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# RECONSTRUCTION OF PRODUCTIVITY GRADIENTS IN THE CANARY ISLAND REGION OFF MOROCCO BY MEANS OF SINKING PARTICLES AND SEDIMENTS

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# Reconstruction of productivity gradients in the Canary Islands region off Morocco by means of sinking particles and sediments

Dissertation
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# ABSTRACT

The Canary Islands region is characterised by a productivity gradient that is formed by the eutrophic trade wind driven upwelling region on the Moroccan shelf, highly productive filament regions, and oligotrophic conditions further offshore. Sinking particles, surface sediments and sediment cores were investigated with the aim to reconstruct productivity gradients in this region. Organic carbon, carbonate and stable carbon isotope ratios served as proxies for the sedimentation of biogenic matter. In addition, the fairly new method of sedimentary stable nitrogen isotope ratios as indicator of nutrient utilisation was applied.

In order to improve the knowledge and the possible pitfalls of stable nitrogen and carbon isotope ratios as paleo-proxies, the processes responsible for their early diagenetic alterations were investigated. Release of dissolved inorganic nitrogen and carbon ($NH_4^+$ and $CO_2$) depleted in $^{15}N$ and $^{13}C$ with respect to the organic source and the remineralisation of organic compounds with isotopic compositions different from the bulk sedimentary organic matter were identified to cause early diagenetic isotopic changes. Furthermore, the influence of ammonium fixed between the lattices of clay on the stable nitrogen isotope ratio of bulk sediment has to be considered especially in sediments poor in organic matter.

The potential of the applied productivity proxies to reconstruct past productivity changes in the investigation area was evaluated by reconstructing present regional productivity gradients in sinking particles and surface sediments and by comparing these with the regional surface water pigment distribution derived from satellite observations. Next to particle production and export from the euphotic zone, lateral particle transport and organic matter degradation were identified as the key processes strongly affecting particle fluxes during settling in the water column and in the surface sediments. A strong imprint of a eutrophic signature on sediment accumulation and the geochemical characteristics was observed in the oligotrophic region north of the Canary Islands. Less than 1 % of the organic matter that was exported from the euphotic zone, resisted degradation and was preserved in the sediments. However, despite of lateral particle transport and organic matter degradation, productivity gradients were recorded, albeit smoothed, in the sediments. Even mesoscale features, such as the highly productive upwelling filament off Cape Ghir, were matched in the surface sediments by geochemical and micropaleontological proxies.

These proxies were used to reconstruct past productivity variations in the investigation area. Both the accumulation of biogenic compounds in time-slices and the geochemical characteristics of time-series studies in the sedimentary record revealed higher productivity during glacial times in the upwelling influenced continental margin area and at an offshore site that was frequently influenced by the Cape Ghir filament. The productivity records at the continental margin were strongly influenced by sea-level changes. In contrast, productivity variation at the filament influenced site was strongly affected by trade wind intensity, as shown in comparison with the pollen record and grain-size of lithogenic matter. Trade wind variations exhibited strong cycles related to precession.

## ZUSAMMENFASSUNG

Die Meeresregion im Bereich der Kanarischen Inseln ist durch einen starken Produktivitätsgradienten gekennzeichnet: Der marokkanische Schelf und die Filamentregionen im Bereich von Kap Ghir und Kap Yubi zeigen insbesondere während der Passatwind- und Auftriebssaison im Sommer hohe Produktivität, während weiter westlich im offenen Ozean oligotrophe Produktionsverhältnisse vorherrschen. In der vorliegenden Studie wurden Sinkstoffe, Oberflächensedimente und Sedimentkerne bearbeitet, um Produktivitätsgradienten im Untersuchungsgebiet zu rekonstruieren. Die Sedimentation biogener Partikel wurde anhand von organischem Kohlenstoff, Karbonat und stabilen Kohlenstoffisotopen untersucht. Zudem wurden sedimentäre Stickstoff-Isotopenverhältnisse als Anzeiger der Nährstoffverfügbarkeit in der euphotischen Zone analysiert.

Da die Isotopenverhältnisse des sedimentären Stickstoffs und des organischen Kohlenstoffs frühdiagenetisch überprägt werden können, wurden zunächst die hierfür verantwortlichen Prozesse untersucht. Es wurde gezeigt, daß bei der Remineralisation der sedimentären organischen Substanz gelöster anorganischer Stickstoff und Kohlenstoff freigesetzt werden, die gegenüber ihrer organischen Quelle an $^{15}$N und $^{13}$C abgereichert sind. Außerdem ist der selektive Abbau von organischen Komponenten mit einer deutlich vom sedimentären Durchschnitt abweichenden Isotopen-Zusammensetzung von Bedeutung. Besonders bei Sedimenten mit geringen Mengen an organischer Substanz kann das zwischen den Schichten von Tonmineralen fixierte Ammonium einen starken Einfluß auf das Isotopenverhältnis des sedimentären Stickstoffs ausüben.

Durch einen Vergleich der Verteilung der analysierten Produktivitätsanzeiger in Sinkstoffen und Oberflächensedimenten mit der regionalen Pigmentverteilung im Oberflächenwasser wurde deren Eignung als Proxy von Produktivitätsgradienten überprüft. Neben Produktion und Export von biogenen Partikeln aus der euphotischen Zone, werden die Partikelflüsse durch lateralen Partikeltransport und Remineralisation von organischer Substanz während des Absinkens und während ihrer Akkumulation im Sediment beeinflußt. Aufgrund der Abbauprozesse in der Wassersäule und in den Oberflächensedimenten bleibt nur weniger als 1% der aus der euphotischen Zone exportierten organischen Substanz im Sediment erhalten. Der Einfluß von lateralem Partikeltransport wird anhand der geochemischen Eigenschaften der Sedimente besonders im oligotrophen Bereich nördlich der Kanarischen Inseln deutlich. Es handelt sich dabei um Partikel aus der vom Auftrieb beeinflußten küstennahen Region vor Marokko. Trotz lateralem Partikeltransport und Abbau organischer Substanz konnten die vorherrschenden Produktivitätsgradienten, wenn auch abgeschwächt, in den Sedimenten rekonstruiert werden. Sogar lokale Besonderheiten, wie die erhöhte Produktivität im Bereich der Auftriebsfilamente vor Kap Ghir und Kap Yubi, wurden in den Oberfächensedimenten anhand ihrer geochemischen und mikropaläontologischen Zusammensetzung angezeigt.

Mit Hilfe dieser Proxies wurden Änderungen der Produktivität für das späte Pleistozän rekonstruiert. In der durch Auftrieb beeinflußten Küstenregion vor Marokko und in der Region, die vom Kap-Ghir-Filament beeinflußt wird, dokumentieren die Akkumulation biogener Komponenten und geochemischen Sedimenteigenschaften eine erhöhte Produktivität zu Glazial-Zeiten. Ein Teil der Produktivitätsschwankungen im küstennahen Bereich kann auf Verlagerungen der Auftriebszellen durch Meeresspiegelschwankungen zurückgeführt werden. Korngrößenanalysen an lithogenem Material und Pollenanalysen zeigen, daß Änderungen der Produktivität im Bereich des Filamenteinflusses westlich von Kap Ghir im wesentlichen durch Änderungen der Passatwindintensität verursacht wurden. Aufgrund von Frequenzanalysen an Zeitserien liegen die Produktivitätsschwankungen in dieser Region hauptsächlich im Frequenzbereich der Präzession und der Exzentrizität.

# PREFACE

In times of anthropogenic perturbations of the climate system due to fossil fuel emissions and other human activities affecting the composition of the atmosphere, the understanding of natural climatic variability is an important topic of research. The marine ecosystem reacts highly sensitive to climate change and occupies a key position in the global carbon cycle by controlling the relative distribution of the greenhouse gas $CO_2$ in the ocean and atmosphere. It is a complex system in which physical (thermohaline and wind-driven circulation, nutrient supply, dust and riverine input, particle aggregation and transport) and biogeochemical processes (particle production, transformation, dissolution, and remineralisation) interact.

In order to contribute to a better understanding of this system, oceanographers of all disciplines collaborated in the MAST III project CANIGO (Canary Islands Gibraltar and Azores Observations) funded by the European Commission. The investigation area off NW Africa offers a manifold of processes and oceanographic conditions extending from the eutrophic continental margin, influenced by coastal upwelling, to the oligotrophic subtropical gyre region. It includes an important frontal systems within the Azores region, the Gibraltar region characterised by water exchange between the North Atlantic and the Mediterranean Sea, and the eastern boundary current interacting with the Canary Islands. Huge amounts of dust transported from the African continent affect surface biogechemical processes and sedimentation in the whole investigation area. The publication on hand is a PhD thesis conducted within Subproject 3 of CANIGO ("Particle flux and paleoceanography in the Eastern Boundary Current System"). The main topic of the present study is the reconstruction of productivity gradients off NW Africa with geochemical methods.

The thesis consists of four main parts. *Chapter 1. Introduction* gives the thematic context of the different studies carried out. The oceanographic background is summarised and methodological aspects are discussed. *Chapter 2. Publications* presents a collection of five separate studies related to the main topic. They reflect the content of manuscripts submitted to peer reviewed international journals. These manuscripts may be modified during the ongoing review process. *Chapter 3. Conclusion* summarises the main results and gives an outlook on the implications of these results and suggested future studies. *Chapter 4. Literature* comprises a reference list for this thesis.

The international collaboration within CANIGO is reflected in the contributions of various co-authors to the publications prepared for this thesis. Experts from the University of Bremen and the Max-Planck Institute of Microbiology participated on a study on "Early diagenetic fractionation of stable nitrogen and carbon isotopes in marine sediments in the Canary Islands region" (manuscript 1) designed to improve the knowledge on methods used for reconstruction of productivity gradients. This study was supplemented by pore water data from Dr. Frank Wenzhöfer and Dr. Matthias Zabel and by organic petrological data from PD. Dr. Thomas Wagner. Manuscript 2 "Influence of lateral particle advection and organic matter degradation on sediment accumulation and stable nitrogen isotope ratios along a productivity gradient in the Canary Islands region" was prepared in close co-operation with Dr. Susanne Neuer who provided the elemental analysis and particulate fluxes determined with sediment traps. Dr. Helge Meggers contributed the stable oxygen isotope data of planktic foraminifera and Bob Davenport the SeaWiFS data. My contribution to the publications on "Surface water properties recorded on the seafloor of the Canary Islands region through the distribution of geochemical and micropaleontological parameters" (manuscript 3, first author Dr. Helge Meggers) and on "Glacial-interglacial variability of particle accumulation in the Canary Basin: A time-slice approach" (manuscript 4, first author Jorijntje Henderiks) consisted of analytical work (elemental analysis and stable nitrogen isotope ratios on bulk sediments, stable carbon isotopes of the organic matter, physical properties) and authorship. For manuscript 5 "Upwelling intensity and filament activity off Morocco during the last 250,000 years" Dr. Helge Meggers provided stable oxygen and carbon isotope data of planktic and benthic foraminfera. The contributions of the other co-authors to this paper consisted of $^{14}$C-data (Jorijntje Henderiks), grain size analyses (Ana Moreno) and susceptibility measurements (Holger Kuhlmann).

Data are available under http://www.pangaea.de/home/tfreudenthal/.

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# 1. INTRODUCTION

Since the early evolution of life on earth, marine productivity is believed to have a major impact on the composition of the atmosphere and thus on earth climate. The revolutionary change from an oxygen-free atmosphere in the Archeozoic Era to the oxygenated atmosphere in the Proterozoic Era would not have taken place without the photosynthetic activity of early forms of marine life. Looking at more recent time scales, the large natural variability of atmospheric $CO_2$ concentrations during glacial/interglacial cycles detected in bubbles of ancient air trapped in ice cores (Barnola et al., 1987) has focussed the interest of climate research on the global carbon cycle. Since the observation of drastically increasing atmospheric concentration of the greenhouse gas $CO_2$ during the last two centuries caused by burning of fossil fuels and other human activities (Keeling et al., 1985; Neftel et al., 1985) combined with a general increase of global temperature, it is clear that the understanding of the natural and anthropogenic variations of $CO_2$ concentrations and there impact on climate is of general importance for our future.

