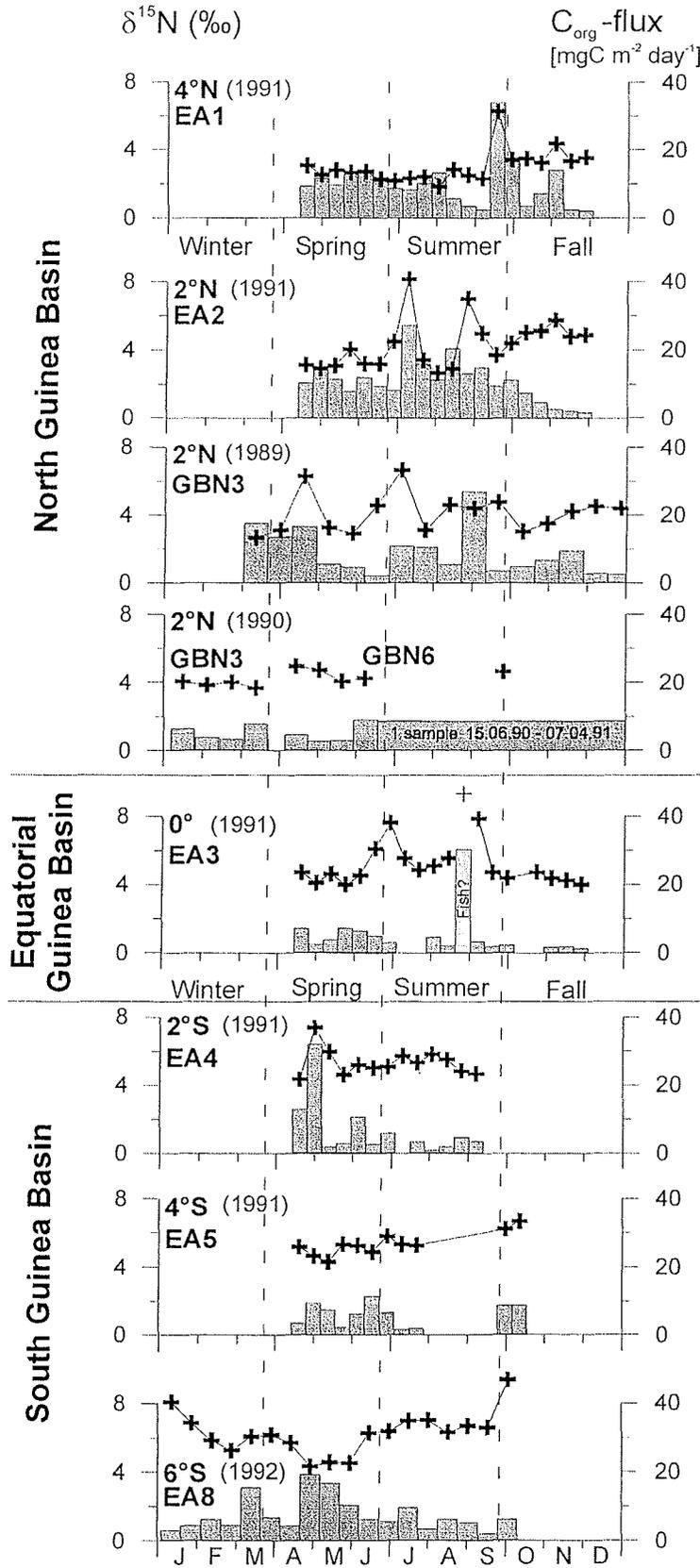


Figure 3  $\delta^{15}\text{N}$  values in ‰ vs. air (+) and  $C_{\text{org}}$  fluxes (bars) from eight different sediment traps at six different stations along a N-S transect at about 10°W in the eastern equatorial Atlantic.

The general pattern is higher  $C_{\text{org}}$  fluxes and lower  $\delta^{15}\text{N}$  values in the northern Guinea Basin (EA1, EA2 and GBN3, GBN6) compared to the equatorial- (EA3) and the southern Guinea Basin (EA4, EA5 and EA8).

The higher  $C_{\text{org}}$  fluxes throughout the transect were mainly registered during spring, in particular in the southern Guinea basin. Only at  $2^\circ\text{N}$  (EA2 and GBN3) the summer  $C_{\text{org}}$  fluxes were higher than the spring fluxes. At the Equator (EA3) and  $2^\circ\text{N}$  (EA2 and GBN3) there were large variations in the  $\delta^{15}\text{N}$  values throughout the sampling period. The actual values though, were generally 1-2‰ higher at the Equator (EA3) compare to  $2^\circ\text{N}$  (EA2 and GBN3). Further to the north (EA1) and south (EA4 and EA5) the  $\delta^{15}\text{N}$  values revealed less variance, with the lowest values at  $2^\circ\text{N}$  (EA1). The southernmost site (EA8) revealed a relatively high seasonality in both  $C_{\text{org}}$  fluxes and  $\delta^{15}\text{N}$  values with a anti-correlation between the two parameters. The higher  $C_{\text{org}}$  fluxes with low  $\delta^{15}\text{N}$  values occurred during spring and lower fluxes and higher  $\delta^{15}\text{N}$  values occurred during summer and winter. For the rest of the transect, only for 1990 at  $2^\circ\text{N}$  (GBN3) were the winter values available. Here the  $C_{\text{org}}$  fluxes were low and the  $\delta^{15}\text{N}$  values remained almost constant ( $3.9 \pm 0.1$ ). During Fall, the  $C_{\text{org}}$  fluxes were mainly low with average to high  $\delta^{15}\text{N}$  values throughout the transect.

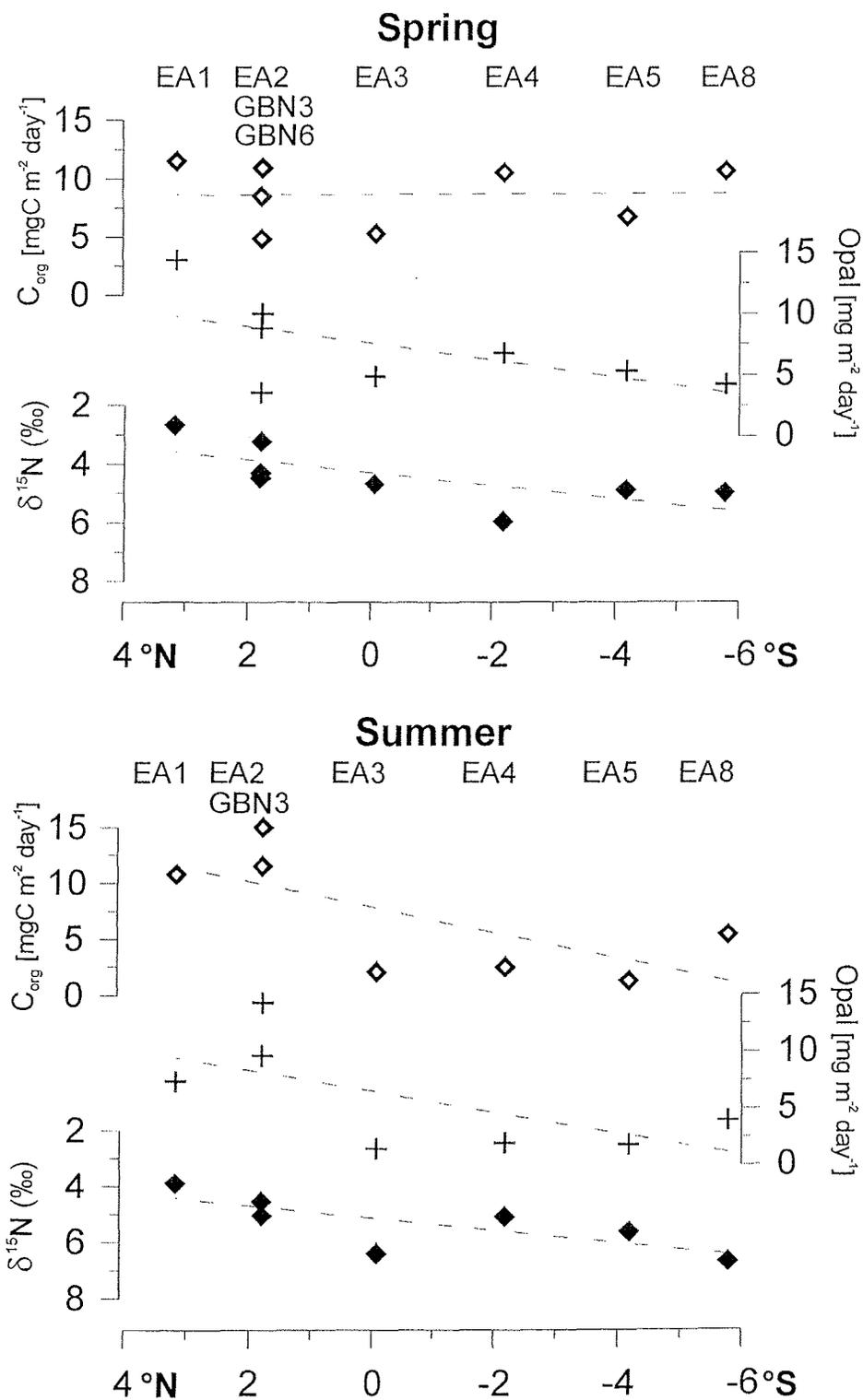
One exceptional peak in the  $C_{\text{org}}$  fluxes (slashed bar) and the  $\delta^{15}\text{N}$  record is due to contamination by swimmers not included in the calculation of mean values for the Equator (EA3). This sample contains no lithogenic material at all (Fischer and Wefer, 1995) and a visual inspection of the samples coarse fraction ( $>1$  mm) revealed many partly dissolved swimmers, thus we are quite certain that this sample is disturbed or altered in some way. EA1 (late summer), EA2 (early summer) and EA4 (early spring) all have one very prominent  $C_{\text{org}}$  flux peak with a very heavy  $\delta^{15}\text{N}$  signal, similar to the one we removed from the EA3 record. These peaks were not found or clearly seen in the diatom and opal fluxes from the respective samples (Fischer and Wefer, 1995; Romero et.al., 1999a). This could be caused by the presence of organic matter from swimmers known to have a heavier  $\delta^{15}\text{N}$  composition than their “food” ( $\sim 3.5$ ‰ per trophic level, Fry, 1988). In the case of these three extreme samples, the presence of organic material from swimmers is one possible explanation for the very heavy  $\delta^{15}\text{N}$  values and the discrepancies between opal and  $C_{\text{org}}$  fluxes. However, as long as we have no positive proof of an alteration, we see no reason to remove these from the records.

**Table 2**  $\delta^{15}\text{N}$  (‰ vs. air), TOC (weight %) and C/N ratios from surface sediment samples between 4°N and 9°S in the Guinea Basin.

Surface sediment samples							
Core	Type	Water depth (m)	Position	Sediment depth (cm)	$\delta^{15}\text{N}$ (‰ vs. air)	C/N	TOC (wt. %)
<b>Northern Guinea Basin</b>							
1406-1	MUC	4523	03°09'2N/ 11°14'4W	0.5	6.1	n.d.	n.d.
1606-7	MUC	4451	03°04'2N/ 11°54'6W	0.5	6.6	9.4	1.00
1607-8	MUC	4318	01°48'0N/ 11°16'2W	0.5	7.6	8.7	0.62
1101-4	GKG	4567	01°39'6N/ 10°58'8W	1	7.4	7.7	0.48
<b>Equatorial Guinea Basin</b>							
1103-3	GKG	4321	00°36'0N/ 09°15'6W	1	8.6	8.6	0.36
1102-3	GKG	4779	00°31'2N/ 08°35'4W	1	8.5	8.0	0.41
1608-9	MUC	4586	00°03'6S/ 10°51'0W	0.5	8.2	8.3	0.57
1104-5	GKG	3724	01°09'6S/ 10°42'6W	1	8.3	7.6	0.32
1403-2	GKG	3692	01°12'0S/ 11°42'6W	1	8.2	7.0	0.35
<b>Southern Guinea Basin</b>							
1105-3	GKG	3232	01°40'2S/ 12°25'8W	1	n.d.	6.5	0.37
1105-3	GKG	3232	01°40'2S/ 12°25'8W	4	8.8	8.8	0.29
1108-3	GKG	3875	02°10'2S/ 09°51'6W	1	8.8	8.3	0.34
1609-9	MUC	3908	02°11'4S/ 10°06'6W	0.5	8.6	7.0	0.45
1115-4	GKG	2921	03°33'6S/ 12°34'8W	1	8.9	6.3	0.32
1116-1	GKG	3471	03°37'2S/ 13°11'4W	1	8.9	6.4	0.27
1117-3	GKG	3977	03°49'2S/ 14°54'0W	1	9.5	6.2	0.24
1612-9	MUC	3513	04°19'2S/ 10°15'0W	0.5	9.1	6.5	0.37
1407-7	GKG	3508	04°18'8S/ 10°15'0W	1	9.7	6.5	0.24
1613-10	GKG	3560	05°51'0S/ 09°31'2W	1	9.6	7.4	0.20
1903-1	GKG	3161	08°40'8S/ 11°50'4W	1	9.5	7.3	0.24

## 5. Seasonal and annual variation

The seasonal timing of the fluxes and their respective N-isotope signals provides us with important information about the surface conditions which govern the sedimentation. To avoid a too detailed and partly speculative discussion about all variations in each record, we will mainly focus on the seasonal mean values presented in Fig. 4 and in Table 1 for the discussion of spatial and seasonal variations. For the comparison between the surface water production/ nitrate availability and the surface sediment along the N-S transect, the sediment trap data are shown as averaged values (Fig. 4 and Table 1).



**Figure 4** Seasonal mean values for the warm spring and the cold summer (upwelling) seasons along the N-S transect at about 10°W in the equatorial Atlantic. Corg fluxes (open diamonds) and Opal fluxes (+) in mg m<sup>-2</sup> day<sup>-1</sup> and the  $\delta^{15}\text{N}$  values (black diamonds) are weighted against the total N-content.

### 5.1. Warm Seasons (Spring, Fall and Winter)

At all sediment trap stations along the N-S transect the total fluxes during spring were high and the corresponding  $\delta^{15}\text{N}$  signals were light compared to the other seasons (Fig. 3 and 4, Table 1). High lithogenic fluxes in the northern Guinea Basin (Table 1), and maximum relative abundance of freshwater and coastal diatoms (~10%) (Lange et al., 1994; 1998; Romero et al., 1999b) during the increased spring fluxes, reflects the southward extension of the coastal and eolian influence through the NE trades. Additional to this external input, enhanced open ocean production took place (Lange et al., 1994; 1998; Wefer and Fischer, 1993; Fischer and Wefer, 1995; Treppke et al., 1996) resulting in the high spring fluxes in the northern Guinea Basin (Fig. 4, Table 1). The elevated fluxes registered during spring at the southern Guinea Basin sites (Table 1) were probably due to a deep chlorophyll maximum with increased primary production at a thermal ridge developing at about 2-3°S during boreal spring (Voituriez and Herbrand, 1977; 1981).

The northern Guinea Basin sites are low in surface nitrate content (Fig. 5b) and is likely to be at its minimum during the warm seasons (Fig. 2) when no supply from the subsurface waters take place. Therefore, a non marine source of nitrate for the primary production is required to explain the high  $C_{\text{org}}$  and opal fluxes during spring (and late winter in 1989) in the northern Guinea Basin. In 1991 (EA1 and EA2) high spring fluxes were recorded and the  $\delta^{15}\text{N}$  values were light (Fig. 4, Table 1). For the 1989 (GBN3) and 1990 (GBN6) records, with lower particle fluxes during spring, the corresponding  $\delta^{15}\text{N}$  values are close to the average for the respective years (Table 1). The most significant difference between the spring fluxes at 2°N in 1989 (GBN3), 1990 (GBN6) and 1991 (EA2), was the much higher lithogenic flux recorded in 1991 (EA2) compared to the two previous years. This suggests a connection between high terrestrial input through dust (lithogenic fluxes) and increased  $C_{\text{org}}$ - and opal fluxes with light  $\delta^{15}\text{N}$  composition. Below we will list and discuss some possible mechanisms to explain the enhanced  $C_{\text{org}}$  fluxes and the connected low  $\delta^{15}\text{N}$  values during spring in the northern Guinea Basin; 1) Considerable amounts of terrestrial organic matter with a light  $\delta^{15}\text{N}$  signature are incorporated in the dust, 2) Nutrients brought by the NE trades (Schütz, 1980) represent a nitrate source with light isotopic composition for the primary production, 3) Trace elements (Fe) brought by the dust causes increased production with nitrogen fixation from air as an important nitrate source.

1) Considering  $\delta^{15}\text{N}$  values from terrestrial plants and organic matter in surface sediments (2.3-7.8‰) and modern lake sediments (5.0-9.0‰) from Ghana, to the NE of the study area (Talbot and Johannessen, 1992), terrestrial organic material is not expected to have very light  $\delta^{15}\text{N}$  composition. This is further confirmed by measurements performed on dust samples from the study area giving  $\delta^{15}\text{N}$  values of  $5.5 \pm 1\text{‰}$  (Manuscript 2) which are heavier than the N-isotope composition recorded in the sediment trap samples in the

northern Guinea Basin. We would also expect higher C/N ratios than 7.6 (Table 1) if the terrestrial organic matter, with C/N ratios ranging between 20 and 200, (Hedges et al., 1986; Talbot and Johannessen, 1992) were dominating the organic content in the POM collected in the sediment traps. A relative amount of ~5% non-marine diatoms during winter and spring (Lange et al., 1994; 1998; Romero et al., 1998) demonstrates that the diatom content is also not significantly influenced by input from the continent.

2)  $\delta^{15}\text{N}$  measurements on nitrate in rainwater reveal values mainly between -15 and 15‰ with the main bulk between 0-4‰ (Kendall, 1998 and references therein), indicates that this could be a source of isotopically light nitrogen for the primary production. We are not able to quantify the amount of nutrients supplied by the NE Trades which precipitate within the ITCZ (Wefer and Fischer, 1993), but recognise this as a potentially significant source of isotopically light nitrogen available for the primary production.

3) Atmospheric transport of dust is probably the dominant source of iron (Fe) into the productive photic zone (Duce and Tindale, 1991) and increased Fe supply is shown to have a positive effect on primary productivity, at least in high nitrogen low chlorophyll regions (HNLC)(Boyd et al., 1998; Hutchins and Bruland, 1998). Takeda (1998) also showed a positive effect of increased iron availability in equatorial Pacific upwelling, a system with similarities to the eastern equatorial Atlantic. The equatorial Atlantic is not a HNLC region, but the light  $\delta^{15}\text{N}$  values could point to nitrogen fixation by cyanobacteria as a likely source of new nitrate. Walsh (1996) estimated an annual variation in the contribution from nitrogen fixation to the nitrate budget, between 34% and 77% in the meso,- to oligotrophic Cariaco Basin, depending on the supply of upwelled marine nitrate.

In the southern Guinea Basin a thermal ridge breaking the thermocline and nutricline at 2-4°S is thought to be the nutrient source for the high spring fluxes during spring (Voituriez and Herbrand, 1977; 1981). A likely explanation for the light  $\delta^{15}\text{N}$  during spring in the southern Guinea Basin is that factors other than nitrate are limiting the primary production at this deep chlorophyll maximum, i.e. light. If no significant utilisation in the available nitrate source appears, then the  $\delta^{15}\text{N}$  signal in the particulate organic material will remain light.

Only in the southernmost part of our study area, 4-6°S (EA5 and EA8), do the fall and winter fluxes significantly contribute to the annual fluxes. The relatively high  $\delta^{15}\text{N}$  values (Table 1) point towards a marine source of nitrate, may be in connection to migrations in the Benguela Ocean Current. Between 0 and 2°S (EA3, EA4), fluxes during fall were very low and thus of minor significance to the formation of the sediments. The presented traps at 0° and 2°S (EA3 and EA4) were not sampling during winter, however Lange et al. (1994) found no significant fluxes in the southern Guinea Basin during winter either. In the northern Guinea Basin (EA1, EA2 and GBN3) the fall and winter fluxes are about the half

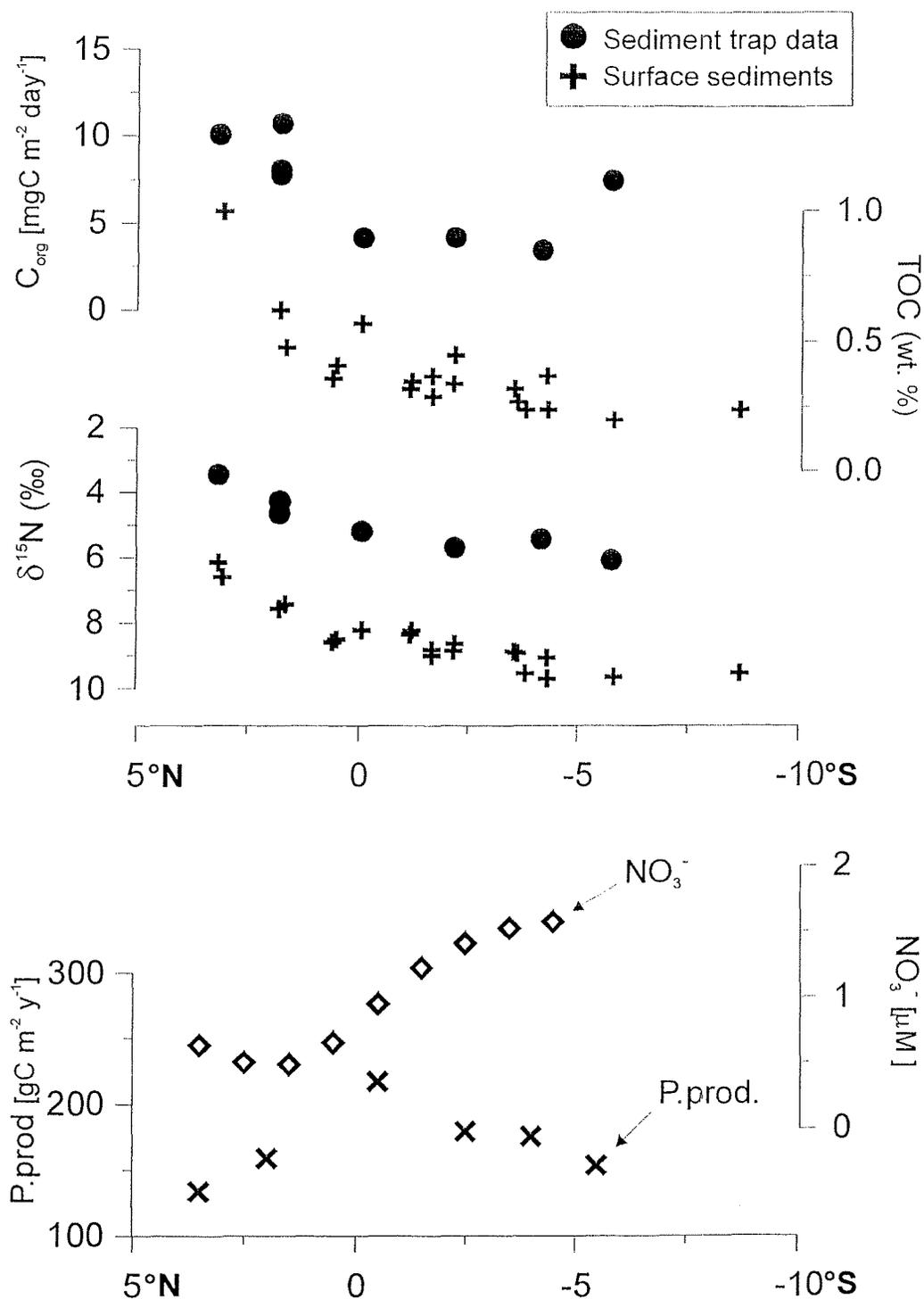
of the spring and summer fluxes (Table 1). Some of the POM trapped during early fall could be related to the end of the high production (cold) season (discussed below), while late fall and winter fluxes relate to surface water conditions, as discussed above for the spring but with considerably less lithogenic input (Table 1). Seasonal  $\delta^{15}\text{N}$  values between 3.5‰ and 3.9‰ during fall and winter (Table 1) in the northern Guinea Basin indicate that nitrogen fixation and nutrients supplied by the ITCZ, were important sources of new nitrate during these periods too.

### 5.2. Cold season (Summer)

Unlike the situation during spring, with several independent sources of new nitrogen available for the primary production in the Guinea Basin, there is only one dominant source during summer. Due to the known source area (0-4°S) of nutrients and high primary production (Fig. 1, 2 and 5b)(Longhurst, 1993; 1995; Antoine, 1996), it is possible to trace the eventual lateral transport of the POM by comparing the fluxes recorded below the high production area (0°-2°S) and the fluxes immediately to the north (2°N) and south (4°S) of the divergence (Fig. 1). For the traps located further away from the high production area (3°N and 6°S) significant contributions from other sources to the recorded summer fluxes may have to be considered.

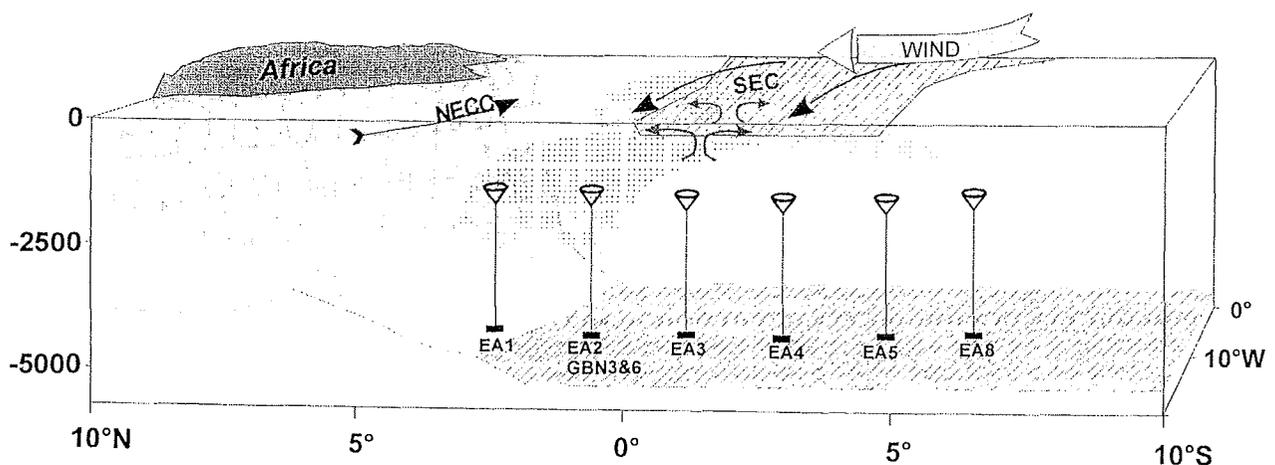
During 1991 (EA1-EA5) the minimum summer fluxes were recorded at 4°S, south of the divergence, and slightly higher fluxes were recorded close to (2°S) and beneath the divergence (0°)(Fig. 4, Table 1). The total particle flux recorded during summer at 2N° was about three times higher than beneath the area of high surface water production (0° and 2°S) (Table 1). By looking specifically at the opal and organic carbon fluxes, the imbalance was even higher, with 7-10 times the fluxes at 2°N compared to the Equator and 2°S (Fig. 4, Table 1), while the primary production is higher at and south of the Equator than in the northern Guinea Basin (Fig. 2 and 5b).

At 2°N, the total flux rates during summer 1989 (GBN3) were slightly lower compared to summer 1991 (EA2), except for carbonate, and the main difference was the much higher lithogenic fluxes during 1991 (Table 1). The enhanced lithogenic input during 1991 could influence the primary production through the supply of trace elements and/or dust could enhance the sinking velocities of POM and thus the opal and  $\text{C}_{\text{org}}$  fluxes (Ramaswamy et al., 1991; Neuer et al., 1996). The lithogenic input did not seem to enhance the influence from nitrogen fixation during summer, as the summer  $\delta^{15}\text{N}$  values from 1989 (GBN3) were lower than for 1991 (EA2).



**Figure 5** A comparison of annual mean values from the sediment traps (EA1-EA5, GBN3, GBN6 and EA8) and surface sediments, to nutrient availability and the primary production along the N-S transect at about 10°W in the equatorial Atlantic a) Mean  $C_{\text{org}}$  fluxes and  $\delta^{15}\text{N}$  values (weighted against the total N-content) for the sediment traps, TOC (weight %) and  $\delta^{15}\text{N}$  data from surface sediments. b) Annual mean nitrate ( $\text{NO}_3^-$ ) concentration in the upper 30 m of the water column (diamonds and left axis)(Conkright et al., 1994) and annual primary production (X and right axis) (Antoine et al., 1996).

Lateral transport of the POM is also indicated by the  $\delta^{15}\text{N}$  data because, directly beneath the source of new nitrate at the Equator (EA3) the  $\delta^{15}\text{N}$  values during summer were higher than at 2°N (EA2). This indicates that the POM collected during summer beneath the Equator is not originating from the centre of the source of new nitrate sited directly above. A relatively heavy isotope signal during an upwelling season would point to a production area distal to the source of new nitrate. Hence, considering the low fluxes and the heavy  $\delta^{15}\text{N}$  at the Equator (EA3) and the high fluxes and low  $\delta^{15}\text{N}$  values at 2°N (EA2) during summer (Fig. 4, Table 1), a lateral displacement towards the north, (schematically illustrated in Fig. 6) is the most likely explanation. The most likely driving mechanism for this transport within the upper 1000 m of the water column are the wind driven surface currents from the south east (SEC, Peterson and Stramma, 1991). Richardson and Walsh (1986) reported surface current velocities up to  $50 \text{ cm s}^{-1}$  in a north-western direction during summer and Picaut et al. (1985) demonstrated strong prevailing winds from the south. The colder water masses from the south could be slowed down as they meet the warm NECC between 2°N and 4°N (Figs. 1 and 6) (Richardson and Walsh, 1986; Peterson and Stramma, 1991).



**Figure 6** A model schematically demonstrating the northward lateral transport in the particulate organic matter from the high production area (thin straight lines) related to the equatorial divergence, at the equator (diverging arrows), and the shallowing of the thermocline during boreal summer.

If the source of the high summer fluxes at 3°N (EA1) was solely the equatorial divergence, heavier rather than lighter  $\delta^{15}\text{N}$  values compared to 2°N (EA2) would be expected due to the large distance to the upwelling centre. However, if the POM is advected northwards beneath the photic zone dipping under the NECC (Fig. 1, Fig. 5), a sorting of the particles due to sinking velocities or an altering of the  $\delta^{15}\text{N}$  signal due to early diagenesis, are possible explanations for this discrepancy. Nakatsuka et al. (1997)

suggested a preferential early degradation of  $^{15}\text{N}$  rich components like amino acids to explain a similar discrepancy with depth.

The lower  $\delta^{15}\text{N}$  values during summer, at 2°S (EA4) and 4°S (EA5) compared to the equatorial site (EA 3) could have several possible explanations e.g.; -different biological composition, - elements other than nitrate were limiting the production, -or, nitrogen fixation from air was influential. Due to the very low fluxes during summer, these  $\delta^{15}\text{N}$  signals are of minor importance for the forming of the sediments in the southern Guinea Basin.

## 6. Mean values and surface sediments

### 6.1. Mean values

The trap transect EA1 - EA5 did not sample during winter and EA8 did not sample through fall. However, considering the moderate to low fluxes during the not sampled seasons at other sites nearby, we expect the mean  $\delta^{15}\text{N}$  values from EA1-5 and EA8 to be close to the annual mean  $\delta^{15}\text{N}$  values from the respective years (Table 1). Due to the low winter and fall fluxes, the mean fluxes presented for EA 1 - EA5 and EA8, are assumed to be slightly higher than the true annual mean. EA2, GBN3 and GBN6 are representing three years (1989, 1990, and 1991) of sampling at the same site (2°N) and the interannual variation in the mean values are low (0.4‰) compared to the regional differences in the Equatorial Atlantic (Table 1). Even though significant differences in total fluxes and diatom fluxes (Lange et al., 1994; 1998; Romero et al., 1999a) occurred between 1989 (GBN3) and 1991 (EA2), the annual  $\delta^{15}\text{N}$  values appear to be almost constant.

### 6.2. Surface sediments

The sedimentation rates for the last 7-8 ka at one of the shallowest sites 2°S (GeoB1105-3, 2,8 cm/ka, G. Mollenhauer, personal comm.) and one of the deepest sites 2°N (GeoB1101-4, 2,9 cm/ka, Bickert, 1992) are similar. Therefore, we assume that the TOC percentages from the box corers (GKG) surface sample mirror the accumulation rates. The surface samples from multiple corers (MUC) contain more fluffy sediment and show a tendency towards higher TOC percentage than nearby located box corer surface samples (Table 2). The  $C_{\text{org}}$  accumulation rates at 2°N ( $0.07 \text{ gC m}^{-2} \text{ y}^{-1}$ , GeoB1101-4), are slightly higher than at 2°S ( $0.06 \text{ gC m}^{-2} \text{ y}^{-1}$ , GeoB1105-3) in the Guinea Basin. By comparison of TOC values/accumulation rates to the particle fluxes in the water column, one should keep in mind that fluxes and burial rates decrease as a function of water depth (Berger and Wefer, 1990).

The constant  $\delta^{15}\text{N}$  offset of  $3.5 \pm 0.6\text{‰}$  higher values at the sediment surface compared to the sinking matter (Fig. 5a), indicates that the conditions governing the  $\delta^{15}\text{N}$  signal have

been relatively stable over the last few hundred years. A stable situation is further confirmed by the good correlation between the mean  $C_{org}$  fluxes and the TOC content in the surface sediments. Similar to the  $\delta^{15}N$  values there is a pronounced North to south trend in the TOC values (Fig. 5a).

Different estimates for the terrestrial contribution to the total  $C_{org}$  in surface sediments exists (Westerhausen et al., 1993; Wagner and Dupont, 1999), but with C/N ratios mainly below 8.5 (Table 2) we consider the terrestrial input to be of minor importance. The northernmost site at 3°N has a somewhat higher C/N ratio (9.4), which could reflect higher terrestrial influence, compared to rest of the transect. Except for this northernmost sample, no pronounced N-S trend is found in the surface sedimentary C/N ratios (Table 2). The high  $\Delta C/N$  between surface sediments and sediment trap at EA1 (2.1), compared to the rest of the transect ( $0.7 \pm 1.1$ ) (Tables 1 and 2), could be the result of higher relative preservation of the terrestrial organic material compared to the marine organic matter in the sediments. A corresponding difference does not appear in the  $\Delta \delta^{15}N$  between surface sediments and trap material, suggesting that the  $\delta^{15}N$  of the terrestrial organic matter has to be somewhere in the middle of these values (3.4‰ and 6.6‰). The low terrestrial influence on the  $\delta^{15}N$  signal in marine sediments, earlier demonstrated by Holmes et al. (1997), is due to the lower nitrogen content (high C/N) in terrestrial organic matter compared to marine organic matter (Müller, 1977). From this we can deduce that the  $\delta^{15}N$  values in the sediment are predominantly reflecting the marine condition.

## 7. Paleoceanographic implications

Taking the whole transect into consideration, the biogenic fluxes ( $C_{org}$  and Opal) during spring are the dominating fluxes to the sediment. This makes the productivity during spring at least as important for the export fluxes as the high production related to the equatorial upwelling (Ekman drift) and the shallowing of the thermocline during summer (Fig. 2, Longhurst, 1995). Consequently, changes in the factors governing the production during the warm season might be as important as changes in summer upwelling intensity for the export production in this area.

Probably the most drastic paleoceanographic implication from our data is that the dominating fluxes towards the sediments beneath the Equator (Fig. 1 and Fig. 6), do not seem to be related to the upwelling of subsurface waters during summer. The output of the high production during summer is found in the more oligotrophic northern Guinea Basin (Fig. 6), as schematically shown in Fig. 4, where the biogenic fluxes during summer exceed the biogenic spring fluxes, in particular at 2°N. As a consequence, changes in the upwelling intensity would not necessarily be well recorded in the sediments below the

equatorial divergence. Additionally, a change in the lateral transport during summer could have a major influence on the sedimentation beneath the divergence. By comparing the  $C_{\text{org}}$  fluxes and  $\delta^{15}\text{N}$  values during summer at the Equator with those in the northern Guinea Basin (Fig. 4, Table 1), it is obvious that if the lateral transport ceased or reduced this would have a strong impact on the sedimentation. This would cause a change towards higher TOC and lighter  $\delta^{15}\text{N}$  values beneath the divergence, which would commonly be interpreted as a change towards higher upwelling intensity.

## 8. Conclusions

High fluxes during the warm spring season occurred all along the presented N-S transect. Due to low fluxes during the cold summer season to the south of Equator, the fluxes during spring dominate the sedimentation at the Equator and in the southern Guinea Basin. Low  $\delta^{15}\text{N}$  values in the sinking matter during spring, suggest nitrogen fixation related to Fe supply through dust and precipitation of nutrients within the ITCZ as important sources of nitrate for new production in the northern Guinea Basin.

High summer fluxes in the northern Guinea Basin is the major difference in the sedimentation of organic matter compared to the equatorial and southern Guinea Basin (EA3 and EA4). Low  $\delta^{15}\text{N}$  values combined with high fluxes suggests an origin close to the source of new nitrate. The only mechanism to explain this is a substantial northward lateral transport of the POM related to the equatorial upwelling during boreal summer as shown in Fig. 5.

## Acknowledgements

We thank the officers, crew and scientists aboard R/V *Meteor* for their help during core recovery and sampling, and Monika Segl and Wolfgang Bevern for the assistance with the mass spectrometry analyses. We also thank Peter J Müller for providing sedimentary C/N data and helpful comments on the manuscript. Special thanks to Albert Benthien, Emma Eades, Gesine Mollenhauer, Oscar Romero, and Laurence Vidal for discussions and comments. This research was funded by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 261 at the University of Bremen, Contribution No. xxx).

## References

- Altabet, M.A., 1988. Variations in nitrogen isotopic composition between sinking and suspended particles; implications for nitrogen cycling and particle transformation in the open ocean. *Deep-Sea Research. Part A* 35 (4), 535-554.
- Altabet, M.A., Deuser, W.G., Honjo, S., Stienen, C., 1991. Seasonal and depth-related changes in the source of sinking particles in the North Atlantic. *Nature* 354, 136-139.
- Altabet, M.A., Francois, R., 1994. Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization. *Global Biogeochemical Cycles* 8 (1), 103-116.
- Antoine, D., Andre, J.M., Morel, A., 1996. Oceanic primary production 2. Estimation at global scale from satellite (coastal zone color scanner) chlorophyll. *Global Biogeochemical Cycles* 10 (1), 57-69.
- Berger, W.H., 1989. Global maps of ocean productivity. In: Berger, W.H., Smetacek, V., Wefer, G. (Eds.), *Productivity in the Ocean: Present and the Past*. John Wiley, Chichester, pp. 429-455.
- Berger, W.H., Wefer, G., 1990. Export production; seasonality and intermittency, and paleoceanographic implications. In: Cloeting, S. (Ed.) *Global and Planetary Change, 3, Geosphere Fluctuations; Short Term Instabilities in the Earth's System*. Elsevier, Amsterdam, Netherlands, pp. 245-254.
- Bickert, T., 1992. Rekonstruktion der spätquartären Bodenwasserzirkulation im östlichen Südatlantik über stabile Isotope benthischer Foraminiferen. *Berichte, Fachbereich Geowissenschaften, 27, Universität Bremen, Bremen*, 205pp.
- Boyd, P., Berges, J.A., Harrison, P.J., 1998. In vitro iron enrichment experiments at iron-rich and -poor sites in the NE subarctic pacific. *Journal of Experimental Marine Biology and Ecology* 227 (1), 133-151.
- Capone, D.G., Zehr, J.P., Pearl, H.W., Bergmann, B., Carpenter, E.J., 1997. *Trichodesmium*, a globally significant cyanobacterium. *Science* 276, 1221-1229.
- de Lange, G.J., van Os, B., Pruyssers, P.A., Middelburg, J.J., Castradori, D., van Santvoort, P., Müller, P.J., Eggemkamp, H., Prahl, F.G., 1994. Possible early diagenetic alteration of palaeo proxies. In: Zahn, R., Pedersen, T.F., Kaminski, M.A., Labeyrie, L. (Eds.), *Nato ASI Series, 1, Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change*. Springer, Berlin, Heidelberg, pp. 225-258.
- DeNiro, M.J., Epstein, S., 1981. Influence of diet on the distribution of nitrogen isotopes in animals. *Geochimica et Cosmochimica Acta* 45 (3), 341-351.
- Duce, R.A., Tindale, N.W., 1991. Atmospheric transport of iron and its deposition in the ocean. *Limnology and Oceanography* 36 (8), 1715-1726.

- Farrell, J.W., Pedersen, T.F., Calver, S.E., Nielsen, B., 1995. Glacial-interglacial changes in nutrient utilization in the equatorial Pacific Ocean. *Nature* 377 (514-517).
- Fischer, G., Wefer, G., 1991. Sampling, preparation and analysis of marine particulate matter. In: Hurd, D.C., Spencer, D.W. (Eds.), *Geophysical Monograph*, 63, Marine Particles; Analysis and Characterization. American Geophysical Union, Washington, DC, pp. 391-397.
- Fischer, G., Wefer, G., 1995. Downward particulate matter fluxes in the eastern and western equatorial Atlantic: a comparison. In: Tsunogai, K., Koike, I.O.T. (Eds.), *Proceedings of the IGBP Symposium on "Global fluxes of carbon and its related substances in the coastal sea-ocean-atmosphere system*. Hokkaido University, Sapporo, Japan, pp. 317-331.
- Francois, R., Altabet, M.A., Yu, E.F., Sigman, D.M., Bacon, M.P., Frank, M., Bohrmann, G., Bareille, G., Labeyrie, L.D., 1997. Contribution of Southern Ocean surface-water stratification to low atmospheric  $\text{CO}_2$  concentrations during the last glacial period. *Nature* 389, 929-935.
- Fry, B., 1988. Food web structure on Georges Bank from stable C, N and S isotopic composition. *Limnology and Oceanography* 33, 1182-1190.
- Gruber, N., Sarmiento, J.L., 1997. Global Patterns of marine nitrogen fixation and denitrification. *Global Biogeochemical Cycles* 11 (2), 235-266.
- Heaton, T.H.E., Spiro, B., Madeline, S., Robertson, C., 1997. Potential canopy influences on the isotopic composition of nitrogen and sulphur in atmospheric deposition. *Oecologia* 109, 600-607.
- Hedges, J.I., Clark, W.A., Quay, P.D., Richey, J.E., Devol, A.H., Santos, U.d.M., 1986. Compositions and fluxes of particulate organic material in the Amazon River. *Limnology and Oceanography* 31 (4), 717-738.
- Holmes, M.E., Müller, P.J., Schneider, R.R., Segl, M., Pätzold, J., Wefer, G., 1996. Stable nitrogen isotopes in Angola Basin surface sediments. *Marine Geology* 134 (1-2), 1-12.
- Holmes, M.E., Schneider, R., Müller, P.J., Segl, M., Wefer, G., 1997. Reconstruction of past nutrient utilization in the eastern Angola Basin based on sedimentary  $^{15}\text{N}/^{14}\text{N}$  ratios. *Paleoceanography* 12 (4), 604-614.
- Holmes, M.E., Müller, P.J., Schneider, R., Segl, M., Wefer, G., 1998. Spatial variations in euphotic zone nitrate utilization based on  $\delta^{15}\text{N}$  in surface sediments. *Geo-Marine Letters* 18 (1), 58-65.
- Hutchins, D.A., Bruland, K.W., 1998. Iron-limited diatom growth and Si:N uptake ratios in a coastal upwelling regime. *Nature* 393, 561-564.