The ocean contains 60 times more $CO_2$ than the atmosphere and plays an important role in the global carbon cycle (Broecker and Peng, 1982). The atmospheric increase of $CO_2$ during the past two centuries would have been even stronger without the buffering capacity of the Ocean (Schlesinger, 1991). Looking at the causes for the natural variability of atmospheric $CO_2$ concentrations during glacial/interglacial time scales, the ocean seems to play again an important role. A variety of theories refer to changes of marine productivity as possible controlling factor (summarised by Broecker and Henderson, 1998).

The high-productive coastal margin areas are of special interest with respect to the global carbon cycle (Sarnthein et al., 1987). At the eastern margins of the subtropical Atlantic and Pacific Oceans trade winds blowing parallel to the coast promote upwelling of $CO_2$ and nutrient enriched subthermocline waters. These regions are characterised both by release of dissolved $CO_2$ to the atmosphere and by high fixation rates of atmospheric $CO_2$ due to biological production and subsequent removal of biogenic matter to the sea floor. Since productivity in these regions depends on the supply of nutrients by upwelling, productivity variations mirror changes in the strength and duration of the trade winds. Thus the investigation of productivity gradients through space and time in these areas is of twofold interest with respect to climate research: 1. to regionally quantify $CO_2$ sources and sinks as important parts of the carbon cycle that control global climate and 2. to detect the history of regional climate. These ultimate goals serve as the context in which the specific questions of this study were elaborated.

I will focus in my thesis on the reconstruction of productivity gradients in the Canary Islands region off NW Africa. In the following paragraphs, I will introduce the investigation area and the general approach that lead to the specific objectives of this work.

## 1.1 The investigation area

### TOPOGRAPHY

The investigation area is located in the vicinity of the Canary Islands, from the Moroccan coast to the westernmost Canary Islands (La Palma and Hierro), between Cape Yubi (27.5°N) and Cape Ghir (31°N) (Fig.1). The passive continental margin of the African plate with a broad shelf region (30 – 100 km wide) and water depths below 200 m forms the eastern border of this area. Water depth gradually increases up to 3500 m along the continental slope. The shelf and slope are deeply incised by the Agadir Canyon west of Cape Ghir. Below 3500 m the deep-sea plain is characterised by rather flat topography with the exception of several sea-mounts that rise from the sea-floor. Hot spot volcanism resulted in the formation of the Canary Islands, which rise from the deep-sea plain to heights of up to 3718 m above sea level.

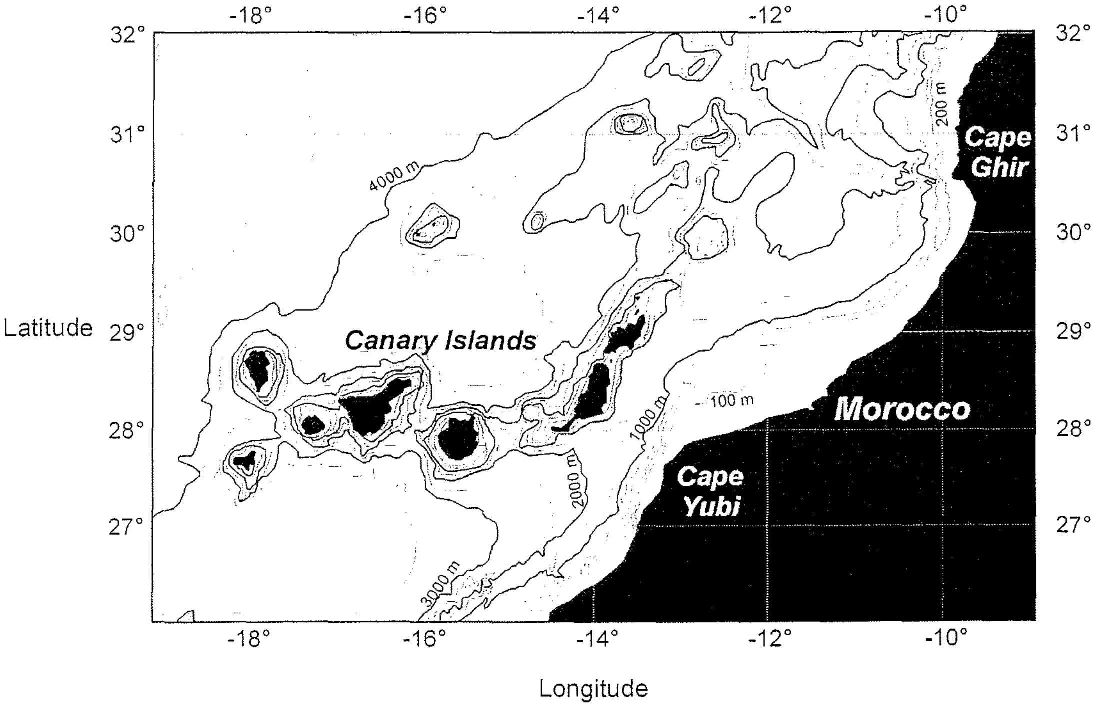

Fig. 1: Bathymetric map of the investigation area

## PRESENT CLIMATE

The Atlas mountain-chain, located north-east of the investigation area, receives humidity from the Atlantic carried by the mid-latitude westerlies especially during boreal winter (Despois and Raynal, 1967). However, rivers draining the Atlas reach the Atlantic Ocean mainly north of the investigation area (Müller-Hohenstein and Popp, 1990). The terrestrial influence on sedimentation in the eastern North Atlantic adjacent to the semi-arid and arid NW African continent is mainly by dust (Summerhayes et al., 1976; Sarnthein et al., 1982).

The eastern margin of the subtropical North Atlantic is one of the four major trade wind driven upwelling regions of the world. The motion of air along the pressure gradient from the subtropical high pressure region to the low pressure system of the Intertropical Convergence Zone (ITCZ) in combination with a westward deflection caused by the Coriolis force result in the formation of the NE Trades (Fig. 2). These winds are blowing parallel to the coast at large parts of the Iberian and NW African margin. At the latitude of the Canary Islands, trade winds are blowing mainly in summer.

## OCEANOGRAPHY

Surface layer Ekman drift during the trade wind season is directed offshore and causes upwelling over the continental shelves. The upwelled waters are cold and enriched in nutrients and promote higher primary production compared to the oligotrophic open ocean where nutrient import to the euphotic zone occurs mainly in winter by turbulent mixing (Sathyendranath et al., 1995). During winter coastal upwelling occurs mainly between 10 and 25°N. Due to the northward displacement of the ITCZ and the subtropical high pressure region during summer, the main upwelling season at the coast of Morocco is in summer and fall (Nykjær and Van Camp, 1994). In some cases additional upwelling was observed at the western margins of the easternmost Canary Islands, Lanzarote and Fuerteventura (Davenport et al., 1999).

Apart from the offshore directed Ekman drift, surface waters in the Canary Islands region are transported mainly southward. As part of the subtropical gyre recirculation system, the eastward flowing Azores Current separates in the eastern subtropical Atlantic into three southward directed branches (Fig. 3). The easternmost branch, the Canary Current, influences the investigation area. It receives additional water from the temperate North Atlantic by the

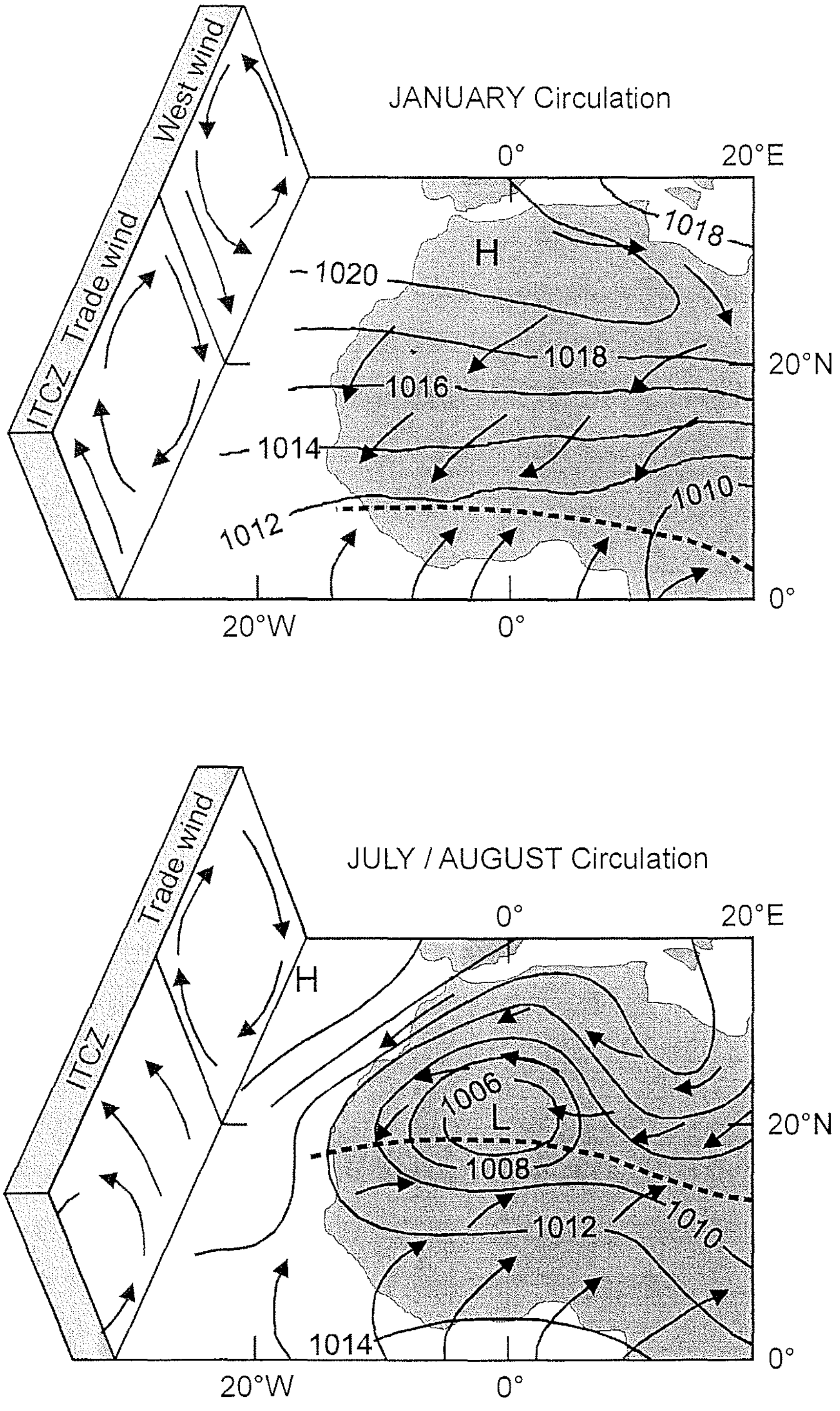

Fig. 2: Schematic of the general patterns of winds and pressure over NW Africa. Dotted lines indicate the Intertropical Convergence Zone (ITCZ). Modified from Nicholson (1996).

Portuguese Current. Current speeds are about 25 to 50 cm $s^{-1}$ over the continental shelf and slope (Mittelstaedt, 1991). The flow of the Canary Current increases during summer and fall (Knoll et al., submitted). The main flow path either between the easternmost Islands and the Moroccan coast or through the Islands is seasonally variable (Stramma and Siedler, 1988;

Barton, 1998; Knoll et al., submitted). Cold eddies with increased primary production are frequently observed at the lee side south of the islands, as a consequence of the interaction of the trade winds, the Canary Current and the Canary Islands (Arístegui et al., 1994). Topographically controlled meandering of the Canary Current results in the formation of filaments at Cape Ghir and Cape Yubi (Johnson and Stevens, 2000). These filaments form a transition zone between the eutrophic coastal upwelling region and the oligotrophic subtropical gyre region further offshore, as nutrient rich coastal upwelling waters may be transported several hundred kilometres into the open ocean at these sites (Van Camp et al., 1991; Barton et al., 1998).