- Karl, D., Leteiler, R., Tupas, L., Dore, J., Christian, J., Hebel, D., 1997. The role of nitrogen fixation in the biochemical cycling in the subtropical North Pacific Ocean. *Nature* 380, 533-538.
- Kendall, C., 1998. Tracing nitrogen sources and cycling in catchments. In: Kendall, C., McDonnell, J.J. (Eds.), *Isotope Tracers in Catchment Hydrology*. Elsevier Science B.V, Amsterdam, pp. 519-576.
- Lange, C.B., Treppke, U.F., Fischer, G., 1994. Seasonal diatom fluxes in the Guinea Basin and their relationship to trade winds, hydrography and upwelling events. *Deep-Sea Research* 41, 859-878.
- Lange, C.B., Romero, O.E., Wefer, G., Gabric, A.J., 1998. Offshore influence of coastal upwelling off Mauritania, NW Africa, as recorded by diatoms in sediment traps at 2195 m water depth. *Deep-Sea Research I* 45 (6), 985-1013.
- Longhurst, A., 1993. Seasonal cooling and blooming in tropical oceans. *Deep-Sea Research I* 40 (11-12), 2145-2165.
- Longhurst, A., 1995. Seasonal cycles of pelagic production and consumption. *Progress in Oceanography* 36 (2), 77-167.
- Michaels, A.F., Bates, N.R., Buesseler, K.O., Carlson, C.A., Knap, A.H., 1994. Carbon-cycle imbalances in the Saragasso Sea. *Nature* 372, 537-540.
- Minagawa, M., Wada, E., 1984. Stepwise enrichment of  $^{15}\text{N}$  along food chains; further evidence and the relation between delta  $^{15}\text{N}$  and animal age. *Geochimica et Cosmochimica Acta* 48 (5), 1135-1140.
- Müller, P.J., 1977. C/N ratios in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. *Geochimica et Cosmochimica Acta* 41, 765-776.
- Müller, P.J., Schneider, R., Ruhland, G., 1994. Late Quaternary  $\text{PCO}_2$  variations in the Angola Current: evidence from organic carbon  $\delta^{13}\text{C}$  and alkenone temperatures. In: Zahn, R., Pedersen, T.F., Kaminski, M.A., Labeyrie, L. (Eds.), *Nato ASI Series, I 17, Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change*. Springer, Berlin, Heidelberg, pp. 343-366.
- Nakatsuka, T., Handa, N., Harada, N., Sugimoto, T., Imaizumi, S., 1997. Origin and decomposition of sinking particulate organic matter in the deep water column inferred from the vertical distributions of its  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$  and  $\delta^{14}\text{C}$ . *Deep-Sea Research I* 44 (12), 1957-1979.
- Neuer, S., Ratmeyer, V., Davenport, R., Fischer, G., Wefer, G., 1997. Deep water particle flux in the Canary Island region: Seasonal trends in relation to long-term satellite derived pigment data and lateral sources. *Deep-Sea Research I* 44 (8), 1451-1466.

- Peterson, R.J., Stramma, L., 1991. Upper level circulation in the South Atlantic Ocean. *Progress in Oceanography* 26, 1-73.
- Picaut, J., Servain, J., Lecomte, P., Seva, M., Lukas, S., 1985. FOCAL Climatic Atlas of the tropical Atlantic: Wind stress and sea surface temperatures 1964-1979. Université de Bretagne Occidentale, Laboratoire d'Océanographie physique, Brest, France.
- Ramaswamy, V., Nair, R.R., Manganini, S., Haake, B., and Ittekkot, V., 1991. Lithogenic fluxes to the deep Arabian Sea measured by sediment traps: *Deep-Sea-Research*, 38, 169-184.
- Reynolds, R.W., Smith, T.M., 1994. Improved global sea surface temperature analyses. *Journal of Climate* 7, 929--948.
- Richardson, P.L., Walsh, D., 1986. Mapping climatological seasonal variations of surface currents in the Tropical Atlantic using ship drifts. *Journal of Geophysical Research* 91 (C9), 10,537-10,550.
- Romero, O.E., Lange, C.B., Fischer, G., Treppke, U.F., Wefer, G., 1999a. Variability in export production documented by downward fluxes and species composition of marine planktic diatoms: Observations from the Tropical and Equatorial Atlantic. In: Fischer, G., Wefer, G. (Eds.), *Use of Proxies in Paleoceanography: Examples from the South Atlantic*. Springer, Berlin Heidelberg, pp. 365-392.
- Romero, O.E., Lange, C.B., Swap, R., Wefer, G., 1999b. Eolian-transported freshwater diatoms and phytoliths across the Equatorial Atlantic record; temporal changes in Saharan dust transport patterns. *Journal of Geophysical Research* 104 (C2), 3211-3222.
- Saino, T., Hattori, A., 1980.  $^{15}\text{N}$  natural abundance in oceanic suspended particulate matter. *Nature* 283, 752-754.
- Saino, T., Hattori, A., 1987. Geographical variation of the water column distribution of suspended particulate organic nitrogen and its  $^{15}\text{N}$  natural abundance in the Pacific and its marginal seas. *Deep-Sea Research* 34 (5/6), 807-827.
- Sarmiento, J.L., Toggweiler, J.R., 1984. A new model for the role of the oceans in determining atmospheric  $\text{PCO}_2$ . *Nature* 308, 621-624.
- Schütz, L., 1980. Long range transport of desert dust with special emphasis on the Sahara. In: Kneip, T.J., Liouy, P.J. (Eds.), *Annals of the New York Academy of Science*, 338, *Aerosols: Anthropogenic and Natural, Sources and Transport*. The New York Academy of Science, New York, pp. 515-532.
- Takeda, S., 1998. Influence of iron availability on nutrient consumption ratio of diatoms in oceanic waters. *Nature* 393, 774-777.
- Talbot, M.R., Johannessen, T., 1992. A high resolution palaeoclimatic record for the last 27 500 years in tropical West Africa from the carbon and nitrogen isotopic composition of lacustrine organic matter. *Earth and Planetary Science Letters* 110 (1-4), 23-37.

- Treppke, U.F., Lange, C.B., Wefer, G., 1996. Vertical fluxes of diatoms and silicoflagellates in the eastern equatorial Atlantic, and their contribution to the sedimentary record. *Marine Micropaleontology* 28, 73-96.
- Voituriez, B., Herbland, A., 1977. Etude de la production pélagique de la zone équatoriale de l'Atlantique à 4°W, I. Relations entre la structure hydrologique et la production primaire. *Cahier ORSTOM, Série Océanographie* 15, 313-331.
- Voituriez, B., Herbland, A., 1981. Primary production in the tropical Atlantic Ocean mapped from oxygen values of Equalant 1 and 2 (1963). *Bulletin of Marine Science* 31, 853-863.
- Wada, E., Kadonaga, T., Matsuo, S., 1975. <sup>15</sup>N abundance in naturally occurring substances and global assessment of denitrification from isotopic viewpoint. *Geochemical Journal* 9, 139-148.
- Wada, E., Hattori, A., 1976. Natural abundance of <sup>15</sup>N in particulate organic matter in the North Pacific Ocean. *Geochimica et Cosmochimica Acta* 40, 249-251.
- Wada, E., 1980. Nitrogen isotope fractionation and its significance in biogeochemical processes occurring in marine environments. In: Goldberg, E.D., Horibe, Y. (Eds.), *Isotopes in Marine Chemistry*, pp. 375-398.
- Wagner, T., Dupont, L.M., 1999. Terrestrial organic matter in marine sediments: Analytical approaches and eolian-marine records in the central equatorial Atlantic. In: Fischer, G., Wefer, G. (Eds.), *The use of Proxies in Paleoceanography: Examples from the South Atlantic*. Springer, Heidelberg, Berlin, pp. 547-574.
- Walsh, J.J., 1996. Nitrogen fixation within a tropical upwelling ecosystem. *Journal of Geophysical Research* 101, 20,607-20,616.
- Wefer, G., Fischer, G., 1993. Seasonal patterns of vertical particle flux in equatorial and coastal upwelling areas of the eastern Atlantic. *Deep-Sea Research I* 40 (8), 1613-1645.
- Westerhausen, L., Poynter, J., Eglinton, G., Erlenkeuser, H., Sarnthein, M., 1993. Marine and terrigenous origin of organic matter in modern sediments of the equatorial East Atlantic; the  $\delta^{13}\text{C}$  and molecular record. *Deep-Sea Research I* 40 (5), 1087-112.
- Wilkerson, F.P., C, D.R., 1992. Measurements of nitrogen productivity in the equatorial Pacific. *Journal of Geophysical Research*. 97, 669-679.

## 7.2 Manuscript 2:

*Various impact from atmospheric dust on the marine record along the African west coast: Reflecting climate and vegetation.*

Abstract .....	56
Results and discussion.....	57
Methods .....	64
Acknowledgments .....	66
References .....	67

## Various impact from atmospheric dust on the marine record along the African west coast: Reflecting climate and vegetation.

Gaute Lavik<sup>1\*</sup>, Jan-Berend Stuut<sup>2</sup>, Lydie Dupont<sup>1</sup>, Peer Helmke<sup>1</sup>, Ralph R Schneider<sup>1</sup>, and Gerold Wefer<sup>1</sup>

<sup>1</sup> University of Bremen, Department of Geoscience, Post box 330440, 28334 Bremen Germany

<sup>2</sup> Utrecht University, Faculty of Earth Sciences, Sedimentology Division, Post Box 80.021, 3508 TA Utrecht, The Netherlands

To be submitted as a *Letter to Nature*

### Abstract

Input of wind blown terrigenous matter to the ocean will have varying biogeochemical impact on the marine sediments depending on vegetation and climate in the source area of the atmospheric dust. In very hot and arid areas like the Sahel and Sahara lowland grasses (C4 plants) dominate the biomass over bushes, shrubs and trees (C3 plants) (Livingstone and Clayton, 1980; White, 1983). Despite a prolonged discussion about possible differences in the biogeochemical influence of the atmospheric dust on the deep sea sediments (Sarntein and Koopmann, 1980; Westerhausen et al., 1993; DeMenocal, 1995; Verardo and Ruddiman, 1996; Bird et al., 1997; Bird and Cali, 1998; Wagner and Dupont, 1999; DeMenocal et al., 2000; Huang et al., 2000), our information about the organic matter in the dust actually entering the ocean is still limited. To interpret the terrigenous component in marine sediments, we need more information about the total organic composition. Here we present  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  data, C/N ratios, grain size distribution and pollen analysis from atmospheric dust collected during R/V Meteor cruise 41/1 in February and March 1998 along with the governing wind-regimes and a satellite image of the dust storms. Along a transect stretching from 33°N to 12°S along the African west coast, large variation in the composition of the dusts OM (organic matter) occurs in relation to the continental vegetation and climatic zones. The registered 7‰ change in the bulk  $\delta^{13}\text{C}$  values we mainly ascribe to the relative amounts of C3 and C4 plant remains contributing to the OM. Based on the difference between  $\delta^{13}\text{C}$  value in C3 (-27‰) and C4 (-14‰) plants (O'Leary, 1988), the contribution from C4 plants varies from >55% of the OM in the dust between 10°N and 20°N to less than 5% between 0 and 5°S. The trends in the  $\delta^{13}\text{C}$  record is supported by pollen analysis in some selected samples. Most of the difference in the C/N ratios (12-29) is ascribed to the relative proportions of plant litter and charcoal compared to inorganic nitrogen absorbed by clay minerals. Nitrogen isotopes is a parameter which until now has not been checked for its possible variations in dust and

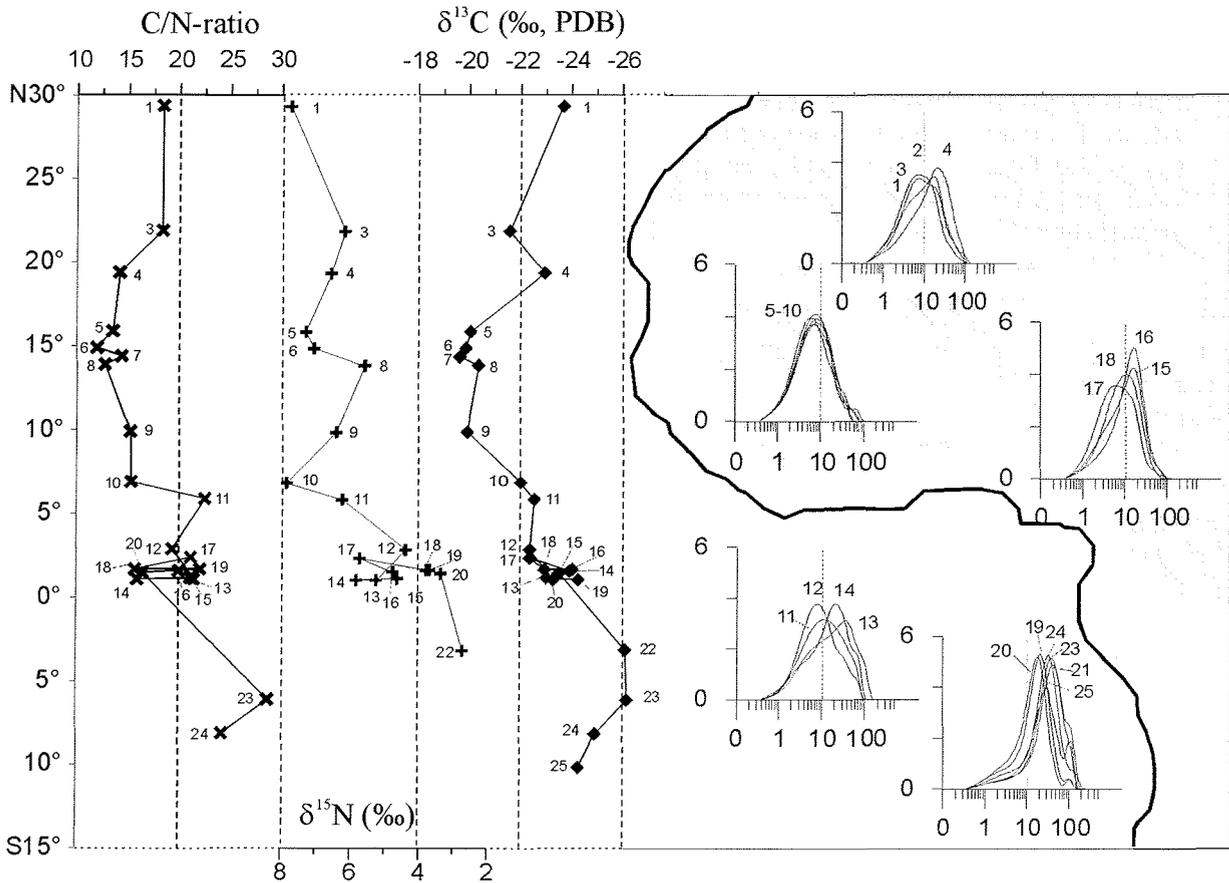
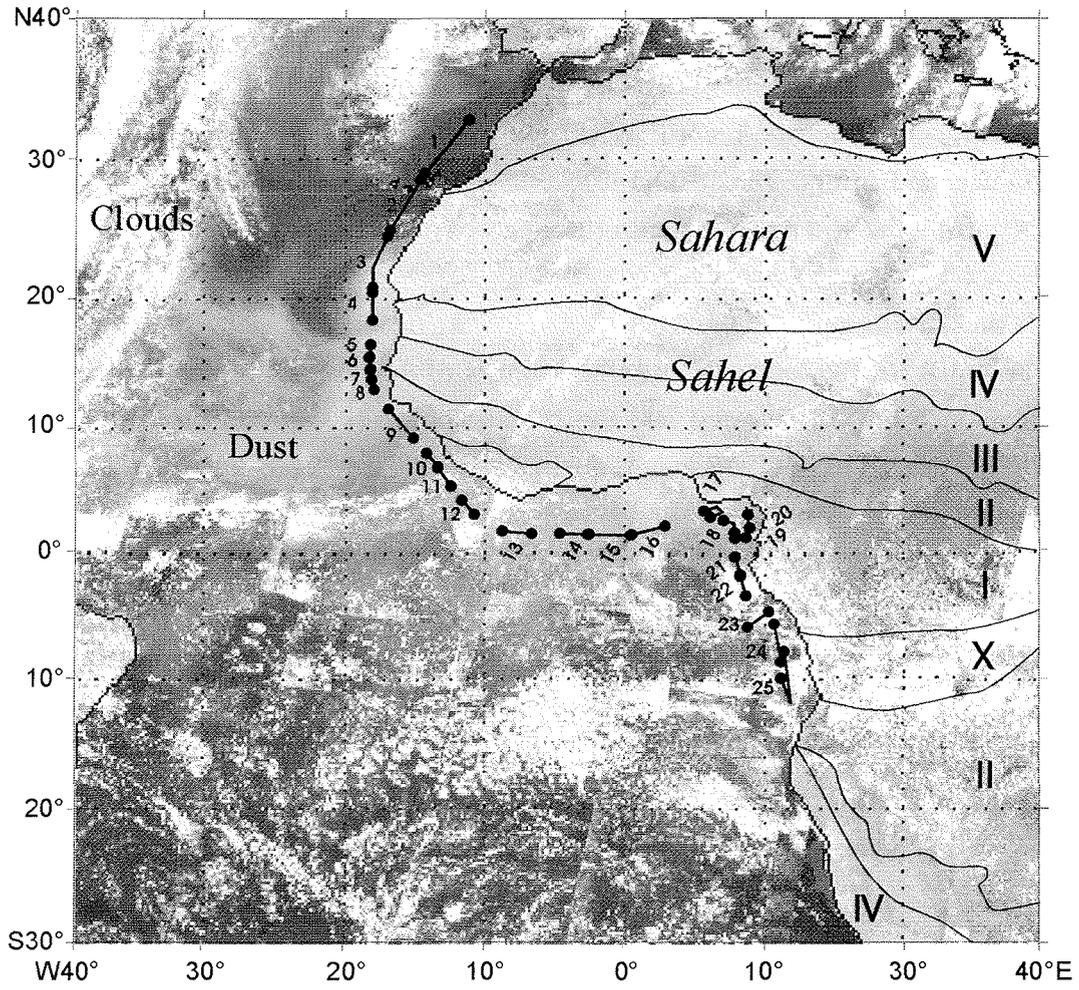
thus, impact on the marine record. When we apply the suggested relation between plant  $\delta^{15}\text{N}$  values and aridity (Heaton, 1987) our data reflect a  $\sim 1000\text{mm y}^{-1}$  precipitation difference from the arid north to the tropical part of our transect.

## Results and discussion

A large part of the total of one billion tonnes of dust transported in Africa every year (D'Almaeida, 1996) is exported into the Atlantic ocean (Prospero et al., 1996; Moulin et al., 1997). The centre of the Saharan dust plume migrates from  $20^\circ\text{N}$  during summer to  $5^\circ\text{N}$  during winter (Moulin et al., 1997), but as seen on our satellite image from early March 1998 (Fig. 1) there is substantial dust amounts in the atmosphere between  $25^\circ\text{N}$  to  $5\text{-}10^\circ\text{S}$ . Although only one to a few percent of this is organic matter (Table 1), its biogeochemical composition is important for the forming of marine sedimentation which again is used to varying extent for reconstructions of past climate history (Sarntein and Koopmann, 1980; Westerhausen et al., 1993; DeMenocal, 1995; Verardo and Ruddiman, 1996; Bird et al 1997; Bird and Cali, 1998; DeMenocal et al., 2000; Huang et al., 2000). To increase the accuracy of these kind of studies we need to confine the possible variation in the biogeochemical impacts from the dust, which is related to a source area with defined climate and vegetation.

**Table 1:** The sample weight used in the calculated values in the table is retrieved from the weight of the material added to the small GF/F filter minus a standard of 16 mg for the glass fibres from the original dust filter which was the average amount retained from clean filters treated the same way. Visual inspection under the microscope indicates that sample weights might be up to 30% overestimated in some samples, and the weight dependant values (TOC and number per mg) in the table are to be considered minimum estimates. Fossilised pollen grains were recognised by their yellow to brownish stain, whereas in 'fresh' pollen, remains of the cell protoplast might be found.

Filter	DS4*	DS6*	DS16*	DS18	DS20*	DS24
Charcoal $\text{mg}^{-1}$	1032	524	2250	245	2070	22
Fungal spores $\text{mg}^{-1}$	1.2.	6.1	8.9	81.6	2.4	5.7
Pollen $\text{mg}^{-1}$	7.8	6.9	20.3	63.7	15.4	21.0
%fresh pollen	90%	30%	98%	95%	100%	100%
%C3	63	66	73	76	87	70
%C4	33	27	14	15	8	13
TOC wt.%	0.7	0.9	2.9	1.9	1.6	2.9
$\delta^{13}\text{C}_{\text{org}}$	22.9	19.9	23.9	22.9	23.5	24.9
Gr. size distr. peak	20 $\mu\text{m}$	10 $\mu\text{m}$	16 $\mu\text{m}$	11 $\mu\text{m}$	18 $\mu\text{m}$	33 $\mu\text{m}$



**Figure 1** Above: The satellite image is a quasi true colour composition of level 1A bands 6, 5 and 1 from the second half of the M41/1 cruise period (03-10.02 1998). The black line between the dots indicates the sampling interval/track for each sample and the numbers are the sample numbers (M41/1 DS1-DS25). Vegetation and precipitation zones after White (1983) are indicated on the left: I) Tropical rain forest, 1500-4000 mm y<sup>-1</sup>, II) Transition zone, 1000-2000 mm y<sup>-1</sup>, III) Dry forest to grass savanna, 500-1500, IV) Wooded grassland to desert grassland, 100-400 mm y<sup>-1</sup>, V) Desert grassland to desert, 10-100 mm y<sup>-1</sup>, VI) Mediterranean vegetation and transition to the northern Sahara, 100-1000 mm y<sup>-1</sup>.

Below: Variation in the  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  signal and C/N ratio of the dust along the cruise transect plotted against the latitude (left) and the sample numbers are written next to the plotted value. The grain size distribution plots (right) are grouped after running numbers and presented as percental amount of particles in the different fraction from 0.4-100 $\mu\text{m}$ . The sample identity is indicated with a number with the exception of DS5-DS10 which have close to identical grain size distribution. For DS8 and DS21, no reliable grain size data were achieved.

To get more information about the dust character and indications about the source area independently from the isotopic composition the material was analysed for grain size and in light microscope additional the governing wind regimes for the sampling periods were plotted. From figure 2 we can deduce that North of Equator the dust transport was performed by the lower (Trade winds) arriving the sampling track from the African continent. The strong higher SAL/Hammatan could possibly carry particles from west (Central America) but from the satellite images it is clear that the main load of dust arrives from the African continent. At and south of the Equator both the higher and lower winds arrives from the continent. Especially in the southernmost part of our study area where the surface winds are weak the higher winds could be important and potentially carry material from east and south-east. The grain size distribution in all samples have about the same range from 0.3 to  $\sim 100\mu\text{m}$  (Fig. 1), but the peak centres vary from  $6\mu\text{m}$ , characterised as long-distance transported dust, to  $30\mu\text{m}$  defined as regional source dust in a study from West Africa by McTinish et al. (1996). We recorded well sorted fine grained material close to the West African coast (Fig. 1) where a regional source is possible and coarser material further offshore in the Guinea Basin getting finer approaching the Central African coast. A possible explanation for this is offered by comparing the charcoal content (black particles ranging in size between 20 and  $\sim 100\mu\text{m}$ ) and grain size distribution of six selected samples (Table 1). We find that the rather coarse samples DS4, DS16 and DS20 contain high amounts of charcoal fragments while the finer grained samples DS6 and DS18 contained clearly less charcoal. The wind directions indicate a change in transport direction, and thus possible source area, between 8 and 5°N from northeast to east (Fig. 2) which relates well to the change in grain size distribution towards coarser dust. To relate this to possible source areas of charcoal, the main burning biomass areas are directly to the north and south of the tropical rain forests (Andreae et al., 1994). The minimum in the

higher winds and thus transport potential, above the sampling area of DS17 and 18 might explain the fine grain size and the low charcoal content (DS18) in these samples. Furthermore, if the charcoal is mainly carried with the higher winds, the source of the charcoal in i.e. DS16 at the Equator is to the south of the equator. Shifting impacts from dust carried by higher winds from east and southeast and surface wind from east and north offer an explanation for the variable character of the dust long the Equator (Fig. 1, 2 and Table 1).

Only the samples from south of the Equator, showed equal amounts of pollen and charcoal particles (Table 1). Pollen concentrations ranged from less than 1 to 10 p\*mg<sup>-1</sup> in the filters exposed northwest of 10°N 15°W (summer dust plume) and from 15 to over 60 p\*mg<sup>-1</sup> in the filters exposed southeast of 5°N 15°W (mostly winter dust plume). A crude estimate of pollen emitted by C<sub>4</sub> plants is given by 0.5 x *Chenopodiaceae-Amaranthaceae* + *Poaceae* pollen counts (Huang et al., 2000). Applying the formula to the filter data gives values of about 30% for the area west of Mauretania and values less than 15% for samples from the Gulf of Guinea. This matches the pattern seen in modern marine sediments albeit the latter show higher 'C<sub>4</sub>-pollen' percentages (over 50 and 15%, respectively). Only in one of the filters (D6) considerable amounts of fossilised pollen (70%) were found. In the other filters almost all pollen was 'fresh', which were emitted or resuspended within the last months or years. Fossilised pollen might have originated in Holocene lake beds of the Sahel and the Sahara which are blown out during sand storms (Petit et al, 1991). Our results indicate, however, that the majority of the filtered pollen grains is not from those lake beds.

The  $\delta^{13}\text{C}$  composition of organic matter reflects the dynamics of carbon assimilation during photosynthesis and the isotopic composition of the inorganic carbon source (Hayes, 1993). Most photosynthetic plants use the C<sub>3</sub>, Calvin-Benson pathway; that discriminates against the <sup>13</sup>C isotope to cause a shift ~-20‰ compared to the source. Hence the terrestrial mean  $\delta^{13}\text{C}$  value is about -27‰ (-7‰ in atm. air)(O'Leary, 1988; Sackett, 1989) and a mean value in marine phytoplankton of -22 to -20‰ ( $\delta^{13}\text{C}$  of marine bicarbonate is ~0‰)(Sackett 1989; Meyers, 1994). The C<sub>4</sub> group of plants, which utilise the C<sub>4</sub>, Hatch-Slack pathway, is dominated by lowland grasses adapted to hot and arid conditions (Livingstone and Clayton, 1980; White, 1983), is discriminating less against the <sup>13</sup>C isotope giving a mean  $\delta^{13}\text{C}$  value of about 14‰ (O'Leary, 1988). When applying a linear regression between -14‰ (100% C<sub>4</sub> plants) and -27‰ (100% C<sub>3</sub> plants) on our measured  $\delta^{13}\text{C}$  data (Fig. 1) we find that the relative amount of organic matter from C<sub>4</sub> plants in the dust varies from over 50% between 20°N and 10°N to below 5% between 0-5°N. Although DS 12- DS20 is sampled along the Equator with prevailing surface winds directly from the East (tropical rain forest), a substantial contribution of C<sub>4</sub> plant material (20-40%) is

found. If this dust were transport by higher winds, the source area would rather be in the vegetational transition zone II South of the Equator rather than the Sahel region to the north ( compare Fig. 1 and 2). South of the Equator, close to the coast along the tropical rain forest area an almost pure C3 origin were found. An increasing C4 contribution presumably from the Kalahari and Namibian desert areas appears in the dust samples taken south of 5°S. The proportions of C3 and C4 pollen shows the same trend as the  $\delta^{13}\text{C}$  data but with a somewhat lower relative contribution from C4 plants (Table 1).

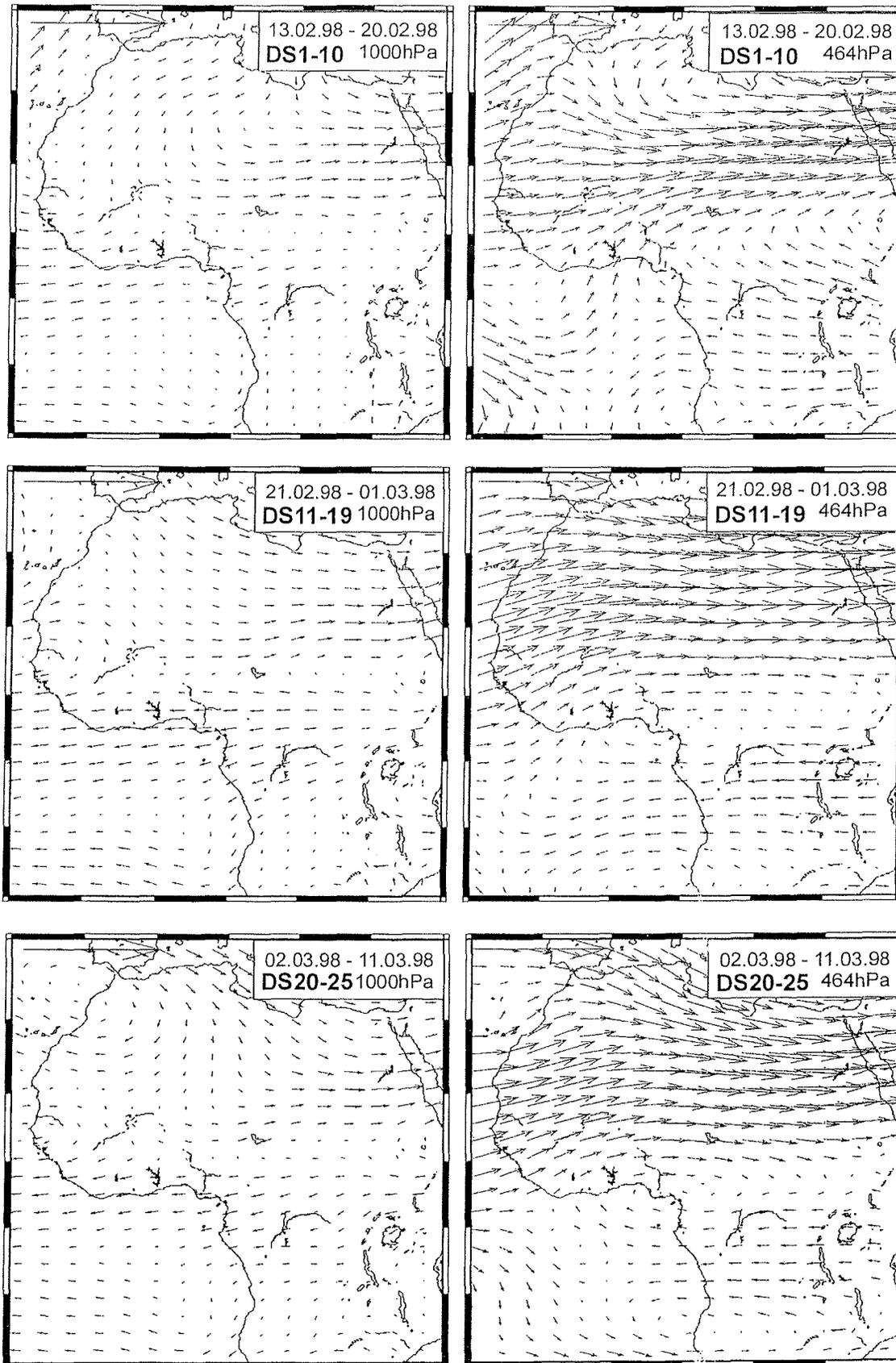
The C/N ratios and  $\delta^{15}\text{N}$  values, are not systematically different in C3 and C4 plants. Thus other compositional and/or climatic factors have to be responsible for the shift from high  $\delta^{15}\text{N}$  values and low C/N ratios outside the Sahara/Sahel region and vice versa outside the tropical areas. C/N ratios determined from elemental analyses of the organic matter in sediments have been widely used to distinguish between *in situ* algal production in marine and lacustrine environments and external input of land plants (Talbot and Johannessen, 1992; Jasper and Gagosian, 1990; Westerhausen et al., 1993; Prahl et al., 1994). The C/N ratios mainly range between 4 and 10 and in protein and lipid rich algal matter and from 20 to >200 in terrestrial organic matter which mainly consists of the nitrogen poor substances lignin and cellulose (Meyers 1994). Due to nitrogen fixing micro-organisms and carbon loss due to microbiological degradation, the terrestrial soils have a mean C/N ratio of 15 (Schlesinger, 1997). Measured C/N ratios have a mean value of 18, and range from 12-15 west of the Sahara/Sahel region to almost 30 south of the Equator demonstrating a notable shift parallel to the change in source area of the dust. A connection between particle size and C/N values in aquatic sediments is well known (Thompson and Eglington, 1978; Prahl et al., 1994; Keil et al., 1994) and is ascribed to two independent factors. More intact land plant litter in the coarser fractions leads to higher C/N ratio in coarser sediments, which is in accordance with our data (Fig. 3). This also accords well to the above mentioned connection between charcoal counts and grain size distribution. On the other hand some clay minerals, which dominate the finest fraction, are negatively charged and can thus absorb ammonium ( $\text{NH}_4^+$ ) and depress the C/N ratios. The negative correlation between the amount of clay and C/N ratio (Fig. 3) is modest but clear and this might explain the low C/N ratios in the dust compared to the terrestrial organic matter. The fine grained DS17 is the only sample that does not fit into this pattern.

The origin and the state of the nitrogen in the samples has implications for the interpretation of the  $\delta^{15}\text{N}$  data. Ammonium and nitrate in natural terrestrial systems is known to have rather low  $\delta^{15}\text{N}$  values ( $0\pm 5\text{‰}$ ) (Kendall, 1998), and this is rather problematic as the higher  $\delta^{15}\text{N}$  values occur in the finer dust outside Sahara and Sahel (Fig. 1). On the other hand, the isotopic composition of nitrate and ammonium, which are the dominant plant nutrients, is usually close to that of the total soil nitrogen (Rennie et al.,

1976), and under normal N-limiting conditions the N-isotopic fractionation during uptake in most land plants is negligible (Nadelhoffer and Fry, 1994).

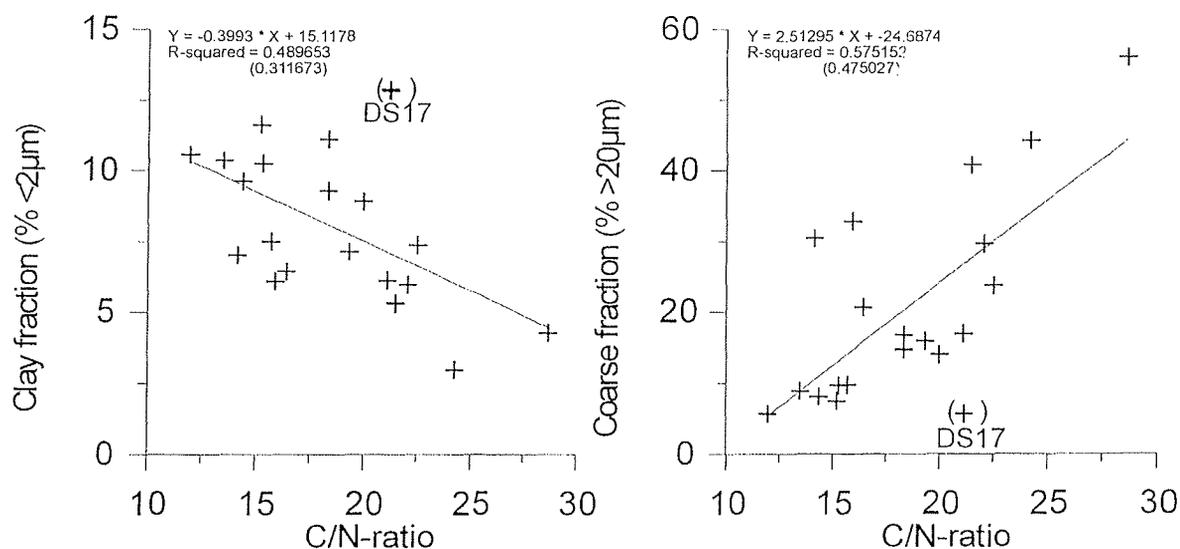
Although not very well understood, a negative correlation between precipitation and  $\delta^{15}\text{N}$  values is reported from earlier studies on a variety of soils (Shearer et al. 1978) and on vegetation in southern Africa (Heaton 1987). Our  $\delta^{15}\text{N}$  data, with 3-5‰ heavier  $\delta^{15}\text{N}$  values in the North (Sahara & Sahel) compared to the southern areas with higher rain forest impact, fits very well with the previously registered connection between continental aridity and  $\delta^{15}\text{N}$  values in soils and land plants. By applying the relation between precipitation and  $\delta^{15}\text{N}$  in terrestrial plants (0.3-0.4‰ per 100 mm  $\text{y}^{-1}$ ) suggested by Heaton (1987), our data reflect a N-S difference in precipitation along the transect of about 1000 mm  $\text{y}^{-1}$ . This is about 50% of the real precipitation difference (~2000 mm  $\text{y}^{-1}$ ) between Sahara and the tropical rain forests. However, there might be a possibility of using  $\delta^{15}\text{N}$  measurements on terrestrial plant debris and oxidation resistant carbon (OREC)(charcoal) from lacustrine,- and marine sediment as paleotracer for continental aridity.

During this short span of time that the studied samples were collected, large differences in the biogeochemical composition of the dust and thus potential impact on the marine sediments were registered. To apply this information in a paleoceanographic and paleoclimatic sense, some other considerations have to be done. The isotopic composition of the dust at the centre of the dust plume between 10 and 20°N (DS5 to DS9) is not very distinguishable from the values found in deep sea sediments, also the C/N values are close to the marine C/N values. However, Bird and Cali (1998) reported high charcoal content in a marine core downwind from the Sahara during late Holocene. These authors interpreted this as a result of human slash and burn agricultural activity because all previous periods of high charcoal content appeared during dry glacial conditions. Consequently, burning of wood in more humid areas related to human activity could produce a surplus of charcoal from C3 plants compared to the pre anthropogenic or "natural" conditions. This could increase the proportion of C3 plant remains and charcoal in the dust arriving from the Sahara and Sahel regions. Along the equatorial part of the transect, however, relatively large variations in the character and biogeochemical composition of the dust are found, and probably caused by variable contributions from source areas to the south of Equator. Considering that the wind fields were in their southernmost position (annually) during the sampling period, the dust contribution from the southern half of the African continent to the marine records in the eastern equatorial Atlantic might be important.



**Figure 2** Average wind speed for the sampled track and potential source area (40°N-20°S/20°W-40°E) during the sampling period at two different pressure levels: -1000hPa (surface) and -464hPa (5000m) representing the Trade Winds and SAL/Harmattan respectively. The upper left corner of each plot shows a standard vector for 75m/s.(Swinbank and O'Neill).

Although the higher dust loads into the Atlantic Ocean comes from the Sahara/Sahel region, the dust input from areas to the South of Equator are considerable in the eastern equatorial Atlantic. Especially in terms the biogeochemical influence the input from areas outside Sahara/Sahel are important. The dust carried by eastern and south-eastern winds are higher in organic content which are isotopically lighter (C and N) and have clearly higher C/N ratios than the marine sediments. Consequently, a change of the climate (Sarntein and Koopmann, 1980, DeMenocal et al., 2000) and vegetation zones (Dupont, 1993) in the continental source areas might be as important as the amount of dust for the biogeochemical impact on marine sediments.



**Figure 3** Relationship between the relative clay fraction against C/N ratio (left) and relative coarse fraction against C/N ratio (right). The r-squared values including the contradicting sample DS17 are presented in brackets.

## Methods

Two different dust samplers consisting of a metal roofed house with a vacuum cleaner engine sucking 1.2-2.0 m<sup>3</sup> air per min. onto filters, were running parallelly. Cellulose filters were used for inorganic samples on which the grain size analyses were performed with the laser particle sizer at the University of Utrecht. Glass fibre (200x250 mm GF/F) filters were used for organic compound and pollen samples. After sampling organic filters were wrapped in aluminium foil and stored at -20°C. In order to release the dust from the original filters, these were put in ultrasonic bath with demineralised water for 15-20 min. and carefully flushed with water. For the isotopic analysis at the laboratories at the

University of Bremen, samples were filtered onto smaller GF/F filters, and decalcified in HCL vapour closed from the atmosphere to remove  $\text{CaCO}_3$ . The filters were then combusted at  $1050^\circ\text{C}$  using a NC 2500 Elemental Analyser connected to a mass spectrometer (Finnigan MAT Delta Plus) with a ConFlo, which enable combined  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  measurements on one sample. Long term standard deviation from repeated measurements is  $<0.2\text{‰}$  for both  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$ , but due to limited sample material and low amounts of nitrogen in some samples the precision of the  $\delta^{15}\text{N}$  data is  $<1.0\text{‰}$ . Due to helium dilution of the sample  $\text{CO}_2$  gas during the combined analysis, the C/N values were calculated and corrected in accordance to the known C/N value of laboratory sediment standard. This adds to the measurement error and the total uncertainty is  $\sim 10\%$  for the C/N values.

Aliquots of the filters have been rinsed with water and examined microscopically for the content of pollen, spores and black particles. The latter probably being charcoal particles and hence named such. To concentrate the organic particles, four filter residues have been treated with HF (\* in Table 1). The others did not receive such treatment. The HF treated samples show more particles than the untreated ones containing between 500-2300 particles per mg dust (p/mg) and 20-500 p/mg, respectively. The filters were exposed between 17 Feb. 1998 and 9 March 1998. Exposure times depended on the amount of dust and varied from almost 3 to more than 20 hours (Schulz et al. 1998).

### **Acknowledgements**

We thank the officers, crew and scientists aboard R/V *Meteor* for their help during sampling recovery, and Monika Segl, Wolfgang Bevern and Albert Benthien for the assistance with the mass spectrometry analyses. We also thank Geoffrey Eglington, Yongsong Huang, Enno Schefuss and Michael Talbot for reading and commenting on an earlier version of this manuscript. The UKMO assimilation data was supplied by the Distributed Active Archive Center, NASA Goddard Space Flight Center, Greenbelt, MD, USA (<http://gcmd.gsfc.nasa.gov/>) This research was funded by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 261 at the University of Bremen, Contribution No.xxx).

## References

- Andreae, M.O., et al., 1994, Biomass Burning in the Global Environment: First results from the IGAC/BIBEX field campaign STARE/TRACE-A/SAFARI-92, in Prinn, R.G., ed.: *Global Atmospheric Biospheric Chemistry*, Plenum, New York, p. 83-101.
- Bird, M.I., and 8-others, 1995, Terrestrial vegetation change inferred from n -alkane  $\delta^{13}\text{C}$  analysis in the marine environment.: *Geochimica-et-Cosmochimica-Acta.*, v. 59, p. 2853-2857.
- Bird, M.I., and Cali, J.A., 1998, A million-year record of fire in sub-Saharan Africa: *Nature*, v. 394, p. 767-769.
- D'Almeida, G.A., 1996, A model for Saharan dust transpor: *Journal-of-Climate-and-Applied-Meteorology.*, v. 25, p. 903-916.
- DeMenocal, P.B., 1995, Plio-Pleistocene African climate.: *Science*, v. 270, p. 53-59.
- DeMenocal, P., Ortiz, J., Guilderson, T., Adkins, J., Sarnthein, M., Baker, L., and Yarusinsky, M., 2000, Abrupt onset and termination of the African Humid period: rapid climate responses to gradual insolation forcing. *Quaternary Science Reviews*, v. 19, issues 1-5, p. 347-361.
- Dupont, L., 1993, Vegetation zones in NW Africa during the Bruhnes Chron reconstructed from marine palynological data: *Quaternary Science Rev.*, v. 12, p. 189-202.
- Hayes, J.M., 1993, Factors controlling  $^{13}\text{C}$  contents of sedimentary organic compounds; principles and evidence, in Parkes, R.J., Westbroek, P., and de Leeuw, J.W., eds., *Marine sediments, burial, pore water chemistry, microbiology and diagenesis*, Volume 113: Amsterdam, Netherlands, Elsevier, p. 111-125.
- Heaton, T.H.E., 1987, The  $^{15}\text{N}/^{14}\text{N}$  ratios of plants in South Africa and Namibia: relationships to climate and coastal/saline enviroments: *Oecologia*, v. 74, p. 236-246.
- Huang, Y., Dupont, L., Sarnthein, M., Hayes, J.M., and Eglinton., 2000(in press), Mapping of  $\text{C}_4$  plant input from North West Africa into North East Atlantic sediments. *Geochimica et Cosmochimica Acta*
- Jasper, J.P., and Gagosian, R.B., 1990, The sources and deposition of organic matter in the Late Quaternary Pigmy Basin, Gulf of Mexico: *Geochimica et Cosmochimica Acta*, v. 54, p. 1117-1132.
- Keil, R.G., Tsamakis, E., Fuh, C.B., Giddings, J.C., and Hedges, J.I., 1994, Mineralogical and textural controls on the organic composition of coastal marine sediments: hydrodynamic separation using SPLITT- fractionation: *Geochimica et Cosmochimica Acta*, v. 58, p. 879-893.