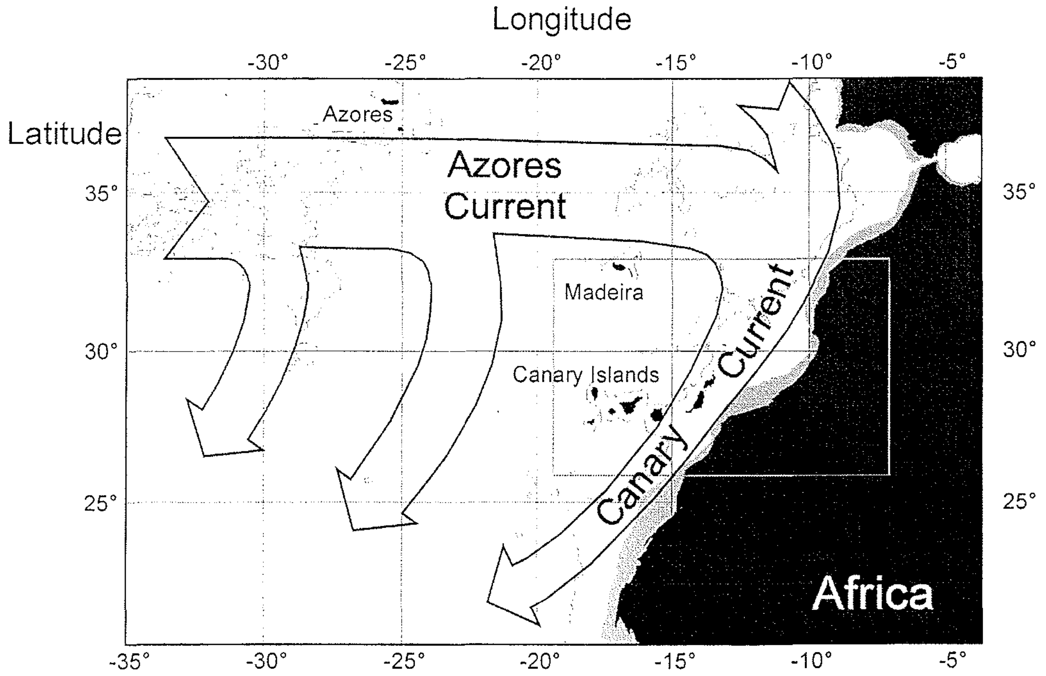

Fig. 3: Main geostrophic transport in the subtropical East Atlantic (modified after Siedler and Onken, 1996). The grey shaded areas indicate the continental shelf (< 200 m water depth). Thin lines represent the 3000 m depth contour.

The distribution of different water masses along NW Africa was reviewed by Sarnthein et al. (1982) and Siedler and Onken (1996). The Canary Current penetrates down to 600 m water depth with subtropical surface waters and North Atlantic Central Water (NACW) being the transported water masses. A deep compensation flow related to upwelling along the NW African margin forms the undercurrent over the continental slope that is responsible for a northward transport of Antarctic Intermediate Water (AIW). In some cases, derivatives of AIW cross the sill between Lanzarote/Fuerteventura and the African continent leading to an imprint of AIW in the northern Canary Islands region (Mittelstaedt, 1991; Knoll et al., submitted).

Mediterranean Outflow Water (MOW), that is characterised by high salinity and high temperature is mainly observed between 1000 and 1500 m water depth. The North Atlantic Deep Water (NADW) below 1500 m shows little variability in temperature and salinity. The transport of MOW and NADW in the eastern subtropical Atlantic is mainly directed southward (Saunders, 1982). Antarctic Deep Water (AADW) with low oxygen concentrations is observed in the North Atlantic below 4000 m water depth.

Neuer et al. (1997b) showed that the general surface and deep water current field north of the Canary Islands may have a strong impact on depth related particle fluxes in the water column. Current induced lateral displacement of biogenic particles has to be considered when investigating the sedimentary productivity record.

### PALEOCLIMATE AND PALEOPRODUCTIVITY

The climate of NW Africa, including the Sahelian area, the Sahara and the Atlas mountains, was more humid during the early Holocene (10.000 - 5.000 BP) than today. In contrast, dry conditions prevailed during the Last Glacial Maximum (LGM) and during the Younger Dryas (Gasse and Fontes, 1992). Analyses of the lithogenic matter in marine sediments off NW Africa indicated stronger trade winds during glacial times compared to interglacial times (Sarnthein and Koopmann, 1980). This interpretation was supported by the investigation of organic carbon accumulation rates indicating higher productivity due to increased upwelling intensity during glacial times (Müller et al., 1983). However, recent investigation indicate that this productivity pattern is not representative for the entire NW African margin (Bertrand et al., 1996). Off Cape Blanc at 20°N, highest productivity was found at the early Holocene and during oxygen isotopic stage 3 and was rather low during the last glacial maximum (Bertrand et al., 1996; Harris et al., 1996; Martinez et al., 1999). Bertrand et al. (1996) conclude, that investigation of several sediment cores within a single upwelling domain is a prerequisite for a profound understanding of changes in upwelling intensity.

## 1.2 Samples and methods

Five sedimentological cruises were lead by the University of Bremen's marine geology department in the Canary Islands region since 1996. During these cruises 80 surface sediment samples (box core and multi core) and 72 sediment cores (gravity core and piston core) were collected. Part of these sediments were used for paleoceanographic studies within the CANIGO project (Canary Islands Azores Gibraltar Observations) funded by the European Commission (MAST III Programme, MAS3-CT96-0060). Sediments were investigated with micropaleontological (University of Bremen, ETH-Zürich, University of Lisbon), sedimentological (University of Barcelona), and geochemical methods (University of Bremen, ETH-Zürich). In addition, moored sediment traps were deployed in order to study the relation of particle fluxes to productivity conditions and dust flux, and to trace their alteration during sedimentation. The focus of the present study, which was conducted as part of the CANIGO project, is the geochemical investigation of sinking particles and sediments in order to evaluate the information of these proxies with respect to productivity variations related to climate change. Regarding the micropaleontological and sedimentological contributions of various colleagues, in several studies a multi-proxy approach was applied to support the interpretation of the geochemical data (see chapter 1.4 and chapter 2 of this thesis). In the following, methodological aspects related to my contribution to these multi-proxy approaches are described.

## CARBONATE AND ORGANIC CARBON

The carbonate shells of important primary (coccoliths) and secondary producers (foraminifera, pteropodes) form the major biogenic part of marine sediments in tropical to temperate climates (Lisitzin, 1972). Carbonate concentrations in sediments of the North Atlantic Ocean during the late Pleistocene typically show high values during warm periods and low values during cold periods, which have been related to dilution by dust (Bacon, 1984; Matthewson et al., 1995). Variations in the accumulation of carbonate in marine sediments may reflect both changes in carbonate production and carbonate dissolution (Milliman, 1993). Different degrees of carbonate dissolution overprint the primary carbonate sedimentation record especially in high-productive continental margin areas and in the deep-sea below the calcite lysocline. Changes of the dominance of primary producers from coccoliths under oligotrophic and mesotrophic conditions to siliceous diatoms and organic walled dinoflagellates under eutrophic conditions have to be considered especially in upwelling influenced continental margin areas (e.g. Karlin et al., 1992). Thus, in these areas carbonate accumulation is not a reliable indicator for productivity variations (Rühlemann et al., 1999).

However, carbonate accumulation in these high-productivity areas has to be considered as an important sink in the global carbon cycle.

Organic carbon in marine sediments is widely used as paleoproductivity indicator especially in continental margin areas (Müller and Suess, 1979; Sarnthein et al., 1987; Rühlemann et al., 1999). The export of organic carbon to the deep-sea sediments is proportional to its production in the euphotic zone. During settling through the water column and within the sediments organic matter is remineralised. The degree of preservation is a function of the amount of organic matter exported to the sea floor, of the exposure time of the biogenic matter to the oxygenated water column (seasonality of flux, water depth, oxygenation of bottom water, sedimentation rate), of the fate of the organic matter (freshly produced or reworked, marine or terrestrial origin), and probably on the surface area of the mineral grains of the sediments (Müller and Suess, 1979; Emerson, 1985; Mayer, 1994). Several attempts have been made to quantify the degree of preservation in case of constant bottom water oxygenation by correlating sedimentary organic carbon accumulation with primary or export production. These regressions are the corner-stone of paleoproductivity equations based on water depth, sedimentation and sediment accumulation rate, and organic carbon concentration (reviewed by Rühlemann et al., 1999)

Carbonate and organic carbon concentrations reported in this thesis were measured either using a LECO CS 244 elemental analyser (LECO) or a Heraeus CHN-O-Rapid elemental analyser (CHN). Measurements of the sediments with CHN yielded simultaneously total nitrogen concentrations. Freeze-dried and homogenised samples were combusted at temperatures above 1000°C. The amount of $CO_2$ released during combustion reflects the carbon content of the sample. Total carbon was measured on unprepared samples while organic carbon was measured after removal of carbonate with hydrochloric acid. Carbonate concentration was calculated from the difference of total and organic carbon, multiplied with 8.333, assuming that calcium carbonate was the only carbonate bearing mineral in the sample. Carbonate and organic carbon concentration in sediments were corrected for the pore water salt content of the sample (see below).

The main differences between the two methods are the preparation of the samples and the detection of the released $CO_2$. In case of the CHN method samples were placed in tin boats for total carbon analysis and in silver boats for organic carbon analysis. For the latter, carbonate was removed by adding 6M HCl to the sample at 80°C. The $CO_2$ released after combustion was detected with a heat conductivity detector. For the measurements of carbon concentrations with LECO, samples were placed in ceramic crucibles. Acidification for carbonate removal was conducted in the crucibles. After addition of combustion accelerator, samples were combusted. The $CO_2$ thus released was detected by an infrared detector.

Similar values were obtained by both methods for total carbon determination (Fig. 4a). Thus, the different detection methods yield comparable results. However organic carbon concentrations measured with LECO were lower compared to those measured with CHN (Fig. 4b). Differences in the carbonate removal procedure may be responsible for this observation. In order to test this hypothesis, samples acidified in ceramic crucibles and in silver boats were both analysed with LECO. Samples acidified in ceramic crucibles yielded lower organic carbon concentrations (Fig. 4b). A significant loss of acid soluble organic carbon through the porous walls of the ceramic crucibles during carbonate removal has to be considered as a systematic error in the analysis of organic carbon concentration using the LECO method. However, this systematic error is not responsible for the total difference of organic concentrations analysed with LECO and with CHN. Samples acidified in silver boats yield still higher organic carbon concentrations when measured with CHN (Fig. 4b). The causes for this difference remain unresolved.

The difference of sedimentary organic carbon concentrations measured either with LECO and ceramic crucibles or with the CHN method using silver boats is rather constant over a wide range of organic carbon concentrations (Fig. 4b). When using the LECO method, an underestimation of organic carbon concentrations has to be considered. However, relative changes in the organic carbon concentration should be detected with both methods.

### C/N RATIO, STABLE CARBON AND NITROGEN ISOTOPE RATIOS

Next to the biogenic particles produced in the marine environment, terrestrial organic matter may contribute to the particulate organic carbon in marine sediments. Especially in the vicinity of great rivers, terrestrial particles are the major source of the sedimentary organic carbon (Schlünz et al., 1999). In our investigation area, riverine input is of minor importance but dust serves as a major source of terrestrial particles (Ratmeyer et al., 1999). Although large parts of NW Africa are poor in vegetation, terrestrial organic matter sedimentation by dust has to be considered when interpreting variations of sedimentary organic carbon with respect to marine productivity gradients.

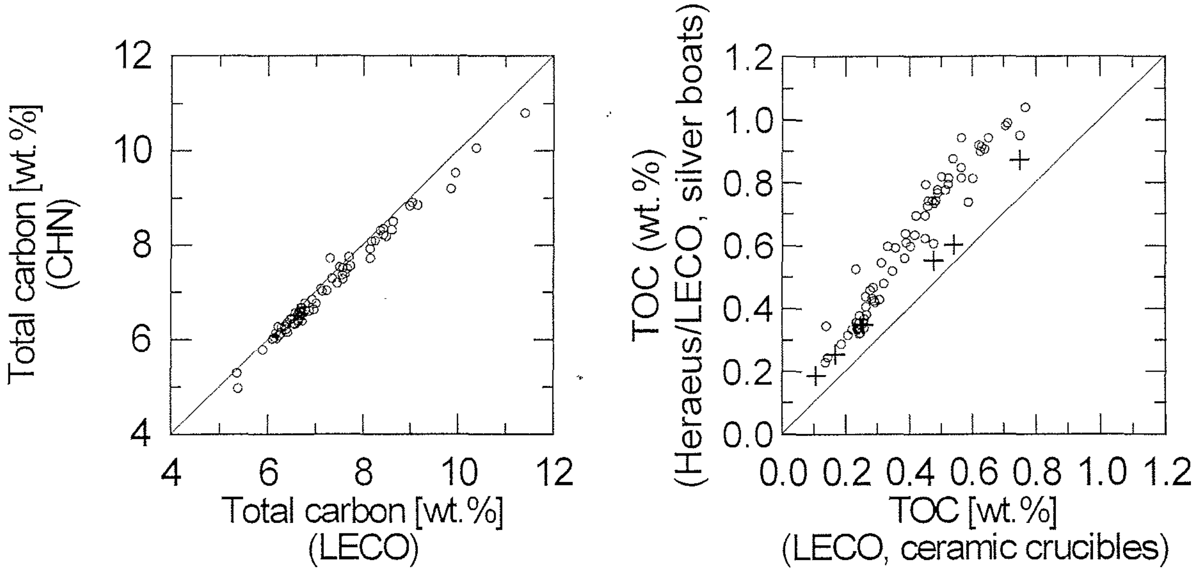

Fig. 4: a) Correlation of total carbon concentrations of surface sediment samples from cruises VH96/1 and M37/1 (0-1 cm sediment depth and the multicore GeoB 4234-1 (1-32 cm sediment depth, 1 cm resolution) determined with the LECO CS 244 elemental analyser in ceramic crucibles and with the Heraeus CHN-O-Rapid elemental analyser in tin boats. b) Correlation of organic carbon concentrations (TOC) acidified in ceramic crucibles measured with the LECO CS 244 elemental analyser and in silver boats measured with the Heraeus CHN-O-Rapid elemental analyser for the same samples as in a) (circles). Four surface samples and two gravity core samples (site GeoB 4242-5; 3 and 18 cm sediment depth) were additionally acidified in silver boats and analysed with the LECO CS 244 analyser for comparison (crosses).

The stable carbon isotope ratio of the organic matter ($\delta^{13}C_{org}$) and the C/N ratio are widely used as indicators of the marine or terrestrial origin of sedimentary organic matter. Terrigenous organic matter derived from C3-plants reveal low $\delta^{13}C_{org}$ values between −25.5 to −29.3 ‰ and C/N ratios from 20 to 200 whereas marine organic matter has typical values between −18.5 to −21.5 ‰ and between 5 to 10 for $\delta^{13}C_{org}$ and C/N ratio, respectively (Romankevich, 1984; Tyson, 1995). If high amounts of the terrestrial organic matter is derived from C4-plants (mainly grasses of the savannah) the terrestrial organic matter is even further enriched in $^{13}C$. The variability of the stable carbon isotope ratio of the marine endmember depends on the phytoplankton community, the $PCO_2$ level and on the growth rate (Burkhardt et al., 1999). Despite of these uncertainties, sedimentary $\delta^{13}C_{org}$ has been used to quantify the relative portion of terrestrial organic matter on the sedimentary organic carbon (e.g. Schneider et al., 1996).

In some cases, the stable nitrogen isotope ratio ($\delta^{15}N$) of sediments and suspended particles was used as indicator of their marine or terrestrial origin (Mariotti et al., 1984; Sweeney and

Kaplan, 1980), based on the differences in the $\delta^{15}N$ of the main nitrogen sources (terrestrial environment: atmospheric $N_2$, 0 ‰; marine environment: dissolved $NO_3^-$, average 5 ‰; Letolle, 1980; Liu and Kaplan, 1989). However, due to the higher C/N ratio of terrigenous organic particles, their imprint on bulk sedimentary $\delta^{15}N$ is less important as in case of $\delta^{13}C_{org}$.

The $\delta^{15}N$ of marine particulate matter depends on the isotopic ratio of the nutrient source and of fractionation processes during nutrient assimilation and trophic transfer (Altabet and Francois, 1994; Wu et al., 1999). Deviations of the isotopic ratio of the nutrient source from the marine average of 5 ‰ is of regional importance in areas where strong water column denitrification or nitrogen fixation occurs (Liu and Kaplan, 1989; Liu et al., 1996). Spatial variations of $\delta^{15}N$ in upwelling regions are interpreted as variations in nutrient utilization: due to the preferential assimilation of $^{14}NO_3^-$, the nutrients in the euphotic zone become progressively enriched in $^{15}NO_3^-$ with increasing amounts of assimilated nitrate, that is with increasing distance to the upwelling area (Altabet and Francois, 1994; Holmes et al., 1999; Hebbeln et al., 2000). In these areas, the sedimentary $\delta^{15}N$ can provide information on the nutrient availability, thus complementing the paleoproductivity records provided by sedimentary organic carbon in combination with $\delta^{13}C_{org}$ and C/N ratio.

Although early diagenesis is known to have a strong impact on sedimentary $\delta^{15}N$ (Francois et al., 1996), the responsible processes are not well understood. Furthermore, the impact of inorganic forms of nitrogen on the $\delta^{15}N$ of bulk sediments is not known. This impact may be considerable, since fixed ammonium contributes up to 40 % to the total sedimentary nitrogen pool, especially in sediments poor in organic matter (Müller, 1977). In some cases, $\delta^{15}N$ was measured on organic matter, that was protected by opaline or carbonate shells of diatoms or foraminifera, to avoid uncertainties arising from diagenetic overprint, inorganic forms of nitrogen or terrestrial organic nitrogen (Altabet and Curry, 1989; Sigman et al., 1999). For the same reason, Sachs and Repeta (1999) measured the nitrogen isotope ratio on chlorines. However, these measurements require high analytical expenditure. In most paleoceanographic studies, stable nitrogen isotope ratios are therefore measured on bulk sediments, assuming that diagenesis results in a constant diagenetic shift which does not overprint the primary variations related to changes in upwelling intensity and nutrient availability (Farrell et al., 1995; Holmes et al., 1997; Müller and Opdyke, 2000).

The stable isotope ratios of carbon and nitrogen were measured simultaneously using an online device of a Heraeus Delta Plus CHN analyzer coupled with a Finnigan MAT mass spectrometer. Samples were combusted at 1050°C with excess oxygen. In a second column, the nitrogen oxides were then reduced with elemental copper at 600°C to $N_2$. After reduction, the gases passed a tube containing Sicapent in order to remove the water. $N_2$ and $CO_2$ were separated by a retention column. The gas is then carried together with a continuous Helium flow into the mass spectrometer, where first the stable nitrogen and afterwards the stable carbon isotope ratio is measured. Reference gases for the isotope ratio measurements are 99.996 % pure tank $N_2$ and Burgbrohl $CO_2$, which were calibrated against air nitrogen and PDB, respectively.

$\delta^{13}C_{org}$ was measured on carbonate free samples. In order to remove the carbonate, samples were decalcified with 1M HCl. After filtering the sample on 0.2 µm Nuclepore filters, samples were dried and removed from the filter. Alternatively samples were acidified in silver boats with 6M HCl. Rühlemann (1996) detected no difference between the $\delta^{13}C_{org}$ of decalcified and acidified samples.

$\delta^{15}N$ was measured either on untreated or decalcified samples. Decalcified samples revealed slightly lower values than untreated samples, indicating a small loss of $^{14}N$-depleted nitrogen compounds during decalcification and filtering of the samples (Fig. 5a). However, correlation between the $\delta^{15}N$ of untreated and decalcified samples was good.

C/N ratio was calculated as weight ratio of organic carbon and total nitrogen determined both with CHN (see above). When CHN data were not available, the peak ratio of $^{12}C$ and $^{14}N$, determined with the Finnigan MAT mass spectrometer on decalcified samples, was used for calculation of the C/N ratio after calibrating against a laboratory sediment standard. Results from both methods (Fig. 5b) showed reasonable correlation (slope significantly different from zero, F-test, $\alpha = 0.05$). However, C/N ratios of decalcified samples are lower compared to the organic carbon to total nitrogen ratio of bulk samples. The loss of organic matter during decalcification and consequent relative increase of inorganic nitrogen may explain this observation.

## PHYSICAL PROPERTIES

Dissolved salt of sedimentary pore waters is precipitated during freeze-drying. This salt affects the measurements of organic carbon and carbonate concentration. In order to avoid misleading results especially in the upper part of the sediments with drastic porosity changes, sedimentary carbon concentrations were corrected for the salt content in this study using a salt

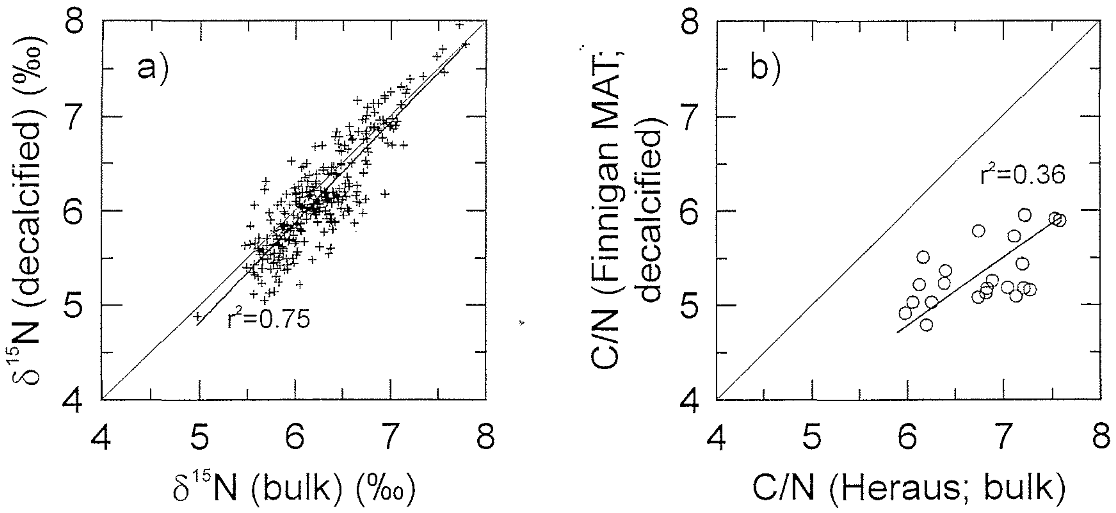

Fig. 5: a) Correlation of $\delta^{15}N$ measured on bulk and decalcified samples of gravity cores GeoB 4223-2 and GeoB 4240-2. b) Correlation of C/N weight ratios measured on bulk samples as organic carbon/total nitrogen ratio determined with Heraeus CHN-O-Rapid elemental analyser and measured on decalcified samples with the Finnigan MAT mass spectrometer. Samples were derived from the multicore GeoB 4234-1.

correction factor (SCF). When inferring from salt corrected carbon concentrations on their accumulation in the sediments, additionally to the sedimentation rate dry bulk density (DBD) has to be known.