- Kendall, C., 1998, Tracing Nitrogen Sources and Cycling in Catchments, *in* Kendall, C., and McDonnell, J.J., eds., *Isotope Tracers in Catchment Hydrology*: Amsterdam, Elsevier Science B V, p. 519-576.
- Livingstone, D.A., and Clayton, W.D., 1980, An altitudinal cline in tropical African grass floras and its paleoecological significance: *Quaternary Research*, v. 13, p. 392-402.
- McTainsh, G.H., Nickling, W.G., and Lynch, A.W., 1997, Dust deposition and particle size in Mali, West Africa: *Catena*, v. 29, p. 307-322.
- Meyers, P.A., 1994, Preservation of elemental and isotopic source identification of sedimentary organic matter, *in* Lee-Cindy, ed., *Chemical Geology*, Volume 114: Amsterdam, Netherlands, Elsevier, p. 289-302.
- Moulin, C., Lambert, C.E., Dulac, F., and Dayan, U., 1997, Control of atmospheric export of dust from North Africa by the North Atlantic Oscillation: *Nature*, v. 387, p. 691-694.
- Müller, P.J., 1977, C/N ratios in Pacific deep-sea sediments: Effect of inorganic ammonium and organic nitrogen compounds sorbed by clays: *Geochimica et Cosmochimica Acta*, v. 41, p. 765-776.
- Nadelhoffer, K.J., and Fry, B., 1994, Nitrogen isotope studies in forest ecosystems, *in* Lajtha, K., and Michener, R.M., eds., *Stable Isotopes in Ecology and Environmental Science*: Oxford, Blackwell Scientific Publishers, p. 22-44.
- O'Leary, M.H., 1988, Carbon isotopes in photosynthesis: *Bioscience*, v. 38, p. 328-336.
- Petit, M., 1991, *Paléoenvironnements du Sahara. Lacs holocènes a Taoudenni*: Mali, CNRS, 239 p.
- Prahl, F.G., Ertel, J.R., Goni, M.A., Sparrow, M.A., and Eversmeyer, B., 1994, Terrestrial organic carbon contributions to sediments on the Washington margin: *Geochimica et Cosmochimica Acta*, v. 58, p. 3035-3048
- Prospero, J.M., Barrett, K., Church, T., Dentener, F., Duce, R.A., Galloway, J.N., Levy, H.I., Moody, J., and Quinn, P., 1996, Atmospheric deposition of nutrients to the North Atlantic Basin: *Biogeochemistry*, v. 35/1, p. 27-73.
- Rennie, D.A., Paul, E.A., and Simmons, L.E., 1976, Natural nitrogen-15 abundance of soil and plant samples: *Canadian Journal of Soil Science*, v. 56, p. 43-50.
- Sackett, W.M., 1989, Stable carbon isotope studies on organic matter in the marine environment, *in* Fritz, P., and Fontes, J.C.; eds., *Handbook of Environmental Isotope Geochemistry*, Volume 3: Amsterdam, Netherlands, Elsevier, p. 39-169.
- Sarnstein, M., and Koopmann, B., 1980, Late Quaternary deep-sea record on Northwest African dust supply and wind circulation, *in* Sarnstein, M., Seibold, E., and Rognon, P., eds., *Sahara and surrounding seas; sediments and climatic changes; proceedings of an international symposium*: Cape Town, South Africa, Balkema., p. 239-253.

- Schlesinger, W.H., 1997, *Biogeochemistry; an analysis of global change*. 2nd ed: San Diego, CA, United States, Academic Press, 588 p.
- Schulz, H.D., and cruise participants, 1998, Report and preliminary results of Meteor Cruise M 41/1, Berrichte, Fachbereich Geowissenschaften, Universität Bremen, 112, 124p.
- Shearer, G.B., Kohl, D.H., and Chien, S.H., 1978, The nitrogen-15 abundance in a wide variety of soils: *Soil Science Society of Am. J.*, v. 42, p. 899-902.
- Swinbank, R., O'Neill, A., 1994, Stratosphere-Troposphere Data Assimilation System: *Monitoring Weather Review.*, v.122, 686-702.
- Talbot, M.R., and Johannessen, T., 1992, A high resolution palaeoclimatic record for the last 27 500 years in tropical West Africa from the carbon and nitrogen isotopic composition of lacustrine organic matter: *Earth and Planetary Science Letters*, v. 110, p. 23-37.
- Thompson, S., and Eglinton, G., 1978, The fractionation of a Recent sediment for organic geochemical analysis: *Geochimica et Cosmochimica Acta*, v. 42, p. 199-208.
- Verardo, D.J., and Ruddiman, W.F., 1996, Late Pleistocene charcoal in tropical Atlantic deep-sea sediments; climatic and geochemical significance: *Geology*, v. 24, p. 855-857.
- Wagner, T., and Dupont, L.M., 1999, Terrestrial organic matter in marine sediments: Analytical approaches and eolian-marine records in the central equatorial Atlantic, *in* Fischer, G., and Wefer, G., eds., *The use of proxies in paleoceanography: Examples from the South Atlantic*: Heidelberg, Berlin, Springer Verlag, p. 547-574.
- Westerhausen, L., Poynter, J., Eglinton, G., Erlenkeuser, H., and Sarnthein, M., 1993, Marine and terrigenous origin of organic matter in modern sediments of the equatorial East Atlantic; the  $\delta^{13}\text{C}$  and molecular record: *Deep-Sea Research. Part I: Oceanographic Research Papers*, v. 40, p. 1087-112.
- White, F., 1983, *The Vegetation of Africa*: Paris, *in* *Natural resources research*, 20. Unesco.

### 7.3 Manuscript 3:

#### *Seasonal variability of $\delta^{15}\text{N}$ in sinking particles in the Benguela upwelling region*

Abstract .....	71
1. Introduction .....	72
2. Study area .....	72
3. Methods .....	74
4. Results .....	75
5. Discussion .....	78
5.1. Temporal variations in the composition of the flux ....	81
5.2. Diagenetic alteration .....	84
5.3. Estimation of nitrate utilization in surface waters .....	85
6. Conclusion .....	90
Acknowledgements .....	91
References .....	92

## Seasonal variability of $\delta^{15}\text{N}$ in sinking particles in the Benguela upwelling region

M. E. Holmes, G. Lavik, G. Fischer, M. Segl, G. Ruhland, and G. Wefer

*All authors at: FB Geowissenschaften, Universität Bremen, Klagenfurter Strasse, 28359 Bremen*

Submitted to Deep-Sea Research

### Abstract

Temporal changes in  $\delta^{15}\text{N}$  values of sinking particles collected with sediment traps in the Benguela upwelling regime off southwest Africa mirrored variations in the input of inorganic nitrogen to the surface water. Reductions in  $\delta^{15}\text{N}$  (to 2.5‰) corresponded to low sea surface temperatures during austral spring and late autumn/early winter, indicating increased nitrate availability due to the presence of recently upwelled water. High particulate fluxes accompanied the low  $\delta^{15}\text{N}$  values and sea surface temperatures, reflecting increased productivity fueled by the upwelled nutrients. High  $\delta^{15}\text{N}$  values (up to 13.5‰) coincided with high sea surface temperatures and low particle flux rates. Satellite images of ocean chlorophyll show that productivity variations coincide with  $\delta^{15}\text{N}$  changes. The observed isotopic pattern does not appear to have been caused by variations in the species composition of the phytoplankton assemblage. Calculations based on  $\delta^{15}\text{N}$  of the sinking particulate nitrogen show that the surface nitrate pool was more depleted during late summer/early fall and mid-winter and less depleted during the intense spring bloom as well as in late fall.

## 1. Introduction

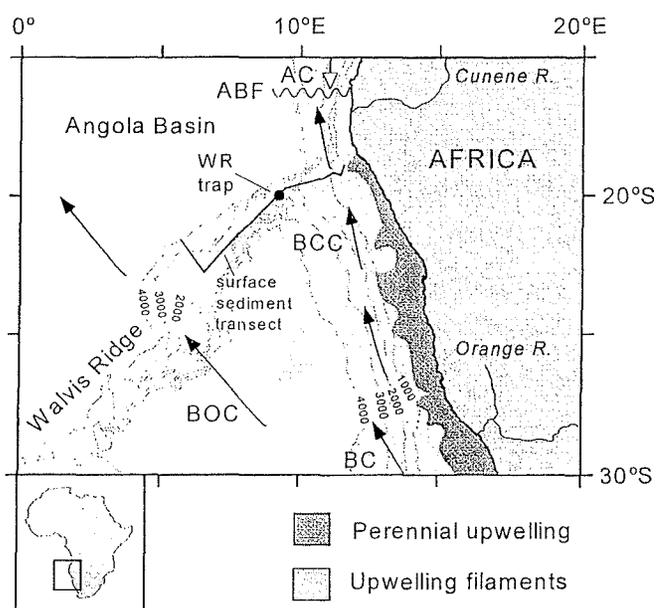
The degree of nutrient utilization in surface waters of the ocean has important implications for primary productivity and CO<sub>2</sub> dynamics in the euphotic zone. Better understanding of seasonal changes in nutrient utilization in productive regions of the ocean will be helpful in evaluating the contribution by such areas to the global carbon inventory. The  $\delta^{15}\text{N}$  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 (Wada, 1980; Altabet et al., 1991). Nitrate is believed to be the limiting nutrient for phytoplankton growth in the Benguela region (Chapman and Shannon, 1985 and references therein). When nitrate in the euphotic zone is abundant, the  $\delta^{15}\text{N}$  of the plankton is low relative to the  $\delta^{15}\text{N}$  of the nitrate due to the preferential uptake of nitrate containing the lighter isotope ( $^{14}\text{N}$ ) (Wada and Hattori, 1978). As nitrate is consumed, the residual nitrate becomes progressively enriched in  $^{15}\text{N}$ . Phytoplankton  $\delta^{15}\text{N}$  also increases as it takes up this residual nitrate. Montoya and McCarthy (1995) investigated isotope fractionation during nitrate uptake by plankton grown in laboratory cultures and it has been shown that the  $\delta^{15}\text{N}$  composition of particulate nitrogen (PN) mirrors nitrate concentrations in surface water over the course of a phytoplankton bloom, with high nitrate concentrations corresponding to low  $\delta^{15}\text{N}_{\text{POM}}$  and vice versa (Nakatsuka et al., 1992). Several authors (including Miyake and Wada (1967), Altabet and McCarthy (1985) and Voss et al. (1996)) have also reported an inverse relationship between photic zone nutrient concentrations and  $\delta^{15}\text{N}$  of suspended and sinking particles. The transfer and preservation of the  $\delta^{15}\text{N}$  signal from the surface water to the sediments makes nitrogen isotopic ratios a valuable tool in paleoceanographic studies (c.f. Farrell et al., 1995; Francois et al., 1992; Nakatsuka et al., 1995, Francois et al., 1997, Holmes et al., 1997 and Kienast, 2000).

The purpose of the present paper is to show that the  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  in sinking particles may be useful in estimating the degree of utilization of nitrate in the euphotic zone.

## 2. 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). A comprehensive review of the Benguela area was written by Shannon and Nelson (1996).



**Figure 1** Map of the study area off the southwest coast of Africa. The sediment trap mooring WR is denoted by the filled circle and the sediment transect used for calculating  $\epsilon$  is also shown. The location of perennial upwelling is represented by the darkly shaded area and the filamentous mixing zone is indicated by the lightly shaded region. The filaments are transient and are not always present near the trap area. The position of the upwelling filaments was redrawn from an infra-red satellite image (METEOSAT) taken in August 1984 and presented in Lutjeharms and Stockton (1987). Black arrows represent cold surface currents and the white arrow indicates 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.

The BC diverges at near 28°S and the main branch, the Benguela Oceanic Current (BOC), continues to the northwest (Peterson and 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 and Hutchings, 1983). Like most eastern boundary systems, the Benguela is characterized by intense coastal upwelling. Southeasterly tradewinds force surface water seaward (Lutjeharms and Meeuwis, 1987) and relatively nutrient-rich ( $10 - 18 \mu\text{M NO}_3^-$ ) South Atlantic Central Water (SACW) from 150-250 m depth comes to the surface off the coast (Calvert and Price, 1971; Jones, 1971). This upwelling supports rates of productivity between  $125$  and  $>300 \text{ g C m}^{-2} \text{ yr}^{-1}$  (Shannon et al., 1987, Fischer et al., 2000). 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 and Meeuwis, 1987; Lutjeharms et al., 1991). The WR sediment trap was not located within the

area where upwelling is permanent, but further seaward in the region where filaments sometimes occur. 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 and Meeuwis, 1987). During parts of the year, especially summer, upwelling filaments are not detectable near the WR mooring. Figure 1 shows an upwelling filament that was redrawn from a 1984 satellite picture. We do not have satellite data during the WR trap deployment. Although the position of the filaments during 1989 - 1991 was likely not exactly as in 1984, similar seaward extension of filaments has been observed during several years (Shannon and Nelson, 1996; Antoine et al., 1996) and there is no evidence that 1989 - 1991 were anomalous in this regard.

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 interannually 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 and 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).

### 3. Methods

Sediment trap samples (representing 12 and 18 day intervals) were collected over a nearly three year period from 18 March 1989 to 17 December 1991. The sediment trap mooring (WR2: March 1989 - March 1990; WR3: March 1990 - April 1991; WR4: April 1991 - December 1991) 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 and Fischer, 1993). The cone-shaped traps (SMT 230; Salzgitter Electronics, Kiel) had 0.5 m<sup>2</sup> collecting areas and were attached to a moored array 599 m and 1648 m below the surface. Because of a trap malfunction, there is a gap in samples from the lower trap between August 1989 and March 1990. In addition, for the upper trap, only samples from March 1989 to March 1990 are presented here, due to a paucity of collected material after March 1990. HgCl<sub>2</sub> was used as preservative in sample bottles and swimmers were removed. The procedures for sample processing were described by Fischer and Wefer (1991). For  $\delta^{15}\text{N}$  measurements of WR2 samples (upper and lower traps), fractions of trap samples were filtered onto precombusted GF/F filters, dried in a drying oven at 50°C overnight and placed in tin

boats.  $\delta^{15}\text{N}$  for WR3 and WR4 were measured on homogenized, freeze-dried material. We found no systematic offset in  $\delta^{15}\text{N}$  between identical samples prepared by the two different methods. WR2-upper samples were combusted at 1050°C in a Hereaus Elemental Analyzer and the  $^{15}\text{N}/^{14}\text{N}$  ratios of the  $\text{N}_2$  gas thus formed was measured using a Finnigan MAT 252 mass spectrometer with trapping box (Fry et al., 1992). Samples from the lower trap (WR2-lower, WR3 and WR4) were measured using a Finnigan MAT Delta Plus mass spectrometer after being combusted at 1050°C in a NC 2500 Elemental Analyzer (CE Instruments).

Isotopic data are presented in permil (‰) in terms of  $\delta$  notation:

$$\delta^{15}\text{N} = \left[ \left( \frac{^{15}\text{N}/^{14}\text{N}_{\text{sample}}}{^{15}\text{N}/^{14}\text{N}_{\text{standard}}} \right) - 1 \right] \times 10^3,$$

$\delta$  values are reported relative to atmospheric air. 99.996% pure tank  $\text{N}_2$  was used as a laboratory working standard gas. The tank  $\text{N}_2$  was calibrated against nitrogen in air and IAEA standards N-1 and N-2. The analytical precision for  $\delta^{15}\text{N}$  sample measurements was  $\leq 0.4\text{‰}$  for WR2-upper and  $\leq 0.2\text{‰}$  for WR2-lower, WR3 and WR4.

Wefer and Fischer (1993) and Fischer and Wefer (1996) reported the fluxes of total particulate, organic carbon, carbonate, biogenic opal and lithogenic components of the WR samples. Diatom and silicoflagellate fluxes were presented by Treppke et al. (1996). SSTs were calculated from samples from the trap at 599 m (Treppke et al., 1996) based on concentrations of di- and tri-unsaturated  $\text{C}_{37}$  alkenones ( $U_{37}^k$  index; Brassel et al., 1986), using the calibration derived by Prahl et al. (1988). SSTs for the lower trap are weekly SSTs blended from ship, buoy and bias-corrected satellite data at 18.5°S, 11.5°E (Reynolds and Smith, 1994).

#### 4. Results

$\delta^{15}\text{N}$  values are listed in Table 1 along with C/N ratios and fluxes of total particulate, organic matter, carbonate, biogenic opal and lithogenic components. The total particulate flux in the upper trap ranged from 12 to 384  $\text{mg m}^{-2} \text{day}^{-1}$  and in the lower trap was between 4 and 341  $\text{mg m}^{-2} \text{day}^{-1}$ . The total flux maxima coincided with peaks in organic material, carbonate, opal and lithogenic fluxes (Table 1). In both traps, the flux consisted mostly of biogenic components, especially carbonate (which was 63.3% and 54.3% of the total flux for the year in the upper and lower traps, respectively). According to Čepek (1994), most of the carbonate material in the trap at 599 m derived from coccolithophorids. Organic matter was the second most predominant component, contributing an average 20% to the total flux at both depths. Marine diatoms were the main contributors of opal

(Treppke et al., 1996), which was 8.3% (599 m) and 12.1 % (1648 m) of the total flux during the study period. Lithogenic material was present only in minor amounts and was 7.8% (599 m) and 13.2% (1648 m) of the total flux.

In,  $\delta^{15}\text{N}$ , total flux rates and sea surface temperatures (SSTs) are shown.  $\delta^{15}\text{N}$  ranged from 2.9 to 8.2‰ in the upper trap while in the lower trap a larger range (2.5 to 13.5‰) was measured. Lowest  $\delta^{15}\text{N}$  values occurred in September - December (austral spring). Total flux rates were between 12.0 and 384.4  $\text{mg m}^{-2} \text{d}^{-1}$  in the upper trap and 3.6 - 340.7  $\text{mg m}^{-2} \text{d}^{-1}$  at 1648 m. Flux maxima were observed in late austral fall (June/July) and spring (September - November).  $U_{37}^k$  SSTs were lowest in austral spring (14.6°C) and highest during fall (up to 23.6°C). The ship, buoy and satellite SSTs ranged from 21.2 - 22.8°C during austral summer/fall and 14.8 - 15.7°C during late winter.

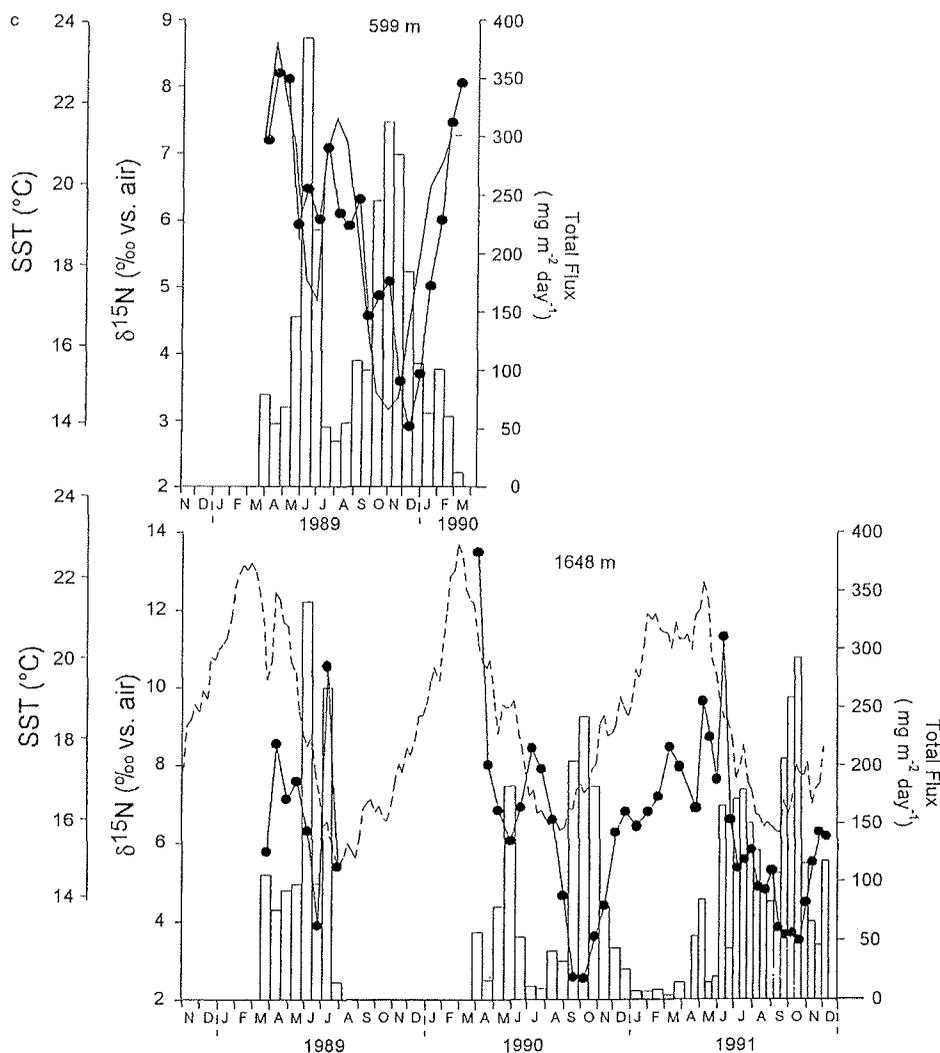
**Table 1**  $\delta^{15}\text{N}$  ( $\pm 0.4$ ), total particle, organic carbon, opal,  $\text{CaCO}_3$  and lithogenic material fluxes and C/N ratios in samples from sediment traps WR-2, 3 and 4 over the Walvis Ridge. Flux data and C/N ratios are from Wefer and Fischer (1993) and Fischer and Wefer (1996).

Sample no.	Collection Time	$\delta^{15}\text{N}$ (‰)	C/N atom	Fluxes ( $\text{mg m}^{-2}\text{day}^{-1}$ )				
				Total	OM	CaCO	Opal	Lithogenic
upper								
1	18.03.89-05.04.89	7.2	9.7	79.1	24.21	37.5	6.8	10.6
2	05.04.89-23.04.89	8.2	8.2	54.2	12.26	35.6	1.7	4.7
3	23.04.89-11.05.89	8.1	7.7	68.7	10.76	56.9	3.6	0.0
4	11.05.89-29.05.89	6.0	9.0	145.8	37.50	76.7	12.8	18.8
5	29.05.89-16.06.89	6.5	8.3	384.4	95.49	205.1	46.9	36.9
6	16.06.89-04.07.89	6.0	9.2	220.0	43.17	123.6	23.4	30.3
7	04.07.89-22.07.89	7.2	6.7	51.3	8.04	38.6	1.4	3.3
8	22.07.89-09.08.89	6.1	6.7	38.9	5.90	30.2	1.0	1.8
9	09.08.89-27.08.89	5.9	6.5	54.9	10.19	38.7	2.5	3.5
10	27.08.89-14.09.89	6.3	6.8	108.0	19.65	78.9	5.4	4.1
11	14.09.89-02.10.89	4.5	6.8	99.8	14.77	80.2	7.3	0.0
12	02.10.89-20.10.89	4.9	7.4	245.1	43.23	159.2	30.0	12.7
13	20.10.89-07.11.89	5.1	7.5	312.0	76.93	180.9	36.7	17.5
14	07.11.89-25.11.89	3.6	8.1	284.2	60.34	162.0	21.9	40.0
15	25.11.89-13.12.89	2.9	6.9	184.4	29.07	140.2	9.6	5.6
16	13.12.89-31.12.89	3.7	6.9	105.6	18.19	78.2	4.9	4.3
17	31.12.89-18.01.90	5.1	7.1	63.1	10.32	48.0	1.7	3.0
18	18.01.90-05.02.90	6.0	8.1	100.7	17.58	75.8	2.6	4.7
19	05.02.90-23.02.90	7.5	8.6	60.4	14.46	38.1	1.7	6.2
20	23.02.90-13.03.90	8.1	6.5	12.0	3.07	8.6	0.2	0.1

Sample no.	Collection Time	$\delta^{15}\text{N}$ (‰)	C/N atom	Fluxes ( $\text{mg m}^{-2}\text{day}^{-1}$ )				
				Total	OM	CaCO	Opal	Lithogenic
lower								
1	18.03.89 -05.04.89	5.8	8.4	105.8	23.38	60.9	8.5	13.0
2	05.04.89 -23.04.89	8.5	7.1	76.2	16.72	50.8	3.3	5.4
3	23.04.89 -11.05.89	7.1	8.7	92.7	11.97	69.6	4.1	7.0
4	11.05.89 -29.05.89	7.6	8.0	98.0	34.47	53.9	5.9	3.7
5	29.05.89 -16.06.89	6.3	8.1	340.7	66.23	238.3	33.7	2.5
6	16.06.89 -04.07.89	3.9	8.8	98.4	25.04	46.4	17.1	9.9
7	04.07.89 -22.07.89	10.6	7.9	266.4	90.00	137.9	31.4	7.2
8	22.07.89 -09.08.89	5.4	6.2	14.4	3.06	9.0	0.7	1.8
21	25.03.90 -13.04.90	13.5	6.2	56.8	58.11	26.8	0.7	0.0
22	13.04.90 -02.05.90	8.0	7.5	16.3	5.34	8.5	0.9	1.5
23	02.05.90 -21.05.90	6.8	8.9	78.8	22.49	33.5	9.8	13.0
24	21.05.90 -09.06.90	6.1	8.9	182.0	50.33	68.3	31.1	32.3
25	09.06.90 -28.06.90	6.9	8.1	52.7	9.57	36.8	4.7	1.6
26	28.06.90 -17.07.90	8.4	8.1	11.1	2.13			
27	17.07.90 -05.08.90	7.9	10.4	9.2	1.60			
28	05.08.90 -24.08.90	6.6	8.3	40.9	9.19	24.4	2.6	4.8
29	24.08.90 -12.09.90	4.6	8.1	32.4	6.44	21.5		
30	12.09.90 -01.10.90	2.6	8.9	203.6	45.11	110.9	22.6	25.0
31	01.10.90 -20.10.90	2.5	9.0	241.6	43.59	140.2	28.0	29.8
32	20.10.90 -08.11.90	3.6	9.6	182.2	22.57	110.7	30.4	18.6
33	08.11.90 -27.11.90	4.4	9.3	78.9	9.66	45.4	11.8	12.0
34	27.11.90 -16.12.90	6.3	8.6	43.8	6.29	29.0	5.6	3.0
35	16.12.90 -04.01.91	6.8	5.9	26.0	3.08	21.0		
36	04.01.91 -23.01.91	6.4	10.4	7.2	1.06			
37	23.01.91 -11.02.91	6.8	5.3	6.8	0.80			
38	11.02.91 -02.03.91	7.2		8.5				
39	02.03.91 -21.03.91	8.5		3.6				
40	21.03.91 -09.04.91	8.0	9.1	14.0	3.36			
41	21.04.91 -03.05.91	6.9	5.5	53.7	6.48	40.4	5.4	1.4
42	03.05.91 -15.05.91	9.6	7.2	84.2	21.08	25.7	8.0	29.4
43	15.05.91 -27.05.91	8.7	6.5	14.4	3.00	8.2	0.6	2.6
44	27.05.91 -08.06.91	7.6	7.4	19.1	3.26	11.9	0.8	3.2
45	08.06.91 -20.06.91	11.3	5.5	165.1	90.10	55.1	6.4	13.5
46	20.06.91 -02.07.91	6.6	6.8	43.0	10.02	20.0	2.0	10.9
47	02.07.91 -14.07.91	5.3	8.1	171.3	30.26	77.7	24.5	38.9
48	14.07.91 -26.07.91	5.6	7.7	179.1	23.53	109.7	18.5	27.5
49	26.07.91 -07.08.91	5.8	6.9	150.4	14.72	107.3	7.2	21.2
50	07.08.91 -19.08.91	4.8	8.2	126.9	14.38	73.5	18.7	20.4
51	19.08.91 -31.08.91	4.8	8.8	90.4	10.86	48.0	13.2	18.3
52	31.08.91 -12.09.91	5.3	5.2	82.6	9.17	76.8	10.7	0.0
53	12.09.91 -24.09.91	3.8	9.7	107.0	16.35	46.5	14.1	30.0
54	24.09.91 -06.10.91	3.6	7.0	205.8	24.25	105.0	39.9	36.6
55	06.10.91 -18.10.91	3.7	7.8	258.5	37.18	96.1	65.1	60.0
56	18.10.91 -30.10.91	3.5	7.5	292.8	45.04	121.9	60.0	65.9
57	30.10.91 -11.11.91	4.5	10.9	115.4	19.69	31.9	17.3	46.5
58	11.11.91 -23.11.91	5.5	4.8	66.1	9.01	55.8	8.6	0.0
59	23.11.91 -05.12.91	6.3	6.6	46.2	3.39	35.6	2.5	4.7
60	05.12.91 -17.12.91	6.2	6.1	117.5	4.12	103.0	2.5	8.0

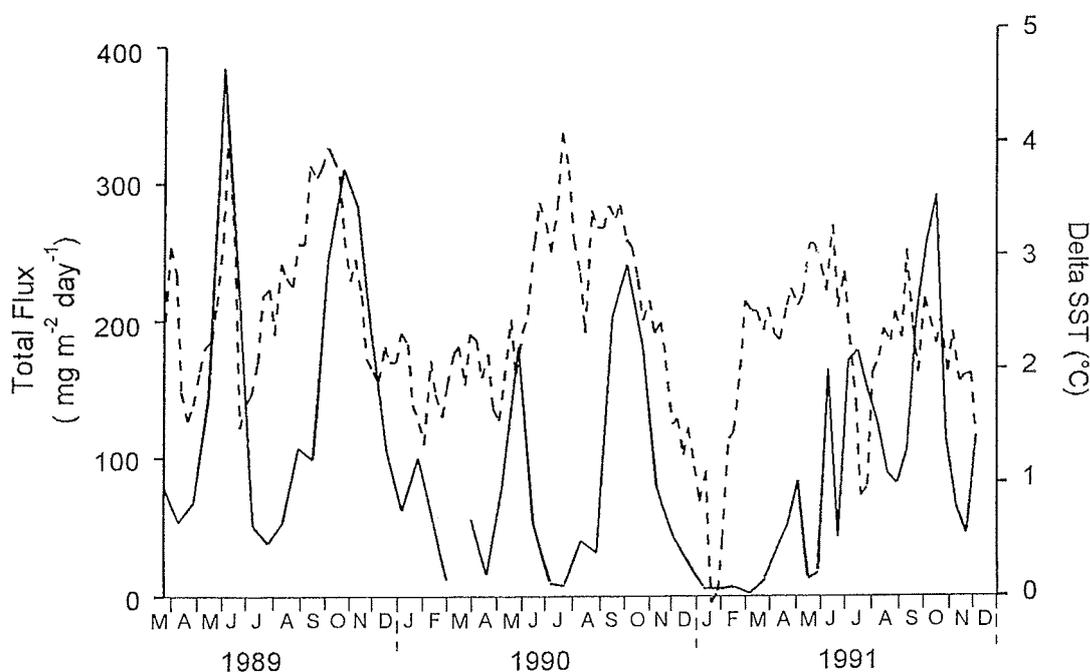
## 5. Discussion

The total flux rate exhibits a clear bimodal pattern, with 2 maxima per year (fall and spring). The  $U_{37}^k$  SST reflects this bimodality, but the ship, buoy and satellite at 18.5°S, 11.5°E do not as clearly show two maxima and minima per year (Fig. 2). Fischer *et al.* (2000), however, reported that satellite-derived primary production estimates (from Antoine *et al.*, 1996) showed two periods of increased primary productivity (in March and November) when upwelling filaments extended seaward to the WR trap position. They surmised that the material collected in the WR traps originated from the east and northeast of the trap position.



**Figure 2**  $\delta^{15}\text{N}$  (‰) values (circles and solid line), SST for upper trap calculated from the  $U_{37}^k$  index (solid line) using the calibration derived by Prah *et al.* (1988):  $\text{SST} = U_{37}^k - 0.039 / 0.034$  (Treppe *et al.*, 1996), SST for lower trap (weekly temperatures blended from ship, buoy and bias-corrected satellite data at 18.5°S, 11.5°E (Reynolds and Smith, 1994)) (dashed line), and total flux (bars) in  $\text{mg m}^{-2} \text{day}^{-1}$  (Wefer and Fischer, 1993; Fischer and Wefer, 1996) from March 1989 to December 1991 at site WR.

Meridional wind stress also peaks twice yearly (up to  $>0.8$  dynes  $\text{cm}^{-2}$ ) off the coast between  $16$  and  $18^\circ\text{S}$  during fall and spring (Shannon and Nelson, 1996). We examined weekly SST data in several sectors of the Benguela region and could not detect anywhere a clear bimodal pattern from 1989 - 1991. SST in several  $1^\circ$  sectors east and northeast of the trap showed a similar pattern to the  $U_{37}^k$  SST for the same period (except for the clear bimodality). SST at  $18.5^\circ\text{S}$ ,  $11.5^\circ\text{E}$  (to the northeast of the WR trap) was most similar in absolute values to the  $U_{37}^k$  SST for the same period and the temperatures from this position were therefore used in this study for comparison to the trap data. A small increase in SST during April/May of 1989 and 1990 and June of 1991 indicates that there is a bimodal pattern, but that it is likely masked by the seasonal drop in temperature. To eliminate the seasonality in SST, we subtracted SST at  $18.5^\circ\text{S}$ ,  $11.5^\circ\text{E}$  (where seasonal variations are combined with changes in upwelling and seaward extension of upwelling filaments) from SST at  $18.5^\circ\text{S}$ ,  $4.5^\circ\text{E}$  (where seasonal variations should be predominant). This brought out the bimodality in SST at  $18.5^\circ\text{S}$ ,  $11.5^\circ\text{E}$  and the correspondence between peaks in the delta SST with particle flux rates is apparent (Fig. 3).



**Figure 3**  $\delta^{15}\text{N}$  (‰) values of sinking particulate matter versus sea surface temperature.  $U_{37}^k$  sea surface temperatures were used for the upper trap (open circles, solid line;  $r^2$  for the regression is .59) and blended fields from Reynolds and Smith (1994) for the lower trap (closed circles, dashed line;  $r^2 = 0.53$ ).

In both traps, total flux and  $\delta^{15}\text{N}$  variations coincide, with lowest  $\delta^{15}\text{N}$  occurring in spring and highest in fall. In the upper trap,  $\delta^{15}\text{N}$  values and flux rates are nearly in sync

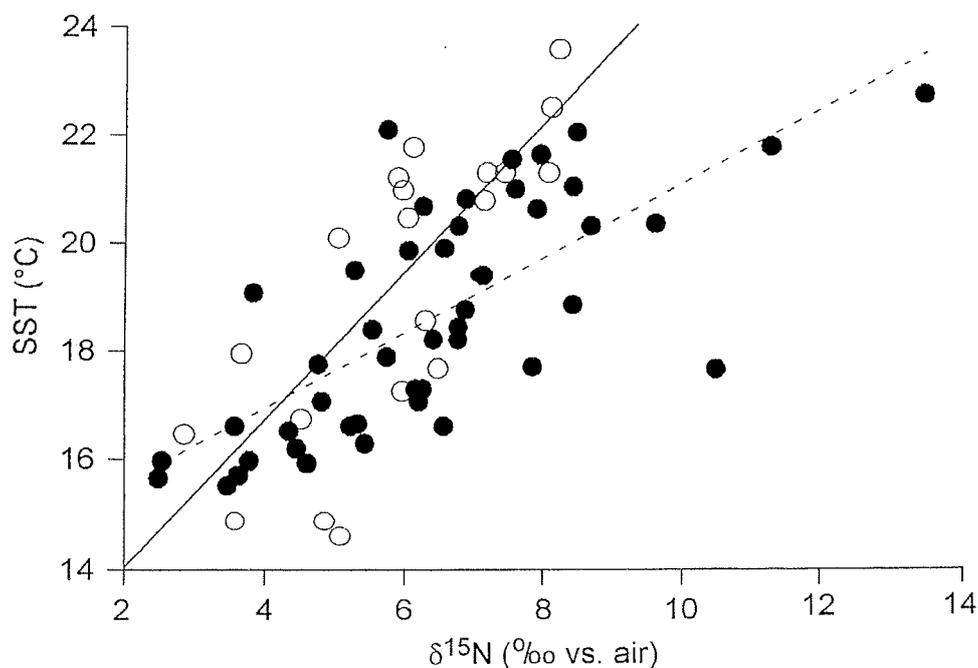
with SST variations because the SST calculated is that recorded when the particles were in surface water. One apparent discrepancy between isotopic values and temperature and flux rates in October - December.  $\delta^{15}\text{N}$  in the 3 samples from October to December preceding the  $\delta^{15}\text{N}$  minimum in December were elevated relative to what would be expected in view of the high flux rates and the decrease in SST. The cause of the higher than expected isotopic values is unclear, but possible explanations are the uptake of  $^{15}\text{N}$ -enriched nitrate during photosynthesis, a reduction in fractionation during nitrate incorporation into plankton, or a temporary change in trophic structure. In the lower trap, SST maxima and minima precede  $\delta^{15}\text{N}$  and flux maxima and minima by about 5 weeks. This lag is due to the time required for particles to sink out of the euphotic zone to the trap. The following discussion takes this lag into account and the time difference will not be referred to each time SST in the deep trap is mentioned.

Decreases in SST were apparent during the major upwelling period in spring, when the lowest values (14 - 16°C) occurred.  $\delta^{15}\text{N}$  minima were attained during spring upwelling (2.9‰ in 1989 in the upper trap (values for lower trap are missing), 2.5‰ in 1990 and 3.5‰ in 1991). A similar, though not so pronounced, pattern occurred in the fall, when a  $\delta^{15}\text{N}$  decrease from 8.2 to 6.0‰ in the shallow trap from April to May was accompanied by a temperature drop from 23.6°C to 17.3°C. Comparable declines can be seen in the lower trap. From April to June 1989,  $\delta^{15}\text{N}$  went from 8.5 to 3.9‰ and  $\delta^{15}\text{N}$  dropped from 13.5 to 6.1‰ between April and May 1990. In 1991, 2 minor  $\delta^{15}\text{N}$  decreases were observed. From March to April,  $\delta^{15}\text{N}$  went from 8.5 to 6.7‰ and from May to early June, isotopic values declined from 9.6 to 7.6‰. The cause of the isotopic and other biogeochemical variations were upwelling-favorable winds off the Namibian coast which peak in late winter/early spring and again in fall (Servain et al., 1985). The strong winds can result in the seaward extension of upwelling filaments to the waters over the sediment trap mooring (Fischer et al., 2000), as seen by the dropping SSTs. 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 ( $^{14}\text{N}$ ) was enhanced and the  $\delta^{15}\text{N}$  of the particulate 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.

Highest  $\delta^{15}\text{N}$  usually occurred in the fall of each year (April /May in 1989, March/April in 1990 and March - June in 1991). This is also when maximal SST and low total flux rates were observed. A second warm period in July/August is evident from the  $U_{37}^k$  SST. This corresponds to a small increase in  $\delta^{15}\text{N}$  from 6.0‰ in June to 7.2‰ in July. SST from ship,

buoy and satellite data rises at around the same time as the  $U_{37}^k$  SST (April 1989, May/June 1990 and July 1991), but the change is less pronounced. The warm temperatures in April 1989 were reflected by a  $\delta^{15}\text{N}$  increase from 3.9‰ in June to 10.6‰ in July. The warming seen in May/June 1990 was followed by an elevation in  $\delta^{15}\text{N}$  from 6.1‰ in June to 8.4‰ in July and the brief rise in SST in July 1991 preceded a small  $\delta^{15}\text{N}$  increase from 4.8‰ in August to 5.3‰ in September.

The close correlation between  $\delta^{15}\text{N}$  and SST seen in Figure 2 is confirmed by the regression between these two parameters shown in Figure 4. SSTs were shifted ahead by 35 days for the regression to compensate for the lag between the time of particle formation in surface water and its sinking to the depth of the trap. The significant  $r^2$  of 0.59 for the upper trap  $\delta^{15}\text{N}$  and  $U_{37}^k$  SST ( $n=20$ ) and  $r^2$  of 0.53 ( $n=48$ ) for  $\delta^{15}\text{N}$  and SST (blended fields) demonstrates the dependence of  $\delta^{15}\text{N}$  in sinking particles in this part of the Benguela region on the input of nitrate into the photic zone.

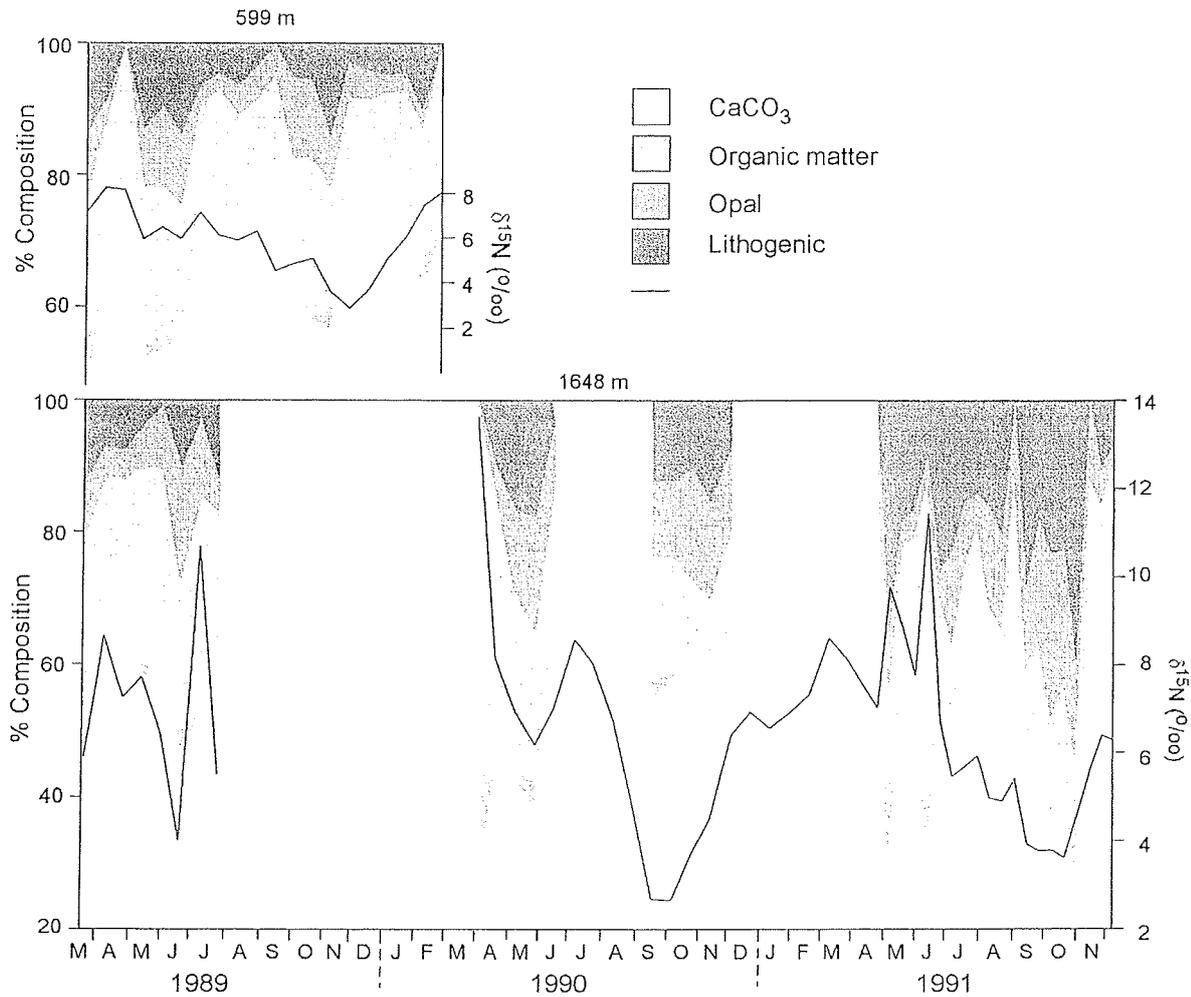


**Figure 4** Delta SST variations at 18.5°S, 11.5°E without seasonal influence (SST at 18.5°S, 4.5°E less SST at 18.5°S, 11.5°E) and total particle flux.