These physical properties were calculated from syringe volume, wet weight (WW) and dry weight (DW) determinations. A pore water salinity of 35 ‰ and a water density of 1.024 g $cm^{-3}$ was assumed. SCF, porosity and DBD were calculated after equations 1, 2, and 3:

eq. 1: $SCF = DW \times (WW - (WW - DW) \times (1 - 0.035)^{-1})^{-1}$

eq. 2: $Porosity = (WW - DW) \times (1 - 0.035)^{-1} \times volume^{-1} \times (1.024\ g\ cm^{-3})^{-1}$

eq. 3: $DBD = (DW - WW \times 0.035) \times (1 - 0.035)^{-1} \times volume^{-1}$

This method is comparable to the one proposed by Weber (1997), with the exception of the volume determination with syringes. Weber (1997) pointed to the high uncertainty of the volume determination (about 0.5 ml). This error causes unreasonable results when the grain density is calculated from DW, WW, and water content. However, the impact of this error on determination of DBD is less important. Total errors according to error propagation calculations are 1.44 % for porosity and 0.016 g $cm^{-3}$ for DBD.

## 1.3 Objectives

The aim of this study is the investigation of productivity gradients in the northern Canary Islands region through space and time. Changes in marine productivity are supposed to reflect changes in regional climate. The emphasis of this studies lies on the reconstruction of these gradients with geochemical proxies (organic carbon, carbonate, $\delta^{13}C_{org}$, $\delta^{15}N$). In addition to the marine productivity other processes may influence their sedimentary record. As already outlined in the previous sections, biogenic matter sedimentation may be affected by terrestrial input, by lateral particle advection, and by early diagenetic processes. This background gives rise to several questions:

- How are the geochemical proxies applied in this study altered during settling and in the surface sediments? What is the influence of lateral particle transport and early diagenesis on the sedimentary productivity record?
- Are the geochemical methods appropriate to "reconstruct" present spatial productivity variations in the Canary Islands region?
- Where are sediment locations sufficiently sensitive to record productivity variations which are related to regional climate?
- How did regional productivity and climate change during the late Pleistocene?

The research that was conducted to answer these questions resulted in the preparation of five manuscripts. These manuscripts which have all been submitted to international journals form the major part of my thesis. Their topics are summarised in the following section.

## 1.4 Overview of research

I. Freudenthal, T., Wagner, T., Wenzhöfer, F., Zabel, M., and Wefer, G. (submitted). Early diagenetic fractionation of stable nitrogen and carbon isotopes in marine sediments in the Canary Islands region. Geochimica et Cosmochimica Acta

The analysis of sedimentary stable nitrogen isotopes as a recorder of past nutrient utilisation is a fairly new method developed especially during the last decade. However, knowledge about the biogeochemical processes in marine sediments resulting in an early diagenetic overprint of the primary signal is still sparse. In this study the impact of fractionation processes during remineralisation of organic matter, of preferential degradation of labile (marine?) versus refractory (terrestrial?) organic compounds and the impact of inorganic nitrogen on sedimentary stable isotope ratios are investigated. We have developed a sequential extraction method in order to obtain information about stable nitrogen isotope ratios of inorganic and organic forms of nitrogen in a short sediment core east of Lanzarote. These results were compared to changes in carbon and nitrogen concentrations, $\delta^{13}C_{org}$, pore water profiles and organic petrological parameters.

II. Freudenthal, T., Neuer, S., Meggers, H., Davenport, R., and Wefer, G. (in press). Influence of lateral particle advection and organic matter degradation on sediment accumulation and stable nitrogen isotope ratios along a productivity gradient in the Canary Islands region. Marine Geology

This study was conducted in order to assess how particle fluxes and their geochemical characteristics are altered during settling and in the surface sediments. We refer to the impact of lateral particle advection and particle degradation on organic carbon, total nitrogen, carbonate and total fluxes and stable nitrogen isotope ratios along a productivity gradient in the Canary Islands region by comparing fluxes in sediment traps with surface sediment accumulation rates and their isotopic characteristics.

III. Meggers, H., Freudenthal, T., Nave, S., Taragona, J., Abrantes, F., Helmke, P., and Davenport, R. (submitted). Surface water properties recorded on the seafloor of the Canary Islands region through the distribution of geochemical and micropaleontological parameters. Deep-Sea Research II.

The reliability of different productivity proxies in the investigation were evaluated by the comparison of different geochemical and micropaleontological parameters of surface sediments with sea surface temperature and productivity inferred from satellite imagery. Despite of lateral particle advection and early diagenesis even meso-scale features like the enhanced productivity in the Cape Ghir filament area are recorded in the surface sediments.

IV. Henderiks, J., Freudenthal, T., Meggers, H., Nave, S., Abrantes, F., Bollmann, J., Thierstein, H.R. (submitted). Glacial-interglacial variability of particle accumulation in the Canary Basin: A time-slice approach. Deep-Sea Research II. (In arrangement with J. Henderiks an abridged version of the submitted manuscript is presented in this thesis)

The accumulation of carbonate, organic carbon, and lithogenic matter as well as the accumulation of carbonate and siliceous microfossils along 4 time-slices (Holocene, Last Glacial Maximum, Last Interglacial Climax, and Penultimate Glacial Maximum) at 5 sediment sites is interpreted with respect to particle degradation, detrital sediment supply and productivity changes. This study confirms the generally accepted theory of increased productivity in the upwelling area off Morocco mainly during the Last Glacial Maximum.

V. Freudenthal, T., Meggers, H., Henderiks, J., Kuhlmann, H., Moreno, A., Wefer, G. (submitted). Upwelling intensity and filament activity off Morocco during the last 250,000 years. Deep-Sea Research II.

In this study four sediment cores, two of them located at the continental slope, the other two located further offshore, were investigated with geochemical methods in order to assess the impact of upwelling intensity and filament activity at each site. Especially at the continental slope sites the signal of climatically induced changes in productivity during glacial/interglacial time-scales was overprinted by the influence of sea-level changes on sedimentation. Productivity variations at the site further offshore that was influenced by the Cape Ghir filament were related to changes in the trade wind system and show precessional and eccentricity cycles.

## 2.1 Manuscript 1:

# Early diagenetic fractionation of stable nitrogen and carbon isotopes in marine sediments in the Canary Islands region

by Tim Freudenthal[1], Thomas Wagner[1], Frank Wenzhöfer[2], Matthias Zabel[1], and Gerold Wefer[1]

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## ABSTRACT

Concentrations and isotopic compositions of inorganic nitrogen (IN), organic nitrogen (ON), total nitrogen (TN) and organic carbon (TOC) were determined on one short core recovered from sediments of the eastern subtropical Atlantic, between the Canary Islands and the Moroccan coast. Changes with depth in concentration and isotopic composition of the different fractions were related to early diagenetic conditions indicated by pore water concentrations of oxygen, nitrate and ammonium. Additionally, the nature of the organic matter was investigated by Rock-Eval pyrolysis and microscopic analysis. A decrease in ON during aerobic organic matter degradation is accompanied by an increase of the $^{15}N/^{14}N$ ratio. Changes in the isotopic composition of ON can be described by Rayleigh fractionation kinetics which are probably related to microbial metabolism. The influence of IN depleted in $^{15}N$ on the bulk sedimentary (TN) isotope signal increases due to organic matter degradation, compensating partly the isotopic changes in ON. In suboxic sediments, fixation of ammonium between clay lattices results in a decrease of stable nitrogen isotope ratio of IN and TN. Changes in the carbon isotopic composition of TOC also can be explained by Rayleigh fractionation during organic matter degradation compensated by an increase of the relative contribution of a hypothetical refractory organic fraction depleted in $^{13}C$. Further studies are needed to characterise this refractory organic fraction, which seems to be depleted in nitrogen.

## INTRODUCTION

Due to the fact that isotope fractionation happens in biogeochemical processes like nutrient and $CO_2$ assimilation, or nitrate reduction, the stable isotope ratios of bulk nitrogen and organic carbon[1] in marine sediments are widely used as proxies to detect variations in past nutrient utilisation, denitrification, atmospheric $CO_2$ concentration, or to distinguish between marine and terrestrial organic matter (e.g., Sweeney and Kaplan, 1980; Müller et al., 1983; Rau et al., 1991; Altabet et al., 1995; Francois et al., 1997; Voß and Struck, 1997). When using these applications it is generally assumed that a) the isotope ratio of bulk nitrogen reflects mainly the organic source and b) diagenetic shifts are constant or do not cause isotopic variations comparable to the primary sedimentary signal.

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[1] Measured as:

$$\delta^{15}N(‰)=\left(\frac{^{15}N/^{14}N_{sample}}{^{15}N/^{14}N_{atm.N_2}}-1\right)\times 1000;\quad \delta^{13}C_{org}(‰)=\left(\frac{^{13}C/^{12}C_{organic}}{^{13}C/^{12}C_{PDB-Std.}}-1\right)\times 1000$$

Especially in sediments with low organic matter content, ammonium fixed between the lattices of clay has been shown to have a major contribution on bulk sedimentary nitrogen concentration (Müller, 1977). However, the impact of fixed ammonium on the bulk sedimentary nitrogen isotope ratio still requires investigation.

Several investigations indicate that early diagenesis has an impact on the stable isotope ratios of organic matter. Incubation experiments with water column particulate matter showed an increase in $\delta^{15}N$ of the particulate matter during organic matter degradation (Holmes et al., 1999). Heterotrophic microbiological activity was shown in laboratory experiments to cause either enrichments or depletion in $^{13}C$ and $^{15}N$ depending on the substrate (Macko and Estep, 1984). An increase in $\delta^{15}N$ and in $\delta^{13}C_{org}$ due to oxic degradation was observed in suspended particulate matter (Altabet, 1988; Libes and Deuser, 1988; Saino, 1992). Surface sediments reveal an increase in $\delta^{15}N$ compared to particles collected by sediment traps. For opal-rich sediments in the Southern Ocean, an apparent diagenetic enrichment by + 5 ‰ relative to the surface signal was described (Altabet and Francois, 1994). The differences in $\delta^{13}C_{org}$ of sinking particulate matter and surface sediments are usually smaller compared to $\delta^{15}N$. The most obvious changes in the isotopic composition of organic carbon related to early diagenetic processes were found in anoxic marine sediments while changes in oxic sediments were usually smaller (Tyson, 1995). In most cases a decrease of sedimentary $\delta^{13}C_{org}$ during organic matter degradation was observed. There are few investigations into early diagenetic changes of sedimentary $\delta^{15}N$ and these produced contrary results: de Lange et al. (1994) observed a decrease in the isotope ratio of total nitrogen while Sigman et al. (1999) found an increase in $\delta^{15}N$ for the organic matter during degradation.

Two main processes have been proposed to explain the observed early diagenetic changes in isotopic composition. Preferential degradation of organic compounds which have different isotopic compositions compared to the preserved organic compounds are assumed to cause the observed shifts in marine sediments. In most cases this process was used to explain negative shifts, since easily degradable organic compounds like amino acids and hydrocarbons or marine organic matter in general are enriched in $^{15}N$ and $^{13}C$ compared to more resistant compounds like lipids, lignin or terrestrial organic matter in general (e.g., Sweeney et al., 1978; de Lange et al., 1994; Prahl et al., 1997; Böttcher et al., 1998). However, the same principle was used to explain a positive shift observed in organic matter from algae mats by diagenetic loss of lipid carbon (Macko et al., 1993).

The second principle process, which may cause early diagenetic changes in isotope composition, is isotope fractionation due to metabolism of the organisms which are responsible for the organic matter degradation. Deamination as well as decarboxylation are reported to cause changes in the isotopic composition of organic matter (Macko and Estep, 1984; Macko et al., 1987; Macko et al., 1993; Holmes et al., 1999). The increase in remaining organic matter in $\delta^{13}C$ and $\delta^{15}N$ as a consequence of bacterial metabolism, which is comparable to the general observation in food webs of enrichment of $^{13}C$ and $^{15}N$ in higher trophic levels, was used to explain the isotopic changes of nitrogen and organic carbon in suspended matter (Saino, 1992) and of sedimentary nitrogen in marine sediments (Nakatsuka et al., 1997; Sigman et al., 1999). Concerning early diagenetic changes of sedimentary $\delta^{13}C_{org}$, fractionation due to microbial metabolism has been neglected in current discussions.

In this study, we test both of these explanations for early diagenetic changes in sedimentary $\delta^{13}C_{org}$ and $\delta^{15}N$. In addition, we investigate the influence of inorganic nitrogen on early diagenetic changes in bulk sedimentary nitrogen isotope composition. For this purpose changes in the concentration and isotopic composition of the main different nitrogen fractions and of organic carbon in marine sediments were determined. The nature of the organic matter was investigated by microscopic analysis and Rock-Eval pyrolysis. Changes in the isotopic composition were related to oxic and suboxic early diagenetic reactions, indicated by the pore water chemistry. The comparison of the pore water results and the distinct changes in nitrogen chemistry in the solid phase yields further insight into processes involved in the early diagenetic changes of bulk sedimentary $\delta^{15}N$.

Our results show that fractionation of organic nitrogen isotopes due to microbial metabolism and changes in the relative contribution of inorganic nitrogen have major impacts on early diagenetic changes in the sedimentary bulk stable nitrogen isotope ratio. Changes in $\delta^{13}C_{org}$ can be described by similar processes assuming fractionation during degradation of reactive organic matter and changes in the relative abundance of a refractory organic phase. Production of biomass enriched in $^{13}C$ and $^{15}N$ by those organisms, which are responsible for organic matter degradation, has to be considered with regard to isotope fractionation in marine sediments.

## STUDY AREA AND METHODS

In the present study, mesotrophic sediments from the eastern subtropical Atlantic between the Canary Islands and the Moroccan coast (Site GeoB 4234, 28°53.4 N, 13°13.6 W) were investigated (Fig. 1). Sediment sampling for pore water and solid phase investigations as well as *in situ* measurements were conducted during Meteor cruise M 37/1 (04.12. - 23.12.1996; Wefer et al., 1997). Sediment samples were recovered with a multicorer from 1360 m water depth. Penetration of cores into the sediment was 32 cm. The sediments consist of a brownish foraminifer nannofossil ooze. The foraminifer content increases below 25 cm sediment depth.

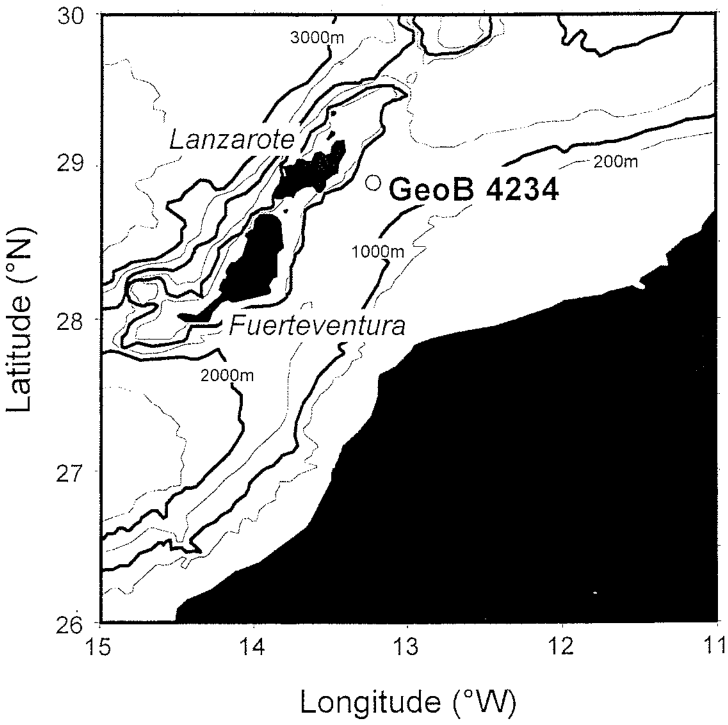

Fig. 1: Map of study area with core position

The pore water oxygen concentration was measured *in situ* with 100 µm step resolution using a profiling lander system equipped with oxygen microelectrodes. Pore water was extracted from slices of 0.5 cm to 5 cm thickness by pressure filtration in a glove box under argon atmosphere. Nitrate concentrations were measured photometrically using a standard analytical method (Grasshoff et al., 1983), whereas ammonium concentrations were determined using a $NH_3$/HCl reactor (rapid flow injection analysis).

A second tube was used for analysis of the solid phase composition. 1 cm slices were stored at –20°C. About 15 g of each sampling depth was freeze-dried and homogenised. Using the weights of wet and freeze-dried samples, and assuming a pore water salinity of 35 ‰ and a grain density of 2.68 g $cm^{-3}$, salt content and porosity was calculated according to Weber et al. (1997).

Pyrolysis was performed on decalcified subsamples (1M HCl) using a Rock-Eval II at the Alfred-Wegener Institute (Bremerhaven) according to the method of Espitalié et al (1977). To account for the immature organic character of the sediments, hydrocarbons detected in the S1 window were added to the S2 yield before hydrogen indices (HI) were calculated. Limitations of this method when applied to TOC-poor deep sea sediments were recently discussed by Wagner and Dupont (1999). Organic petrologic analysis were performed on decalcified (1M HCl) subsamples from 6 depth intervals using a Zeiss Axiophot. Thoroughly crushed samples were embedded under vacuum conditions in a low-viscous resin, then stored for at least two days before grinding and polishing of the specimen surface was performed. Organic particle identification was conducted at 500- and 1000-fold magnification using both normal and ultraviolet light mode.

All carbon and nitrogen elemental analysis were done using a Perkin CHN-analyser. Analytical standard deviation is 1.6 % (relative) for carbon and 2.0 % (relative) for nitrogen concentration. For the determinations of stable nitrogen isotope ratios, sediment samples were placed in tin boats and combusted at 1050°C in a NC 2500 Elemental Analyser (CE Instruments). $\delta^{15}N$ of the gas produced was measured using a Finnigan MAT Delta Plus mass spectrometer. The laboratory working standard gas (99.996 % pure tank $N_2$) was calibrated against IAEA standards N-1 and N-2. For the determination of carbon isotope ratios, sediment samples were combusted in a HERAEUS oven and the resulting $CO_2$ was trapped in a trapping box. $\delta^{13}C$ of the gas was measured using a Finnigan MAT Delta E mass spectrometer. The laboratory working standard gas (Burgbrohl $CO_2$ gas) was calibrated against NBS-22 standard. The $\delta^{15}N$ values are reported relative to air, $\delta^{13}C$ values are reported relative to PDB (Pee Dee Belemnite). Long term reproducibility calculated from repeated measurements on a laboratory sediment standard was < 0.2 ‰ for $\delta^{15}N$ and < 0.1 ‰ for $\delta^{13}C$.

Concentrations and isotopic composition of nitrogen and carbon were determined on different fractions (Fig. 2). The total carbon content (TC) was measured on untreated samples. The total organic carbon content (TOC) was measured on samples acidified in silver boats. Total nitrogen (TN) concentrations reported in this study are calculated averages of measured nitrogen contents of untreated and acidified samples. TC, TN and TOC were calculated on salt free basis. Carbonate content was calculated by difference of TC and TOC, assuming that calcium carbonate was the only carbonate bearing mineral. The isotope ratio of total nitrogen ($\delta^{15}N_{TN}$) was measured on untreated samples. Exchangeable ammonium ($NH_4^+{}_{exch}$) was extracted using 2M KCl (Keeney and Nelson, 1982). Ammonium concentrations were determined in solution using the rapid flow injection method. The stable nitrogen isotope ratio was measured on washed and dried residuals ($\delta^{15}N_{KCl}$). For the determination of fixed nitrogen ($N_{KOBr}$) and its isotopic composition ($\delta^{15}N_{KOBr}$), sediments were decalcified with 1M HCl-solution and oxidised with KOBr-solution (Silva and Bremner, 1966). The stable carbon isotope ratio of organic matter ($\delta^{13}C_{org}$) was measured on decalcified samples.

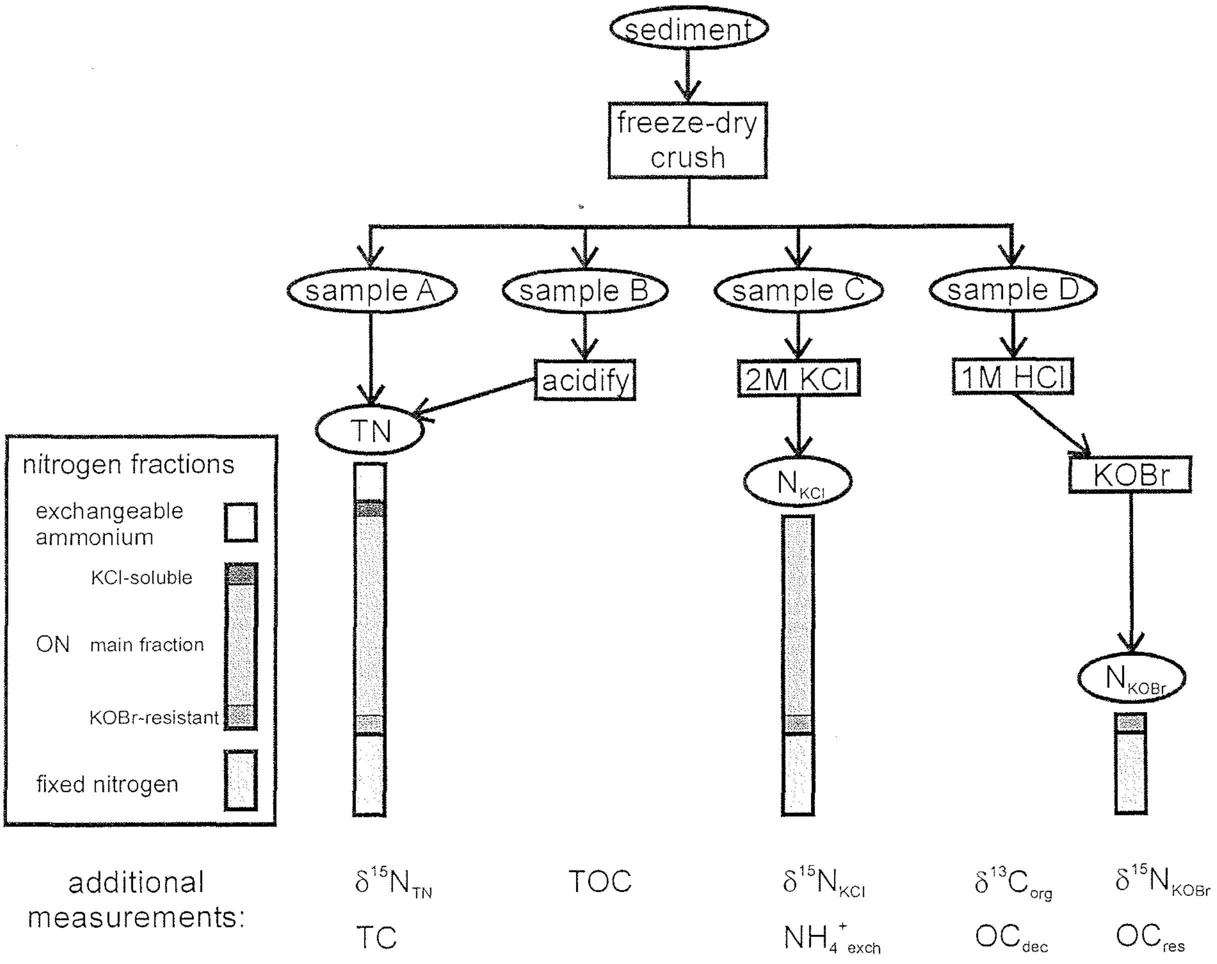

Fig. 2: Flow chart of the extraction procedure for the different forms of inorganic (exchangeable ammonium [$NH_4^+{}_{exch}$], fixed nitrogen [main fraction of $N_{KOBr}$]) and organic nitrogen (ON). ON was divided into three operational fractions: the main fraction, the fraction which may be dissolved by the KCl solution ($N_{KCl}$ represents the nitrogen concentration in the sediments after KCl extraction) and the fraction which may resist the KOBr-attack. The carbon that resisted the KOBr attack ($OC_{res}$) was measured and compared to carbon concentrations of decalcified sediments in order to quantify the success of organic matter oxidation. Total carbon (TC) and organic carbon (TOC) concentrations were measured on bulk and acidified sediments, respectively. Stable nitrogen isotope ratios were measured on bulk sediment ($\delta^{15}N_{TN}$), after KCl-extraction ($\delta^{15}N_{KCl}$), and after KOBr attack ($\delta^{15}N_{KOBr}$). Stable carbon isotope ratios of the organic matter were analysed on decalcified samples.