### 5.1 Temporal variations in the composition of the flux

Although the correlation between  $\delta^{15}\text{N}$ , SST and flux rates is strong evidence that surface nitrate concentration is the most important control on  $\delta^{15}\text{N}$  of sinking particles, we examined relative differences in the fluxes in order to determine whether changes in the

bulk species composition of the material reaching the trap could have significantly influenced the observed variations in  $\delta^{15}\text{N}$ . 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  $\delta^{15}\text{N}$  of the produced organic matter because different species may fractionate nitrogen isotopes to varying degrees. 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 the particle flux components are shown in order to compare how the relative contributions of carbonate, organic matter, opal and lithogenic material varied during the year.  $\text{CaCO}_3$  was the dominant component in the trap samples all year (31% to 88%). Organic matter was the second most predominant constituent, ranging from 4% to 68%. Opal and lithogenic material made minor contributions to the total flux (1% -25% and 0% - 40%, respectively). Regression analyses were performed between  $\delta^{15}\text{N}$  and each flux component and C/N ratios and showed no relationship between  $\delta^{15}\text{N}$  and any of the other parameters. An increase in the number of zooplankton in the plankton population could elevate the  $\delta^{15}\text{N}$  of the sinking organic matter due to the enrichment in  $^{15}\text{N}$  associated with higher trophic levels. Unfortunately it is impossible to distinguish the proportions of auto- and heterotrophic organisms based on the available flux data. Nevertheless, the absence of any clear change in the ratios of the fluxes in relation to  $\delta^{15}\text{N}$  variations is taken as evidence that changes in the bulk composition of the particulate flux did not noticeably affect  $\delta^{15}\text{N}$  values of the particles. More support for this idea comes from the observation that where nitrate concentrations are high, food chains tend to have fewer trophic steps (Biggs et al., 1989; Wu et al., 1997). Analyses of species-specific biomarkers further support our assumption that changes in the bulk composition of the sinking particles were not the cause of the  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  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  $\delta^{15}\text{N}$  fluctuations.



**Figure 5** Composition of sediment trap material in percentage values with  $\delta^{15}\text{N}$  (solid line) for comparison.

Changes in the amount of terrestrial material in particles sinking to the trap could also affect  $\delta^{15}\text{N}$  of these particles. In some areas, terrigenous material has been shown to be depleted in  $^{15}\text{N}$  relative to that of marine origin (Sweeney and Kaplan, 1980; Wada et al., 1987), although in other regions, terrestrially derived organic matter shows no clear divergence from typical marine values (Holmes et al., 1996). Dust from southern Africa, with a nitrogen isotope value of around 5‰, is not very different from nearshore marine values (Manuscript 2). 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. Low concentrations of lithogenic material in the trap samples and low C/N (average  $7.6 \pm 1.0$ ) ratios indicate that the organic matter was predominantly of marine origin. Further, the relative uniformity of the amount 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.

### 5.2 Diagenetic alteration

Holmes et al. (1998) found that surface sediments underlying the sediment trap WR exhibited a  $\delta^{15}\text{N}$  value of 7.1‰. The nitrogen flux-weighted mean  $\delta^{15}\text{N}$  of the upper trap samples was 5.5‰, yielding a difference between sinking particles at 599 m and sediment of +1.6‰. At the deeper trap, the flux weighted mean was 7.2‰, almost indistinguishable from the surface sediments. These results are in line with the findings that in general, degradation of organic matter during sinking and settling on the sea floor results in an increase in  $\delta^{15}\text{N}$  (Saino and Hattori, 1980; Altabet and McCarthy, 1985). In contrast, Libes and Deuser (1988), Fry et al. (1991) and Voss et al. (1997) reported light  $\delta^{15}\text{N}$  in organic matter from anoxic deep waters and proposed that the low isotopic values were due to the presence of high proportions of bacterial biomass. This paradox may be partly explained by laboratory experiments that suggest that fractionation by bacteria during uptake of dissolved inorganic nitrogen in anoxic waters may result in decreases in  $\delta^{15}\text{N}$  with depth. However, Altabet et al., (1991) and Nakatsuka et al. (1997) measured decreasing  $\delta^{15}\text{N}$  with depth in sinking particles where anoxia was not apparent. These authors attributed the observed variations, in part, to preferential degradation of  $^{15}\text{N}$ -rich compounds. Nitrogen isotopic ratios in the few sampling periods from which data from both traps are available do not show any systematic offset between the shallow and deeper depths, but meaningful comparisons are not possible due to the gaps in the data. In any case, the overall increase in  $\delta^{15}\text{N}$  with depth observed in our study suggests that the effect of any  $^{14}\text{N}$ -enrichment in the sinking particles that may have occurred was outweighed by removal of light nitrogen during “normal” degradation processes.

According to Francois et al. (1997) and Manuscript 4, there is a constant diagenetic offset of 4‰ in the open ocean between sinking particulate nitrogen and sediments. Altabet et al. (1999) found a smaller diagenetic offset (1‰) between sediment trap  $\delta^{15}\text{N}$  and underlying sediments in a productive ocean margin setting. The authors ascribed the difference to better organic matter preservation at their study site. The 1.6‰ offset between the upper trap and sediments in the present work may also be explained this way, since productivity rates at the upwelling-influenced site are high. Alternatively, the comparatively small difference measured between Walvis Ridge sinking particles and sediments may be due to degradation of the particles during sinking through the euphotic zone before reaching the trap. Saino and Hattori (1980) and Montoya et al. (1992), for instance, demonstrated a depletion in  $^{14}\text{N}$  in residual organic matter in or just below the euphotic zone due to

rem mineralization. Nakatsuka et al. (1995 and 1997) also reported that  $\delta^{15}\text{N}$  in sinking particles can show large changes in the upper water column. The data of Altabet et al. (1991) and Holmes et al. (1999) indicate that below the euphotic zone,  $\delta^{15}\text{N}$  in sinking particles does not change significantly, at least when flux rates are high. The uncertainties associated with diagenesis on nitrogen isotopic ratios demonstrates the need for more detailed work on the effect of degradation on sinking particulate matter.

### 5.3 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 water (Altabet and Francois, 1994). We calculated the relative depletion of surface nitrate to determine whether reasonable estimates could be obtained based on the available data. The nitrogen isotopic composition of organic matter in the ocean is determined by the  $\delta^{15}\text{N}$  of the inorganic nitrogen substrate ( $\text{NO}_3^-$  in the Benguela system) taken up during photosynthesis and by Rayleigh fractionation effects, as discussed by Mariotti et al. (1981). The  $\delta^{15}\text{N}$  of the nitrate at a given time ( $\delta^{15}\text{NO}_3^-_{(t)}$ ) is given by:

$$\delta^{15}\text{NO}_3^-_{(t)} = \delta^{15}\text{NO}_3^-_{(f=1)} - \epsilon \times \ln f \quad (1)$$

where  $\delta^{15}\text{NO}_3^-_{(f=1)}$  is the  $\delta^{15}\text{N}$  value of the original nitrate pool prior to any biological utilization,  $\epsilon$  is the fractionation factor associated with nitrate uptake and  $f$  is the fraction of unutilized nitrate in surface waters.

The  $\delta^{15}\text{N}$  of PN produced at a particular time and degree of nitrate utilization (instantaneous product) can be approximated by the following equation:

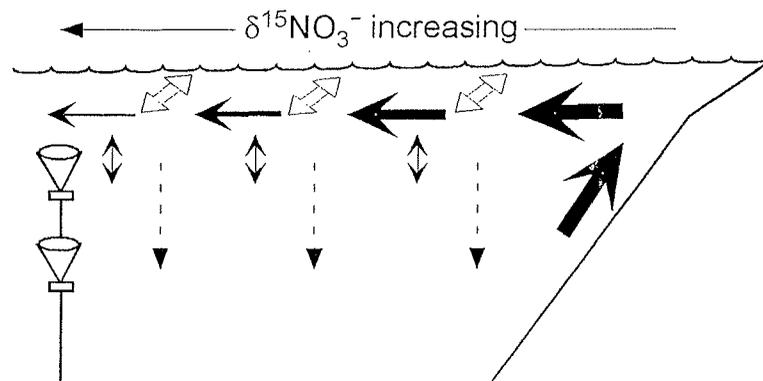
$$\delta^{15}\text{N-PN}_{(t)} = \delta^{15}\text{NO}_3^-_{(t)} - \epsilon \quad (2)$$

where  $\delta^{15}\text{N-PN}_{(t)}$  is the measured  $\delta^{15}\text{N}$  value of the particulate nitrogen.  $\delta^{15}\text{N}$  in PN can also be representative of an accumulated product of all the nitrogen that has been extracted from the nitrate pool:

$$\delta^{15}\text{N-PN}_{(t)} = \delta^{15}\text{NO}_3^-_{(t)} + \epsilon [(f \times \ln f)/(1-f)] \quad (3)$$

In both the instantaneous and the accumulated product scenarios, no new nitrate may be added to the original nitrate pool in order for these equations to be strictly accurate in representing the isotopic fractionation. Additionally, no nitrate may be removed from the original pool, except after being transformed into particulate nitrogen via photosynthesis.

An instantaneous PN product might arise, for example, in sinking PN where the surface nitrate is being advected laterally away from its point of upwelling into surface water, no new nitrogen is introduced and the particles sink immediately. The accumulated product equation would be suitable in sediments underlying a water column in which there is no lateral removal of either DIN or PN. In most marine systems the PN is produced under conditions somewhere between these 2 extreme cases. The physical oceanography characteristics of the Benguela suggests that the instantaneous product equation should most closely represent the nitrogen dynamics in our study area. Here, water is upwelled at the coast and then advected seaward under the influence of tradewinds, and becomes progressively more depleted in  $\text{NO}_3^-$  with distance from the site of upwelling. (Fig. 6). The situation here is similar to that in the equatorial Pacific, where water upwelled at the equator is advected to the north and the south. As in the Benguela region, nitrate concentrations decrease with distance from the upwelling center while particulate nitrogen and surface sediment  $\delta^{15}\text{N}$  increases (Altabet and Francois, 1994). Phytoplankton takes up the nitrate in the surface water, convert it into biomass which eventually sinks out of the surface layer. Particles may be advected some distance before sinking out of the euphotic zone, however, potentially lowering the  $\delta^{15}\text{N}$  of the material in the trap and thus the apparent relative nitrate utilization.



**Figure 6** Diagram of nitrate dynamics in the Benguela coastal region. Solid arrows represent the flow of nitrate with line thickness indicating relative nitrate concentrations. The vertical, two-ended arrows denote vertical exchange of nitrate and open arrows depict lateral transport of nitrate away from the surface water pool that is relevant to the trap. The dashed arrows symbolize downward export of particulate nitrogen.

Another complicating factor is that there may be mixing of water into the originally upwelled pool of surface water along its flow path. This allochthonous water may be laterally advected into the original pool or be mixed upward from below. In the case of laterally transported water, the added water could be either lower or higher in nitrate. If

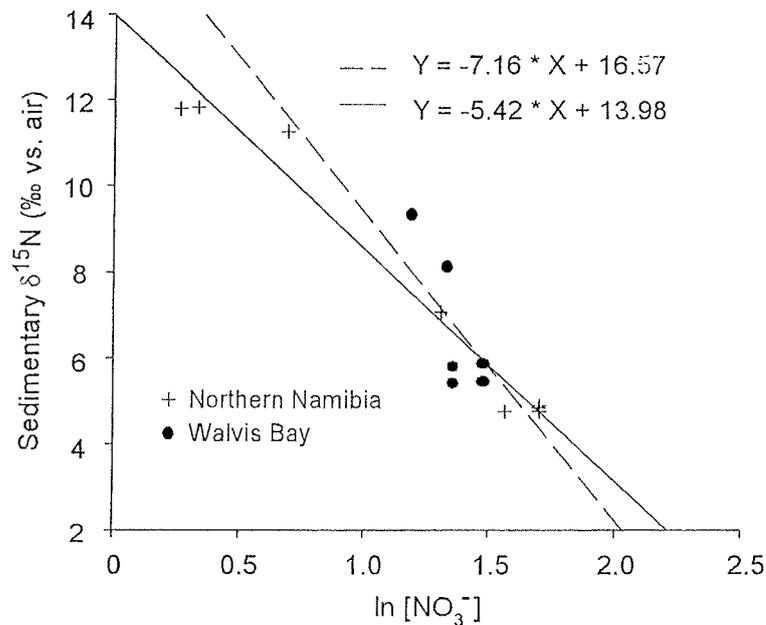
nitrate concentrations were lower, the  $\delta^{15}\text{N}$  of the nitrate in the original pool would not be significantly affected. On the other hand, the additional water could have higher nitrate concentrations, and depending on its  $\delta^{15}\text{N}$  value, it may or may not have a measurable effect on the isotopic composition of PN produced from the nitrate pool. Additionally, some of the nitrate from the original pool will also have been transported away, to some extent balancing this input of “foreign” nitrate. Therefore, this addition of nitrate to the water over the trap is likely negligible. A more significant impact on  $\delta^{15}\text{NO}_3^-_{(f)}$  could be caused by vertical mixing. During this process, new nitrate with a lower isotopic composition may be introduced to the “old” nitrate already in the euphotic zone over the trap, decreasing the  $\delta^{15}\text{N}$  of the PN. These processes should have a greater impact on the isotopic value of the sinking PN during low-flux periods and are probably not important when flux rates are high because the nitrate pool from the coastal upwelling which fuels the high productivity is much larger than the smaller amounts of nitrate which may be added to surface water from lateral or vertical mixing.

In order to estimate relative surface nitrate utilization,  $\delta^{15}\text{NO}_3^-_{(f=1)}$  in equation 1 was set equal to 5‰ because the average value for nitrate from oxygenated waters of the deep sea is around 5‰ (Wada et al., 1975; Liu and Kaplan, 1989; Sigman et al., 1997). The source of upwelled water in this area is South Atlantic Central Water (SACW), which is well oxygenated and should thus exhibit nitrate isotopic values similar to other subsurface waters.  $\epsilon$  was estimated as 5.4‰ for the northern part of the Benguela region by Holmes et al. (1998) from a plot of surface sediment  $\delta^{15}\text{N}$  (see Fig. 1 for location of transect) versus  $\ln [\text{NO}_3^-]$  (objectively analyzed one-degree latitude-longitude mean fields from World Ocean Atlas data set; Conkright et al., 1994) (Fig. 7). The resulting equation was:

$$\text{Sedimentary } \delta^{15}\text{N} = -5.4 * \ln [\text{NO}_3^-] + 13.98 \quad (4)$$

According to Altabet and Francois (1994), the slope of the linear regression between these two parameters is equivalent to  $\epsilon$ . The value obtained for  $\epsilon$  (5.4‰) is similar to the 5‰ fractionation factor reported by Wu et al. (1997) and Altabet et al. (1999) and is within the range of field estimates compiled by Montoya (1994). Since our  $\epsilon$  is based on sedimentary  $\delta^{15}\text{N}$  values, it represents an average fractionation factor for the past few to several hundred years. As discussed above, local vertical mixing of nitrate into the photic zone would serve to lower the  $\delta^{15}\text{N}$  of the PN, a process which becomes especially important where surface nitrate concentrations are low (Altabet and Francois, 1994). The isotopic values of the 3 sediment samples with the highest isotopic values in Fig. 6 appear to be less enriched in  $^{15}\text{N}$  than were horizontally advected nitrate the only source of this nutrient. This may indicate the influence of some new nitrate on the PN although the

surface water overlying the was not very depleted in  $\text{NO}_3^-$  (concentrations were  $\geq 1.3 \mu\text{M}$ ). If the 3 samples associated with the most nitrate-depleted water are omitted from the regression,  $\epsilon$  of 7.2‰ is obtained. We therefore calculated relative nitrate utilization using  $\epsilon = 5.4\text{‰}$  and 7.2‰ to give a potential range off.

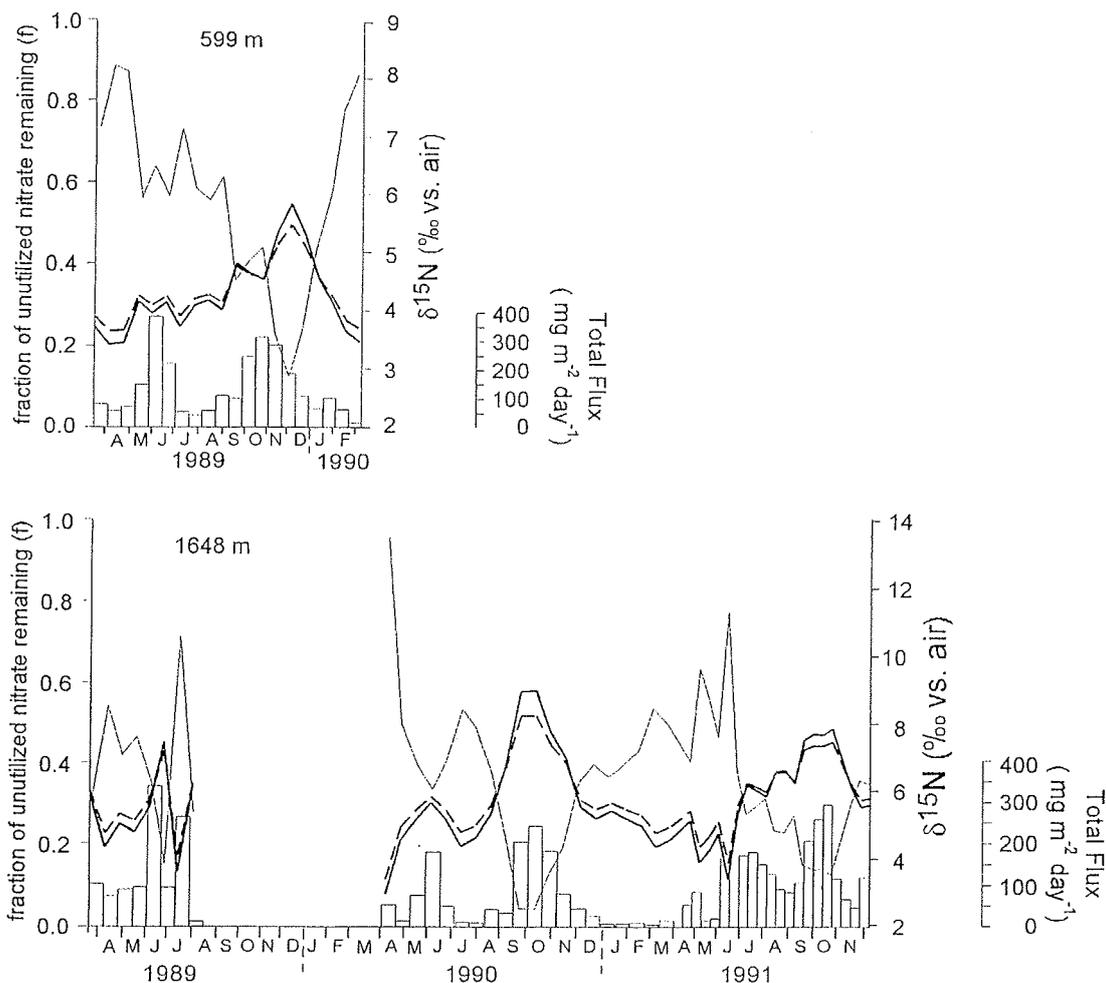


**Figure 7**  $\delta^{15}\text{N}$  (‰) values of bulk surface sediments versus  $\ln[\text{NO}_3^-]$  ( $\mu\text{M}$ ) from northern Benguela ( $23^\circ 4'S$ ,  $19^\circ 2'E$ ) from Holmes *et al.* 1998. The solid line is a regression including the 3 samples with the highest  $\delta^{15}\text{N}$  values. The dashed line shows the slope when these 3 samples are excluded from the regression.  $\epsilon$  used in the present study was obtained from the slopes of the regression lines.

Table 2 and Fig. 8 show the values for  $f$  calculated from equation (1) above, with  $\epsilon = 5.4\text{‰}$  and  $7.2\text{‰}$  and  $\delta^{15}\text{NO}_3^- (f=1) = 5\text{‰}$ . Based on  $\delta^{15}\text{N}$  in the shallow trap,  $f$  was between .55 and .20, when  $\epsilon = 5.4\text{‰}$ , indicating that between 45% and 80% of the original upwelled nitrate had been utilized. For  $\epsilon = 7.2\text{‰}$ ,  $f$  was generally higher than the values for  $\epsilon = 5.4\text{‰}$ .  $f$  was lowest during the fall (Fig. 7), 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 similar pattern is seen in the  $f$  values calculated from the deep trap. Nitrate utilization calculated from the deep trap was 42 to 92% ( $f = .58 - .08$ ). Due to the uncertainty regarding the effect of remineralization on  $\delta^{15}\text{N}$ , our calculations for  $f$  must be viewed as qualitative estimates.

**Table 2:**  $\delta^{15}\text{NO}_3^-$  (f) and f (the fraction of unutilized nitrate remaining in surface water) calculated from equations (1) and (2) using  $\delta^{15}\text{N}$  of sinking particles and  $\varepsilon = 5.4\text{‰}$  and  $\varepsilon = 7.2\text{‰}$ .

Sample	$\varepsilon_{\text{u}}=5.4\text{‰}$		$\varepsilon_{\text{u}}=7.2\text{‰}$		Sample	$\varepsilon_{\text{u}}=5.4\text{‰}$		$\varepsilon_{\text{u}}=7.2\text{‰}$	
	$\delta^{15}\text{NO}_3^-$ (f) (‰)	f	$\delta^{15}\text{NO}_3^-$ (f) (‰)	f		$\delta^{15}\text{NO}_3^-$ (f) (‰)	f	$\delta^{15}\text{NO}_3^-$ (f) (‰)	f
upper									
1	12.6	0.25	14.4	0.27	27	13.3	0.22	15.1	0.25
2	13.6	0.20	15.4	0.23	28	12.0	0.27	13.8	0.30
3	13.5	0.21	15.3	0.24	29	10.0	0.39	11.8	0.39
4	11.4	0.31	13.2	0.32	30	8.0	0.58	9.8	0.52
5	11.9	0.28	13.7	0.30	31	7.9	0.58	9.7	0.52
6	11.4	0.31	13.2	0.32	32	9.0	0.48	10.8	0.45
7	12.6	0.25	14.4	0.27	33	9.8	0.41	11.6	0.40
8	11.5	0.30	13.3	0.31	34	11.7	0.29	13.5	0.31
9	11.3	0.31	13.1	0.32	35	12.2	0.26	14.0	0.29
10	11.7	0.29	13.5	0.31	36	11.8	0.28	13.6	0.30
11	9.9	0.40	11.7	0.39	37	12.2	0.26	14.0	0.29
12	10.3	0.38	12.1	0.37	38	12.6	0.25	14.4	0.27
13	10.5	0.36	12.3	0.36	39	13.9	0.19	15.7	0.23
14	9.0	0.48	10.8	0.45	40	13.4	0.21	15.2	0.24
15	8.3	0.55	10.1	0.49	41	12.3	0.26	14.1	0.28
16	9.1	0.47	10.9	0.44	42	15.0	0.16	16.8	0.19
17	10.5	0.36	12.3	0.37	43	14.1	0.18	15.9	0.22
18	11.4	0.30	13.2	0.32	44	13.0	0.23	14.8	0.26
19	12.9	0.23	14.7	0.26	45	16.7	0.11	18.5	0.15
20	13.5	0.21	15.3	0.24	46	12.0	0.27	13.8	0.30
lower					47	10.7	0.35	12.5	0.35
1	11.2	0.32	13.0	0.33	48	11.0	0.33	12.8	0.34
2	13.9	0.19	15.7	0.23	49	11.2	0.32	13.0	0.33
3	12.5	0.25	14.3	0.27	50	10.2	0.38	12.0	0.38
4	13.0	0.23	14.8	0.26	51	10.2	0.38	12.0	0.38
5	11.7	0.29	13.5	0.31	52	10.7	0.35	12.5	0.35
6	9.3	0.45	11.1	0.43	53	9.2	0.46	11.0	0.43
7	15.6	0.13	17.8	0.17	54	9.0	0.47	10.8	0.44
8	10.8	0.34	12.6	0.35	55	9.1	0.47	10.9	0.44
21	18.9	0.08	20.7	0.11	56	8.9	0.49	10.7	0.45
22	13.4	0.21	15.2	0.24	57	9.9	0.41	11.7	0.40
23	12.2	0.26	14.0	0.29	58	10.9	0.34	12.7	0.34
24	11.5	0.30	13.3	0.32	59	11.7	0.29	13.5	0.31
25	12.3	0.26	14.1	0.28	60	11.6	0.30	13.4	0.31
26	13.8	0.19	15.6	0.23					



**Figure 8** The range of  $f$  (the fraction of unutilized nitrate remaining in surface water) calculated from  $\delta^{15}\text{N}$  of the sinking particles. The thick solid line is the  $f$  expected from  $\epsilon = 5.4\text{‰}$  and the thick dashed line in the shaded area is the  $f$  expected if  $\epsilon = 7.2\text{‰}$ .  $\delta^{15}\text{N}$  is shown for comparison as the thin solid line and the bars are particle flux rates from Fig. 2.

## 6. Conclusion

We have shown that stable nitrogen isotope ratios in sinking particles at the Walvis Ridge in the Benguela system are controlled mainly by changes in relative nitrate utilization in surface water. Nitrogen isotope values are correlated with changes in sea surface temperatures and flux rates. In this area, the seaward extension of upwelling filaments, which usually occurs twice yearly, brings nutrient-rich water to the euphotic zone and leads to elevated productivity and relatively lower  $\delta^{15}\text{N}$  values of the particulate nitrogen. We attempted to calculate changes in the degree of nitrate utilization from  $\delta^{15}\text{N}$  values of the sinking particles. The main uncertainty associated with these estimates is the effect of diagenesis on  $\delta^{15}\text{N}$  and possible variability in preservation of the isotope signal between

periods of high and low particle flux. Also questionable is the fractionation factor, which might vary with nutrient conditions. In spite of these complications, our study demonstrates the potential of stable nitrogen isotopes as a proxy for surface nitrate utilization and attests to the usefulness of  $\delta^{15}\text{N}$  for paleoceanographic studies.

### **Acknowledgements**

We gratefully acknowledge I. Pesza and B. Meyer-Schack for technical assistance with the mass spectrometer. We thank N. Andersen for allowing us to use his unpublished data. Discussions with S. Neuer and M. Voss were of great help during the writing of the manuscript. Comments by Dr. Takeshi Nakatsuka and 2 anonymous reviewers greatly improved the quality of the paper. Access to sea surface temperature data was facilitated by the LDEO/IRI Data Library (<http://ingrid.ldeo.columbia.edu>). The research was funded by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 261 at Bremen University, Contribution No. xxx) and by the Bundesminister für Bildung, Wissenschaft, Forschung and Technologie (BMBF).

## References

- Altabet, M. and McCarthy, J. (1985) Temporal and spatial variation in the natural abundance of  $^{15}\text{N}$  in PON from a warm-core ring. *Deep-Sea Research*, **32**, 755-772.
- Altabet, M. and Francois, R. (1994) Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization. *Global Biogeochemical Cycles*, **8**, 103-116.
- Altabet, M., Deuser, W. G., Honjo, S. and Steinen, C. (1991) Seasonal and depth-related changes in the source of sinking particles in the North Atlantic. *Nature*, **354**, 136-139.
- Altabet, M. A., Pilska, C., Thunell, R., Pride, C., Sigman, D., Chavez, F. and Francois, R. (1999) The nitrogen isotope biogeochemistry of sinking particles from the margin of the Eastern North Pacific. *Deep-Sea Research Part I*, **46**, 655-679.
- Antoine, D., André, J.-M. and Morel, A. (1996) Oceanic primary production-2. Estimation at global scale from satellite (coastal zone colour scanner) chlorophyll. *Global Biogeochemical Cycles*, **10**, 57-69.
- Biggs, D. C., Berkowitz, S.P., Altabet, M. A., Bidigare, R. R., DeMaster, D. J., Macko, S. A., Ondrusek, M. E. and Noh, I. L. (1989) A cooperative study of the upper ocean particulate fluxes. In *Proc. ODB Init. Repts.* **119**, eds. J. Barron, J. Anderson, J. G. Baldauf, B. Larsen, College Station, TX, pp. 109-120.
- Boyd, A. J., Salat, J. and Masó, M. (1987) The seasonal intrusion of relatively saline water on the shelf off northern and central Namibia. *South African Journal of Marine Science*, **5**, 107-120.
- Brassel, S. C., Eglinton, G., Marlowe, I. T., Pflaumann, U. and Sarrnthein, M. (1986) Molecular stratigraphy: a new tool for climatic assessment. *Nature*, **320**, 129-133.
- Calvert, S. E. and Price, N. B. (1971) Upwelling and nutrient regeneration in the Benguela Current, October, 1968. *Deep-Sea Research*, **18**, 505-523.
- Čepek M (1994) Zeitliche und räumliche Variationen von Coccolithophoriden-Gemeinschaften im subtropischen Ost-Atlantik: Untersuchungen an Plankton, Sinkstoffen und Sedimenten. PhD. dissertation Berichte Fachbereich Geowissenschaften, Universität Bremen, **86**, 155 pp.
- Chapman, P. and Shannon, L. V. (1985) The Benguela ecosystem Part II. Chemistry and related processes. *Oceanography and Marine Biology Annual Review*, **23**, 183-251.
- Conkright, M. E., Levitus, S. and Boyer, T. P. (1994) World Ocean Atlas 1994, Vol. 1: Nutrients. NOAA Atlas NESDIS 1. U.S. Dept. of Commerce, NOAA, NESDIS.
- Farrell, J.W., Pedersen, T.F., Calvert, S.E. and Nielsen, B. (1995) Glacial-interglacial changes in nutrient utilization in the equatorial Pacific Ocean. *Nature*, **377**, 514-517.

- Fischer, G. and Wefer, G. (1991) Sampling, preparation and analysis of marine particulate matter. In *Marine Particles: Analysis and Characterization*, eds. D. C. Hurd and D. W. Spencer, Geophysical Monograph, **63**, pp. 391-397.
- Fischer, G. and Wefer, G. (1996) Long-term observation of particle fluxes in the eastern Atlantic: seasonality, changes of flux with depth and comparison with the sediment record. In *The South Atlantic: Present and Past Circulation*, eds. G. Wefer, W. H. Berger, G. Siedler and D. Webb, Springer-Verlag, Berlin, Heidelberg, pp. 325-344.
- Fischer, G., Ratmeyer, V. and Wefer, G. (2000) Organic carbon fluxes in the Atlantic and the Southern Ocean: relationship to primary production compiled from satellite radiometer data. *Deep-Sea Research II*, **47**, 1961-1997.
- Francois, R., Altabet, M. A., and Burkle, L. H. (1992) Glacial to interglacial changes in surface nitrate utilization in the Indian sector of the Southern Ocean as recorded by sediment  $\delta^{15}\text{N}$ . *Paleoceanography*, **7**, 589-606.
- Francois, R., Altabet, M. A., Yu, E., Sigman, D. M., Bacon, M. P., Frank, M., Bohrmann, G., Bareille, G. and Labeyrie, L. D. (1997) Contribution of Southern Ocean surface-water stratification to low atmospheric  $\text{CO}_2$  concentrations during the last glacial period. *Nature*, **389**, 929-935.
- Fry, B., Brand, W., Mersch, F., Tholke, K. and Garritt, R. (1992) Automated analysis system for coupled  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  measurements. *Analytical Chemistry*, **64**, 288-291.
- Holmes, M. E., Müller, P. J., Schneider, R. R., Segl, M., Pätzold, J. and Wefer, G. (1996) Stable nitrogen isotopes in Angola Basin surface sediments. *Marine Geology*, **134**, 1-12.
- Holmes, M. E., Schneider, R. R., Müller, P. J., Segl, M., and Wefer, G. (1997) Reconstruction of past nutrient utilization in the eastern Angola Basin based on sedimentary  $^{15}\text{N}/^{14}\text{N}$  ratios. *Paleoceanography*, **12**, 604-614.
- Holmes, M. E., Müller, P. J., Schneider, R. R., Segl, M. and Wefer, G. (1998) Spatial variations in euphotic zone nitrate utilization based on  $\delta^{15}\text{N}$  in surface sediments. *Geo-Marine Letters*, **18**, 58-65.
- Holmes, M. E., Eichner, C., Struck, U. and Wefer, G. (1999) Reconstruction of surface ocean nitrate utilization using stable nitrogen isotopes in sinking particles and sediments. In *Use of Proxies in paleoceanography: Examples from the South Atlantic*, eds. G. Fischer and G. Wefer, Springer-Verlag, Berlin, Heidelberg, pp. 447-468.
- Jones, P. G. W. (1971) The southern Benguela Current region in February, 1966: Part I. Chemical observations with particular reference to upwelling. *Deep-Sea Research*, **18**, 193-208.
- Kienast, M. (2000) Unchanged nitrogen isotopic composition of organic matter in the South China Sea during the last climatic cycle: Global implications. *Paleoceanography*, **15**, 244-253.

- Lavik, G., Fischer, G., Mueller, P. J., Schneider, R. R. and Wefer, G.  $\delta^{15}\text{N}$  values on sinking matter and surface sediments in the Eastern Equatorial Atlantic: Evidence of a northward lateral particle transport. Submitted to Deep-Sea Research.
- Libes, and Deuser, (1988) The isotope geochemistry of particulate nitrogen in the Peru Upwelling area and the Gulf of Maine. *Deep-Sea Research*, **35**, 517-533.
- Liu, K.-K. and Kaplan, I. R. (1989) The eastern tropical Pacific as a source of  $^{15}\text{N}$ -enriched nitrate in seawater off southern California. *Limnology and Oceanography*, **34**, 820-830.
- Lutjeharms, J. R. E. and Meeuwis, J. M. (1987) The extent and variability of southeast Atlantic upwelling. *South African Journal of Marine Science*, **5**, 51-62.
- Lutjeharms, J. R. E., Shillington, F. A. and Duncombe Rae, C. M. (1991) Observations of extreme upwelling filaments in the Southeast Atlantic Ocean. *Science*, **253**, 774-776.
- Mariotti, A., Germon, J. C., Hubert, P., Kaiser, P., Letolle, R., Tardieux, A. and Tardieux, P. (1981) Experimental determination of nitrogen kinetic isotope fractionation: some principles; illustration for the denitrification and nitrification processes. *Plant and Soil*, **62**, 413-430.
- Meeuwis, J. M. and Lutjeharms, J. R. E. (1990) Surface thermal characteristics of the Angola-Benguela Front. *South African Journal of Marine Science*, **9**, 261-279.
- Miyake, Y. and Wada, E. (1967) The abundance ratio of  $^{15}\text{N}/^{14}\text{N}$  in marine environments. *Rec. Oceanogr. Wks Japan* **9**, 37-53.
- Montoya, J. P. (1994) Nitrogen isotope fractionation in the modern ocean: implications for the sedimentary record. In: *Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change*, R. Zahn et al., editors, NATO Asi Series, Series C, Vol. I 17, Springer, Berlin, Heidelberg, New York, 259-279.
- Montoya, J. P. and McCarthy, J. J. (1995) Isotopic fractionation during nitrate uptake by phytoplankton grown in continuous cultures. *J. Plankton Res.*, **17**, 436-464.
- Montoya, J. P., Wiebe, P. H. and McCarthy, J. J. (1992) Natural abundance of  $^{15}\text{N}$  in particulate nitrogen and zooplankton in the Gulf Stream region and Warm-Core Ring 86A. *Deep-Sea Research*, **39**, Suppl. 1, S363-S392.
- Nakatsuka, T., Handa, N., Wada, E. and Wong, C. S. (1992) The dynamic changes of stable isotopic ratios of carbon and nitrogen in suspended and sedimented particulate organic matter during a phytoplankton bloom. *Journal of Marine Research*, **50**, 267-296.
- Nakatsuka, T., Watanabe, K., Handa, N., Matsumoto, E. and Wada, E. (1995) Glacial to interglacial surface nutrient variations of Bering deep basins recorded by  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  of sedimentary organic matter. *Paleoceanography*, **10**, 1047-1061.
- Nakatsuka, T., Handa, N., Harada, N., Sugimoto, T. and Imaizumi, S. (1997) Origin and decomposition of sinking particulate organic matter in the deep water column inferred

- from the vertical distributions of its  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$  and  $\delta^{14}\text{C}$ . *Deep-Sea Research I*, **44**, 1957-1979.
- Nelson, G. and Hutchings, L. (1983) The Benguela upwelling area. *Progress in Oceanography*, **12**, 333-356.
- Peterson, R. G. and Stramma, L. (1991) Upper-level circulation in the South Atlantic Ocean. *Progress in Oceanography*, **26**, 1-73.
- Prahl, F. G., Muehlhausen, L. A. and Zahnle, D. L. (1988) Further evaluation of long-chain alkenones as indicators of paleoceanographic conditions. *Geochimica et Cosmochimica Acta*, **52**, 2303-2310.
- Reynolds, R.W. and Smith, T.M. (1994) Improved global sea surface temperature analyses. *J. Climate*, **7**, 929-948.
- Saino, T. and Hattori, A. (1980)  $^{15}\text{N}$  natural abundance in oceanic suspended particulate matter. *Nature*, **283**, 752-754.
- Schell, I. I. (1970) Variability and persistence in the Benguela Current and upwelling off Southwest Africa. *Journal of Geophysical Research*, **75**, 5225-5241.
- Servain, J., Picaut, J. and Busalacchi, A. J. (1985) Interannual and seasonal variability of the tropical Atlantic ocean depicted by sixteen years of sea-surface temperature and wind stress. In *Coupled Ocean-Atmosphere Models*, ed. J. C. J. Nihoul, Elsevier, New York, pp. 211-237.
- Shannon, L. V. (1985) The Benguela ecosystem. Part I. Evolution of the Benguela, physical features and processes. *Oceanography and Marine Biology Annual Review*, **23**, 105-182.
- Shannon, L. V. and Nelson, G. (1996) The Benguela: Large scale features and processes and system variability. In *The South Atlantic: Present and past circulation*, eds. G. Wefer, et al., Springer-Verlag Berlin Heidelberg, 163-210.
- Shannon, L. V., Boyd, A. J., Bundrit, G. B. and Taunton-Clark, J. (1986) On the existence of an El Niño-type phenomenon in the Benguela system. *Journal of Marine Research*, **44**, 495-520.
- Shannon, L. V., Hutchings, L., Bailey, G. W. and Shelton, P. A. (1987) Large- and mesoscale features of the Angola-Benguela front. *South African Journal of Marine Science*, **5**, 11-34.
- Sigman, D. M., Altabet, M. A., Michener, R., McCorkle, D. C., Fry, B. and Holmes, R. M. (1997) Natural abundance-level measurement of the nitrogen isotopic composition of oceanic nitrate: an adaptation of the ammonia diffusion method. *Marine Chemistry*, **57**, 227-242.
- Sweeney, R. E. and Kaplan, I. R. (1980) Natural abundances of  $^{15}\text{N}$  as a source indicator for near-shore marine sedimentary and dissolved nitrogen. *Marine Chemistry*, **9**, 81-94.

- Treppke, U. F., Lange, C. B., Donner, B., Fischer, G., Ruhland, G. and Wefer, G. (1996) Diatom and silicoflagellate fluxes at the Walvis Ridge: an environment influenced by coastal upwelling in the Benguela system. *Journal of Marine Research*, **54**, 991-1016.
- Voss, M., Altabet, M. and von Bodungen, B. (1996)  $\delta^{15}\text{N}$  in sedimenting particles as indicator for euphotic zone processes. *Deep-Sea Research*, **43**, 33-47.
- Voss, M., Nausch, G. And Montoya, J. (1997) Nitrogen stable isotope dynamics in the central Baltic Sea: Influence of deep water renewal on the N-cycle changes. *Mar. Ecol. Prog. Ser.* **158**, 11-21.
- Wada, E. (1980) Nitrogen isotope fractionation and its significance in biogeochemical processes occurring in marine environments. In *Isotope Marine Chemistry*, eds. E. D. Goldberg et al., 375-398.
- Wada, E. and Hattori, A. (1978) Nitrogen isotope effects in the assimilation of inorganic nitrogenous compounds by marine diatoms. *Geomicrobiology Journal*, **1**, 85-101.
- Wada, E., Kadonaga, T. and Matsuo, S. (1975)  $^{15}\text{N}$  abundance in nitrogen of naturally occurring substances and global assessment of denitrification from isotopic viewpoint. *Geochemical Journal*, **9**, 139-148.
- Wada, E., Minagawa, M., Mizutani, H., Tsuji, T., Imaizumi, R. and Karasawa, K. (1987) Biogeochemical studies on the transport of organic matter along the Otsuchi River watershed, *Japanese Estuary and Coastal Shelf Science*, **25**, 321-336.
- Wefer, G. and Fischer, G. (1993) Seasonal patterns of vertical particle flux in equatorial and coastal upwelling areas of the eastern Atlantic. *Deep-Sea Research*, **40**, 1613-1645.
- Wu, J., Calvert, S. E. and Wong, C. S. (1997) Nitrogen isotope variations in the subarctic northeast Pacific: Relationships to nitrate utilization and trophic structure. *Deep-Sea Research (Part I)* **44**, 287-314.

## 7.4 Manuscript 4:

### *Nitrogen isotopes in the Benguela Upwelling system: Sea level related offshore migration in the upwelling cell and variable impact of denitrification*

Abstract .....	98
1 Introduction .....	99
1.1 Nitrogen isotopes .....	99
1.2 Oceanographic and physiographic settings .....	101
1.3 Past changes.....	102
2 Material and methods .....	103
3 Stratigraphy .....	103
4 Results .....	106
5 Discussion .....	109
5.1 Sea-level change.....	109
5.2 Processes.....	112
5.2.1 The present situation.....	112
5.2.2 Down core variation.....	115
5.3 Core transect GeoB 1710, 1711 and 1712 .....	116
5.3.1 The interglacials (0-14 ka and 111-128 ka) .....	116
5.3.2 The early glacial period (71-111 ka).....	117
5.3.3 The late glacial period (14-71 ka).....	118
5.3.4 The pre-128 ka period.....	121
5.4 Periodicity of the variation .....	121
6. Conclusions .....	122
Acknowledgements .....	123
References .....	124

## **Nitrogen isotopes in the Benguela Upwelling system: Sea level related offshore migration in the upwelling cell and variable impact of denitrification**

Gaute Lavik<sup>1</sup>, Christiane Eichner<sup>2</sup>, Gesine Mollenhauer<sup>1</sup>, Peter J. Müller<sup>1</sup>, Ralph R. Schneider<sup>1</sup>, Ulrich Struck<sup>1,3</sup> and, Gerold Wefer<sup>1</sup>

<sup>1</sup>*FB Geowissenschaften, Universität Bremen, Klagenfurter Strasse, D-28359 Bremen*

<sup>2</sup>*Institut für Ostseeforschung, Seestrasse 15, D-18119 Rostock*

<sup>3</sup>*Pal. Institut, Universität Muenchen. Richard Wagner Strasse 10, D-80333 Muenchen*

To be submitted to *Paleoceanography*

### **Abstract**

Abrupt changes in the  $\delta^{15}\text{N}$  records in a three core transect from the continental shelf to the lower slope off Walvis Bay, south-western Africa, are probably caused by migrations in the upwelling cell related to changes in sea-level. Only during full interglacial conditions (marine isotope stage 1 and 5.5) are the sea-level high enough to allow the subsurface waters to overflow the inner shelf before emerging at the surface. After marine isotope stage 5.5 (at 111k) the upwelling of subsurface waters shifted away from the shore and emerged at the mid shelf break about 80km off the modern coastline. The return to the interglacial mode of upwelling happens equally abrupt at 14ka and 128ka. Surface sediment  $\delta^{15}\text{N}$  data from the continental shelf along with CTD measurements provide evidence of notable water-column denitrification beneath the zone of perennial upwelling. To a various degree denitrification has also influenced the  $\delta^{15}\text{N}$  records from the upper slope (GeoB1712 and GeoB1711) during intensified upwelling, especially during marine isotope stage 3. The core from the lower slope (GeoB 1710) seems not have been directly influenced by denitrification at any time during the last 25ka and mainly reflects the nutrient availability in the surface waters. This is further confirmed by a inverse correlation to the organic content.

## 1 Introduction

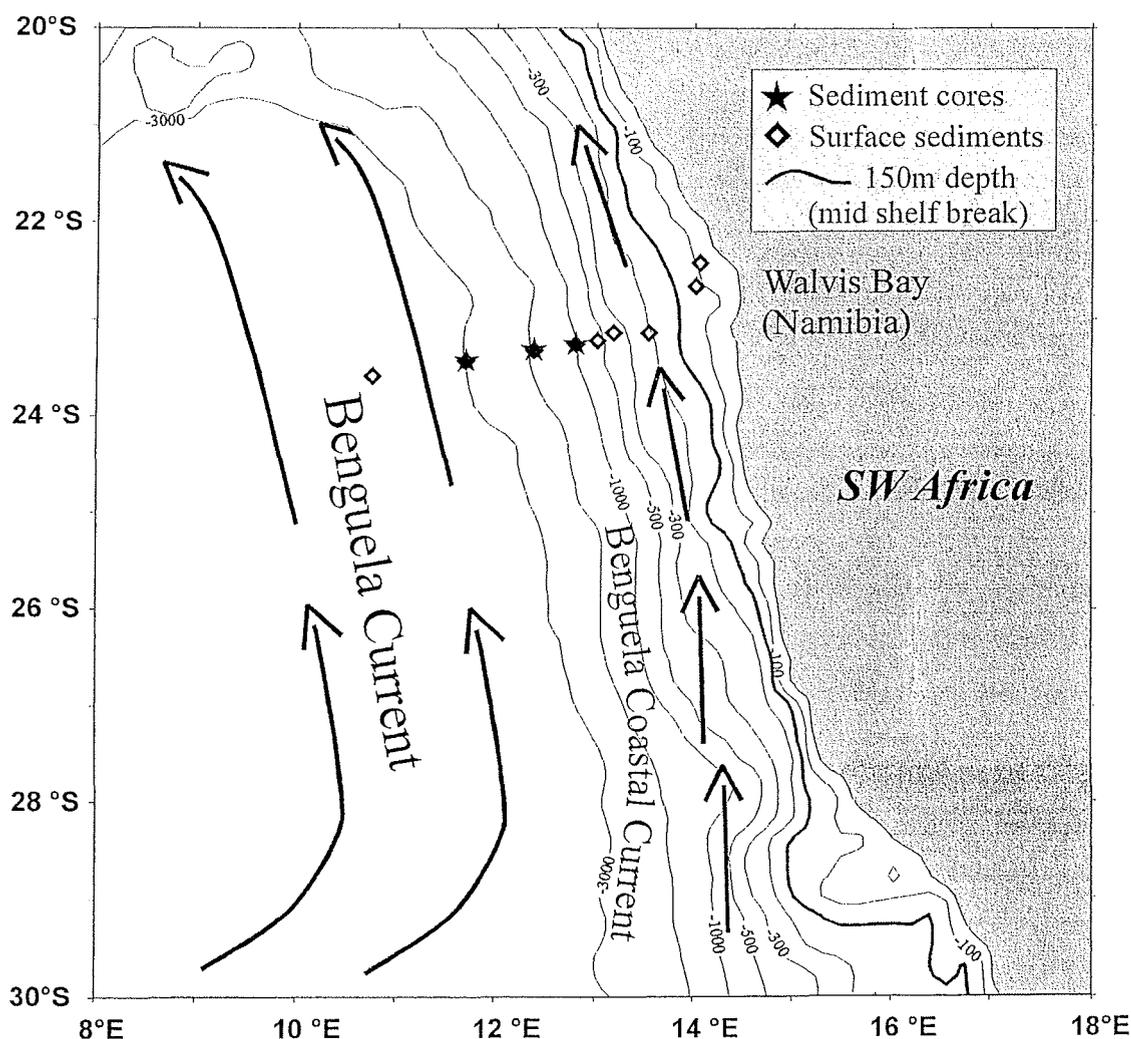
A number of past studies have focused on and aimed to reconstruct the past changes in and around the Benguela Upwelling system based on a wide variety of parameters like; - foraminifera assemblages (Little et al., 1997a; 1997b; Jansen et al., 1996), foraminifera isotopes (Schneider et al., 1992), -diatoms (Abrantes, 2000), - alkenone sea surface temperatures (SST)(Kirst et al., 1999), -and multi-proxy studies (Diester-Haass, 1985; Diester-Haass et al., 1988, Schneider et al., 1992; Summerhayes et al., 1995). Here we present a study based on sedimentary nitrogen isotopes on a three core-transect from the upper slope towards the deep basin. We will attempt to reconstruct the changes in the Walvis Bay upwelling cell based on a parameter which is not directly affected by changes in temperature of the upwelled water, SST, carbonate dissolution and other depth related processes. A three core transect is required to single out the complex processes governing the sedimentary  $\delta^{15}\text{N}$  in an high production zone and to better view the changes in the offshore extent of the upwelling filament. Special focus will be set on the possible impact of sea-level change on the upwelling system and the possible impact of denitrification on the  $\delta^{15}\text{N}$  records.

### 1.1 Nitrogen isotopes

Sedimentary nitrogen isotopes in upwelling areas have been demonstrated to mainly reflect either denitrification variability (Ganeshram, 1995; Altabet et al., 1995; 1999a; Pride et al., 1999) or past relative nitrate utilisation (Francois et al., 1992; Altabet and Francois, 1994; Farrell et al., 1995; Holmes et al., 1996; 1997, 1998;), which would give an opposite relationship between upwelling intensity and sedimentary  $\delta^{15}\text{N}$  values.

The preferential uptake of  $^{14}\text{N}$  by phytoplankton leads to a depletion of  $^{15}\text{N}$  in organic matter compared to the nitrate source (Wada and Hattori, 1978; Montoya, 1994) which leaves the nitrate source relatively enriched in  $^{15}\text{N}$  as the nutrients are utilised. The nitrogen isotopic composition of organic matter produced in the photic zone depends on the isotopic composition of the surrounding nutrient and thus, the degree to which the inorganic nitrogen pool is utilised (Wada, 1980; Altabet et al., 1991; Voss et al., 1996). Reconstruction of past nutrient utilisation then requires that the surface-water- $\delta^{15}\text{N}$ -signal carried by the particles are preserved in the sediments. Although a series of processes alter the original signal through diagenesis in both the water column (Nakatsuka, 1997) and at the sediment water interface (Saino and Hattori, 1980; Altabet and McCarthy, 1985; Francois et al., 1992), there seems to be an persistent transfer of the surface water  $\delta^{15}\text{N}$  signal to the sediment (Francois, et al. 1992; Altabet, 1996; Manuscript 1). These authors reported a consistent  $4\pm 1\%$   $^{15}\text{N}$ -enrichment in the sediments compared to sinking matter in

different regions. However, Altabet et al. (1999b) demonstrated that this difference is less than 1‰ in high production areas and ascribed this to the better N-preservation, due to higher sedimentation rates in a coastal upwelling zone. Directly to the north of our study area at the Walvis Ridge a difference of ~1‰ or less (depending on year) between sediment trap and surface sediments was found at 2200 m water depth 400km off the coast (Manuscript 3) indicating a rather low diagenetic effect at our core locations (Fig. 1). In the same study a close relationship between upwelling intensity and  $\delta^{15}\text{N}$  on particulate matter was stated, where intensified upwelling (reduced SST) lowered the  $\delta^{15}\text{N}$  due to decreased relative nitrate utilisation. Rising sedimentary  $\delta^{15}\text{N}$  values away from the nutrient source off the shelf in our study region indicate that the surface sediment  $\delta^{15}\text{N}$ -values mainly reflect relative nutrient utilisation (Holmes et al., 1998; 1999).



**Figure 1:** Bathymetric map over the study area with the main oceanic currents indicated with arrows and the sediment core (star) and surface sediment sample (diamonds) locations plotted.

When oxygen is in short supply in some part of the water-column denitrifying bacteria can use nitrate as electron acceptor during respiration. Denitrification could occur under strictly local anoxic conditions in microzone (Allredge and Cohen, 1987) but do first get efficient at oxygen concentrations of  $0.2 \text{ mL L}^{-1}$  or less (Packard et al., 1983). Due to the preferential use of  $^{14}\text{NO}_3^-$  by bacterial respiration water column denitrification is accompanied by a large isotopic fractionation (20-40‰, Cline and Caplan, 1975; Collister and Hayes, 1991; Brandes et al., 1998). Water column-denitrification is commonly associated with high export production (high particle flux) where the oxic degradation of organic matter exceeds the oxygen supply in the sub surface waters and  $\text{NO}_3^-$  is used as an alternative electron acceptor by denitrifying bacteria. Hence, increasing upwelling/production would relate to increasing  $\delta^{15}\text{N}$  values due to increasing denitrification (Altabet et al., 1995; 1999a; Ganeshram et al., 1995; Pride et al., 1999). Brandes and Devol (1997) found no large systematic fractionation by denitrification in sediments and ascribed this to the limited supply of reactants into and within the sediments.

Nitrogen fixation is another main actor in the marine nitrogen cycle but because it is a metabolically expensive process it mainly occurs where nitrate is limited (Carpenter, 1983).

### *1.2 Oceanographic and physiographic settings*

The Namibian continental margin is characterised by a distinctly wide shelf area with the shelf edge at 350-400 m water depth between 100 and 160 km offshore. Outside Walvis Bay (Fig. 1) the shelf consists of a relatively wide inner platform reaching about 80 km off the coast with a rather abrupt step down to the lower shelf at ~140 depth. The lower shelf is about 60 km wide and gently sloping from 250 to 350 m depth. A distinct trough is crossing the lower shelf in a north-western direction outside the Walvis Bay (Calvert and Price, 1983). The sediment on the inner shelf is anoxic diatom ooze with abundant organic carbon (TOC of 5 to <15%) and less than 25%  $\text{CaCO}_3$ . On the lower shelf the  $\text{CaCO}_3$  dominate the sediment (<50%) and the TOC reduces to less than 5% (Calvert and Price, 1983).

The hydrography along the Namibian coast is controlled by the coastal branch of the Benguela current and the more or less perennial upwelling of subsurface water masses along the coast (Fig. 1). The Benguela Current System (BCS) is previously described in detail by several authors (Shannon, 1985; Lutjeharms and Meeuwis, 1987; Lutjeharms and Stockton, 1987; Peterson and Stramma, 1991; Summerhayes et al., 1995; Shannon and Nelson, 1996). The prevailing winds (trade winds) from south-south-west and south-west

(Servain, 1982, Picaut, 1985) drives surface water offshore during most of the year and is consequently causing the upwelling of subsurface waters along the Namibian Coast. The south-east Atlantic coastal upwelling consists of eight upwelling cells between 15° and 35°S in which the centres do not overlap (Lutjeharms and Meeuwis, 1987). The Walvis Bay upwelling cell is the proximate one to our core locations, but the Lüderitz cell to the south, which is the most intense one, might also be influential for our sites (Fig. 1). The mean surface water temperatures (SST) are 16-17°C at the centres of these two cells and their filaments have an average seaward extension of about 250 km. The main difference between these two upwelling cells is the frequency of the upwelling events, being more than twice as high and of a more perennial character at Lüderitz (Lutjeharms and Meeuwis, 1987). The cold and nutrient rich subsurface water are upwelled from about 300 m depth (Shillington et al., 1990). Additionally to the wind driven coastal upwelling, several studies have described an upwelling above the continental slope related to the oceanographic front at the shelf edge (e.g. Hart and Currie, 1960; Bang, 1971 and 1973; Bang and Andrews, 1974; Shannon et al., 1985; Hutchings et al., 1986). This phenomenon is most important along the southern Benguela region, but it is also confirmed to occur off the Namibian shelf edge (Nelson, 1989; Barange and Pillar, 1992; Barange et al., 1992). Summerhayes et al. (1995). argued that, because this is not related to the seasonal winds but to the equatorward flowing currents, the shelf edge upwelling is probably a perennial phenomena. Nevertheless, the primary production has a pronounced maximum during austral summer both above the shelf and the slope (Antoine et al., 1996) following the seasonality in the wind-driven upwelling. This is also reflected in the fluxes towards the sediments as seen in sediment trap studies (Fischer et al., 2000; Manuscript 3).

### *1.3 Past changes*

Although some controversy exists (Diester-Haass 1985, Diester-Haass et al, 1988; Schmidt, 1992;), it is generally accepted that the upwelling intensity and productivity was mainly higher during the glacial periods compared to the interglacials in the Benguela system (Oberhänsli, 1991; Summerhayes, 1995; Little et al, 1997a; 1997b; Kirst et al, 1999). Summerhayes et al. (1995) concluded that the upwelling was intensified off Namibia during the last glacial (isotope stages 2-4) due to a ~5° northwards shift in the South Atlantic high pressure cell strengthening the upwelling favourable southern trade winds. The upwelling seems to have been at its maximum during interstadial isotope stage 3. For isotope stage 2 they concluded from increasing alkenone SST, that the trade-winds were less favourable for coastal upwelling compared to stage 3. For a more detailed description see Summerhayes et al. (1995). Changes in the upwelling intensity on sub-

Milankovitch time scales were reported by Little et al. (1997a; 1997b) and related to changes in the trade wind intensity and linked to the so called Heinrich events and Dansgaard-Oeschger cycles on the northern hemisphere (i.e. Bond et al, 1993; Dansgaard et al., 1993; van Kreveld, et al., 1996).

## 2 Material and methods

The three gravity cores from the continental slope off Namibia we present in this study (GeoB 1710-3, 23.43°S/11.70°E, 2987 m water depth, 1045 core length; GeoB 1711-4, 23.32°S/12.38°E, 1967m water depth, 1066 cm core length; GeoB 1712-4, 23.26°S/112.81°E, 998 m water depth), and the box cores GeoB 1709-1714, were recovered during RV „Meteor“ cruise M20/2 (Schulz et al., 1992). The general descriptions of the core sediments were light green carbonate ooze for GeoB 1710-3 and olive green carbonate ooze for GeoB 1711-4 and GeoB 1712-4.

For the determination of total organic carbon (TOC) and nitrogen in the core material and surface sediments, sub-samples from the freeze-dried and homogenised material were decalcified using 6M HCl in silver boats and dried at 60°C. The samples were combusted at 1050°C in excess oxygen using a commercial Hereaus CHN analyser (Fischer and Wefer 1991; Müller et al., 1994).

The  $\delta^{15}\text{N}$  measurements were performed on a Finnigan Delta Plus attached to a Carlo/Erba NC2500 automatic elemental analyser as preparation line. The stable isotope determination was made from  $\text{N}_2$  gas released by flash combustion in excess oxygen at 1050°C. Depending on organic content, between 5-100 mg of bulk material (freeze-dried and homogenised) was weighted in and measured against 99.996% pure  $\text{N}_2$  tank gas. One internal standard (WST2 6.66‰) was measured for every fifth sample. The  $\text{N}_2$  tank gas and the WST2 house standard were calibrated against the IAEA standards N-1 and N-2. Standard deviation on replica measurements were better than 0.2‰.

## 3 Stratigraphy

The stratigraphic control of the cores GeoB 1710 and GeoB 1711 is based on oxygen isotope analyses of the benthic foraminifera species *Cibicidoides wuellerstorfi*. For the time period between 12 and 38 ka BP, radiocarbon age datings give additional information for core GeoB 1711. GeoB 1712 is correlated to the other two cores using a multi-parameter approach involving  $\text{CaCO}_3$ -, SST- and TOC- records next to the oxygen isotope curve determined from tests of the planktic foraminifera species *Globigerina bulloides*.

Based on the radiocarbon datings and the benthic oxygen isotope ( $\delta^{18}\text{O}$ ) record, the age control of GeoB 1711 is considered most reliable out of the three cores on the transect (Table 1). In contrast to previously published age models for GeoB 1711 (Little et al., 1997b; Kirst et al., 1999; Vidal et al., 1999), we re-evaluated the existing radiocarbon data and discarded several. The measurements for determining radio carbon age published in the studies of Kirst et al. (1999) and Little et al. (1997b) were performed using tests of the planktic foraminifera species *Globorotalia inflata*.

**Table 1:**

GeoB 1710-3		GeoB 1711-4		GeoB1712-4	
Core depth (m)	Age (ka)	Core depth (m)	Age (ka)	Core depth (m)	Age (ka)
0.13	3	0.43	6	0.03	2
0.83	16.1	0.93	11	0.93	13.5
2.13	28.2	1.03 <sup>a</sup>	12.15	1.98	24
2.53	32.5	1.08 <sup>a</sup>	12.68	2.93	32.8
3.45	59.5	1.48	16.1	4.33	57
3.83	66.4	2.88 <sup>b</sup>	29.13	4.88	62.5
4.73	84.1	3.93 <sup>c</sup>	38	5.58	69.4
5.63	108.5	4.98	59	6.23	78.8
6.33	127	5.58	65	6.78	85.8
6.63	135	6.08	71	7.63	110
7.23	146	6.83	80	8.53	134
7.58	151	7.43	87	9.98	151
8.38	171	8.23	99		
8.78	183	8.73	107		
8.93	186	9.73	122		
9.18	194	10.23	128		
9.48	205	10.63	135		
9.73	216				
10.08	228				
10.43	238				
10.58	245				

<sup>a</sup> radiocarbon datum performed on samples of *Globorotalia inflata* from Little et al. 1997b

<sup>b</sup> radiocarbon datum performed on samples of *Globigerina bulloides* from Vidal et al. 1999

<sup>c</sup> radiocarbon datum: KIA3269, 38000 +350, -340 ka  $^{14}\text{C}$ ,  $\delta^{13}\text{C}$ : 0 ‰; *G. bulloides*

In two recent studies, the joint effect that varying species abundance over time and bioturbation have on the radiocarbon age of a given monospecific samples was pointed out (Broecker et al., 1999, Mollenhauer et al., submitted). In the latter study, an age difference of 4600  $^{14}\text{C}$  years was observed for two samples from box-corer sediments from the core location GeoB 1711. One of these two samples was measured on *G. inflata*, which is one of the less common species in the assemblage (Little et al., 1997a), the other on the dominant species in the assemblage, *Neogloboquadrina pachyderma* dextral.

Therefore, we decided to only use datings performed on *G. inflata* from core depths where species abundance is stable and above 10 %. This occurs between 80 and 120 cm core depth. Vidal et al. (1999) performed additional radiocarbon datings using the common planktic species *Globigerina bulloides*. During  $^{14}\text{C}$  measurements,  $\delta^{13}\text{C}$  of the same sample is determined as quality control and for data correction (Nadeau et al., 1997). One age datum given by a *G. bulloides* analysis from Vidal et al. (1999) was discarded because the  $\delta^{13}\text{C}$  measurement suggests sample contamination. For the core levels below 400 cm corresponding to ages older than the range of reliable radiocarbon dating, the age model is based on visual correlation with the normalised SPECMAP standard record (Imbrie et al., 1984) identifying isotopic events. Besides, the interval of the last glacial maximum is identified as the period of highest benthic oxygen isotope values and assigned an age of 16.1 - 19.5  $^{14}\text{C}$  years following the agreement made on the EPILOG workshop in Delmenhorst, Germany, in May 1999 (Mix et al., submitted). The stratigraphy presented here is equal to the one presented in Vidal et al. (1999) for sediments below 493 cm.

The age model for GeoB 1710 is based on peak-to-peak correlation of the *C. wuellerstorfi* oxygen isotope record to that from GeoB 1711. A very good match between the two cores can be achieved spanning the last 135 ka and is also evident in the records of  $\text{CaCO}_3$ , TOC and SST (Fig. 2). Below 663 cm core depth, the level corresponding to 135 ka, we adopt the stratigraphy for GeoB 1710 based on visual correlation with the SPECMAP standard record from Bickert and Wefer (1999).

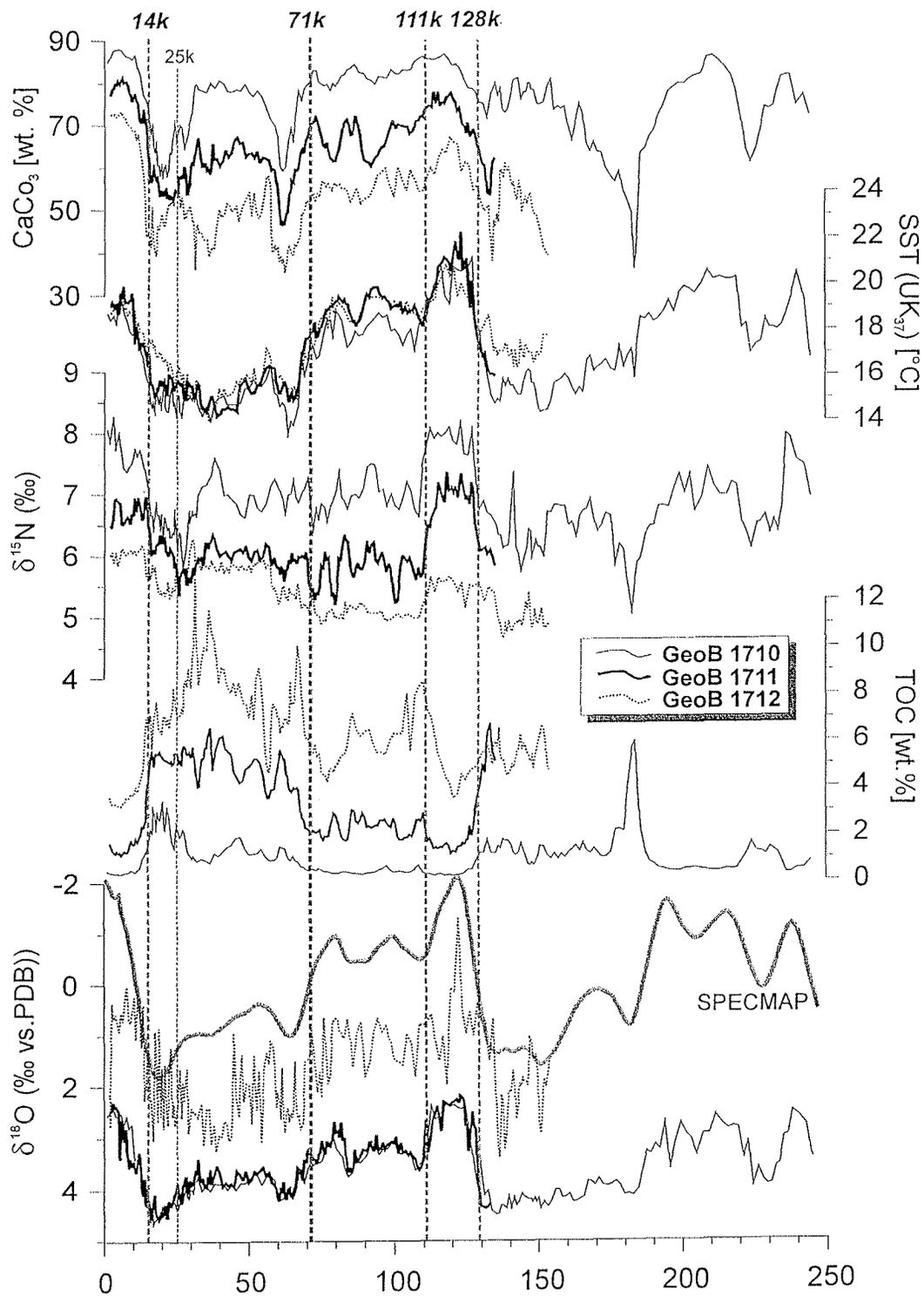
The oxygen isotope record of the planktic foraminifera *G. bulloides* in core GeoB 1712 is very variable and does not allow to unambiguously identify isotopic events. However, a good match between cores can be achieved by using other sediment parameters. This is deduced from the fact that the correlation of GeoB 1710 and GeoB 1711 based on benthic foraminifera isotope records, commonly regarded as a reliable method, results in a good match between the SST- and  $\text{CaCO}_3$ - records. Thus, a multi-parameter correlation, primarily based on SST and  $\text{CaCO}_3$  and supplemented by the TOC-data, was performed for GeoB 1712. A best match for all parameters including  $\delta^{18}\text{O}$  in all three cores was sought.

#### 4 Results

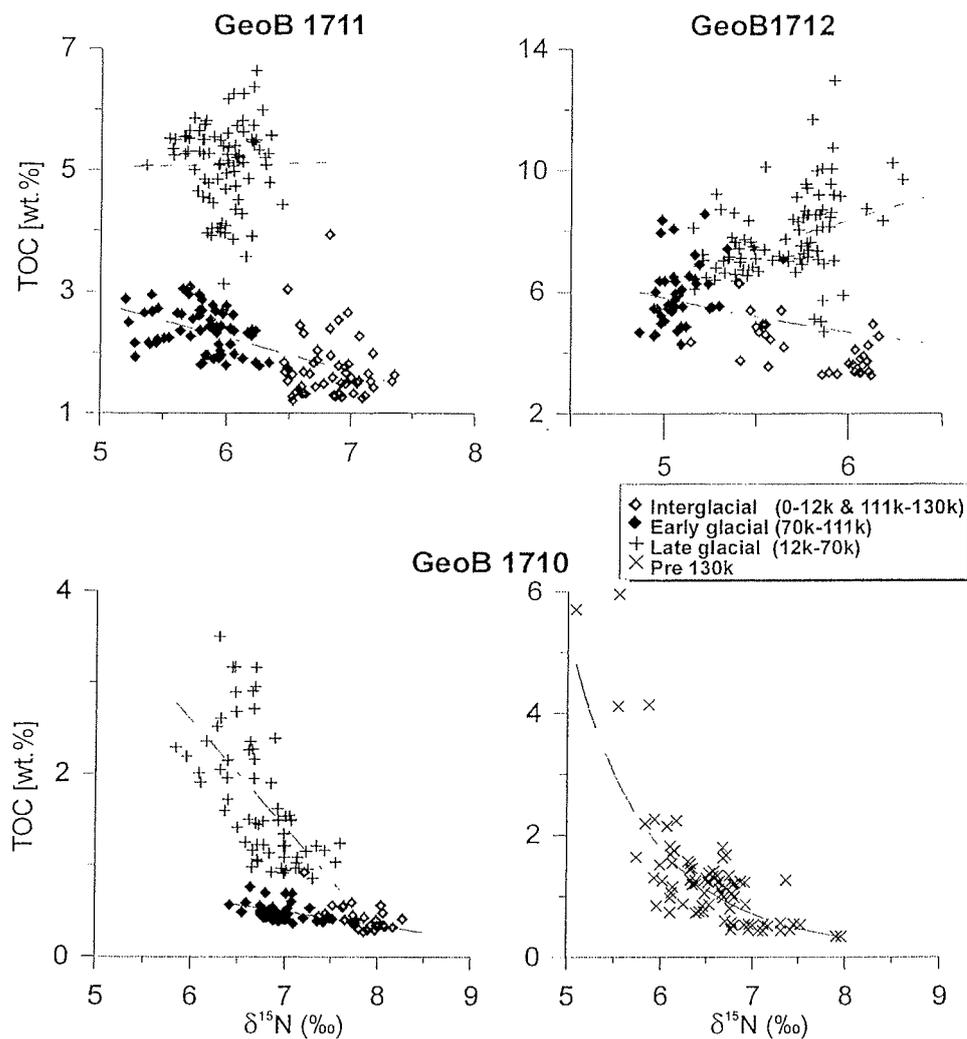
In this section we will point to the most relevant features and coincidences in our data for the later discussions on the impact of sea-level change and upwelling intensity. We consider the  $\delta^{15}\text{N}$  data and the TOC data as the most relevant for reflecting upwelling intensity and proximity to the nutrient source, and thus mainly focus on these data. We prefer to use the TOC (wt %) instead of accumulation rates because the periodicity/frequency of the variations is mainly shorter than the resolution of stratigraphic control. The  $\delta^{15}\text{N}$  and TOC records in the different cores reveal the same main features but with decreasing TOC and increasing  $\delta^{15}\text{N}$  values offshore from GeoB 1712 to GeoB 1710. The major breaks or changes in the records occur at 14ka, 71ka, 111ka and 128ka (Fig. 2). We have no indication longer periods of anoxic sedimentary conditions at any stage in our records (laminated sediments).

The mean  $\delta^{15}\text{N}$  values for the last 14ka were 7.7 (GeoB 1710), 6.7 (GeoB 1711) and 6.1 (GeoB 1712) and for GeoB 1710 and GeoB 1711 these were about the same for the period 111ka-128ka (Fig. 2). The  $\delta^{15}\text{N}$  for GeoB 1712 were 0.5‰ lower through this period compared to the last 14ka. The difference of about 1‰ between GeoB 1710 and GeoB 1711 is, with a few exceptions, maintained throughout the records and the mean  $\delta^{15}\text{N}$  values between 111ka and 14ka were 5.8‰ (GeoB 1711) and 6.8‰ (GeoB 1710). From 111ka to 60-71ka the  $\delta^{15}\text{N}$  records from GeoB 1710 and GeoB 1711 reveal parallel rhythmic variations of 0.5-1‰ magnitude. This pattern continued throughout the glacial period in the GeoB 1710 record but were reduced in GeoB 1711 between 60-71 and ~25ka. During this period (60ka to 30ka) the  $\delta^{15}\text{N}$  values in GeoB 1712 rise approximately to the level of GeoB 1711.

In general, there is a good agreement between the  $\delta^{15}\text{N}$  and the TOC records from GeoB 1710 and GeoB 1711, with high TOC content corresponding to low (light)  $\delta^{15}\text{N}$  values (Fig. 2 and 3). In GeoB 1712, only the breaks in the TOC at 128ka, 111ka and 14ka are reflected by a negative correlation in the  $\delta^{15}\text{N}$  record. During some periods, especially 71ka to 24ka, there appeared to be a positive correlation between the TOC and  $\delta^{15}\text{N}$  values (Fig. 2 and 3). For about the same period (71-30ka) in the GeoB 1711, the negative correlation between TOC and  $\delta^{15}\text{N}$  ceased and was occasionally reversed (Fig. 2 and 3). In GeoB 1710 the TOC content for the whole period 128ka to 71ka is mainly below 0.5% and the variability in the TOC record is low (Fig. 2). It should be noted though, that the relative change i.e. at 111ka (20-50% increase) is about the same magnitude as in the other two cores.



**Figure 2** Sedimentary records from sediment cores GeoB 1710 (thin curve), GeoB 1711 (thick curve), and GeoB 1712 (dotted curve). Vertical dotted lines indicates the main breaks in the sedimentary record. The alkenone ( $\text{UK}_{37}$ ) SST data are from Kirst et al., (1999).



**Figure 3** Organic content (TOC) plotted against  $\delta^{15}\text{N}$ -values for the sediment cores GeoB 1712, GeoB 1711 and GeoB 1710. The data are grouped after the time-spans defined in the text and the discontinuous lines are trend lines from a linear, except the pre 128k in 1710 (power log).

The SST reconstructions from the alkenone  $U_{37}^k$  index revealed very similar patterns throughout the three cores, with a tendency to colder SST in the deepest core (GeoB 1710). The variation in the SST mainly follows the global climate pattern (SPECMAP) but with an exceptionally cold period through most of isotope stage 3. This and the early warming during isotope stage 2 at the site of GeoB 1712 are previously described and discussed by Kirst et al. (1999).

The changes in the  $\text{CaCO}_3$  content were mainly parallel in the three cores, with the larger shifts related to the coldest isotope stages (2, 4, 6.2 and 6.6). One notable exception is the reduced  $\text{CaCO}_3$  content in GeoB 1712 between 30ka and 50ka, which did not occur in the other two cores (Fig. 2).

## 5 Discussion

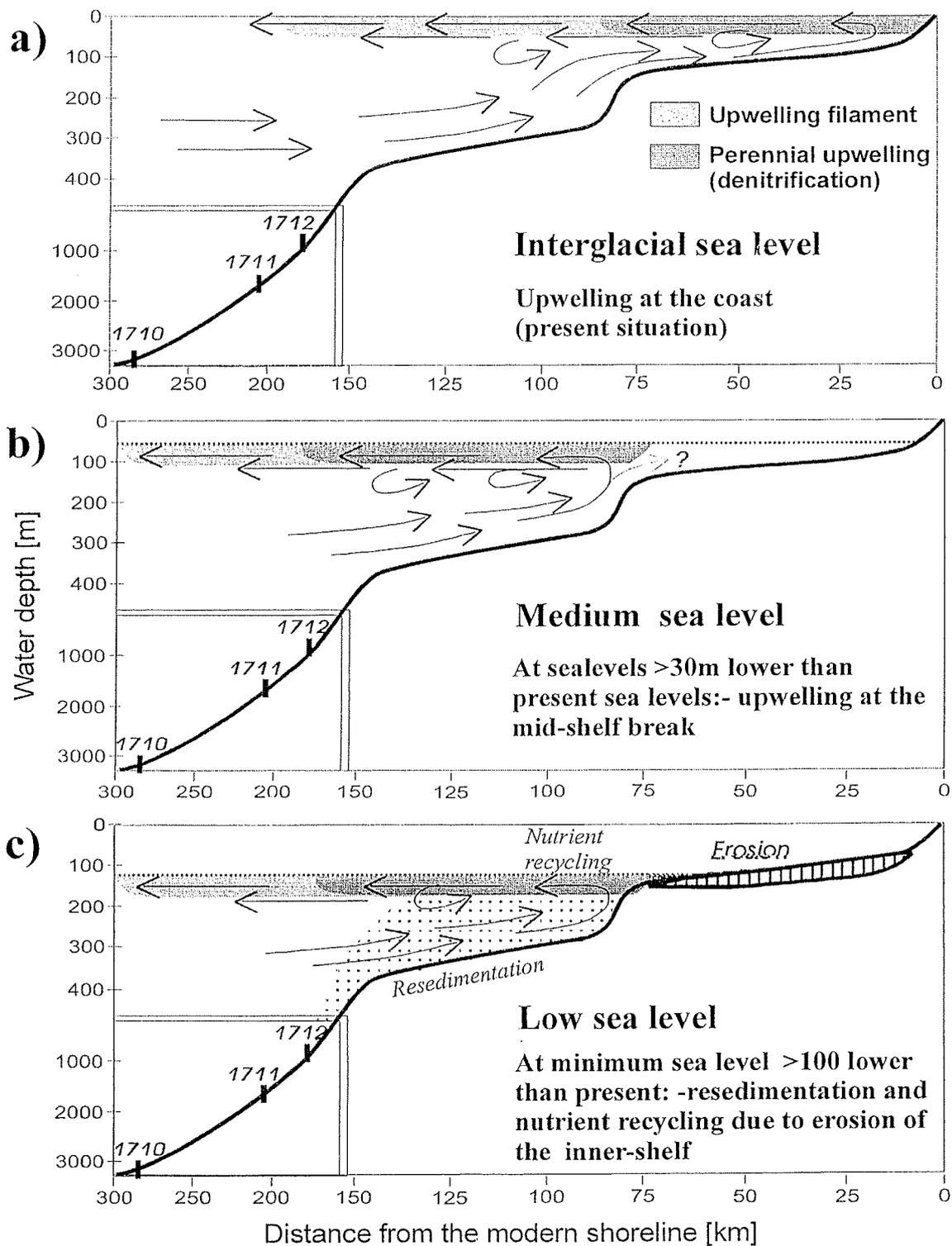
Changes in the nutrient inventory and its  $\delta^{15}\text{N}$  values might have occurred, but a common global glacial to interglacial connection, like for the oxygen isotopes (i.e. SPECMAP), is still not found and might not exist. Altabet et al. (1995; 1999a) and Ganeshram et al (1995) argue that reduced denitrification intensity during glacials in the Arabian Sea and the tropical North Pacific might have increased the nutrient inventory of the world ocean and caused increased global marine productivity during these periods. In contrast to the water that carries the  $\delta^{18}\text{O}$  signal globally with the conveyor belt circulation, the nutrients which carry the  $\delta^{15}\text{N}$  signal get depleted in the surface waters and thus do not return from the Indian,- and Pacific Oceans. This constrains the possible impacts from processes affecting the nutrient budget and  $\delta^{15}\text{N}$  in the Indian-Pacific sector on the Atlantic Ocean's nutrient budget and  $\delta^{15}\text{N}$  signal.

Increased nitrogen fixation due to increasing input of micro nutrients with dust during glacial periods is suggested by Broecker and Henderson (1998). Except in the Cariaco Basin (Haug et al, 1998) this is not confirmed by core data so far, but this may have caused higher nutrient content with lower  $\delta^{15}\text{N}$  values in the southern Atlantic Ocean.

Whatever the causes are, comparing sedimentary  $\delta^{15}\text{N}$  records from different regions most reflect lighter  $\delta^{15}\text{N}$  values during glacial periods compared to interglacials mainly following the major glacial cycles (23k and 41k)(Altabet and Francois; 1994; Farrell et al., 1995; Ganeshram et al, 1995; Haug et al.,1995,1998; Holmes et al., 1997; Altabet et al., 1999a). This indicates that if we should expect changes in the upwelled subsurface waters it would be more nutrients with lighter  $\delta^{15}\text{N}$  signal during marine stage 2, 4 and 6 as compared to 1, 3, and 5 (Altabet et al., 1999a). The major exception is the Southern oceans where the sedimentary  $\delta^{15}\text{N}$  values are higher during the LGM and are ascribed to higher nitrate utilisation due to water column stratification (Francois et al., 1997; 1992; Sigman et al., 1999). The most characteristic differences from the  $\delta^{15}\text{N}$  records presented in this study (Fig. 2) and the records from most of the above mentioned works, are the special shape of the full interglacial periods and the lack of 23k and/or 41k cycles.

### 5.1 Sea-level change

The abrupt changes in the records before and after the full interglacial periods are best explained by a sea-level related seaward shift in the upwelling cell during the glacial periods. By a relatively small change (<30 m) in sea level the upwelling of sub surface water probably shifted from the shore to the mid shelf break about 80 km offshore as illustrated in the cartoon (Fig. 4a and b).



**Figure 4** Suggested model for impact from changing sea-level on the coastal upwelling cell outside Walvis Bay, south-western Africa.

The main evidence of this are the  $\delta^{15}\text{N}$  records, where the difference in  $\delta^{15}\text{N}$  values between GeoB 1711 and GeoB 1710 (80 km further offshore) perfectly matches the abrupt change in the  $\delta^{15}\text{N}$  records (Fig. 2). The glacial  $\delta^{15}\text{N}$  values in GeoB 1710 are at the same level as the interglacial values in GeoB 1711. If these changes were caused by variations in the nutrient inventory of the subsurface waters similar changes should also have been detected in  $\delta^{15}\text{N}$  records from other regions like neighbouring Angola basin (Holmes et al., 1997).

Considering the duration of the interglacial compared to the glacial mode, the present situation with upwelling directly at the coast/shore is the exception and upwelling at the mid shelf break the rule. The sea-level rise during sub-stage 5.1 and 5.3 was not sufficient to allow the upwelling to migrate shorewards and limit the sea-level stand for upwelling at the shore to >30m below the present sea level (Martinson et al., 1987; Winograd et al., 1992). The sensitivity to sea-level change for the present mode of upwelling, is further stated during isotope stage 7 (only represented in GeoB 1710), which did not reach the high sea levels of Stage 1 and 5.5 (Imbrie et al., 1984; Martinson et al., 1987; Winograd et al., 1992; Eisenhauer et al., 1996). In the  $\delta^{15}\text{N}$  data from GeoB 1710 isotope stage 7 there is only a short period during sub-stage 7.5 where a shoreward shift in the upwelling cell is indicated by increasing  $\delta^{15}\text{N}$  values.

Considering the timing of the shifts, it appears that the onshore migration of the upwelling cell (14ka and 128ka) related to the termination of the glacials occurred at lower sea levels than the offshore migration (111ka) during dropping sea level. The timing of the onshore migration during Termination 1 (14ka) coincides with the results from Bard et al. (1996) who concluded that there was a large rise in sea level shortly before 13.8k. For Termination 2, there is some controversy about the timing of this event between the orbitally tuned marine isotope records (Imbrie et al., 1984; Martinson et al., 1987) and U/Th dated sea-level changes (Winograd et al., 1992; Eisenhauer et al., 1996). To avoid this discussion we use the transition in the benthic  $\delta^{18}\text{O}$  records for GeoB 1711 and GeoB 1710 as an indicator for global sea-level change. Considering the changes in the  $\delta^{18}\text{O}$  records, onshore shifts of the upwelling according to the  $\delta^{15}\text{N}$  records (14ka and 128ka) occurred at a relatively early stage of sea-level rise, but the offshore shift at 111ka coincide with the initial change in the  $\delta^{18}\text{O}$  record. Erosion of the inner shelf during the lowest sea-level stands might offer an explanation for this. If the inner shelf was eroded down to the basement during the lowest sea-level stands, this might have caused a lowering of the surface of the inner shelf and thus, allowed the upwelling water to reach the shore at lower sea-level stands. A dependence on the sediment package is also supported by the  $\delta^{15}\text{N}$  data from isotope stage 7 (GeoB 1710), where an onshore migration might have occurred only

during sub-stage 7.5, although the sea-level stand was slightly higher during 7.3 and 7.1 (Imbrie et al., 1984; Martinson et al., 1987; Winograd et al., 1992).

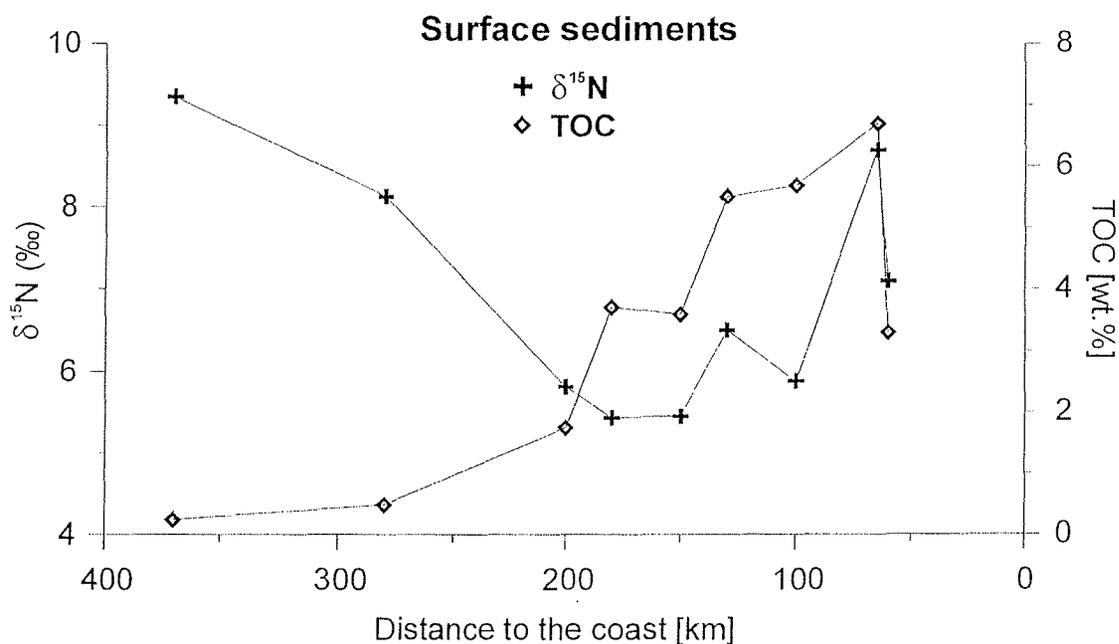
## 5.2 Processes

### 5.2.1 The present situation

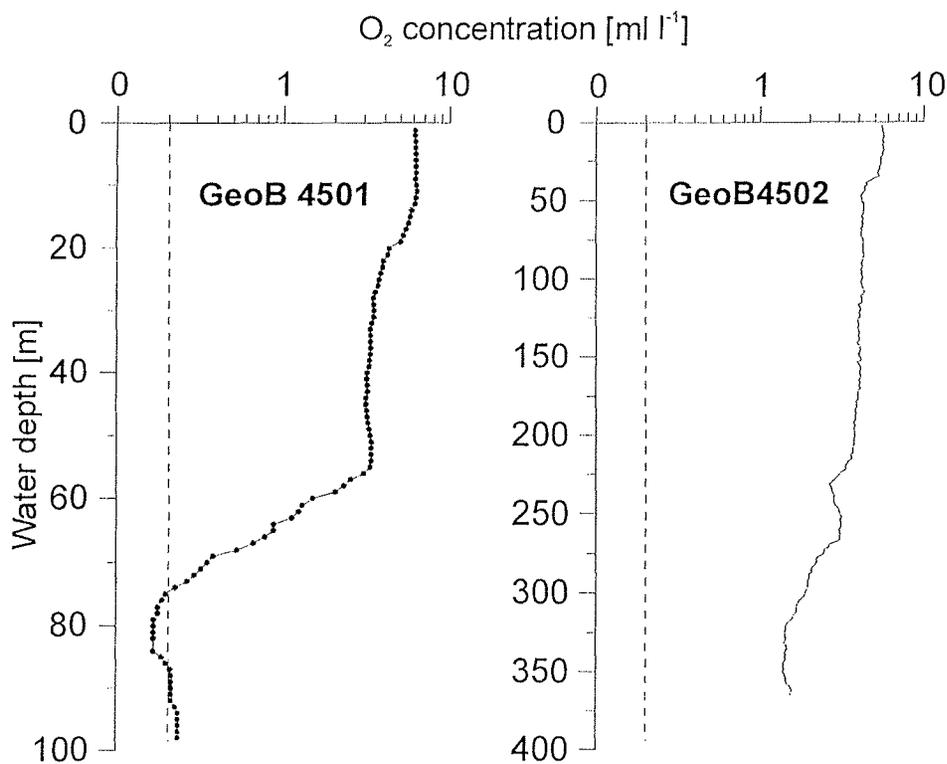
For our study area, the Benguela Upwelling system, Holmes et al. (1998, 1999) concluded that denitrification had not largely influenced the sedimentary  $\delta^{15}\text{N}$  values on the outer shelf and the continental slope, based on the decreasing  $\delta^{15}\text{N}$  values with increasing nutrient content towards the upwelling area. In Table 2 (Fig.5) we have added some surface-sediment samples closer to the coast, and it is evident that the  $\delta^{15}\text{N}$  values on the inner shelf are higher than the ones from the outer shelf and the upper continental slope. With the additional information that the amount of dissolved oxygen in the water column above site GeoB 4501 drops below the critical value for denitrification ( $0.2\text{mL L}^{-1}$ , Packard et al., 1983) in the lower part of the water-column (Fig. 6), it is likely to explain the high  $\delta^{15}\text{N}$  values on the inner shelf with water column denitrification. Mixing and recycling the nitrate relatively enriched in  $^{15}\text{N}$  due to denitrification, with the newly upwelled nitrate to the surface, would lead to a heavier isotopic composition of the nitrate source. The resulting  $^{14}\text{N}/^{15}\text{N}$  composition of the nitrate source would depend on the extent/strength of the denitrification and the relative amounts of the two nitrate sources, new and recycled additional to the relative nitrate utilisation.