One aim of the analyses summarised in Figure 2 is to determine the concentration of organic nitrogen (ON) based on the difference between TN and inorganic nitrogen forms (IN). The isotopic composition of ON ($\delta^{15}N_{ON}$) can be determined according to mass balance calculations (see Appendix) from the weighted difference of the isotopic composition of TN and IN. Two different forms of inorganic nitrogen, exchangeable ammonium ($N_{KCl}$) and ammonium fixed between the lattices of clay minerals ($N_{KOBr}$), were determined. The amount of fixed ammonium may be overestimated if significant amounts of organic nitrogen have resisted oxidation by the KOBr-treatment. In order to investigate the success of organic matter oxidation, carbon content was measured on decalcified samples before ($OC_{dec}$) and after KOBr treatment ($OC_{res}$). $OC_{res}$ reflects the portion of organic matter that has resisted the KOBr-treatment and amounts to about 10 % of the carbon content of the decalcified samples ($OC_{dec}$) in this study. However, concentration changes of $OC_{res}$ are not reflected by $N_{KOBr}$, resulting in a weak correlation at least for the upper 25 cm of the investigated sediments (Fig. 3). We conclude that the KOBr-resistant organic fraction is poor in nitrogen and $N_{KOBr}$ is dominated by ammonium fixed between the lattices of clay.

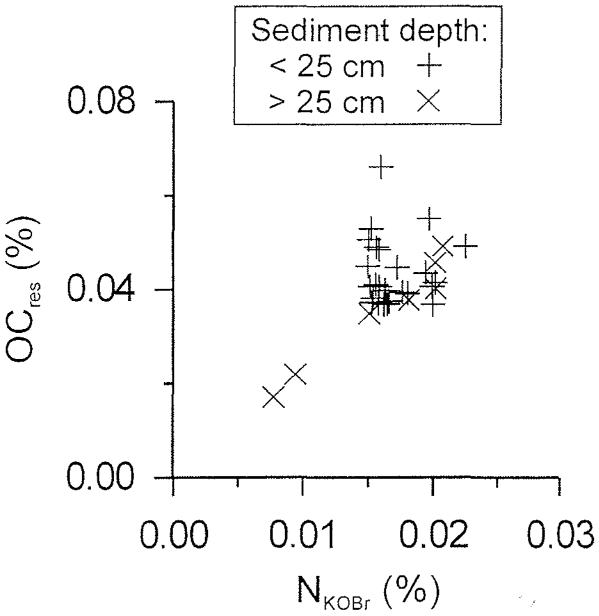

Fig. 3: Correlation of oxidation resistant nitrogen ($N_{KOBr}$) and carbon ($OC_{res}$) in samples of sediment core GeoB 4234

# RESULTS

## Sedimentary environment and geochemical characterisation

In the upper part of the investigated sediments, carbonate contents (about 51%) were constant within the detection limit (Fig. 4). The porosity decreased in the uppermost centimetres due to compaction from 82% to 70%, below it was fairly constant down to 25 cm sediment depth. TOC contents decreased from the sediment surface (0.8%) down to 12 cm, where values remained constant (about 0.35%) down to 25 cm. Below 25 cm a change in the sedimentation condition was characterised by a decrease in porosity (< 60 %) and TOC concentration (< 0.25 %), and an increase in the carbonate content (up to 67 %).

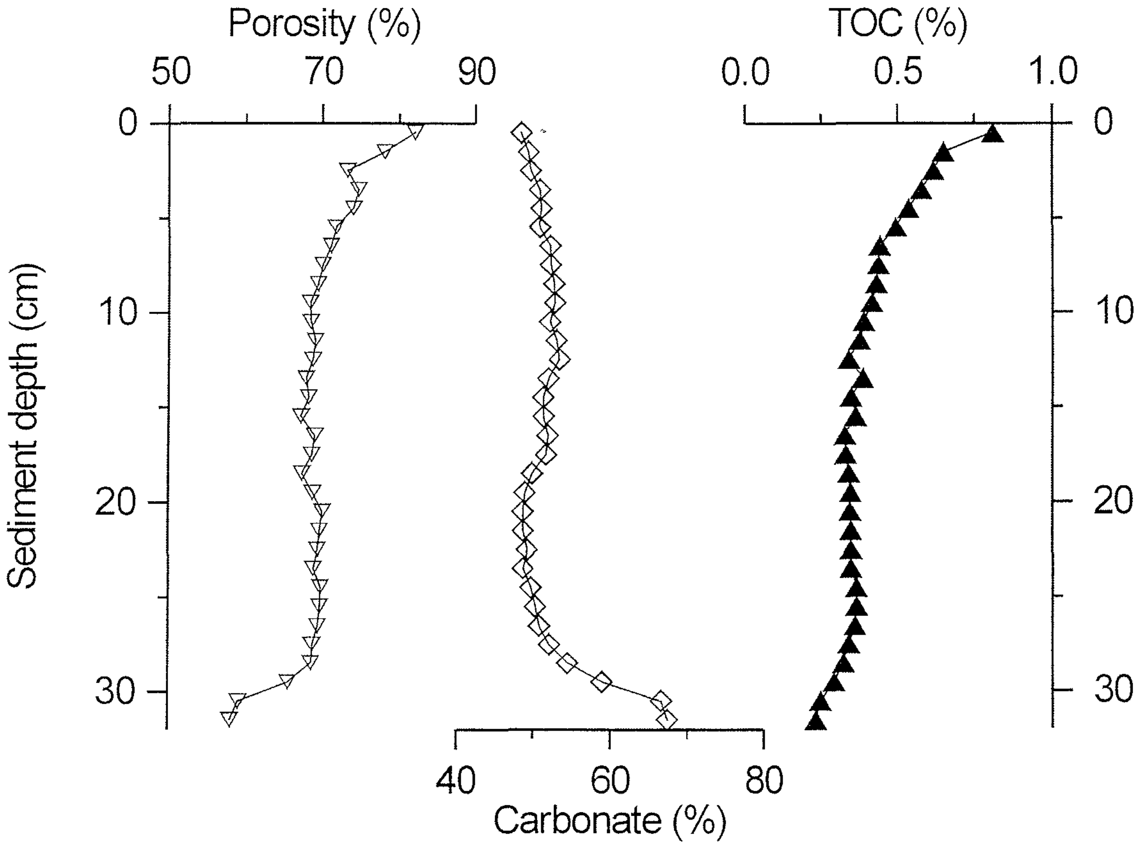

Fig. 4: Porosity, carbonate and TOC contents of sediments at site GeoB 4234

The TOC decrease in the upper part of the sediments is explained by oxic organic matter degradation which is confirmed by the availability of oxygen within the first 10 cm (Fig. 5a). Aerobic organic matter degradation and the consequent oxidation of ON in the upper 10 cm was also documented by the nitrate concentration profile (Fig. 5b) indicating nitrification processes near the sediment surface. A part of the released nitrate diffuses into the suboxic zone below 10 cm and may be used as an oxidant for organic matter degradation as well. The ammonium concentration was low in the oxic zone (Fig. 5b). The expected generation of ammonium in anoxic parts of the sediment and subsequent diffusion and oxidation in the oxic/suboxic boundary at about 10 cm was corroborated by one measurement in the suboxic part of the sediment revealing a higher ammonium concentration.

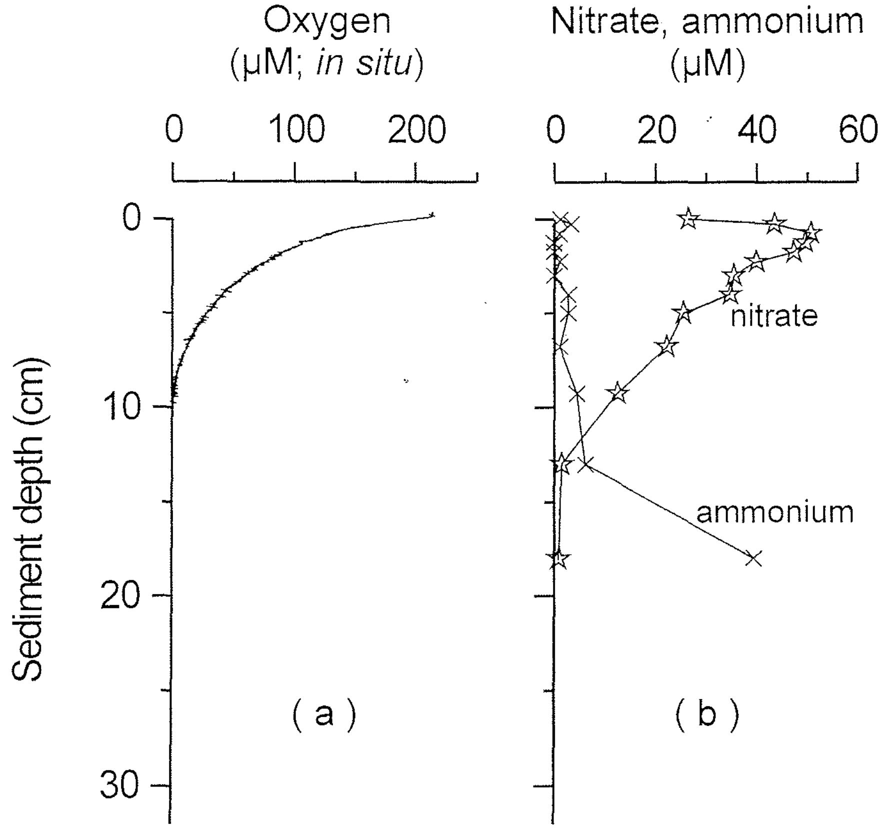

Fig. 5: Pore water concentrations of a) *in situ* oxygen and b) nitrate and ammonium at site GeoB 4234

Nature of the organic matter

In the present study, microscopic investigation as well as Rock-Eval pyrolysis give indications for high microbial activity in a system dominated by marine organic matter.

Microscopic inspections revealed that the organic matter consists mainly of marine structured organic matter (Liptonite, Liptodetrinite) in the upper centimetres which changed into organic amorphous matter (AOM) with increasing depth. AOM occurred as unstructured aggregates showing a brownish red fluorescence. Dominance of AOM is typical for sediments characterised by high fluxes of labile (mostly marine) organic matter and by high microbial activity (ten Haven et al., 1989; Lückge et al., 1996; Littke et al., 1997). The terrestrial fraction (huminites/vitrinites and inertinites, mainly detritic) comprised a background signal of the bulk organic matter. Throughout the core no significant change in their abundance occurred.

Rock-Eval pyrolysis showed a decrease from 1.8 to 0.5 mg HC/gSed with depth in volatisable hydrocarbon yield, mainly trapped in the kerogen fraction (S2) (Fig. 6a). This is in correspondence with the decrease in $OC_{dec}$ (Fig. 6b). Notably, volatile HC detected in the S1 window is significantly elevated at 8-10 cm and 15-16 cm sediment depth, which may be an indication for local chemoautotrophic and heterotrophic microbial activity. The normalisation of the hydrocarbon yield to the organic carbon content, results in hydrogen indices of 75-160, which is fairly low for marine sediments dominated by labile (marine) organic matter (Stein, 1991).