**Table 2:**

<b>Surface sediment samples</b>					
Sample	Position	Distance to coast	Water depth	TOC %	$\delta^{15}\text{N}$ ‰
GeoB1709	23.35S/10.46E	370	3837	0.24	9.35
GeoB1710	23.26S/11.42E	280	2983	0.49	8.13
GeoB1711	23.19S/12.23E	200	1964	1.74	5.81
GeoB1712	23.15S/12.48E	180	1007	3.71	5.43
GeoB1713	23.13S/13.01E	150	597	3.6	5.45
GeoB4502	23.08S/13.11E	130	370	5.5	6.5
GeoB1714	23.08S/13.33E	100	200	5.69	5.88
NAM1	22.40S/14.00E	65	125	6.7	8.7
GeoB4501	22.25S/14.03E	60	98	3.3	7.1



**Figure 5** Organic content (TOC) and bulk  $\delta^{15}\text{N}$  values from surface sediments along a West to east-transect around 23°S. For sample identity see Table 2.



**Figure 6** Oxygen concentration in the water column at two stations GeoB 4501 and GeoB 4502 calculated from CTD profiles. The critical level for efficient denitrification 0.2 [ml l<sup>-1</sup>] are indicated with a dotted line.

Heavier N-isotopic composition of the nutrient source due to denitrification at Walvis Bay compared to Northern Namibia (with less intense upwelling, Lutjeharms and Meeuwis, 1987) could explain the heavier  $\delta^{15}\text{N}$  composition 100-200 km off the coast at Walvis Bay (6.5-5.4, Table 2, Fig 5) compared to Northern Namibia (4.8-4.7, Holmes et al, 1998). However, finding lower  $\delta^{15}\text{N}$  values on the outer shelf and upper slope compared to the inner shelf (Table 2, Fig. 5), indicates that the water column denitrification above the inner shelf rather affects the nitrogen exported to the sediment at the inner shelf than the presumably common source. A separate study would be needed to fully understand the extent, timing and impact of the denitrification in the water column over the inner shelf. Nevertheless, we would suggest the following hypothesis to explain the registered sedimentary  $\delta^{15}\text{N}$  values from Table 2: -Over the inner shelf upwelling and high production is present more or less through the whole year but the strong upwelling events causing increased production above the outer shelf and continental slope is seasonal (Lutjeharms and Meeuwis, 1987; Lutjeharms and Stockton, 1987). If the water column denitrification is stronger over the inner shelf when the supply of well oxygenated subsurface waters is less, between the strong upwelling events, this would explain the stronger impact from denitrification on the export production over the inner shelf. Moreover, when the supply of new, isotopically light, nitrate is large this would dilute the impact from denitrification when the high production is extended further offshore.

Another mechanism with influence on the sedimentary  $\delta^{15}\text{N}$  values from the inner shelf towards the upper continental slope at least, is the onshore bottom transport on the inner shelf and the offshore bottom transport on the outer shelf described by Giraudeau et al. (2000). This transport brings particles from the mid-shelf with heavier isotopic composition towards the outer shelf and the upper slope and could smoothen the visible/recorded impact from denitrification. Considering our core locations (GeoB 1710, GeoB 1711 and GeoB 1712), the direct influence from denitrification seems to be minor during the present situation due to the continuously rising  $\delta^{15}\text{N}$  values combined with decreasing organic content (TOC) seaward from GeoB 1712 (Table 2). Although some material from the shelf might be deposited by bottom transport at the uppermost site GeoB 1712 (Giraudeau et al., 2000), there is a clear negative correlation between  $\delta^{15}\text{N}$  and TOC offshore. On the contrary, the correlation between TOC and  $\delta^{15}\text{N}$  shoreward from GeoB 1713 is positive (rising  $\delta^{15}\text{N}$  with rising TOC, Fig. 5).

Increasing diagenetic effect with lower fluxes/burial rates (Altabet et al., 1999b) offshore along the transect might have added to the spatial difference related to the degree of relative nitrate utilisation (Holmes et al., 1998). By using the results from Manuscript 3, revealing limited ( $\sim 0.5\%$ ) diagenetic fractionation at the Walvis Ridge (400km offshore,

2196 m water depth, and 0.46 wt.% TOC), as an analogue, the sediment cores at least (Fig. 5, Table 2) should have limited isotopic fractionation due to diagenesis at the sediment water interface. Limited difference in the diagenetic effect between GeoB 1710 and GeoB 1711 is further indicated during the abrupt changes in the  $\delta^{15}\text{N}$  records (Fig. 2) where the change in the TOC record does not fully match the difference between the cores like it is in the  $\delta^{15}\text{N}$  records.

### 5.2.2 Down core variation

From the discussion above, these two mechanisms (nitrate utilisation and denitrification) potentially governing the sedimentary  $\delta^{15}\text{N}$  values could be singled out down core by the relation to export production best represented by TOC content. A positive correlation indicates that water column denitrification was directly influencing the  $\delta^{15}\text{N}$  signal at this site. By a negative correlation, the relative nutrient utilisation reflecting upwelling intensity was governing the sedimentary  $\delta^{15}\text{N}$  record. This is of course not straight forward, because both processes probably would be of importance at the same time near an upwelling centre. Therefore, by changing dominance between denitrification and nutrient utilisation week to no relations would be expected. Additionally, it should be kept in mind that the TOC content would also depend on factors like carbonate dissolution and silicate accumulation. Still, plotting the data like in Figure 3 could give valuable information about the mechanisms governing the sedimentary  $\delta^{15}\text{N}$  values.

In GeoB 1710 there is a clear negative correlation between TOC and  $\delta^{15}\text{N}$  throughout the core and there is no reason to assume that this site was directly influenced by water column denitrification. Indirect influence (affected source), could possibly explain the apparent shift in relation between the inter- and early glacial periods to the late glacial period. The change between inter- and early glacial to late glacial is more drastic in GeoB 1711 with no systematic relation between TOC and  $\delta^{15}\text{N}$  during the late glacial. This indicates that this site, at least periodically, during the late glacial was directly influenced by water column denitrification. In GeoB 1712 there also seems to be a similar shift between the inter- and early glacial period to the late glacial, but with a positive correlation during the late glacial indicating a predominant impact on the  $\delta^{15}\text{N}$  values from water column denitrification. The apparent negative correlation from the inter- and early glacial periods might be a pseudo relation, because the negative correlation between TOC and  $\delta^{15}\text{N}$  is rather from one period to the other and not within each of the periods.

From this we can deduce that even if none of the core sites are directly influenced from water column denitrification at the present, this at least periodically influenced the sites of GeoB 1712 and, although to a lesser extent, GeoB 1711. This reduced or reversed the (negative) correlation between the  $\delta^{15}\text{N}$  signal and the productivity/upwelling intensity.

Therefore we would have to consider both denitrification and relative nitrate utilisation under changing conditions in our records. However, by using three well correlated cores along a transect away from the upwelling cell we have a good chance to isolate the governing processes for the nitrogen isotopes and their environmental implications.

### 5.3 Core transect GeoB 1710, 1711 and 1712

The similarities in the GeoB 1710 and GeoB 1711  $\delta^{15}\text{N}$  records and the negative correlation between to the TOC records makes us confident that these two cores mainly reflect the relative nutrient utilisation, except from 60-30ka in the GeoB 1711 (Fig. 2 and 3). The low variability and the mainly positive correlation to the TOC record, in the  $\delta^{15}\text{N}$  values from GeoB 1712, suggest that factors other than nitrate utilisation have to be taken into account. Additionally to the above discussed water column denitrification, resuspended material (Summerhayes et al, 1995) and particle transport from the shelf related offshore flowing bottom currents (Giraudeau et al., 2000) could wipe out or smoothen the upwelling related  $\delta^{15}\text{N}$  variation. Due to the good correlation between the alkenone temperatures in GeoB 1712 and the other two cores, we reckon that large scale resedimentation from the inner shelf during periods of lower sea level did not occur. One exception is the last glacial maximum (14ka-24ka) where the planktic  $\delta^{18}\text{O}$ -record reveals large oscillations and the alkenone temperatures in GeoB 1712 were distinctly warmer than in the other two cores. This could have been caused by a large scale resedimentation of older sediments, possibly from the last interglacial period and is discussed later. Summerhayes et al. (1995) estimated the amount of resedimented material as high as 40% during this period (LGM) at the same depth close to GeoB 1712.

To compare the records under the same frame conditions, we will discuss in order of periods that are defined by the main breaks in the records, previously described in the result chapter.

#### 5.3.1 The interglacials (0-14ka and 111-128ka)

The two extended interglacial periods appear to have been quite similar, particularly according to the records from GeoB 1710 and GeoB 1711 (Fig. 2). The variability of the upwelling intensity within the interglacials seems to be lower than during the glacial periods, with only minor changes in the TOC and  $\delta^{15}\text{N}$  records. However, the negative correlation between TOC and  $\delta^{15}\text{N}$  (Fig. 3) and the synchronous changes the  $\delta^{15}\text{N}$  values in GeoB 1710 and GeoB 1711 (Fig. 2), suggest that these data reflect small scale variations in the upwelling intensity with a frequency of 5 to 10k.

In GeoB 1712 there is a tendency towards lighter  $\delta^{15}\text{N}$  values with increasing depth, especially seen by comparing the interglacial periods. We can not say for sure if this is an environmental change or a diagenetic effect due to loss of Nitrogen from the sediment. Higher TOC content point towards stronger upwelling during the last interglacial compared to Holocene (Imbrie et al., 1984; Martinson et al., 1987; Winograd et al., 1992), which for some reason was not influencing the other two cores. A more oxygenated water column, and thus less impact from denitrification at the site of GeoB 1712 during the last interglacial period, could also have caused this discrepancy. This is, however, contradictory to the rest of the record. The possibility of a diagenetic process is supported by steadily increasing C/N ratios with depth in this core (data not presented here). Consequently, there had to be a preferable loss of nitrogen species with heavy isotopic composition from the sediment, a diagenetic effect opposite of the better known early diagenesis (i.e. Francois et al., 1997, Manuscript 1). To find out which nitrogen species eventually were lost, pore water analysis with  $\delta^{15}\text{N}$  analysis on the specific nitrogen species have to be performed on fresh core material.

### 5.3.2 The early glacial period (71-111ka)

Within this period the upwelling took place at the mid shelf-break, but the basic characteristics of the upwelling were about the same as during the interglacials. The higher TOC and lower  $\delta^{15}\text{N}$  values compared to the interglacials were probably caused by the offshore migration in the upwelling centre and do not necessarily imply increased upwelling. From the  $\delta^{15}\text{N}$  and TOC records (Fig. 2), a somewhat larger variability in the upwelling intensity compared to the interglacials seems to have occurred.

The shift in the  $\delta^{15}\text{N}$  values equals the difference between the records (Fig. 2) and thus matches the offshore migration of the upwelling cell (Fig. 4). The shift in the TOC content, though, is somewhat less than the difference between the records (Fig. 2). This could be a matter of depth difference between the core sites, as burial rates of organic carbon are reduced as a function of depth. Another factor that could play a role is the bottom transport from the lower shelf and upper slope as described by Giraudeau et al. (2000). This transport and its impact on the sedimentation is related to the slope and the distance from the shelf edge (higher impact at the site of GeoB 1712 and ceasing towards GeoB 1710) which would not necessarily change with the offshore shift of the upwelling centre.

Throughout this period the  $\delta^{15}\text{N}$  records from GeoB 1710 and GeoB 1711 correlate very well and reveal variation on sub-Milankowich time-scales (5-15k cycles). The  $\delta^{15}\text{N}$  reveals a negative correlation to the TOC content with approximately the same linear trend as the interglacial periods (Fig. 3). This suggests that the  $\delta^{15}\text{N}$  signal in these two cores reflect variation in relative nitrate utilisation related to changes in the upwelling intensity.

Moreover, the TOC content in GeoB 1712 is positively correlated to its own  $\delta^{15}\text{N}$  record, reflecting more anoxic conditions with increasing upwelling but, except for 71ka to 85ka, the TOC in GeoB 1712 negatively correlates to the  $\delta^{15}\text{N}$  in the other two cores (Fig. 2).

At the present there are no lower surface-sediment  $\delta^{15}\text{N}$ -values onshore from GeoB 1712 (Table 2) that could explain the  $\sim 0.5\%$  shift to lighter  $\delta^{15}\text{N}$  values at 111k in GeoB 1712. This might indicate a reduction in denitrification as the upwelling is moved to larger water depth at the mid-shelf break. However, a reduction in the bottom-current transport (Giraudeau et al., 2000) might also cause a similar effect by transporting less particle from the area with a suboxic water column to the upper slope. We will not be able to resolve this here as differences in bottom current systems due the shape and depth of the shelf additional to surface currents is a complex issue (Giraudeau et al., 2000).

### 5.3.3 The late glacial period (14-71ka)

During this period a substantial increase in the productivity seems to have occurred (Oberhänsli, 1991; Summerhayes, 1995; Little et al, 1997a; 1997b; Kirst et al, 1999) and is well documented in our data by a major increase in the TOC content in all three cores at about 71ka (Fig. 2). Between 60k and 71ka the good coherency in the  $\delta^{15}\text{N}$  data from GeoB 1710 and GeoB 1711 fades out (Fig. 2) and there is no consistent correlation between TOC and  $\delta^{15}\text{N}$  in GeoB 1711 (Fig. 2). At about the same time (75k-60ka) an increase occurred in the  $\delta^{15}\text{N}$  values from GeoB 1712, and from  $\sim 60\text{k}$  to 24ka the  $\delta^{15}\text{N}$  values in GeoB 1711 and GeoB1712 are partly overlapping (Fig.3). Increasing influence from water column denitrification both seaward (GeoB 1711) and in intensity (GeoB 1712) is the likely cause of this change in the respective  $\delta^{15}\text{N}$  records. Between 24ka and 30ka, when the upwelling probably was at its maximum (discussed below), the  $\delta^{15}\text{N}$  values in GeoB 1712 are mainly higher than in GeoB1711. This situation could be analogue to the present situation closer to the upwelling centre. The  $\delta^{15}\text{N}$  GeoB 1712 is similar to GeoB 1713 and even closer to the upwelling, at the site of GeoB 1714, the  $\delta^{15}\text{N}$  value increases (Table 2, Fig. 5). We will not go into a detailed discussion on these two cores during this period, not only because of the complex relationship between  $\delta^{15}\text{N}$  and upwelling intensity when water column denitrification occurs, but also due to a complex relationship between TOC and upwelling very close to the upwelling centre where silicate is dominating the sedimentation (Calvert and Price, 1983). Additionally, controversy exists about the change in carbon preservation in the sediment relying on oxygen availability (Emerson and Hedges; 1988; Canfield 1989; Pedersen and Calvert, 1990; Ming et al., 1993).

Only core GeoB 1710 seems to have been unaffected by water column denitrification during this period (24ka-71ka) and continuously reflects relative nitrate utilisation. There are no change in the mode of variation in the GeoB 1710  $\delta^{15}\text{N}$ -record compared to the

early glacial period until ~35ka (Fig. 2). The low/decreasing  $\delta^{15}\text{N}$  values from 35ka to 30ka were accompanied by increasing TOC content and probably reflect increased upwelling intensity. However, instead of returning back towards less upwelling, which was the pattern from 111k to 35ka, there seems to have been a further strong enhancement at about 30ka. After explaining the characteristic drop in the  $\delta^{15}\text{N}$  from the interglacial to the glacial mode by a sea-level related offshore shift in the upwelling, a further shift, i.e. to the shelf edge, might offer an explanation for this break in the rhythmical variation in the  $\delta^{15}\text{N}$  record. There are two main arguments against this scenario; 1) this does not appear at a period with a drastic change in the sea level (Martinson et al., 1987; Imbrie et al., 1984; Winograd et al., 1992), and 2) the other offshore movements in the upwelling cell are clearly recognised in all three records, this one is not. Moreover, this incident in GeoB 1710 coincides with a strong upwelling period north of the Walvis Ridge, registered in low  $\delta^{15}\text{N}$  and high TOC content in core GeoB 1016 (Holmes et al., 1997). Similar coincidences exist between these two cores during isotope stage 6 and will be further discussed under the pre-128ka section.

Although we consider the  $\delta^{15}\text{N}$  in GeoB 1710 to reflect the upwelling intensity, a notable change in the relationship between TOC and  $\delta^{15}\text{N}$  occurred at about 71ka (Fig. 2). Above we interpreted from the  $\delta^{15}\text{N}$  values that a further offshore extension of the upwelling cell compared to the early glacial period, is only evident after ~30ka. There are two possible explanations for this abrupt change in the relation between TOC and  $\delta^{15}\text{N}$ , where one does not exclude the other:

- 1) Enhanced denitrification as indicated by the GeoB 1711 and GeoB 1712 records affects the  $\delta^{15}\text{N}$  of the nutrient source due to increased loss of isotopically light nitrate. This could compensate for expected lighter  $\delta^{15}\text{N}$  values by increasing upwelling intensity. This would reduce the amplitude in the  $\delta^{15}\text{N}$  variation because the denitrification would be stronger by high upwelling intensity as the  $\delta^{15}\text{N}$  values are at the minimum. Albeit this is partly contradictory to the very light  $\delta^{15}\text{N}$  (>6‰) combined with the high TOC between 33 and 24ka.

- 2) A change towards more perennial upwelling, like at the Lüderitz upwelling cell at the present day situation, could have caused an enhancement in the productivity without a further offshore extension of the upwelling cell. If the wind, either through strength or direction, were causing stronger upwelling events, extending further offshore, this would be seen in the  $\delta^{15}\text{N}$  records with lighter values. However, the sedimentary  $\delta^{15}\text{N}$  values would depend on the  $\delta^{15}\text{N}$  values from the dominating particles fluxes during the upwelling events (see introduction), thus the sedimentary  $\delta^{15}\text{N}$  would not necessarily record whether these high fluxes occurred once or twice a year. Considering that the offshore extension of the Namibian and Lüderitz upwelling cells are about the same, but

the upwelling frequency is almost three times higher at the Lüderitz cell (Lütjeharms and Meeuwis, 1987), we would suggest a more perennial upwelling as the most likely explanation for the enhanced productivity during the period from 71ka to 24ka.

Based on our data alone we can not decide if this is a change in the wind/upwelling pattern at the existing Namibian cell or if this is caused by an equatorward migration of the Lüderitz cell. The timing of this shift coincides well with the suggested equatorward migration in the Subtropical Convergence (STC) during isotope stage 4-2 (Morley, 1989; Howard and Prell, 1992), and would be an argument for the latter explanation. A further indication for a change towards a perennial upwelling is the lowering in the alkenone temperatures, known in general to reflect annual mean SST (Prahl et al., 1988, Müller et al., 1998) and warm seasons from surface sediments in this area (Kirst et al., 1999) rather than upwelling temperatures. Consequently, if the upwelling was perennial the upwelling temperature was the annual mean temperature.

The period from 24ka to 14ka is the period of minimum sea-level stand (LGM) and most of the 80 km of inner shelf was exposed to erosion either from tidal currents, winds, and rain. We previously mentioned that resedimentation from the upper shelf, during this period, could explain the discrepancies between the alkenone temperatures in GeoB 1712 and the two other cores and the large oscillations in the planktic  $\delta^{18}\text{O}$  curve from GeoB 1712. If large areas of the inner shelf were eroded and large scale resedimentation took place, we have to assume that this also influenced the two cores further away from the shelf (GeoB 1711 and GeoB 1710). Not only the direct resedimentation, which might be of less importance further down the continental slope, have to be considered. We would suggest that potentially more important is the huge amounts of nutrients that eventually would be released. This could be a large source of nutrients for primary production additional to the upwelling during this period and partly be responsible for the very high TOC content during this period (Fig. 2) when Summerhayes et al. (1995) concluded that the winds were less favourable for coastal upwelling. The rather light  $\delta^{15}\text{N}$  values but increasing offshore from GeoB 1712 to GeoB 1710 (Fig. 2) indicate high production due to recycling of nutrients rather than direct resedimentation as the most important factor for the high TOC. This is because sediments from the inner shelf would not be expected to have a light  $\delta^{15}\text{N}$  signature (Table 2) and there is no reason why the  $\delta^{15}\text{N}$  of the resedimented material should be different further away from the source. It is difficult to predict the exact impact this nutrient recycling would have had on the  $\delta^{15}\text{N}$  records, but during this period there is again a coherency between the  $\delta^{15}\text{N}$  records from GeoB 1710 and GeoB 1711.

### 5.3.4 The pre 128ka period

The most striking event during isotope stage 6, both in the  $\delta^{15}\text{N}$  and the TOC records, is the overall highest peak in the TOC accompanied by the lightest  $\delta^{15}\text{N}$  values during isotope stage 6.6. The same event is previously reported from the eastern Angola basin, particularly in core GeoB 1016 north of the Walvis Ridge (Holmes et al., 1997). Additionally (as mentioned above), both cores reveal similar features during the last glacial period (24-30ka). Although the  $\delta^{15}\text{N}$  records in these two cores seem to be governed by different processes/cycles (GeoB 1016 is dominated by the orbital precessional cycles), they appear to share these two events. It is beyond the task of this paper to find the common cause for this event, but as these cores are from different ocean basins we would suggest that the connection can be found in the wind driven upwelling intensity rather than changes in the water masses. Although we can not exclude a over-regional change in the nutrient budget of the ocean.

The GeoB 1710  $\delta^{15}\text{N}$  record from the rest of isotope stage 6 mainly shows variations in a similar frequency as for the last glacial period (5-15ka) with a general drop in the  $\delta^{15}\text{N}$  values at about ~150ka. We interpret these variations as changes in the relative nitrate utilisation due to changes in the wind driven upwelling intensity. The  $\delta^{15}\text{N}$  record from GeoB 1712 is positively correlated to the TOC content and thus mainly reflects increasing water column denitrification with increasing upwelling intensity.

The increasing  $\delta^{15}\text{N}$  values in GeoB 1710 and GeoB 1712 before the rise in sea level is accompanied by high TOC content and suggest that resedimentation and nutrient recycling, as suggested for the last glacial maximum, could explain this feature. The increased difference in the alkenone temperatures between the two cores (GeoB 1712 and GeoB 1710) comparable to the LGM supports this.

### 5.4 Periodicity of the variation

In the above sections we have discussed the large changes in the records related to sea-level change and frontal zones but just mentioned the sub- Milankowich variation best recorded in the  $\delta^{15}\text{N}$  record of GeoB 1710. Variations on these time-scale have been described in earlier studies, both on land (Stokes et al., 1997) and in the upwelling intensity (Little et al., 1997a; 1997b). Although this is a complex issue and beyond the main scope of this study we will discuss it briefly on the base of the  $\delta^{15}\text{N}$  data.

The works from Little et al. (1997a; 1997b) based on planktic foraminifera includes core GeoB 1711 and it would have been natural to make a direct comparison to our  $\delta^{15}\text{N}$  data from the same core. However, from 60ka to 20ka where they registered most of the „PS-events“ (*Neogloboquadrina pachyderma sinistral*) the  $\delta^{15}\text{N}$  record from GeoB 1711

was probably influenced by water column denitrification and thus not reflecting relative nutrient utilisation.

Due to the negative correlation between  $\delta^{15}\text{N}$  and TOC in  $\delta^{15}\text{N}$  throughout most of GeoB 1710, we think that the  $\delta^{15}\text{N}$  record mainly reflects the relative nutrient utilisation which again we interpret as change in the strength of the wind driven coastal upwelling. The latter is an assumption that we so far have not cleared for. Potentially a change in; 1) the shelf edge upwelling, 2) the nutrient pool of the upwelled water could have caused similar changes.

1) Changes in the shelf edge upwelling intensity have been suggested by Summerhayes et al. (1995), but this would probably change with the frontal zones following the major glacial cycles (41k and 23k) (Morley, 1989; Howard and Prell, 1992; Summerhayes et al, 1995) rather than sub-Milankovich cycles. Secondly, the water upwelled at the shelf edge is originating from above the thermocline (Barange and Pillar, 1992) which is known to have a somewhat heavier  $\delta^{15}\text{N}$  signal ( $>8\text{‰}$ ) compared to the deeper waters  $\sim 5\text{‰}$  (Sigman, 1997). Thus, an enhancement in the shelf edge upwelling could increase the productivity but would probably not lower the  $\delta^{15}\text{N}$  values.

2) By increasing the amount of nutrients in the upwelled water it is imaginable that the production increases and the relative nutrient utilisation above the core site is reduced, and thus lowered  $\delta^{15}\text{N}$  values. This would be difficult to distinguish from an enhancement in the wind driven upwelling by using  $\delta^{15}\text{N}$  and TOC, because the effect would be exactly the same. Although we cannot exclude this as a influential factor, changes in the oceans interior nutrient pool would rather follow the major glacial cycles, due to changes in the relationship between denitrification and nitrogen fixation (Altabet et al., 1999a).

We will not go further into the mechanisms that change the wind driven upwelling. Although we would point to the periodicity of change in the  $\delta^{15}\text{N}$  record (GeoB 1710) between 35ka and 105ka, where factors other than upwelling intensity seem to have been of minor importance. There are nine peaks indicating minimum upwelling (we counted the maximum  $\delta^{15}\text{N}$  values because they are more defined than the minima) during this period which fits the number of interstadials (IS) in the GRIP2 ice core from Greenland (Grootes et al., 1993).

## 6 Conclusions

Water-column denitrification occurs at present above the inner shelf, presumably with the larger impact during periods with less upwelling and thus supply of well oxygenated upwelling water.

An abrupt offshore migration of the upwelling cell to the mid shelf break about 80 km seaward from the present shoreline occurred with less than 30 m sea-level change. The upwelling directly at the coast of Walvis bay like the present situation, occurred only during the interglacial periods 128-111ka and 14ka to present (extended isotope stage 5.5 and 1 respectively).

A change toward more perennial upwelling at the Walvis Bay upwelling cell, like at Lüderitz for the present situation, took place during isotope stage 2-4. This also extended the zone affected by water column denitrification further offshore, with a maximum in the denitrification during isotope stage 3.

Two distinct maximums in the offshore extent of the upwelling filaments occur at the end of isotope stage 3 and in early isotope stage 6 and is of inter-regional character as they coincide with similar events in the Angola basin.

Erosion of the inner shelf during the lower sea-level stands, especially LGM, probably released large amounts of nutrients and thus notably enhanced the production in this region independently from the upwelling intensity during LGM.

### **Acknowledgements**

We thank the officers, crew and scientists aboard R/V *Meteor* for their help during core recovery and sampling, and Monika Segl and Wolfgang Bevern for the assistance with the mass spectrometry analyses. Special thanks to Emma Eades for correcting the English and commenting on a previous version of this manuscript. This research was funded by the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 261 at the University of Bremen, Contribution No.xxx).

## References

- Abrantes, F., 2000, 200000 yrs diatom records from Atlantic upwelling sites reveal maximum productivity during LGM and a shift in phytoplankton community structure at 185000 yr: *Earth and Planetary Science*, v. 176, p. 7-16.
- Allredge, A.L., and Cohen, Y., 1987, Can microscale chemical patches persist in the sea? Microelectrode study of marine snow, fecal pellets: *Science*. 1987. 235, v. 235, p. 689-691.
- Altabet, M.A., and McCarthy, J.J., 1985, Temporal and spatial variations in the natural abundance of  $^{15}\text{N}$  in PON from a warm-core ring: *Deep-Sea Research*, v. 32, p. 755-772.
- Altabet, M.A., Deuser, W.G., Honjo, S., and Stienen, C., 1991, Seasonal and depth-related changes in the source of sinking particles in the North Atlantic.: *Nature*, v. 354, p. 136-139.
- Altabet, M.A., and Francois, R., 1994, Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization.: *Global-Biogeochemical-Cycles*, v. 8, p. 103-116.
- Altabet, M.A., Francois, R., Murray, D.W., and Prell, W.L., 1995, Climate-related variations in denitrification in the Arabian Sea from sediment  $^{15}\text{N}/^{14}\text{N}$  ratios.: *Nature*, v. 373, p. 506-509.
- Altabet, M.A., 1996, Nitrogen and carbon isotope tracers of the source and transformation of particles in the deep sea. *in* V.Ittekkot et al., eds.: *Particle Flux in the ocean*. John Wiley, New York, p. 155-184.
- Altabet, M.A., Murray, D.W., and Prell, W.L., 1999a, Climatically linked oscillations in Arabian Sea denitrification over the past 1 m.y.: Implications for the marine N cycle: *Paleoceanography*, v. 14, p. 732-743.
- Altabet, M.A., Pilskaln, C., Thunell, R., Pride, C., Sigman, D., Chavez, F., and Francois, R., 1999b, The nitrogen isotope biogeochemistry of sinking particles from the margin of the eastern North Pacific: *Deep-Sea Research Part I: Oceanographic Research Papers*, v. 46, p. 655-679.
- Antoine, D., and Morel, A., 1996, Oceanic primary production 1. Adaptation of a spectral light- photosynthesis model in view of application to satellite chlorophyll observations.: *Global-Biogeochemical-Cycles*, v. 10, p. 43-55.
- Bang, N.D., 1971, The Benguela Current region in February 1966. Bathythermography and air sea interactions: *Deep-Sea Research*, v. 18, p. 209-265.
- Bang, N.D., 1973, Characteristics of an intense ocean frontal system in the upwelling regime west of Cape Town.: *Tellus*, v. XXV, p. 256-265.

- Bang, N.D., and Andrews, W.R.H., 1974, Direct current measurements of a shelf-edge frontal jet in the southern Benguela system: *Journal of Marine Research*, v. 32, p. 405-417.
- Barange, M., and Pillar, S.C., 1992, Cross-shelf circulation, zonation and maintenance mechanisms of *Nyctiphanes capensis* and *Euphausia hanseni* (*Euphausiacea*) in the northern Benguela upwelling system: *Continental Shelf Research*, v. 12, p. 1027-1042.
- Barange, M., Pillar, S.C., and Hutchings, L., 1992, Major pelagic borders of the Benguela upwelling system according to the euphausiid species distribution: *South African Journal of Marine Science*, v. 12, p. 3-17.
- Bard, E., Hamelin, B., Arnold, M., Montaggioni, L., Cabioch, G., Faure, G., and Rougerie, F., 1996, Deglacial sea-level record from Tahiti corals and the timing of global meltwater discharge: *Nature*, v. 382, p. 241-244.
- Bickert, T., and Wefer, G., 1999, South Atlantic and benthic foraminifer  $\delta^{13}\text{C}$ -deviations: Implications for reconstructing the Late Quaternary deep-water circulation.: *Deep-Sea Research*.
- Bond, G., and others, 1993, Correlations between climate records from North Atlantic sediments and Greenland ice: *Nature*, v. 365, p. 143-147.
- Brandes, J.A., and Devol, A.H., 1997, Isotopic fractionation of oxygen and nitrogen in coastal marine sediments: *Geochimica et Cosmochimica Acta*, v. 61, p. 1793-1801.
- Broecker, W., Matsumoto, K., Clark, E., Hajdas, I., and Bonani, G., 1999, Radiocarbon age differences between coexisting foraminiferal species: *Paleoceanography*, v. 14, p. 431-436.
- Broecker, W.S., and Henderson, G.M., 1998, The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial  $\text{CO}_2$  changes: *Paleoceanography*, v. 13, p. 352-364.
- Calvert, S.E., and Price, B.N., 1983, Coastal upwelling, its sediment records; Part A, Responses of the sedimentary regime to present coastal upwelling, in Suess, E., and Thiede, J., eds.: *NATO conference series IV, marine sciences*: New York, United States, Plenum Press, p. 337-375.
- Canfield, D.E., 1989, Sulfate reduction and oxic respiration in marine sediments: implications for organic carbon preservation in euxinic environments: *Deep Sea Research*, v. 36, p. 121-138.
- Carpenter, E.J., 1983, Nitrogen fixation by marine *Oscillatoria* (*Trichodesmium*) in the world's oceans.- in Carpenter, E.J. ed: *Nitrogen in the Marine Environment*. London and New York (Academic Press). p. 65-103.

- Cline, J.D., and Kaplan, I.R., 1975, Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical North Pacific Ocean.: *Marine Chemistry.*, v. 3, p. 271-299.
- Dansgaard, W., and others, 1993, Evidence for general instability of past climate from a 250-kyr ice-core record: *Nature*, v. 364, p. 218-220.
- Diester-Haass, L., 1985, Late Quaternary sedimentation on the Eastern Walvis Ridge, SE Atlantic ( HPC 532 and four piston cores): *Marine Geology*, v. 65, p. 145-189.
- Diester-Haass, L., Heine, K., Rothe, P., and Schrader, H., 1988, Late Quaternary history of continental climate and the Benguela Current off south west Africa: *Palaeogeography, Palaeoclimatology, Paleoecology*, v. 65, p. 81-91.
- Eisenhauer, A., Zhu, Z.R., Collins, L.B., Wyrwoll, K.H., and Eichstatter, R., 1996, The Last Interglacial sea level change: new evidence from the Abrolhos Islands, west Australia: *Geologische Rundschau*, v. 85, p. 606-614.
- Emerson, S., and Hedges, J.I., 1988, Processes controlling the organic carbon content of open ocean sediments: *Paleoceanography*, v. 3, p. 621-634.
- Farrell, J.W., Pedersen, T.F., Calver, S.E., and Nielsen, B., 1995, Glacial-interglacial changes in nutrient utilization in the equatorial Pacific Ocean: *Nature*, v. 377.
- Fischer, G., and Wefer, G. (1991). Sampling, preparation and analysis of marine particulate matter. In "Marine particles; analysis and characterization." (D. C. e. Hurd, and D. W. e. Spencer, Eds.), pp. 391-397. Geophysical Monograph. American Geophysical Union. Washington, DC, United States. 1991.
- Fischer, G., Ratmeyer, V., and Wefer, G., 2000, Organic carbon fluxes in the Atlantic and the Southern Ocean: relationship to primary production compiled from satellite radiometer data.: *Deep-Sea Research Part II: Topical Studies in Oceanography*. v. 47, Issues 9-11. p. 1961-1997
- Francois, R., Altabet, M.A., and Burckle, L.H., 1992, Glacial to interglacial changes in surface nitrate utilization in the Indian sector of the Southern Ocean as recorded by sediment  $\delta^{15}\text{N}$ .: *Paleoceanography.*, v. 7, p. 589-606.
- Francois, R., Altabet, M.A., Yu, E.F., Sigman, D.M., Bacon, M.P., Frank, M., Bohrmann, G., Bareille, G., Labeyrie, L.D., 1997. Contribution of Southern Ocean surface-water stratification to low atmospheric  $\text{CO}_2$  concentrations during the last glacial period. *Nature* 389, 929-935.
- Ganeshram, R.S., Pedersen, T.F., Calvert, S.E., and Murray, J.W., 1995, Large changes in oceanic nutrient inventories from glacial to interglacial periods: *Nature*, v. 376, p. 755-758.
- Giraudeau, J., Bailey, G.W., and Pujol, C., 2000, A high-resolution time-series analyses of particle fluxes in the Northern Benguela coastal upwelling system: carbonate record of

- changes in biogenic production and particle transfer processes: Deep-Sea Research Part II, Topical Studies in Oceanography, v. 47, p. 1999-2028.
- Grootes, P.M., Stuiver, M., White, J.W.C., Johnsen, S., and Jouzel, J., 1993, Comparison of oxygen isotope records from the GISP2 and GRIP Greenland ice cores: *Nature*, v. 366, p. 552-554.
- Hart, T.J., and Currie, R.I., 1960, The Benguela Current: Discovery report, v. 31, p. 123-298.
- Haug, G.H., Pedersen, T.F., Sigman, D.M., Calvert, S.E., Nielsen, B., and Peterson, L.C., 1998, Glacial/interglacial variations in production and nitrogen fixation in the Cariaco Basin during the last 580 kyr: *Paleoceanography*, v. 13, p.427-432.
- Holmes, M.E., Muller, P.J., Schneider, R.R., Segl, M., Patzold, J., and Wefer, G., 1996, Stable nitrogen isotopes in Angola Basin surface sediments.: *Marine Geology*, v. 134, p. 1-12.
- Holmes, M.E., Muller, P.J., Schneider, R., Segl, M., and Wefer, G., 1998, Spatial variations in euphotic zone nitrate utilization based on  $\delta^{15}\text{N}$  in surface sediments.: *Geo-Marine-Letters*, v. 18, p. 58-65.
- Holmes, M.E., Schneider, R., Muller, P.J., Segl, M., and Wefer, G., 1997, Reconstruction of past nutrient utilization in the eastern Angola Basin based on sedimentary  $^{15}\text{N}/^{14}\text{N}$  ratios: *Paleoceanography*, v. 12, p. 604-614.
- Holmes, M.E., Eichner, C., Struck, U., and Wefer, G., 1999, Reconstruction of Surface Ocean Nitrate Utilization Using Stable Nitrogen Isotopes in Sinking Particles and Sediments, *in* Fisher, G., and Wefer, G., eds, 1999: Use of Proxies in Paleooceanography: Examples from the South Atlantic. Springer. Berlin Heidelberg New York. p.447-468.
- Howard, W.R., and Prell, W.L., 1992, Late Quaternary surface circulation of the southern Indian Ocean and its relationship to orbital variations: *Paleoceanography*, v. 7, p. 79-117.
- Hutchings, L., Armstrong, D.A., and Mitchell-Innes, B.A., 1986, The frontal zone in the southern Benguela Current, *in* Nihoul, J.C.J., ed., *Marine Interfaces Ecohydrodynamics*, Volume 42: Elsevier Oceanography Series, p. 67-94.
- Imbrie, J., and et al., 1984, The orbital theory of Pleistocene climate: support from a revised chronology of the marine  $\delta^{18}\text{O}$  record: *Milankovitch and climate*, v. 1, p. 269-305.
- Jansen, J.H.F., Ufkes, E., and Schneider, R.R., 1996, Late Quaternary movements of the Angola-Benguela Front, SE Atlantic, and implications for advection in the equatorial ocean: The South Atlantic: present and past circulation. G. Wefer, W.H. Berger, G. Siedler & D. Webb (eds.).

- Kirst, G.J., Schneider, R.R., Muller, P.J., von Storch, I., and Wefer, G., 1999, Late quaternary temperature variability in the Benguela Current System derived from Alkenones: *Quaternary Research*, v. 52, p. 92-103.
- Kreveld van, S.A., Knappertsbusch, M., Ottens, J., Ganssen, G.M., and Van-Hinte, J.E., 1996, Biogenic carbonate and ice-rafted debris (Heinrich layer) accumulation in deep-sea sediments from a northeast Atlantic piston core: *Marine Geology*, v. 131, p. 21-46.
- Little, M.G., Schneider, R.R., Kroon, D., Price, B., Bickert, T., and Wefer, G., 1997a, Rapid palaeoceanographic changes in the Benguela upwelling system for the last 160 000 years as indicated by abundances of planktonic foraminifera: *Palaeogeography, Palaeoclimatology, Palaeoecology*, v. 130, p. 135-161.
- Little, M.G., Schneider, R.R., Kroon, D., Price, B., Summerhayes, C.P., and Segl, M., 1997b, Trade wind forcing of upwelling, seasonality, and Heinrich events as a response to sub-Milankovitch climate variability: *Paleoceanography*, v. 12, p. 568-576.
- Lutjeharms, J.R.E., and Meueuwis, J.M., 1987, The extent and variability of South-east Atlantic upwelling, *in* Payne, A.I.L., Gulland, J.A., and Brink, K.H., eds., *The Benguela Comparable Ecosystems, Volume 5: South African Journal of Marine Science*, p. 51-62.
- Lutjeharms, J.R.E., and Stockton, P.L., 1987, Kinematics of the upwelling front off southern Africa, *in* Payne, A.I.L., Gulland, J.A., and Brink, K.H., eds., *The Benguela Comparable Ecosystems: South African Journal of Marine Science*, p. 35-49.
- Martinson, D.G., Pisias, N.G., Hays, J.D., Imbrie, J., Moore-Jr, T.C., and Shackleton, N.J., 1987, Age dating and the orbital theory of the ice ages: development of a high-resolution 0 to 300 000-year chronostratigraphy: *Quaternary Research*, v. 27, p. 1-29.
- Ming Yi, S., Lee, C., and Aller, R.C., 1993, Anoxic and oxic degradation of <sup>14</sup>C-labeled chloropigments and a <sup>14</sup>C-labeled diatom in Long Island Sound sediments: *Limnology and Oceanography*, v. 38, p. 1438-1451.
- Mix, A.C., Bard, E., and Schneider, R., submitted, Environmental Processes of the Ice age: Land, Oceans, Glaciers (EPILOG): *Quaternary Science Reviews*.
- Mollenhauer, G., Bickert, T., Grootes, P.M., Segl, M., and Wefer, G., submitted, Differences in South Atlantic surface sediment radiocarbon ages obtained from coexisting planktic foraminifera species living in different depth habitats and ecological provinces: *Paleoceanography*.
- Montoya, J.P., 1994, Nitrogen isotope fractionation in the modern ocean: implications for the sedimentary record, *in* Zahn, R., and al., e., eds., *NATO ASI Series, Volume 1*, p. 260-279.
- Morley, J.J., 1989, Variations in high-latitude oceanographic fronts in the southern Indian Ocean: an estimation based on faunal changes: *Paleoceanography*, v. 4, p. 547-554.

- Müller, P.J., Kirst, G., Ruhland, G., Von Storch, I., and Rosell Mele, A., 1998, Calibration of the alkenone paleotemperature index UK<sup>37</sup> based core-tops from the eastern South Atlantic and the global ocean (60°N-60°S): *Geochimica et Cosmochimica Acta*, v. 62, p. 1757-1772.
- Müller, P.J., Schneider, R., and Ruhland, G., 1994, Late Quaternary PCO<sub>2</sub> variations in the Angola Current: Evidence from organic carbon  $\delta^{13}\text{C}$  and alkenone temperatures, *in* Zahn, R., and et al, eds., NATO ASI Series, p. 343-365.
- Nadeau, M.-J., Schleicher, M., Grootes, P.M., Erlenkeuser, H., Gott dang, A., Mous, D.J.W., Sarnthein, J.M., and Willkomm, H., 1997, The Leibniz-Labor AMS facility at the Christian-Albrechts University, Kiel, Germany, *in* Andersen, H.H., and Rehn, L.E., eds., Nuclear Instruments and Methods in Physics Research Beam interactions with materials and atoms, Volume B123: North-Holland, Elsevier, p. 22-30.
- Nakatsuka, T., Handa, N., Harada, N., Sugimoto, T., and Imaizumi, S., 1997, Origin and decomposition of sinking particulate organic matter in the deep water column inferred from the vertical distributions of its  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$  and  $\delta^{14}\text{C}$ .: *Deep-Sea Research. Part I: Oceanographic Research Papers*, v. 44, p. 1957-1979.
- Nelson, G., 1989, Poleward motion in the Benguela area, *in* Neshbya, A.J., Moores, C.N.K., Smith, R., and Barber, T.J., eds., Poleward Flows along Eastern Boundaries, Volume 34: Coastal and Estuarine Studies: New York, Springer-Verlag, p. 110-130.
- Oberhansli, H., 1991, Upwelling signals at the northeastern Walvis Ridge during the past 500 000 years: *Paleoceanography*, v. 6, p. 53-71.
- Packard, T.T., Garfield, P.G., and Martinez, R., 1983, Respiration and respiratory enzyme activity in aerobic and anaerobic cultures of the marine denitrifying bacterium, *Pseudomonas perfectomarinus*: *Deep Sea Research*, v. 30, p. 227-243.
- Pedersen, T.F., and Calvert, S.E., 1990, Anoxia vs. productivity: what controls the formation of organic- carbon-rich sediments and sedimentary rocks?: *American Association of Petroleum Geologists Bulletin*, v. 74, p. 454-466.
- Peterson, R.J., and Stramma, L., 1991, Upper level circulation in the South Atlantic Ocean: *Progress in Oceanography*, v. 26, p. 1-73.
- Picaut, J., Servain, J., Lecomte, P., Seva, M., and Lukas, S., 1985, FOCAL Climatic Atlas of the tropical Atlantic: Wind stress and sea surface temperatures 1964-1979, Université de Bretagne Occidentale, Laboratori d'Océanographie physique, Brest, France.
- Prahl, F.G., Muehlhausen, L.A., and Zahnle, D.L., 1988, Further evaluation of long-chain alkenones as indicators of paleoceanographic conditions.: *Geochimica et Cosmochimica Acta*, v. 52, p. 2303-2310.

- Pride, C., Thunell, R., Sigman, D., Keigwin, L., Altabet, M., and Tappa, E., 1999, Nitrogen isotopic variations in the Gulf of California since the last deglaciation: Response to global climate change: *Paleoceanography*, v. 14, p. 397-408.
- Saino, T., and Hattori, A., 1980,  $^{15}\text{N}$  natural abundance in oceanic suspended particulate matter: *Nature*, v. 283, p. 752-754.
- Schmidt, H., 1992, Der Benguela-Strom im Bereich des Walfisch Rückens im SpätQartär [Doctoral thesis]: Bremen, Universität Bremen.
- Schneider, R., Dahmke, A., Kolling, A., Muller, P.J., Schulz, H.D., and Wefer, G., 1992, Strong deglacial minimum in the  $\delta^{13}\text{C}$  record from planktonic foraminifera in the Benguela upwelling region: palaeoceanographic signal or early diagenetic imprint?, *Upwelling systems: evolution since the early Miocene*, Volume Special Publication, 64: London, Geological Society, p. 285-297.
- Schulz, H., and participants, 1992, Bericht und erste Ergebnisse über die Meteor Fahrt M20/2, Abidjan - Dakar 27.12.1991 - 3.2.1992: Berichte, Fachbereich Geowissenschaften, v. 25, p. 173.
- Servain, J., Picaut, J., and Merle, J., 1982, Evidence of remote forcing in the equatorial Atlantic Ocean: *Journal of Physical Oceanography*, v. 12, p.457-463.
- Shannon, L.V., Walters, N.M., and Mostert, S.A., 1985, Satellite observation of surface temperature and near surface chlorophyll in the southern Benguela Region, *in* Shannon, L.V., ed., *South African Ocean Colour and Upwelling Experiment*: Cape Town, S.A., Sea Fisheries Research Institute, p. 183-210.
- Shannon, L.V., and Nelson, G., 1996, The Benguela: Large Scale Features and Processes and System Variability *in* Wefer, G., Berger, W.H., Sieder, G., and Webb, D.J., eds.: *The South Atlantic: Present and past circulation*. Springer, Berlin Heidelberg New York, p.163-210.
- Shillington, F.A., Peterson, W.T., Hutchings, L., Probyn, T.A., Waldron, H.N., and Agenbag, J.J., 1990, A cool upwelling filament off Namibia, southwest Africa: preliminary measurements of physical and biological features: *Deep-Sea Research*, v. 37, p. 1753-1772.
- Sigman, D.M., 1997, The role of biological production in Pleistocene atmospheric carbon dioxide variations and the nitrogen isotope dynamics of the Southern Ocean. [Doctoral thesis]: Cambridge, MA, United States.
- Sigman, D.M., Altabet, M.A., Francois, R., McCorkle, D.C., and Gaillard, J.F., 1999, The isotopic composition of diatom-bound nitrogen in Southern Ocean sediments: *Paleoceanography*, v. 14, p. 118-134.
- Stokes, S., Thomas, D.G., and Washington, R., 1997, Multiple episodes of aridity in southern Africa since the last interglacial period: *Nature*, v. 388, p. 154-158.

- Summerhayes, C.P., and others, 1995, Variability in the Benguela Current upwelling system over the past 70 000 years: *Progress in Oceanography*, v. 35, p. 207-251.
- Vidal, L., Schneider, R.R., Bickert, T., and Wefer, G., 1999, Link between the North and the South Atlantic related to the Heinrich Events during the last glacial period: *Climate Dynamics*, v. 15, p. 909-919.
- Voss, M., Altabet, M.A., and Bodungen, B.V., 1996,  $\delta^{15}\text{N}$  in sedimenting particles as indicator of euphotic-zone processes.: *Deep-Sea Research, Part I.*, v. 43, p. 33-47.
- Wada, E., 1980, Nitrogen isotope fractionation and its significance in biogeochemical processes occurring in marine environments, *in* Goldberg, E.D., and Horibe, Y., eds., *Isot. Mar. Chem.*, p. 375-398.
- Wada, E., and Hattori, A., 1978, Nitrogen isotope effects in the assimilation of inorganic nitrogenous compounds by marine diatoms: *Geomicrobiology Journal*, v. 1, p. 85-100.
- Winograd, I.J., and 8 others, 1992, Continuous 500 000-year climate record from vein calcite in Devils Hole, Nevada: *Science*, v. 258, p. 255-260.

## 8 Conclusions

The intention of this work was to increase the knowledge about how to interpret the sedimentary  $\delta^{15}\text{N}$  signal in the Southern Atlantic in terms of paleoceanography. From this study following conclusions can be drawn:

1) The regional differences in nutrient sources is large and important to consider by paleo interpretations. In the Benguela upwelling area the nutrients are almost solely provided by the upwelling of subsurface waters and a close relation between the  $\delta^{15}\text{N}$  in sinking matter and upwelling related parameters like SST and particle fluxes exists. On the contrary, in the equatorial upwelling area of the eastern Atlantic ocean, alternative nitrate sources supplied by nitrogen fixation and possibly precipitation during the warm oligotrophic season are as important for the annual export production as the nitrate supplied by the upwelling of subsurface water.

2) Dust is vital as a supplier of micro-nutrients for nitrogen fixation in the meso,- and oligotrophic regions. Additionally, the dust carries organic and inorganic nitrogen into the ocean which could influence the sedimentary bulk  $\delta^{15}\text{N}$  signal in oligotrophic regions. The potential impact from dust is not constant but varies with the climatic conditions of the source area of the dust. However, the  $\delta^{15}\text{N}$  values of the dust is not systematically different from the marine sediments and the influence from dust on the deep sea sediments are larger in parameters like C/N-ratio and  $\delta^{13}\text{C}$ .

3) In at least parts of the Benguela upwelling region water column denitrification over the inner shelf influences the sedimentary  $\delta^{15}\text{N}$  signal at the present situation and thus represents a loss of isotopically light nitrogen from the marine nitrogen cycle to the atmosphere. A sea-level related offshore migration of the upwelling cell during glacial periods are revealed in the  $\delta^{15}\text{N}$  records with abrupt changes towards lighter values. At minimum sea-level stands, erosion of the exposed shelf areas probably added surplus nutrients for the primary production. During periodically intensified upwelling, especially during isotope stage 3, the impact of denitrification are detectable in the sedimentary  $\delta^{15}\text{N}$  records more than 100km further offshore than at the present situation.

It is still many uncertainties connected to the use of sedimentary  $\delta^{15}\text{N}$  as a paleoceanographic proxy and it is very important to use it along with other related proxies, like i.e. sea surface temperature and organic content and composition, to interpret the sedimentary  $\delta^{15}\text{N}$  records. Nevertheless, it is important to continue the studies of bulk sedimentary  $\delta^{15}\text{N}$  along with studies on the  $\delta^{15}\text{N}$  of water and specific primary producers to increase our understanding of the nutrient dynamics and the  $\delta^{15}\text{N}$  signal. The system as a

---

unit will probably be best reflected in the bulk sample. For paleo studies of  $\delta^{15}\text{N}$ , both on bulk sediments and on specific parts of the sediment, in the Atlantic Ocean it would be of major importance to reveal the glacial to interglacial variations in the oceans nutrient pool and its  $\delta^{15}\text{N}$  signal. To overview these variations in the deeper and intermediate waters of the Atlantic Ocean is of global importance as these water masses are transported into the Pacific-, and Indian Ocean and where they are upwelled into the photic zone. To achieve this, more studies on both sinking matter and sediment cores in the Atlantic Ocean have to be done to better estimate the sources, nitrogen fixation and recycling of nutrients by erosion, and the sinks, sedimentation and loss of nitrate to the atmosphere by denitrification.

## 9 References

- Allredge, A.L., Cohen, Y., 1987. Can microscale chemical patches persist in the sea? Microelectrode study of marine snow, faecal pellets. *Science* 235 (4789), 689-691.
- Altabet, M.A., McCarthy, J.J., 1985. Temporal and spatial variations in the natural abundance of  $^{15}\text{N}$  in PON from a warm-core ring. *Deep Sea Research* 32 (7A), 755-772.
- Altabet, M.A., 1988, Variations in nitrogen isotopic composition between sinking and suspended particles; implications for nitrogen cycling and particle transformation in the open ocean.: *Deep-Sea Research. Part A: Oceanographic Research Papers.*, v. 35, p. 535-554.
- Altabet, M.A., Curry, W.B., 1989. Testing models of past ocean chemistry using foraminifera  $^{15}\text{N}/^{14}\text{N}$ . *Global Biogeochemical Cycles* 3 (2), 107-119.
- Altabet, M.A., Deuser, W.G., Honjo, S., Stienen, C., 1991. Seasonal and depth-related changes in the source of sinking particles in the North Atlantic. *Nature* 354 (6349), 136-139.
- Altabet, M.A., Francois, R., Murray, D.W., Prell, W.L., 1995. Climate-related variations in denitrification in the Arabian Sea from sediment  $^{15}\text{N}/^{14}\text{N}$  ratios. *Nature* 373 (6514), 506-509.
- Altabet, M.A., Francois, R. (Eds.) 1994. NATO ASI Series, 1, The use of nitrogen isotopic ratio for reconstruction of past changes in surface ocean nutrient utilization., 281-306.
- Altabet, M.A., Murray, D.W., Prell, W.L., 1999 a. Climatically linked oscillations in Arabian Sea denitrification over the past 1 m.y.: Implications for the marine N cycle. *Paleoceanography* 14 (6), 732-743.
- Altabet, M.A., Pilskaln, C., Thunell, R., Pride, C., Sigman, D., Chavez, F., Francois, R., 1999b. The nitrogen isotope biogeochemistry of sinking particles from the margin of the eastern North Pacific. *Deep Sea Research Part I: Oceanographic Research Papers* 46 (4), 655-679.
- Antoine, D., Andre, J.M., Morel, A., 1996. Oceanic primary production 2. Estimation at global scale from satellite (coastal zone colour scanner) chlorophyll. *Global-Biogeochemical-Cycles* 10 (1), 57-69.
- Berelson, W.M., Hammond, D.E., O'Neill, D., Xu, X.M., Chin, C., Zukin, J., 1990. Benthic fluxes and pore water studies from sediments of the central equatorial north Pacific: nutrient diagenesis. *Geochimica et Cosmochimica Acta* 54 (11), 3001-3012.
- Bertrand, P., Pedersen, T.F., Martinez, P., Calvert, S., Shimmiel, G., 2000. Sea level impact on nutrient cycling in coastal upwelling areas during deglaciation: Evidence from nitrogen isotopes. *Global Biogeochemical Cycles* 14 (1), 341-355.

- Brandes, J.A., Devol, A.H., 1997. Isotopic fractionation of oxygen and nitrogen in coastal marine sediments. *Geochimica et Cosmochimica Acta* 61 (9), 1793-1801.
- Brandes, B., Godbold, D.L., Kuhn, A.J., Jentschke, G., 1998. Nitrogen and phosphorus acquisition by the mycelium of the ectomycorrhizal fungus *Paxillus involutus* and its effect on host nutrition. *New Phytologist* 140 (4), 735-743.
- Brandes, J.A., Devol, A.H., Yoshinari, T., Jayakumar, D.A., Naqvi, S.W.A., 1998. Isotopic composition of nitrate in the central Arabian Sea and eastern tropical North Pacific: A tracer for mixing and nitrogen cycles. *Limnology and Oceanography* 43 (7), 1680-1689.
- Broecker, W.S., Henderson, G.M., 1998. The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial CO<sub>2</sub> changes. *Paleoceanography* 13, 352-364.
- Capone, D.G., Carpenter, E.J., 1982. Nitrogen fixation in the marine environment. *Science* 217 (4565), 1140-1142.
- Capone, D.G., Zehr, J.P., Pearl, H.W., Bergmann, B., Carpenter, E.J., 1997. *Trichodesmium*, a globally significant cyanobacterium. *Science* 276, 1221-1229.
- Carpenter, E.J., Harvey, H.R., Fry, B., Capone, D.G., 1997. Biogeochemical tracers of the maine cyanobacterium, *Trichodesmium*. *Deep Sea Research, Part 1* 44, 27-38.
- Chapman, P., Shannon, L.V., 1985. The Benguela ecosystem Part II. Chemistry and related processes. *Oceanography and Marine Biology Annual Review* 23, 183-251.
- Cline, J.D., Kaplan, I.R., 1975. Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical North Pacific Ocean. *Marine Chemistry* 3 (4), 271-299.
- Codispoti, L.A., 1989. Phosphorus and nitrogen limitation of new and export production. In: Berger, W.H., Smetacek, V.S., Wefer, G. (Eds.), *Productivity of the Oceans: Present and Past*. John Wiley, New York, pp. 377-394.
- Collister, J.W., Hayes, J.M., 1991. A preliminary study of the carbon and nitrogen isotopic biogeochemistry of lacustrine sedimentary rocks from the Green River Formation, Wyoming, Utah, and Colorado. *US-Geological-Survey-Bulletin* 1973 (A-G), C1-C16.
- Cornell, S., Rendell, A., Jickells, T., 1995. Atmospheric inputs of dissolved organic nitrogen to the oceans. *Nature* 376 (6537), 243-246.
- DeMenocal, P.B., 1995. Plio-Pleistocene African climate. *Science* 270 (5233), 53-59.
- DeNiro, M.J., Epstein, S., 1981. Influence of diet on the distribution of nitrogen isotopes in animals. *Geochimica et Cosmochimica Acta* 45 (3), 341-351.
- Devol, A.H., Christensen, J.P., 1993. Benthic fluxes and nitrogen cycling in sediments of the continental margin of the eastern North Pacific. *Journal of Marine Research* 51, 345-372.

- Eichner, C., 2000. Mikrobielle Modifikation der Isotopensignatur des Stickstoffs in marinem partikulären Material, PhD Thesis, Universität Rostock, (98pp).
- Farrell, J.W., Pedersen, T.F., Calvert, S.E., Nielsen, B., 1995. Glacial-interglacial changes in nutrient utilization in the equatorial Pacific Ocean. *Nature* 377 (514-517).
- Fischer, G., Wefer, G., 1991. Sampling, preparation and analysis of marine particulate matter. In: Hurd, D.C., Spencer, D.W.E. (Eds.), *Geophysical Monograph*, 63, Marine particles; analysis and characterization. American Geophysical Union. Washington, DC, United States. 1991, 391-397.
- Francois, R., Altabet, M.A., Burckle, L.H., 1992. Glacial to interglacial changes in surface nitrate utilization in the Indian sector of the Southern Ocean as recorded by sediment  $\delta^{15}\text{N}$ . *Paleoceanography* 7 (5), 589-606.
- Francois, R., Altabet, M.A., Yu, E.F., Sigman, D.M., Bacon, M.P., Frank, M., Bohrmann, K.G., Bareille, G., Labeyrie, L.D., 1997. Contribution of Southern Ocean surface-water stratification to low atmospheric  $\text{CO}_2$  concentrations during the last glacial period. *Nature* 389 (6654), 929-935.
- Ganeshram, R.S., Pedersen, T.F., Calvert, S.E., Murray, J.W., 1995. Large changes in oceanic nutrient inventories from glacial to interglacial periods. *Nature* 376, 755-758.
- Georgiadis, M.M., Komiya, P., Chakrabarti, D., Woo, J., Rees, D.C., 1992. Crystallographic structure of the nitrogenase iron protein from *Azotobacter vinelandii*. *Science* 257, 1653-1659.
- Gruber, N., Sarmiento, J.L., 1997. Global Patterns of marine nitrogen fixation and denitrification. *Global Biogeochemical Cycles* 11 (2), 235-266.
- Haug, G.H., Pedersen, T.F., Sigman, D.M., Calvert, S.E., Nielsen, B., Peterson, L.C., 1998. Glacial/interglacial variations in production and nitrogen fixation in the Cariaco Basin during the last 580 kyr. *Paleoceanography* 13 (5), 427-432.
- Holmes, M.E., Muller, P.J., Schneider, R.R., Segl, M., Patzold, J., Wefer, G., 1996. Stable nitrogen isotopes in Angola Basin surface sediments. *Marine Geology* 134 (1-2), 1-12.
- Holmes, M.E., Schneider, R., Muller, P.J., Segl, M., Wefer, G., 1997. Reconstruction of past nutrient utilization in the eastern Angola Basin based on sedimentary  $^{15}\text{N}/^{14}\text{N}$  ratios. *Paleoceanography* 12 (4), 604-614.
- Holmes, M.E., Muller, P.J., Schneider, R., Segl, M., Wefer, G., 1998. Spatial variations in euphotic zone nitrate utilization based on  $\delta^{15}\text{N}$  in surface sediments. *Geo Marine Letters* 18 (1), 58-65.
- Holmes, M.E., Eichner, C., Struck, U., and Wefer, G., 1999, Reconstruction of Surface Ocean Nitrate Utilization Using Stable Nitrogen Isotopes in Sinking Particles and Sediments, in Fisher, G., and Wefer, G., eds, 1999: Use of Proxies in

- Paleoceanography: Examples from the South Atlantic. Springer. Berlin Heidelberg New York. p.447-468.
- Howarth, R.W., Cole, J.J., 1985. Molybdenum availability, nitrogen limitation, and phytoplankton growth in natural waters. *Science* 229 (4714), 653-655.
- Howarth, R.W., 1988. Nutrient limitation of net primary production in marine ecosystems. In: Johnston, R.F. (Ed.) 19, *Annual review of ecology and systematics*. Annual Reviews Inc., Palo Alto.
- Karl, D., Leteiler, R., Tupas, L., Dore, J., Christian, J., Hebel, D., 1997. The role of nitrogen fixation in the biochemical cycling in the subtropical North Pacific Ocean. *Nature* 380, 533-538.
- Kendall, C., 1998. Tracing Nitrogen Sources and Cycling in Catchments. In: Kendall, C., McDonnell, J.J. (Eds.), *Isotope Tracers in Catchment Hydrology*. Elsevier Science B V, Amsterdam, 519-576.
- Kim, J., Rees, D.C., 1992. Structural models for metal centres in nitrogenase-molybdeniumrich protein. *Science* 257, 1677-1682.
- Knauer, G.A., 1993. Productivity and new production in the oceanic system. In: Wollast, R., MacKenzie, F.T., Chou, L. (Eds.), *Interactions of C, N, P and S Biogeochemical Change*. Springer Verlag, New York, 211-231.
- Kumar, P.P., Manohar, G.K., Kandalgaonkar, S.S., 1995. Global distribution of nitric oxide produced by lightning and its seasonal variation. *Journal of Geophysical Research* 100 (D6), 11,203-11,208.
- Mariotti, A., Germon, J.C., Hubert, P., Kaiser, P., Letolle, R., Tardieux, A., Tardieux, P., 1981. Experimental determination of nitrogen kinetic isotope fractionation: some principles; illustration for the denitrification and nitrification processes. *Plant and Soil* 62, 413-430.
- Mariotti, A., 1983. Atmospheric nitrogen is a reliable standard for natural  $^{15}\text{N}$  abundance measurements. *Nature* 303 (5919), 685-687.
- Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. In: Lee Cindy (Ed.), *Chemical Geology* 114. Elsevier, Amsterdam, Netherlands, 289-302.
- Michaels, A.F., Bates, N.R., Buesseler, K.O., Carlson, C.A., Knap, A.H., 1994. Carbon-cycle imbalances in the Saragasso Sea. *Nature* 372, 537-540.
- Minagawa, M., Wada, E., 1984. Stepwise enrichment of  $^{15}\text{N}$  along food chains; further evidence and the relation between  $\delta^{15}\text{N}$  and animal age. *Geochimica et Cosmochimica Acta* 48 (5), 1135-1140.

- Minagawa, M., Wada, E., 1986. Nitrogen isotope ratios of red tide organisms in the East China Sea: A characterization of biological nitrogen fixation. *Marine Chemistry* 19, 245-249.
- Miyake, Y., Wada, E., 1971. The isotope effect on the nitrogen in biochemical, oxidation-reduction reactions. *Rec. Oceanogr. Works Jpn.* 11, 1-6.
- Montoya, J.P., McCarthy, J.J., 1995. Isotopic fractionation during nitrate uptake by phytoplankton grown in continuous culture. *Journal of Plankton Research* 17 (3), 439-464.
- Nakatsuka, T., Handa, N., Wada, E., Chi, S.W., 1992. The dynamic changes of stable isotopic ratios of carbon and nitrogen in suspended and sedimented particulate organic matter during a phytoplankton bloom. *Journal of Marine Research* 50 (2), 267-296.
- Nakatsuka, T., Handa, N., Harada, N., Sugimoto, T., Imaizumi, S., 1997. Origin and decomposition of sinking particulate organic matter in the deep water column inferred from the vertical distributions of its  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$  and  $\delta^{14}\text{C}$ . *Deep Sea Research. Part I: Oceanographic Research Papers* 44 (12), 1957-1979.
- O'Leary, M.H., 1988. Carbon isotopes in photosynthesis. *Bioscience* 38, 328-336.
- Packard, T.T., Garfield, P.G., Martinez, R., 1983. Respiration and respiratory enzyme activity in aerobic and anaerobic cultures of the marine denitrifying bacterium, *Pseudomonas perfectomarinus*. *Deep Sea Research* 30 (3A), 227-243.
- Palit, S., Sharma, A., Talukder, G., 1994. Effects of cobalt on plants. *Botanical review* 60, 149-181.
- Paulsen, D.M., Paerl, H.W., Bishop, P.E., 1991. Evidence that molybdenum-dependent nitrogen fixation is not limited by high sulfate concentrations in marine environments. *Limnology and Oceanography* 36 (7), 1325-1334.
- Pennock, J.R., Velinsky, D.J., Ludlam, D.J., Sharp, J.H., Vogel, M.L., 1996. Isotopic fractionation of ammonium and nitrate during uptake by *Skeletonema costatum*: Implications for  $\delta^{15}\text{N}$  dynamics under bloom conditions. *Limnology and Oceanography* 41, 451-459.
- Pomeroy, L.R., Deibel, D., 1986. Temperature regulation of bacterial activity during the spring bloom in Newfoundland coastal waters. *Science* 233 (4761), 359-361.
- Pride, C., Thunell, R., Sigman, D., Keigwin, L., Altabet, M., Tappa, E., 1999. Nitrogen isotopic variations in the Gulf of California since the last deglaciation: Response to global climate change. *Paleoceanography* 14 (3), 397-408.
- Ridley, B.A., Dye, J.E., Walega, J.G., Zheng, J., Grahek, F.E., Rison, W., 1996. On the production of active nitrogen by thunderstorms over New Mexico. *Journal of Geophysical Research* 101 (D15), 20985-21005.

- Rühlemann, C., 1996. Akkumulation von Carbonat und organischem Kohlenstoff im tropischen Atlantik: Spätquartäre Produktivitäts-Variationen und ihre Steuerungsmechanismen. Doctoral Thesis, Universität Bremen, Bremen, 140pp.
- Sackett, W.M., 1989. Stable carbon isotope studies on organic matter in the marine environment. In: Fritz, P., Fontes, J.C. (Eds.), 3, Handbook of Environmental Isotope Geochemistry. Elsevier, Amsterdam, 39-169.
- Schimel, D.S., 1995. Terrestrial biogeochemical cycles: global estimates with remote sensing. *Remote Sensing of Environment* 51 (1), 49-56.
- Schlesinger, W.H., Hartley, A.E., 1992. A global budget for atmospheric NH<sub>3</sub>. *Biogeochemistry* 15 (3), 191-211.
- Schlesinger, W.H., 1997. *Biogeochemistry; an analysis of global change*. 2nd ed. Academic Press, San Diego, CA, United States, 588pp.
- Sigman, D.M., 1997. The role of biological production in Pleistocene atmospheric carbon dioxide variations and the nitrogen isotope dynamics of the Southern Ocean. Doctoral, Cambridge, MA, United States.
- Sigman, D.M., Altabet, M.A., Francois, R., McCorkle, D.C., Gaillard, J.F., 1999. The isotopic composition of diatom-bound nitrogen in Southern Ocean sediments. *Paleoceanography* 14 (2), 118-134.
- Sigmann, D.M., Altabet, M.A., R, M., McCorkle, D.C., Fry, B., Holmes, R.M., 1997. Natural abundance-level measurement of the nitrogen isotopic composition of oceanic nitrate; an adaptation of the ammonia diffusion method. *Marine Chemistry*. 57 (3-4), 227-242.
- Sweeney, R.E., Liu, K.K., Kaplan, I.R. (Eds.) 1975. *Stable Isotope in the Earth Science*, Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen, 9-26.
- Tyrell, J.J., 1999. The relative influence of nitrate and phosphorus on oceanic primary production. *Nature* 400, 525-531.
- Verardo, D.J., Ruddiman, W.F., 1996. Late Pleistocene charcoal in tropical Atlantic deep-sea sediments; climatic and geochemical significance. *Geology* 24 (9), 855-857.
- Vitousek, P.M., Howarth, R.W., 1991. Nitrogen limitation on land and in the sea: how can it occur? *Biogeochemistry* 13 (2), 87-115.
- Wada, E., Kadonaga, T., Matsuo, S., 1975. <sup>15</sup>N abundance in naturally occurring substances and global assessment of denitrification from isotopic viewpoint. *Geochemical Journal* 9, 139-148.
- Wada, E., Hattori, A., 1978. Nitrogen isotope effects in the assimilation of inorganic nitrogenous compounds by marine diatoms. *Geomicrobiology Journal* 1 (1), 85-100.

- Wada, E., 1980. Nitrogen isotope fractionation and its significance in biogeochemical processes occurring in marine environments. In: Goldberg, E.D., Horibe, Y. (Eds.), *Isot. Mar. Chem*, 375-398.
- Wagner, T., Dupont, L.M., 1999. Terrestrial organic matter in marine sediments: Analytical approaches and eolian-marine records in the central equatorial Atlantic. In: Fischer, G., Wefer, G. (Eds.), *The use of proxies in paleoceanography: Examples from the South Atlantic*. Springer Verlag, Heidelberg, Berlin, 547-574.
- Walsh, J.J., 1984. The role of oceanic biota in accelerated ecological cycles: A temporal view. *Bioscience* 34, 499-507.
- Walsh, J.J., Dieterle, D.A., Meyers, M.B., 1988. A simulation analysis of the fate of phytoplankton within the Mid-Atlantic Bight. *Continental Shelf Research* 8 (5-7), 757-787.
- Waser, N.A., Yin, K., Yu, Z., Tada, K., Harrison, J., Turpin, D.H., Calvert, S., 1998. Nitrogen isotope fractionation during nitrate, ammonium and urea uptake by marine diatoms and coccolithophores under various conditions of N availability. *Marine Ecology Progress Series* 169, 29-41.
- Westerhausen, L., Poynter, J., Eglinton, G., Erlenkeuser, H., Sarnthein, M., 1993. Marine and terrigenous origin of organic matter in modern sediments of the equatorial East Atlantic; the  $d^{13}C$  and molecular record. *Deep-Sea Research. Part I: Oceanographic Research Papers* 40 (5), 1087-112.
- Wilkerson, F.P., Dugdale, R.C., 1992. Measurements of nitrogen productivity in the equatorial Pacific. *Journal of Geophysical Research* 97, 669-679.
- Wolff, T., Mulitza, S., Rühlemann, C., Wefer, G., 1999. Response of the tropical Atlantic thermocline to late Quaternary trade wind changes. *Paleoceanography* 14 (3), 374-383.
- Wu, J., Calvert, S.E., Wong, C.S., 1997. Nitrogen isotope variations in the subarctic north east Pacific: relationships to nitrate utilization and trophic structure. *Deep Sea Research* 44 (2), 287-314.

## 10 Appendix

### 10.1 Table 1

Parallel double measurements on material from sediment trap GBN3(o), on freeze dried material and split samples filtered onto GF/filters.

GBN3(o) Sample No.	1.run fr.dr $\delta^{15}\text{N}$ (‰)	2.run fr.dr $\delta^{15}\text{N}$ (‰)	1. run GF/F $\delta^{15}\text{N}$ (‰)	2. run GF/F $\delta^{15}\text{N}$ (‰)
1	2.60	2.74	2.70	2.92
2	3.10	3.14	3.00	3.13
3	6.18	6.42	6.48	6.31
4	3.29	3.24	3.38	3.60
5	2.92	2.94	3.01	3.16
6	4.66	4.51	4.02	4.40
7	6.57	6.75	7.11	7.27
8	3.19	3.08	3.15	2.32
9	4.43	4.81	4.66	4.64
10	4.48	4.35	4.57	4.65
11	4.75	4.80	4.65	4.73
12	3.01	3.10	3.12	3.22
13	3.42	3.62	3.50	3.58
14	4.22	4.23	4.28	4.62
15	4.39	4.62	4.46	4.34
16	4.34	4.45	4.21	4.40
17	4.02	4.09	4.35	4.71
18	3.89	3.82	4.26	4.21
19	4.23	3.84	3.43	3.52
20	3.64	3.72	3.80	3.84

**10.2 Table 2**

Parallel measurements of the total- and dechlorinated sediment for gravity cores GeoB 1105, GeoB1710, and GeoB 1523 presented in the methods chapter 5

GeoB 1523			
Depth (cm)	<sup>15</sup> N Decal. (‰)	<sup>15</sup> N tot. Sed. (‰)	Difference (‰)
3	6,15	6,26	0,11
8	6,63	6,41	-0,22
13	6,16	7,10	0,94
18	6,17	7,14	0,97
23	6,37	6,92	0,55
28	6,06	6,77	0,71
33	5,13	6,19	1,06
38	5,59	6,07	0,48
43	5,62	6,08	0,47
48	5,35	6,07	0,72
53	6,17	6,18	0,01
58	5,99	6,09	0,10
63	5,83	6,35	0,52
68	6,13	6,18	0,05
73	6,27	6,44	0,17
78	6,59	6,61	0,02
83	6,67	6,70	0,03
88	6,57	6,87	0,30
93	6,50	6,59	0,08
98	6,33	6,58	0,25
103	5,41	6,52	1,11
108	5,75	5,95	0,19
113	5,50	6,47	0,98
118	5,91	6,49	0,58
123	5,71	6,32	0,61
128	5,66	6,67	1,00
133	6,17	6,90	0,73

GeoB 1710			
Depth (cm)	<sup>15</sup> N Decal. (‰)	<sup>15</sup> N tot. Sed. (‰)	Difference (‰)
138	6,28	6,61	0,34
143	6,29	6,43	0,15
148	6,25	6,47	0,21
153	6,38	6,31	-0,07
158	6,30	6,31	0,01
163	6,39	6,39	0,00
168	6,35	6,36	0,01
173	6,54	6,77	0,23
178	6,29	6,27	-0,02
183	6,22	6,16	-0,06
188	6,31	6,39	0,08
193	6,25	6,38	0,13
198	6,01	6,08	0,08
203	5,65	5,84	0,18
208	5,75	5,95	0,19
213	5,96	6,10	0,14
218	6,46	6,49	0,03
223	6,56	6,70	0,14
228	6,56	6,58	0,02
233	6,70	6,72	0,02
238	6,65	6,66	0,00
243	6,47	6,71	0,23
248	6,49	6,65	0,17

GeoB 1710			
Depth (cm)	<sup>15</sup> N Decal. (‰)	<sup>15</sup> N tot. Sed. (‰)	Difference (‰)
3	7,72	8,06	0,34
8	7,90	7,87	-0,03
13	7,98	8,28	0,30
18	7,84	7,77	-0,06
23	7,77	7,99	0,22
28	7,70	7,74	0,04
33	7,46	7,45	-0,01
38	7,34	7,37	0,03
43	7,25	7,44	0,19
48	7,35	7,52	0,17
53	7,59	7,74	0,15
58	7,45	7,64	0,19
63	7,57	7,73	0,15
68	7,32	7,55	0,23
73	7,10	7,34	0,24
78	6,99	7,07	0,08
83	6,52	6,65	0,13
88	6,59	6,67	0,08
93	6,38	6,46	0,09
98	6,58	6,65	0,07
103	6,62	6,89	0,27
108	6,56	6,68	0,12
113	6,45	6,67	0,22
118	6,34	6,48	0,14
123	6,36	6,69	0,33
128	6,22	6,29	0,08
133	6,13	6,63	0,50

10.2 Table 2 (continued)

GeoB 1523			
Depth (cm)	<sup>15</sup> N Decal. (‰)	<sup>15</sup> N tot. Sed. (‰)	Difference (‰)
138	6,02	6,71	0,69
143	5,87	6,54	0,66
148	6,21	6,60	0,39

GeoB 1105			
Depth (cm)	<sup>15</sup> N Decal. (‰)	<sup>15</sup> N tot. Sed. (‰)	Difference (‰)
4	n. d.	8,80	n. d.
7	n. d.	9,06	n. d.
10	n. d.	8,98	n. d.
13	n. d.	9,14	n. d.
16	n. d.	9,11	n. d.
19	n. d.	9,80	n. d.
23	n. d.	9,73	n. d.
28	n. d.	9,36	n. d.
33	n. d.	8,85	n. d.
38	7,72	6,99	-0,73
43	n. d.	8,84	n. d.
48	n. d.	8,56	n. d.
53	8,93	9,34	0,40
58	7,96	8,29	0,33
63	6,86	7,15	0,29
68	6,89	6,94	0,06
73	6,54	6,71	0,17
78	6,54	n. d.	n. d.
83	6,53	6,86	0,34
88	n. d.	7,10	n. d.
93	6,27	6,42	0,15
98	n. d.	6,49	n. d.
103	6,16	6,52	0,37
108	5,94	n. d.	n. d.
113	n. d.	6,60	n. d.
118	6,45	6,75	0,30
123	6,38	6,69	0,31

GeoB 1105			
Depth (cm)	<sup>15</sup> N Decal. (‰)	<sup>15</sup> N tot. Sed. (‰)	Difference (‰)
128	6,70	7,00	0,30
133	6,72	6,85	0,13
138	6,77	6,90	0,12
143	7,10	7,37	0,28
148	6,76	7,04	0,28
153	6,84	7,05	0,21
158	6,26	6,82	0,57
163	6,66	6,90	0,23
168	6,54	6,87	0,33
173	6,50	6,84	0,34
178	6,47	7,04	0,58
183	n. d.	6,99	n. d.
188	n. d.	6,95	n. d.
193	6,79	7,07	0,27
198	6,87	7,12	0,25
203	6,26	6,83	0,58
208	6,36	7,07	0,71
213	6,57	6,92	0,34
218	n. d.	6,98	n. d.
223	7,20	7,25	0,05
228	6,66	7,22	0,57
233	7,04	7,42	0,38
238	n. d.	7,65	n. d.
243	7,67	8,02	0,35
248	n. d.	7,56	n. d.
253	n. d.	7,81	n. d.
258	n. d.	8,10	n. d.

10.2 Table 2 (continued)

GeoB 1105			
Depth (cm)	<sup>15</sup> N Decal. (‰)	<sup>15</sup> N tot. Sed. (‰)	Difference (‰)
263	n. d.	8,03	n. d.
268	n. d.	7,65	n. d.
273	n. d.	7,57	n. d.
278	n. d.	7,80	n. d.
283	n. d.	7,39	n. d.
288	n. d.	6,99	n. d.
293	n. d.	6,48	n. d.
298	n. d.	6,65	n. d.
303	n. d.	6,59	n. d.
308	n. d.	6,12	n. d.
313	n. d.	6,59	n. d.
318	n. d.	6,09	n. d.
323	n. d.	6,09	n. d.
328	n. d.	6,35	n. d.
333	n. d.	6,79	n. d.
338	n. d.	7,04	n. d.
343	n. d.	6,86	n. d.
348	n. d.	7,73	n. d.
353	n. d.	6,99	n. d.
358	n. d.	7,50	n. d.
363	n. d.	7,18	n. d.
368	n. d.	7,31	n. d.
373	n. d.	8,40	n. d.
378	n. d.	8,47	n. d.
383	n. d.	8,07	n. d.
388	n. d.	7,21	n. d.
393	n. d.	6,49	n. d.

GeoB 1105			
Depth (cm)	<sup>15</sup> N Decal. (‰)	<sup>15</sup> N tot. Sed. (‰)	Difference (‰)
398	n. d.	7,18	n. d.
403	6,55	n. d.	n. d.
408	n. d.	6,72	n. d.
413	n. d.	6,56	n. d.
418	5,96	6,58	0,62
423	6,38	6,89	0,50
428	6,56	7,20	0,64
433	6,33	7,28	0,96
438	6,62	7,40	0,78
443	7,19	7,78	0,59
448	n. d.	7,92	n. d.
453	n. d.	n. d.	n. d.
458	6,35	7,99	1,63
463	6,67	7,79	1,12
468	6,11	6,89	0,77
473	6,10	6,68	0,58
478	5,69	6,16	0,47
483	6,22	6,77	0,54
488	6,02	6,49	0,47
493	5,92	n. d.	n. d.
498	5,86	6,35	0,49
503	5,94	6,84	0,90
508	6,41	7,27	0,86
513	6,39	7,62	1,22
518	6,42	7,31	0,89
523	7,28	8,00	0,72
528	n. d.	6,68	n. d.

GeoB 1105			
Depth (cm)	<sup>15</sup> N Decal. (‰)	<sup>15</sup> N tot. Sed. (‰)	Difference (‰)
533	7,07	8,19	1,12
538	n. d.	7,86	n. d.
543	n. d.	6,59	n. d.
548	5,63	6,34	0,70
553	5,46	6,49	1,02
558	6,20	7,43	1,22
563	6,36	6,75	0,40
568	7,32	7,85	0,52
573	7,44	8,08	0,65
578	7,18	7,42	0,24
583	6,14	6,37	0,23
588	6,48	7,07	0,59
593	6,10	6,44	0,34
598	6,39	6,90	0,52
603	6,27	7,07	0,80
608	6,36	6,91	0,55

### 10.3 Table 3

The  $\delta^{15}\text{N}$  values from the sediment traps presented in Manuscript 1.

Sample No.	EA1 $\delta^{15}\text{N}$ (‰)	EA2 $\delta^{15}\text{N}$ (‰)	EA3c $\delta^{15}\text{N}$ (‰)	EA4 $\delta^{15}\text{N}$ (‰)	EA5 $\delta^{15}\text{N}$ (‰)	EA8a $\delta^{15}\text{N}$ (‰)	GBN3(o) $\delta^{15}\text{N}$ (‰)	GBN6(o) $\delta^{15}\text{N}$ (‰)
1	3.06	3.13	4.69	4.34	5.19	8.11	3.12	4.97
2	2.55	2.93	4.08	7.38	4.67	6.90	6.30	4.76
3	2.80	3.08	4.62	5.97	4.33	5.84	3.27	4.10
4	2.67	4.05	3.99	4.62	5.33	5.26	2.93	4.29
5	2.74	3.20	4.50	5.21	5.27	6.08	4.58	4.65
6	2.28	3.20	6.11	5.04	4.89	6.18	6.66	
7	2.19	4.50	7.64	5.12	5.84	5.68	3.13	
8	2.34	8.19	5.52	5.72	5.32	4.33	4.62	
9	2.42	3.43	4.83	5.33	5.27	4.58	4.42	
10	1.85	2.67	5.08	5.83		4.55	4.77	
11	2.86	2.91	5.55	5.52		6.29	3.06	
12	2.54	7.04	9.36	4.84		6.36	3.52	
13	2.34	5.01	7.87	4.66		6.98	4.23	
14	6.30	3.71	4.68			7.02	4.50	
15	3.43	4.40	4.36		6.23	6.33	4.40	
16	3.49	5.03			6.68	6.68	4.05	
17	3.25	5.14	4.71			6.55	3.85	
18	4.38	5.77	4.35			9.38	4.04	
19	3.35	4.80	4.24			7.51	3.68	
	3.55							
20		4.88	3.98			8.35	2.67	

**10.4 Table 4**

Combined measurements of  $\delta^{15}\text{N}$ ,  $\delta^{13}\text{C}$  and C/N ratio in the Dust samples M41/1 DO1 - DO25. The decalcified samples are presented in manuscript 2. In the methods chapter 5 the  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}$  from not decalcified secondary filters and of small parts of the original filter (the rawfilter) are presented too.

Sample	Decalcified secondary filter					Not decalcified secondary filter			Rawfilter	
	Amount of dust (mg)	Signal (V)	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}$ (‰)	C/N-ratio	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}$ (‰)	C/N-ratio	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}$ (‰)
DO1 M41_1	11,10	0,60	7,75	-23,64	15,94					-16,59
DO3 M41_1	10,40	0,39	6,17	-21,56	16,08					-15,34
DO4 M41_2	28,50	0,57	6,57	-22,92	12,38					-19,88
DO5 M41_1	33,40	1,01	7,30	-20,03	11,80					-17,24
DO6 M41_1	28,00	0,95	7,06	-19,85	10,47					-17,88
DO7 M41_2	8,40			-19,61	12,58					-19,40
DO8 M41_1	24,80	0,79	5,58	-20,36	11,18					-18,14
DO9 M41_1	21,10	0,58	6,39	-19,90	13,32	6,99	-18,99	12,84		-18,57
DO10 M41_1	6,50	0,71	7,86	-22,00	13,39		-21,46	15,31	4,67	-20,71
DO11 M41_1	8,60	0,40	6,24	-22,52	19,71	5,61	-22,31	20,50		-25,55
DO12 M41_1	8,10	0,43	4,40	-22,35	16,92	5,04	-21,04	16,66	4,33	-20,05
DO13 M41_1	11,60	0,39	5,25	-23,26	18,83				3,89	-21,74
DO14 M41_1	17,80	1,18	5,82	-24,26	13,94					-23,19
DO15 M41_1	4,60	0,33	4,64	-23,00	18,51	7,03	-22,71	21,28	5,41	-21,40
DO16 M41_1	8,00	0,51	4,76	-23,93	17,50	5,26	-23,40	21,76	5,39	-22,38
DO17 M41_1	10,60	0,48	5,73	-22,36	18,54	7,29	-20,15	18,15	5,61	-19,88
DO18 M41_1	9,80	0,53	3,80	-22,94	13,74	6,53	-21,67	15,88	5,97	-20,21
DO19 M41_1	8,90	0,28	3,71	-24,03	19,35				6,79	-23,23
DO20 M41_1	9,40	0,40	3,38	-23,50		4,75	-21,29	14,15	5,38	-22,19
DO21 M41_1				-22,90						-22,78
DO22 M41_1	10,40	0,22	2,75	-26,10						-23,84
DO23 M41_1	3,20	0,12	4,82	-26,16	24,19					-23,00
DO24 M41_1	4,20			-24,93	20,45					
DO25 M41_1	2,10			-24,25						-24,13

### 10.5 Table 5

The data from gravity cores; GeoB 1710, -1711, and -1712 presented in Manuscript 4

GeoB 1710						GeoB 1710					
Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ C.wüll.	$\delta^{15}\text{N}$	Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ C.wüll.	$\delta^{15}\text{N}$
(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)	(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)
0.03	1.13	0.48	84.9	2.58	8.06	2.03	27.27	2.29	66.6	4.23	5.84
0.08	2.06	0.43	86.1	2.50	7.87	2.08	27.73	2.19	64.9	4.09	5.95
0.13	3.00	0.41	87.8	2.43	8.28	2.13	28.20	1.91	66.2	3.94	6.10
0.18	3.94	0.40	88.0	2.57	7.77	2.18	28.74	1.41	67.8	4.11	6.49
0.23	4.87	0.40	88.1	2.58	7.99	2.23	29.28	1.22	70.5	4.15	6.70
0.28	5.81	0.37	87.9	2.52	7.74	2.28	29.81	1.25	71.1	3.98	6.58
0.33	6.74	0.41	87.0	2.75	7.45	2.33	30.35	1.04	73.3	3.98	6.72
0.38	7.68	0.44	86.3	2.58	7.37	2.38	30.89	1.16	77.0	4.04	6.66
0.43	8.61	0.47	86.2	2.80	7.44	2.43	31.43	1.06	79.5	3.84	6.71
0.48	9.55	0.56	85.8	2.73	7.52	2.48	31.96	0.97	79.7	3.82	6.65
0.53	10.49	0.45	86.8	3.40	7.74	2.53	32.50	0.91	78.7	3.75	6.99
0.58	11.42	0.56	83.8	3.40	7.64	2.58	33.97	1.02	78.3	4.02	7.13
0.63	12.36	0.59	81.9	3.50	7.73	2.63	35.43	0.96	77.9	3.92	7.16
0.68	13.29	1.03	77.5	3.84	7.55	2.68	36.90	0.85	80.1	4.02	7.30
0.73	14.23	1.21	76.3	3.94	7.34	2.73	38.37	1.24	78.9	3.86	7.59
0.78	15.16	1.49	74.5	4.00	7.07	2.78	39.84	1.16	80.6	3.88	7.43
0.83	16.10	2.27	68.6	4.57	6.65	2.83	41.30	1.34	79.9	3.88	6.99
0.88	16.57	2.16	69.9	4.42	6.67	2.88	42.77	1.53	78.1	3.98	7.00
0.93	17.03	3.17	65.4	4.66	6.46	2.93	44.24	1.62	78.0	3.89	6.92
0.98	17.50	2.90	64.1	4.58	6.65	2.98	45.71	1.90	78.5	3.98	6.85
1.03	17.96	2.39	65.8	4.57	6.89	3.03	47.17	1.95	78.2	3.86	6.67
1.08	18.43	2.95	60.7	4.50	6.68	3.08	48.64	1.50	79.8	3.86	6.61
1.13	18.89	2.71	60.8	4.47	6.67	3.13	50.11	1.21	77.9	3.78	7.01
1.18	19.36	2.68	58.6	4.51	6.48	3.18	51.58	1.21	76.8	3.69	6.98
1.23	19.82	3.16	60.4	4.48	6.69	3.23	53.04	1.22	78.1	3.72	6.78
1.28	20.29	3.50	58.3	4.31	6.29	3.28	54.51	1.44	75.9	3.89	6.72
1.33	20.75	2.35	60.3	4.33	6.63	3.33	55.98	1.13	74.6	3.75	6.84
1.38	21.22	2.26	60.7	4.40	6.61	3.38	57.45	0.96	71.7	3.70	7.12
1.43	21.68	3.17	58.3	4.43	6.43	3.43	58.91	0.95	70.2	3.80	7.25
1.48	22.15	2.89	59.7	4.42	6.47	3.48	60.04	1.08	67.5	4.09	7.14
1.53	22.62	2.61	63.7	4.34	6.31	3.53	60.95	1.54	60.5	4.19	7.05
1.58	23.08	2.05	63.4	4.26	6.31	3.58	61.86	1.49	59.3	4.17	6.93
1.63	23.55	1.72	66.5	4.22	6.39	3.63	62.77	1.46	60.0	4.12	6.69
1.68	24.01	1.60	69.1	4.23	6.36	3.68	63.68	1.08	65.9	4.05	6.99
1.73	24.48	1.48	70.7	4.23	6.77	3.73	64.58	0.94	69.4	4.06	7.01
1.78	24.94	2.52	66.6	4.33	6.27	3.78	65.49	1.15	66.6	4.13	7.23
1.83	25.41	2.36	67.8	4.18	6.16	3.83	66.40	0.96	72.1	4.01	6.97
1.88	25.87	2.15	69.4	4.33	6.39	3.88	67.38	0.92	78.3	3.64	6.86
1.93	26.34	1.96	70.3	4.25	6.38	3.93	68.37	0.69	76.1	3.75	7.02
1.98	26.80	2.01	69.7	4.18	6.08	3.98	69.35	0.69	78.8	3.84	7.09

10.5 Table 5 (continued)

GeoB 1710						GeoB 1710					
Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ C.wüll.	$\delta^{15}\text{N}$	Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ C.wüll.	$\delta^{15}\text{N}$
(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)	(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)
4.03	70.33	0.53	79.7	3.55	7.28	6.33	127.00	0.56	78.6	3.37	8.04
4.08	71.32	0.54	80.4	3.46	6.88	6.38	128.33	0.92	77.8	3.87	7.22
4.13	72.30	0.57	82.8	3.53	6.42	6.43	129.67	1.23	75.4	3.50	6.75
4.18	73.28	0.51	82.9	3.44	6.76	6.48	131.00	1.24	75.0	4.12	6.87
4.23	74.27	0.59	80.3	3.47	6.60	6.53	132.33	1.80	71.7	4.03	6.67
4.28	75.25	0.52	79.7	3.43	6.85	6.58	133.67	1.24	77.4	4.42	6.64
4.33	76.23	0.47	79.4	3.25	6.79	6.63	135.00	1.22	79.7	4.50	6.52
4.38	77.22	0.49	79.7	3.13	6.55	6.68	135.92	1.53	76.9	4.47	6.33
4.43	78.20	0.43	78.2	3.18	6.79	6.73	136.83	1.44	78.5	4.32	6.32
4.48	79.18	0.40	79.9	2.97	6.89	6.78	137.75	1.82	73.7	4.32	6.11
4.53	80.17	0.41	79.2	3.20	7.03	6.83	138.67	1.75	72.9	4.37	6.14
4.58	81.15	0.39	80.5	3.27	7.35	6.88	139.58	1.75	73.7	4.14	6.16
4.63	82.13	0.46	81.7	3.35	6.95	6.93	140.50	1.62	76.4	4.36	6.68
4.68	83.12	0.47	81.9	3.60	6.89	6.98	141.42	1.26	80.4	4.15	7.36
4.73	84.10	0.46	83.2	3.74	6.76	7.03	142.33	1.15	80.9	4.31	6.14
4.78	85.46	0.41	83.5	3.68	6.98	7.08	143.25	1.25	81.1	4.25	6.03
4.83	86.81	0.40	84.4	3.39	7.01	7.13	144.17	1.64	76.2	4.08	5.74
4.88	88.17	0.39	82.5	3.48	6.94	7.18	145.08	1.30	77.7	4.15	5.94
4.93	89.52	0.36	82.3	3.40	7.10	7.23	146.00	0.97	77.8	4.18	6.11
4.98	90.88	0.38	81.0	3.32	7.42	7.28	146.71	0.75	79.9	4.20	6.42
5.03	92.23	0.42	80.5	3.06	7.49	7.33	147.43	0.72	79.9	4.19	6.39
5.08	93.59	0.44	79.6	3.18	7.47	7.38	148.14	0.84	78.3	4.25	5.96
5.13	94.94	0.52	81.4	3.32	7.03	7.43	148.86	0.73	78.4	4.17	6.11
5.18	96.30	0.60	81.3	3.21	7.08	7.48	149.57	0.87	76.5	4.26	6.25
5.23	97.66	0.70	81.1	3.22	6.80	7.53	150.29	1.06	74.8	4.18	6.12
5.28	99.01	0.49	83.1	3.11	7.00	7.58	151.00	1.54	74.8	4.38	6.13
5.33	100.37	0.43	82.2	3.13	6.82	7.63	152.25	1.51	75.3	4.25	5.99
5.38	101.72	0.49	82.1	3.31	6.75	7.68	153.50	1.14	79.0	4.34	6.70
5.43	103.08	0.47	83.0	3.31	6.94	7.73	154.75	0.98	80.7	4.22	6.69
5.48	104.43	0.42	82.9	3.26	7.20	7.78	156.00	1.21	73.5	4.02	6.81
5.53	105.79	0.46	83.2	3.39	7.05	7.83	157.25	0.98	74.3	4.01	6.80
5.58	107.14	0.56	84.9	3.63	6.75	7.88	158.50	1.19	73.7	4.17	6.79
5.63	108.50	0.76	85.7	3.50	6.64	7.93	159.75	1.05	74.3	4.15	6.79
5.68	109.82	0.41	86.1	3.45	7.52	7.98	161.00	1.27	69.6	4.09	6.49
5.73	111.14	0.37	85.8	3.16	7.77	8.03	162.25	1.37	66.5	4.24	6.53
5.78	112.46	0.34	85.6	2.39	8.07	8.08	163.50	1.56	70.8	4.23	6.30
5.83	113.79	0.29	85.4	2.64	7.90	8.13	164.75	1.33	75.0	4.19	6.62
5.88	115.11	0.34	85.8	2.60	8.00	8.18	166.00	1.67	72.8	4.15	6.72
5.93	116.43	0.34	86.1	2.49	7.93	8.23	167.25	1.33	65.8	3.83	6.75
5.98	117.75	0.29	86.8	2.36	7.98	8.28	168.50	1.22	63.8	3.84	6.92
6.03	119.07	0.33	85.5	2.41	8.09	8.33	169.75	1.41	65.9	3.93	6.58
6.08	120.39	0.27	84.0	2.37	7.86	8.38	171.00	1.25	63.5	3.79	6.38
6.13	121.71	0.30	84.4	2.43	7.81	8.43	172.50	1.05	63.3	3.91	6.48
6.18	123.04	0.32	83.0	2.45	8.17	8.48	174.00	1.04	59.9	3.94	6.67
6.23	124.36	0.40	80.8	2.38	7.65	8.53	175.50	1.23	57.9	3.90	6.63
6.28	125.68	0.54	78.8	2.90	7.63	8.58	177.00	2.19	56.4	3.85	5.83

**10.5 Table 5 (continued)**

GeoB 1710					
Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ C.wüll.	$\delta^{15}\text{N}$
(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)
8.63	178.50	2.24	58.7	3.94	6.17
8.68	180.00	2.15	54.2	4.12	6.07
8.73	181.50	4.12	52.1	4.09	5.54
8.78	183.00	5.71	49.2	4.13	5.09
8.83	184.00	5.96	35.9	4.06	5.55
8.88	185.00	4.14	44.0	3.99	5.87
8.93	186.00	2.26	63.1	3.69	5.94
8.98	187.60	1.26	64.3	3.27	6.33
9.03	189.20	0.84	66.9	3.33	6.46
9.08	190.80	0.75	68.5	3.15	6.47
9.13	192.40	0.57	71.8	3.24	6.78
9.18	194.00	0.52	74.1	2.73	6.79
9.23	195.83	0.45	77.7	3.58	6.77
9.28	197.67	0.43	78.7	3.09	7.07
9.33	199.50	0.43	79.6	2.73	7.31
9.38	201.33	0.52	79.5	2.93	7.00
9.43	203.17	0.56	80.7	3.03	7.31
9.48	205.00	0.59	81.3	3.34	6.70
9.53	207.20	0.53	81.8	2.94	6.91
9.58	209.40	0.45	85.7	2.94	7.41
9.63	211.60	0.43	86.1	2.58	7.12
9.68	213.80	0.45	84.9	2.75	6.96
9.73	216.00	0.53	83.2	2.85	6.96
9.78	217.71	0.51	81.4	2.80	7.17
9.83	219.43	0.53	77.6	2.83	7.12
9.88	221.14	0.86	71.0	3.39	6.53
9.93	222.86	1.19	64.0	3.08	6.35
9.98	224.57	1.68	61.1	3.94	6.11
10.03	226.29	1.29	64.2	3.60	6.50
10.08	228.00	1.23	68.9	3.84	6.53
10.13	229.43	1.12	74.1	3.93	6.64
10.18	230.86	1.45	73.6	3.90	6.34
10.23	232.29	1.32	74.2	3.58	6.57
10.28	233.71	1.20	78.0	3.52	6.38
10.33	235.14	0.80	81.1	3.00	6.76
10.38	236.57	0.34	81.5	2.96	7.96
10.43	238.00	0.34	81.6	2.51	7.91
10.48	240.33	0.53	74.6	2.62	7.53
10.53	242.67	0.54	76.9	2.77	7.45
10.58	245.00	0.86	72.2	3.41	6.93

10.5 Table 5 (continued)

GeoB 1711						GeoB 1711					
Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ C.wüll.	$\delta^{15}\text{N}$	Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ C.wüll.	$\delta^{15}\text{N}$
(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)	(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)
0.03	2.00	1.69	77.1	2.48	6.47	2.03	21.22	5.23	55.4	4.28	6.09
0.08	2.50	1.54	78.6	2.46	6.49	2.08	21.68	5.21	52.8	4.55	6.07
0.13	3.00	1.38	78.9	2.30	6.59	2.13	22.15	5.16	54.0	4.27	6.00
0.18	3.50	1.32	79.9	2.39	6.92	2.18	22.62	5.13	52.6	4.21	6.12
0.23	4.00	1.27	79.8	2.39	6.93	2.23	23.08	5.20	53.3	4.31	6.09
0.28	4.50	1.34	80.6	2.44	6.90	2.28	23.55	5.07	52.8	4.25	6.05
0.33	5.00	1.28	80.0	2.48	6.88	2.33	24.01	5.12	53.3	4.16	6.01
0.38	5.50	1.30	80.7	3.40	6.86	2.38	24.48	5.51	54.5	4.08	5.81
0.43	6.00	1.21	81.3	2.64	6.54	2.43	24.94	5.55	54.4	4.02	5.89
0.48	6.50	1.28	80.3	2.77	6.53	2.48	25.41	5.55	54.5	3.86	5.65
0.53	7.00	1.35	80.4	3.05	6.56	2.53	25.87	5.08	58.2	4.11	5.36
0.58	7.50	1.32	80.4	2.80	6.61	2.58	26.34	5.27	57.4	4.08	5.66
0.63	8.00	1.33	79.7	3.26	6.64	2.63	26.80	5.01	58.4	4.26	5.74
0.68	8.50	1.45	78.0	3.56	6.60	2.68	27.27	5.65	57.6	3.91	5.77
0.73	9.00	1.65	77.4	3.39	6.53	2.73	27.73	5.86	60.4	3.87	5.74
0.77	9.50	1.84	75.9	3.54	6.70	2.78	28.20	5.76	58.5	3.72	5.82
0.83	10.00	1.66	76.8	3.43	6.67	2.83	28.66	5.53	53.7	3.91	5.54
0.88	10.50	1.67	77.7	3.53	6.96	2.88	29.13	5.51	55.1	4.05	5.58
0.93	11.00	1.88	76.0	3.65	6.73	2.93	29.55	5.57	56.3	3.80	5.67
0.98	11.58	1.77	75.5	3.45	6.95	2.98	29.97	5.36	60.4	3.93	5.57
1.03	12.15	1.96	71.5	3.27	6.84	3.03	30.40	5.53	61.6	3.84	5.69
1.08	12.68	2.04	70.9	3.59	6.73	3.08	30.82	5.82	60.6	3.86	5.83
1.13	13.11	2.45	70.9	3.96	6.59	3.13	31.24	5.31	62.7	3.76	5.68
1.18	13.54	2.32	74.0	4.10	6.62	3.18	31.66	4.79	63.9	3.60	5.85
1.23	13.96	2.54	71.4	3.76	6.90	3.23	32.09	4.46	65.9	3.70	5.88
1.28	14.39	2.66	71.8	4.22	6.98	3.28	32.51	4.09	67.1	3.41	5.99
1.33	14.82	3.94	64.6	4.31	6.82	3.33	32.93	4.12	64.9	3.63	5.96
1.38	15.25	4.44	62.4	4.18	6.44	3.38	33.35	4.85	62.6	3.80	5.92
1.43	15.67	5.09	58.4	4.30	6.31	3.43	33.78	5.26	60.6	3.82	6.00
1.48	16.10	5.38	56.7	4.57	6.01	3.48	34.20	5.28	60.9	3.76	5.85
1.53	16.57	5.64	57.1	4.39	6.12	3.53	34.62	5.40	60.2	3.86	5.96
1.58	17.03	4.98	60.9	4.27	6.05	3.58	35.04	5.74	61.2	3.93	6.20
1.63	17.50	5.41	58.5	4.08	6.06	3.63	35.47	5.74	59.6	3.94	6.20
1.68	17.96	5.51	57.4	4.49	6.19	3.68	35.89	6.26	60.0	3.78	6.13
1.73	18.43	5.48	57.7	4.50	6.19	3.73	36.31	6.37	59.1	3.81	6.21
1.78	18.89	5.50	55.2	4.56	6.23	3.78	36.73	6.63	58.6	3.59	6.23
1.83	19.36	5.58	53.3	4.51	6.35	3.83	37.16	5.99	61.1	3.88	6.28
1.88	19.82	5.46	54.8	4.41	6.21	3.88	37.58	4.80	65.7	3.77	6.34
1.93	20.29	5.34	53.5	4.48	6.25	3.93	38.00	5.20	62.1	3.71	6.30
1.98	20.75	5.28	54.0	4.45	6.33	3.98	39.00	5.82	62.1	3.52	6.12

10.5 Table 5 (continued)

GeoB 1711						GeoB 1711					
Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ C.wüll.	$\delta^{15}\text{N}$	Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ C.wüll.	$\delta^{15}\text{N}$
(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)	(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)
4.03	40.00	6.18	60.6	3.67	6.00	6.38	74.60	2.24	68.8	3.27	5.50
4.08	41.00	6.26	61.5	3.91	6.05	6.43	75.20	1.97	67.4	3.05	5.84
4.13	42.00	5.74	64.2	3.85	6.07	6.48	75.80	1.83	65.3	3.20	5.81
4.18	43.00	5.62	62.7	3.90	6.00	6.53	76.40	1.98	64.9	3.32	6.06
4.23	44.00	5.50	63.4	3.87	5.94	6.58	77.00	1.96	65.9	3.06	5.94
4.28	45.00	4.74	66.4	3.93	6.06	6.63	77.60	1.97	64.1	3.16	5.96
4.33	46.00	4.51	67.2	3.62	6.09	6.68	78.20	2.36	62.4	3.09	5.63
4.38	47.00	4.28	65.8	3.69	6.11	6.73	78.80	2.65	62.0	3.04	5.35
4.43	48.00	4.35	66.0	3.80	6.06	6.78	79.40	2.95	61.5	2.69	5.41
4.48	49.00	4.86	62.7	3.62	6.17	6.83	80.00	2.88	61.6	2.89	5.20
4.53	50.00	4.95	63.4	3.83	5.99	6.88	80.58	2.67	62.9	2.86	5.41
4.58	51.00	5.09	63.5	3.77	5.93	6.93	81.17	2.44	64.1	2.99	5.96
4.63	52.00	5.26	62.4	3.64	6.06	6.98	81.75	2.14	66.5	2.70	5.94
4.68	53.00	5.25	63.8	3.67	6.09	7.03	82.33	1.91	69.1	3.04	6.13
4.73	54.00	5.11	61.1	3.62	5.94	7.08	82.92	1.84	70.4	2.99	6.34
4.78	55.00	4.69	62.4	3.56	5.98	7.13	83.50	1.79	70.9	3.39	6.27
4.83	56.00	3.91	62.1	3.70	6.20	7.18	84.08	1.84	71.4	3.66	6.24
4.88	57.00	3.57	61.8	3.66	6.15	7.23	84.67	2.14	70.3	3.55	6.03
4.93	58.00	3.96	59.4	3.84	5.84	7.28	85.25	2.87	67.8	3.66	5.81
4.98	59.00	3.96	59.8	3.89	5.98	7.33	85.83	3.08	67.9	3.57	5.71
5.03	59.50	4.54	57.6	3.98	5.85	7.38	86.42	3.05	70.1	3.22	5.65
5.08	60.00	4.85	55.2	4.11	5.82	7.43	87.00	2.61	72.3	3.47	5.79
5.13	60.50	5.27	51.5	4.21	5.81	7.48	87.75	2.54	70.2	3.40	5.87
5.18	61.00	5.66	48.4	3.95	5.70	7.53	88.50	2.70	67.5	3.33	5.79
5.23	61.50	5.51	46.4	4.06	5.80	7.58	89.25	2.96	63.6	3.23	5.79
5.28	62.00	5.31	47.2	3.83	5.78	7.63	90.00	2.78	61.6	3.24	5.89
5.33	62.50	5.25	46.6	4.11	5.57	7.68	90.75	2.36	61.3	3.25	6.23
5.38	63.00	4.66	49.1	4.18	5.76	7.73	91.50	2.40	61.1	3.07	6.03
5.43	63.50	4.56	49.7	3.99	5.80	7.78	92.25	2.32	60.3	3.17	6.17
5.48	64.00	4.05	53.8	3.97	5.94	7.83	93.00	2.37	61.3	3.26	6.20
5.53	64.50	3.92	54.5	4.11	5.87	7.88	93.75	2.43	62.3	2.95	5.92
5.58	65.00	3.86	57.0	4.13	6.05	7.93	94.50	2.42	62.8	3.23	5.88
5.63	65.60	4.04	56.5	3.98	5.92	7.98	95.25	2.64	64.1	3.20	5.97
5.68	66.20	3.99	59.5	3.91	5.94	8.03	96.00	2.62	64.8	3.10	6.05
5.73	66.80	4.04	59.4	3.56	5.88	8.08	96.75	2.68	65.1	3.21	5.92
5.78	67.40	3.96	60.1	3.58	5.98	8.13	97.50	2.56	66.7	3.13	5.73
5.83	68.00	3.13	63.1	3.60	5.98	8.18	98.25	2.43	68.4	3.11	5.86
5.88	68.60	2.77	64.3	3.80	6.00	8.23	99.00	2.37	69.9	3.07	5.79
5.93	69.20	2.70	63.5	3.41	5.98	8.28	99.80	2.73	71.1	3.09	5.46
5.98	69.80	2.36	66.6	3.46	6.06	8.33	100.60	2.50	69.2	2.98	5.22
6.03	70.40	2.33	67.4	3.24	5.92	8.38	101.40	1.93	70.2	3.30	5.28
6.08	71.00	2.25	69.3	3.18	5.54	8.43	102.20	1.81	70.0	3.10	5.80
6.13	71.60	2.16	70.9	3.37	5.44	8.48	103.00	1.80	69.9	3.27	6.00
6.18	72.20	2.22	70.5	3.41	5.46	8.53	103.80	1.91	69.6	3.25	5.94
6.23	72.80	2.16	70.9	3.42	5.27	8.58	104.60	1.90	69.7	3.33	5.90
6.28	73.40	2.14	72.3	3.49	5.39	8.63	105.40	2.03	68.1	3.28	5.95
6.33	74.00	2.17	70.9	3.32	5.38	8.68	106.20	1.96	68.5	3.35	5.85

10.5 Table 5 (continued)

GeoB 1711					
Sed. depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ C.wüll.	$\delta^{15}\text{N}$
(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)
8.73	107.00	2.27	69.7	3.41	5.71
8.78	107.75	2.65	71.1	3.55	5.61
8.83	108.50	2.70	71.1	3.61	5.81
8.88	109.25	2.63	72.1	3.54	5.64
8.93	110.00	2.96	71.9	3.36	5.70
8.98	110.75	2.28	73.6	2.67	6.20
9.03	111.50	1.76	74.3	3.29	6.49
9.08	112.25	1.85	74.6	3.02	6.46
9.13	113.00	1.69	74.2	2.66	6.62
9.18	113.75	1.44	77.9	2.53	6.72
9.23	114.50	1.49	75.1	2.40	6.78
9.28	115.25	1.43	77.9	2.59	7.19
9.33	116.00	1.50	74.5	2.88	7.06
9.38	116.75	1.49	75.4	2.31	6.96
9.43	117.50	1.60	75.1	2.33	6.85
9.48	118.25	1.64	76.5	2.36	7.36
9.53	119.00	1.54	76.9	2.38	7.07
9.58	119.75	1.25	77.5	2.33	7.10
9.63	120.50	1.33	76.3	2.30	7.03
9.68	121.25	1.29	75.6	2.26	7.12
9.73	122.00	1.51	73.5	2.34	6.93
9.78	122.60	1.53	74.0	2.20	7.16
9.83	123.20	1.53	72.5	2.23	7.33
9.88	123.80	1.66	70.1	2.30	7.14
9.93	124.40	1.60	70.0	2.79	7.00
9.98	125.00	1.79	68.1	2.79	6.90
10.03	125.60	1.82	70.6	3.27	6.98
10.08	126.20	2.40	67.3	2.91	6.83
10.13	126.80	1.99	67.9	2.51	7.18
10.18	127.40	2.27	69.1	2.76	7.07
10.23	128.00	3.04	67.8	2.85	6.49
10.28	128.88	3.64	65.6	3.86	6.32
10.33	129.75	4.13	63.6	4.32	6.07
10.38	130.63	5.03	60.9	4.35	6.09
10.43	131.50	4.66	60.3	4.37	6.12
10.48	132.38	6.34	54.0	4.34	6.02
10.53	133.25	6.79	53.6	4.27	6.08
10.58	134.13	5.50	61.0		5.97
10.63	135	5.14	62.1		5.82

10.5 Table 5 (continued)

GeoB 1712						GeoB 1712					
Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ G.bull.	$\delta^{15}\text{N}$	Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ G.bull.	$\delta^{15}\text{N}$
(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)	(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)
0.03	2.00	3.66	72.6	2.76	6.01	2.03	24.46	7.72	55.2	2.75	5.43
0.08	2.64	3.36	72.8	0.36	6.07	2.08	24.93	7.38	54.8	2.60	5.78
0.13	3.28	3.36	72.8	0.66	5.90	2.13	25.39	7.15	53.6	2.28	5.78
0.18	3.92	3.36	72.2	0.57	6.06	2.18	25.85	7.09	54.9	1.98	5.74
0.23	4.56	3.29	72.1	0.74	5.86	2.23	26.32	7.18	50.8	1.64	5.68
0.28	5.19	3.31	73.1	0.91	5.94	2.28	26.78	7.51	53.1	2.60	5.74
0.33	5.83	3.27	73.4	0.54	6.12	2.33	27.24	7.26	51.6	1.89	5.76
0.38	6.47	3.40	72.2	0.70	6.11	2.38	27.71	8.44	48.3	2.25	5.76
0.43	7.11	3.39	72.2	0.25	6.04	2.43	28.17	8.67	48.3	1.88	5.76
0.48	7.75	3.63	70.6	0.01	6.03	2.48	28.63	8.39	50.1	1.64	5.70
0.53	8.39	3.60	70.3	0.61	6.08	2.53	29.09	9.20	50.2	2.89	5.84
0.58	9.03	3.74	69.6	0.73	6.10	2.58	29.56	8.74	51.2	2.72	6.09
0.63	9.67	3.82	68.7	0.53	6.07	2.63	30.02	8.35	49.7	2.42	6.18
0.68	10.31	3.75	68.9	0.23	6.10	2.68	30.48	9.71	47.7		6.29
0.73	10.94	4.11	66.5	1.06	6.04	2.73	30.95	10.25	47.9		6.23
0.78	11.58	3.90	68.1	0.26	6.08	2.78	31.41	12.96	36.0		5.92
0.83	12.22	4.25	64.6	0.25	6.11	2.83	31.87	10.06	45.9		5.86
0.88	12.86	4.54	61.9	1.21	6.16	2.88	32.34	9.55	46.7	2.59	5.90
0.93	13.50	4.94	58.3	0.39	6.13	2.93	32.80	8.46	44.9		5.90
0.98	14.00	5.89	50.9	2.27	5.97	2.98	33.66	9.42	44.9	2.33	5.78
1.03	14.50	7.01	43.9	2.01	5.68	3.03	34.53	10.06	43.2	3.13	5.91
1.08	15.00	6.65	44.7	1.42	5.71	3.08	35.39	9.99	43.1	2.45	5.83
1.13	15.50	6.91	44.0	1.52	5.75	3.13	36.26	11.69	39.2	2.42	5.80
1.18	16.00	7.18	41.4	2.20	5.62	3.18	37.12	10.76	41.5	3.10	5.91
1.23	16.50	5.73	50.9		5.86	3.23	37.99	10.42	40.9	2.73	
1.28	17.00	6.91	42.0	3.04	5.75	3.28	38.85	9.55	46.1	3.24	5.77
1.33	17.50	7.35	40.6	0.90	5.83	3.33	39.71	8.53	50.2	2.95	5.78
1.38	18.00	7.74	39.4	1.48	5.66	3.38	40.58	9.20	48.5	2.98	5.92
1.43	18.50	7.09	46.4	2.69	5.50	3.43	41.44	9.13	49.0	2.66	5.72
1.48	19.00	6.58	45.3	0.84	5.38	3.48	42.31	8.52	51.6	2.71	5.82
1.53	19.50	6.54	47.9	2.61	5.45	3.53	43.17	8.30	51.4	3.04	5.73
1.58	20.00	6.37	49.3	1.63	5.39	3.58	44.04	8.14	49.8	2.98	5.89
1.63	20.50	7.11	46.7	2.82	5.42	3.63	44.90	8.56	50.3	0.93	5.84
1.68	21.00	7.14	46.2	1.58	5.36	3.68	45.76	8.03	51.2	2.25	5.83
1.73	21.50	6.73	49.3	2.44	5.43	3.73	46.63	8.56	47.4	2.59	5.78
1.78	22.00	7.04	51.2	2.75	5.59	3.78	47.49	8.14	50.5	1.36	5.86
1.83	22.50	6.63	51.8	1.46	5.33	3.83	48.36	7.62	51.7	2.29	5.79
1.88	23.00	7.16	51.4	1.22	5.35	3.88	49.22	7.60	53.2	1.94	5.78
1.93	23.50	7.39	53.2	2.59	5.49	3.93	50.09	7.06	54.3	1.97	5.84
1.98	24.00	8.35	51.2	2.34	5.46	3.98	50.95	8.04	48.6	2.72	5.73

10.5 Table 5 (continued)

GeoB 1712						GeoB 1712					
Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ G.bull.	$\delta^{15}\text{N}$	Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ G.bull.	$\delta^{15}\text{N}$
(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)	(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)
4.03	51.81	6.92	53.9	1.37	5.87	6.38	80.71	5.06	56.0	0.69	5.00
4.08	52.68	8.70	49.8	2.46	5.86	6.43	81.35	5.23	56.0	0.92	4.98
4.13	53.54	9.16	48.1	1.69	5.95	6.48	81.98	5.38	55.2	0.94	5.04
4.18	54.41	8.61	49.5	3.08	5.90	6.53	82.62	5.46	55.3	1.04	4.96
4.23	55.27	7.02	53.2	1.66	5.92	6.58	83.25	5.47	55.0	0.93	5.25
4.28	56.14	5.11	57.7	1.33	5.82	6.63	83.89	5.74	54.6	0.68	5.06
4.33	57.00	4.70	57.9	1.55	5.87	6.68	84.53	6.28	53.4	0.94	5.17
4.38	57.50	5.03	55.0	1.09	5.85	6.73	85.16	6.91	51.7	1.10	5.19
4.43	58.00	7.39	40.2	1.14	5.54	6.78	85.80	7.22	52.9	1.62	5.17
4.48	58.50	7.64	40.4	1.25	5.47	6.83	87.22	6.53	55.3	0.93	5.14
4.53	59.00	7.50	41.9	1.61	5.48	6.88	88.65	6.27	51.7	0.71	5.24
4.58	59.50	7.42	40.6	2.40	5.41	6.93	90.07	6.43	52.6	1.82	5.17
4.63	60.00	7.08	41.5	2.11	5.35	6.98	91.49	6.49	53.0	1.56	5.05
4.68	60.50	7.04	38.0	2.25	5.21	7.03	92.92	5.94	55.0	0.95	5.06
4.73	61.00	6.40	39.3	2.64	5.27	7.08	94.34	5.53	57.9	0.66	5.06
4.78	61.50	6.73	37.6	1.63	5.46	7.13	95.76	5.53	58.8	0.92	5.10
4.83	62.00	6.68	38.6	2.59	5.51	7.18	97.19	5.46	59.8	0.81	4.95
4.88	62.50	6.98	35.4	2.88	5.41	7.23	98.61	6.01	55.6	1.09	4.95
4.93	62.99	7.03	37.0	2.47	5.32	7.28	100.04	6.36	53.1	1.49	5.00
4.98	63.49	6.80	40.4	2.42	5.28	7.33	101.46	6.34	60.1	1.51	5.06
5.03	63.98	6.81	41.9	2.69	5.48	7.38	102.88	6.37	57.2	1.58	4.98
5.08	64.47	8.60	40.7	2.52	5.38	7.43	104.31	8.08	54.5	0.95	5.05
5.13	64.96	7.65	39.6	2.60	5.38	7.48	105.73	5.60	59.4	1.14	5.02
5.18	65.46	7.63	39.7	2.34	5.39	7.53	107.15	7.96	57.2	1.82	4.98
5.23	65.95	7.80	42.2	1.49	5.37	7.58	108.58	8.37	54.4	0.77	4.99
5.28	66.44	8.72	41.8	2.43	5.30	7.63	110.00	8.57	54.5	0.79	5.22
5.33	66.94	10.12	42.5	2.60	5.55	7.68	111.33	7.43	57.7	0.71	5.34
5.38	67.43			2.58	5.48	7.73	112.67	7.08	59.9	0.58	5.65
5.43	67.92	9.24	43.7	2.83	5.28	7.78	114.00	6.30	58.3	1.12	5.41
5.48	68.41	8.11	49.1		5.16	7.83	115.33	5.39	61.9	1.50	5.64
5.53	68.91	7.24	49.3	2.68	5.21	7.88	116.67	4.95	64.1	1.02	5.56
5.58	69.40	6.48	50.4	1.51	5.23	7.93	118.00	4.45	63.3	1.97	5.58
5.63	70.12	6.10	52.3		5.17	7.98	119.33	4.20	67.0	0.06	5.65
5.68	70.85	6.10	51.3	1.45	5.10	8.03	120.67	3.56	66.0	0.15	5.57
5.73	71.57	5.54	53.3	0.88	5.30	8.08	122.00	3.77	65.4	-1.32	5.42
5.78	72.29	5.51	53.9		5.26	8.13	123.33	4.62	59.0	0.49	5.55
5.83	73.02	5.91	51.8		5.08	8.18	124.67	4.37	61.1	0.96	5.15
5.88	73.74	5.39	53.9	2.12	5.04	8.23	126.00	4.69	60.7	0.51	5.52
5.93	74.46	5.46	53.0	1.71	5.02	8.28	127.33	4.86	54.4	1.00	5.50
5.98	75.18	4.68	56.5	2.22	4.87	8.33	128.67	4.95	55.9	0.35	5.54
6.03	75.91	4.61	56.7	0.63	4.95	8.38	130.00	5.40	52.0	0.71	5.47
6.08	76.63	4.56	55.6		4.95	8.43	131.33	5.56	49.7	0.73	5.25
6.13	77.35	4.29	56.2	1.95	5.09	8.48	132.67	5.77	51.0	1.50	5.48
6.18	78.08	4.86	55.1	1.80	5.09	8.53	134.00	5.00	37.9	0.67	5.41
6.23	78.80	4.86	54.6	0.73	5.12	8.58	134.59	5.85	47.3	1.75	5.38
6.28	79.44	4.73	56.4	0.70	5.07	8.63	135.17	5.98	45.9	2.50	5.21
6.33	80.07	4.97	55.6	0.65	4.98	8.68	135.76	5.76	49.1	3.14	5.05

**10.5 Table 5 (continued)**

GeoB 1712					
Sed.depth	Age	TOC	CaCO <sub>3</sub>	$\delta^{18}\text{O}$ G.bull.	$\delta^{15}\text{N}$
(m)	(ka)	(wt.%)	(wt.%)	(‰ vs. PDB)	(‰)
8.73	136.34	6.58	47.1	3.39	4.93
8.78	136.93	5.28	59.4	2.18	4.87
8.83	137.52	5.21	59.2	2.42	4.70
8.88	138.10	5.14	57.3	3.22	4.64
8.93	138.69	4.70	61.2	2.95	4.92
8.98	139.28	4.54	58.9	2.20	4.75
9.03	139.86	4.64	60.1	2.11	4.93
9.08	140.45	4.76	58.2	2.14	4.82
9.13	141.03	5.04	55.6	1.70	4.76
9.18	141.62	4.88	56.5	1.95	4.85
9.23	142.21	5.24	53.5	2.65	4.89
9.28	142.79	5.55	52.2	2.39	4.91
9.33	143.38	5.61	56.8	1.95	4.90
9.38	143.97	6.30	54.6	2.01	4.95
9.43	144.55	5.65	49.4	1.84	4.85
9.48	145.14	5.92	51.8	1.92	5.01
9.53	145.72	5.75	53.0	1.92	5.24
9.58	146.31	5.55	51.3	1.99	5.12
9.63	146.90	5.27	53.0	1.02	5.40
9.68	147.48	5.13	53.9	1.13	5.00
9.73	148.07	5.45	51.8	1.41	4.80
9.78	148.66	4.79	49.8	1.47	4.88
9.83	149.24	5.39	48.9	1.39	5.11
9.88	149.83	5.60	48.7	1.77	4.88
9.93	150.41	5.98	46.9	2.75	4.90
9.98	151.00	6.29	45.4	2.94	5.00
10.03	151.59	6.68	43.3	2.20	5.14
10.08	152.17	6.56	41.0	1.87	4.87
10.13	152.76	5.98	40.4	2.01	4.80
10.18	153.34	4.96	39.4	1.75	4.83
10.23	153.93	4.75	39.3	1.48	4.90

Publications of this series:

- No. 1**      **Wefer, G., E. Suess and cruise participants**  
Bericht über die POLARSTERN-Fahrt ANT IV/2, Rio de Janeiro - Punta Arenas, 6.11. - 1.12.1985.  
60 pages, Bremen, 1986.
- No. 2**      **Hoffmann, G.**  
Holozänstratigraphie und Küstenlinienverlagerung an der andalusischen Mittelmeerküste.  
173 pages, Bremen, 1988. (out of print)
- No. 3**      **Wefer, G. and cruise participants**  
Bericht über die METEOR-Fahrt M 6/6, Libreville - Las Palmas, 18.2. - 23.3.1988.  
97 pages, Bremen, 1988.
- No. 4**      **Wefer, G., G.F. Lutze, T.J. Müller, O. Pfannkuche, W. Schenke, G. Siedler, W. Zenk**  
Kurzbericht über die METEOR-Expedition No. 6, Hamburg - Hamburg, 28.10.1987 - 19.5.1988.  
29 pages, Bremen, 1988. (out of print)
- No. 5**      **Fischer, G.**  
Stabile Kohlenstoff-Isotope in partikulärer organischer Substanz aus dem Südpolarmeer  
(Atlantischer Sektor). 161 pages, Bremen, 1989.
- No. 6**      **Berger, W.H. and G. Wefer**  
Partikelfluß und Kohlenstoffkreislauf im Ozean.  
Bericht und Kurzfassungen über den Workshop vom 3.-4. Juli 1989 in Bremen.  
57 pages, Bremen, 1989.
- No. 7**      **Wefer, G. and cruise participants**  
Bericht über die METEOR - Fahrt M 9/4, Dakar - Santa Cruz, 19.2. - 16.3.1989.  
103 pages, Bremen, 1989.
- No. 8**      **Kölling, M.**  
Modellierung geochemischer Prozesse im Sickerwasser und Grundwasser.  
135 pages, Bremen, 1990.
- No. 9**      **Heinze, P.-M.**  
Das Auftriebsgeschehen vor Peru im Spätquartär. 204 pages, Bremen, 1990. (out of print)
- No. 10**     **Willems, H., G. Wefer, M. Rinski, B. Donner, H.-J. Bellmann, L. Eißmann, A. Müller,  
B.W. Flemming, H.-C. Höfle, J. Merkt, H. Streif, G. Hertweck, H. Kuntze, J. Schwaar,  
W. Schäfer, M.-G. Schulz, F. Grube, B. Menke**  
Beiträge zur Geologie und Paläontologie Norddeutschlands: Exkursionsführer.  
202 pages, Bremen, 1990.
- No. 11**     **Wefer, G. and cruise participants**  
Bericht über die METEOR-Fahrt M 12/1, Kapstadt - Funchal, 13.3.1990 - 14.4.1990.  
66 pages, Bremen, 1990.
- No. 12**     **Dahmke, A., H.D. Schulz, A. Kölling, F. Kracht, A. Lücke**  
Schwermetallspuren und geochemische Gleichgewichte zwischen Porenlösung und Sediment  
im Wesermündungsgebiet. BMFT-Projekt MFU 0562, Abschlußbericht. 121 pages, Bremen, 1991.
- No. 13**     **Rostek, F.**  
Physikalische Strukturen von Tiefseesedimenten des Südatlantiks und ihre Erfassung in  
Echolotregistrierungen. 209 pages, Bremen, 1991.
- No. 14**     **Baumann, M.**  
Die Ablagerung von Tschernobyl-Radiocäsium in der Norwegischen See und in der Nordsee.  
133 pages, Bremen, 1991. (out of print)
- No. 15**     **Kölling, A.**  
Frühdigenetische Prozesse und Stoff-Flüsse in marinen und ästuarinen Sedimenten.  
140 pages, Bremen, 1991.
- No. 16**     **SFB 261 (ed.)**  
1. Kolloquium des Sonderforschungsbereichs 261 der Universität Bremen (14.Juni 1991):  
Der Südatlantik im Spätquartär: Rekonstruktion von Stoffhaushalt und Stromsystemen.  
Kurzfassungen der Vorträge und Poster. 66 pages, Bremen, 1991.
- No. 17**     **Pätzold, J. and cruise participants**  
Bericht und erste Ergebnisse über die METEOR-Fahrt M 15/2, Rio de Janeiro - Vitoria,  
18.1. - 7.2.1991. 46 pages, Bremen, 1993.
- No. 18**     **Wefer, G. and cruise participants**  
Bericht und erste Ergebnisse über die METEOR-Fahrt M 16/1, Pointe Noire - Recife,  
27.3. - 25.4.1991. 120 pages, Bremen, 1991.
- No. 19**     **Schulz, H.D. and cruise participants**  
Bericht und erste Ergebnisse über die METEOR-Fahrt M 16/2, Recife - Belem, 28.4. - 20.5.1991.  
149 pages, Bremen, 1991.