The temperature ($T_{max}$) of maximum HC yield of the Kerogen (S2) fraction, which is usually used in fossil sediments as an indicator of thermal maturity of organic matter, ranged between 390 and 440°C (Fig. 6c), with higher fluctuations in the upper 10 cm which may be an indication for bioturbation. The pyrolysis results are indicative of immature organic matter as expected for modern sediments (Stein, 1991; Wagner and Dupont, 1999).

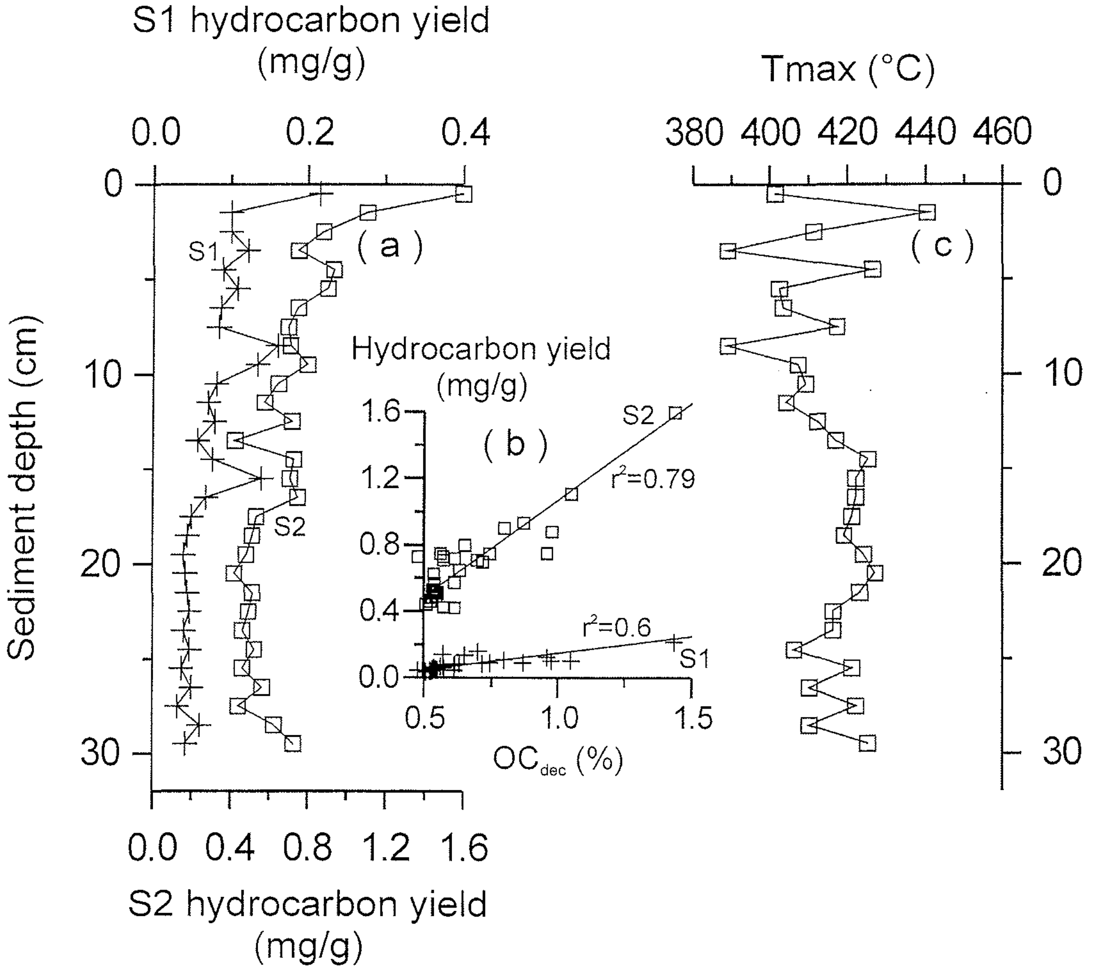

Fig. 6: Results of Rock-Eval pyrolysis at site GeoB 4234: amount of volatisable hydrocarbons (crosses S1: 90 - 300°C; squares S2: 300 - 550°C) plotted against a) depth and b) organic carbon content of decalcified samples and c) Tmax temperature of maximum hydrocarbon release of Kerogen (S2) plotted against depth

Nitrogen speciation and isotopic compositions of nitrogen and organic carbon

The TN profile (Fig. 7) was similar in shape to the TOC profile, decreasing from 0.11 % at the surface to 0.055 % between 10 and 25 cm depth. Below 25 cm TN concentration decreased down to 0.025 %. A closer look at the data shows a decrease of the TOC/TN weight ratio with depth from about 7.5 to 6 (Fig. 7). The sedimentation change below 25 cm is marked by higher TOC/TN ratios up to 9.4. The exchangeable ammonium at its maximum accounts only for 1 % of TN (Fig. 7). In spite of low pore water ammonium concentrations, exchangeable ammonium reached relatively high values in the oxic zone with a maximum of nearly 6 ppm in the section 0 - 1 cm. Comparably high values of exchangeable ammonium in oxic surface sediments have been determined also by Boatman and Murray (1982) and may reflect high amounts of fresh bacterial organic matter, which has stored ammonium in the cells. In the suboxic zone, the amount of exchangeable ammonium increased with depth from 2.2 to 5 ppm, which was expected, assuming that pore water ammonium concentration increases with depth (Boatman and Murray, 1982). Below 25 cm exchangeable ammonium content decreased down to 2.6 ppm. The $N_{KOBr}$ fraction, which contains ammonium fixed between the lattices of clay minerals, remained constant at 0.016 % in the upper 13 cm and increased below, to up to 0.021 % (Fig. 7). Below 25 cm $N_{KOBr}$ contents decreased.

These results indicate that fixed ammonium is the major form of inorganic nitrogen at site GeoB 4234. Thus, taking $N_{KOBr}$ as IN and calculating the amount of ON as the difference between TN and IN, the TOC/ON shows a slight increase from 8.7 at the surface to about 9.5 at 12 cm sediment depth (Fig. 7), reflecting preferential degradation of organic compounds rich in nitrogen (Cowie and Hedges, 1991). Because of the scatter between 13 and 25 cm depth, neither a general increase nor a decrease in the TOC/ON ratio is observable. The calculated TOC/ON ratios of 9-10 are typical for sediments dominated by marine organic matter (Müller, 1977). Below 25 cm the TOC/ON ratio increases up to nearly 14.

The stable nitrogen isotope ratios of the different measured nitrogen fractions and of $\delta^{13}C_{org}$ are shown in Figure 8. $\delta^{15}N_{TN}$ values ranged from 6.5 to 7.3 ‰. They showed an increase of 0.8 ‰ in the oxic zone and a decrease of 0.4 ‰ in the suboxic zone. Values of $\delta^{15}N_{KCl}$ are similar to $\delta^{15}N_{TN}$. The values of $\delta^{15}N_{KOBr}$ showed a decrease in the suboxic zone from 5.8 to 5 ‰.

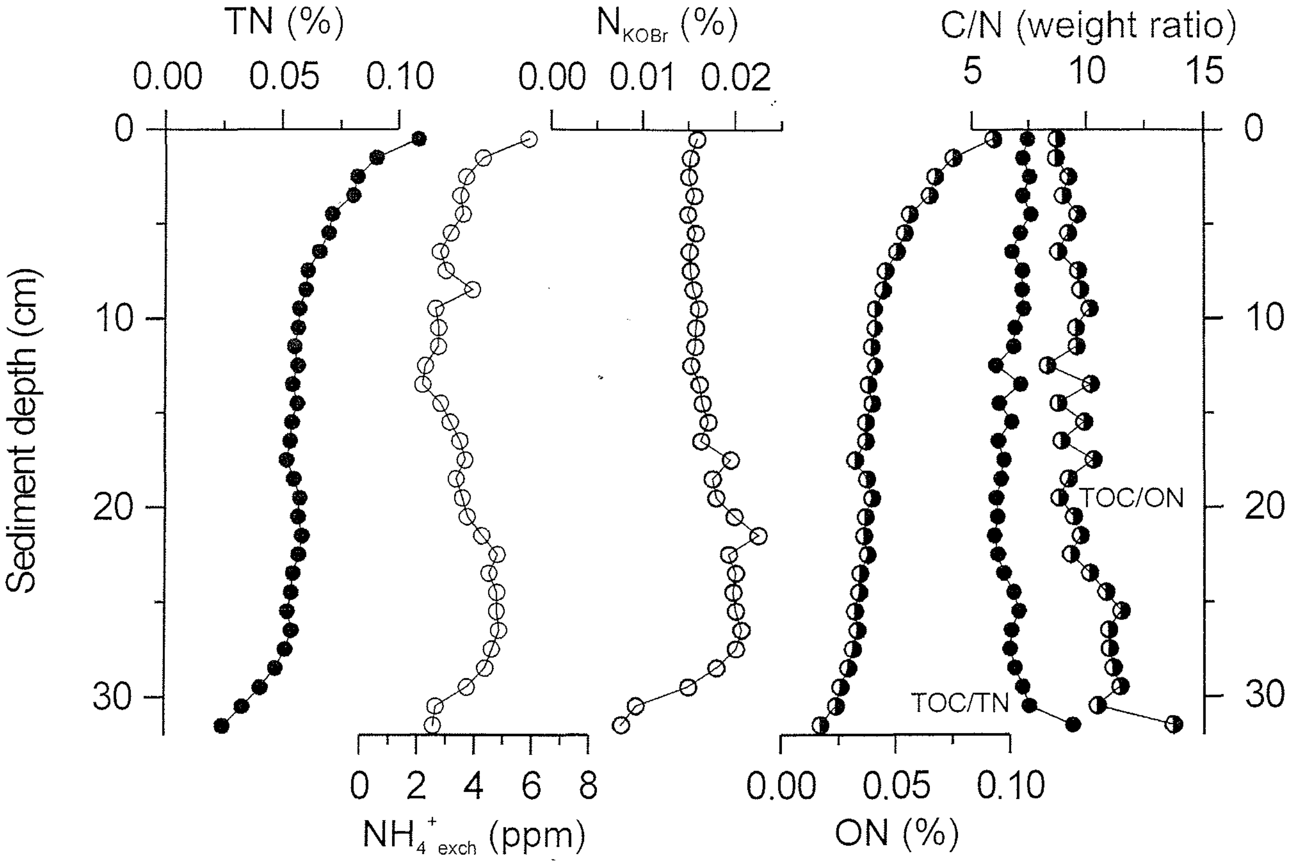

Fig. 7: Sedimentary concentrations at site GeoB 4234 of TN, $NH_4^+{}_{exch}$, $N_{KOBr}$ and ON and C/N ratios (TOC/TN: filled circles; TOC/ON: half-full circles). $N_{KOBr}$ concentrations which were measured on decalcified sediments, were calculated based on total sediments. ON was calculated as difference between TN and $N_{KOBr}$ (see text).

Since the amount of exchangeable ammonium did not exceed 1% of TN and $\delta^{15}N_{KCl}$ was not significantly different from $\delta^{15}N_{TN}$, we neglected exchangeable ammonium in mass balance calculations concerning the estimation of $\delta^{15}N_{ON}$ (defining $N_{KOBr}$ as IN and $\delta^{15}N_{KOBr}$ as $\delta^{15}N_{IN}$; see methods section). The values of $\delta^{15}N_{ON}$ increased from 6.6 ‰ at the 0 - 1 cm sample to about 7.8 ‰ at the 9 - 10 cm sediment sample (Fig. 8). Below this depth $\delta^{15}N_{ON}$ remained rather constant.

An increase of the $\delta^{13}C_{org}$ value was observed from –19.9 ‰ at the surface sediment sample up to -19.2 ‰ at the maximum at 3-4 cm depth. Below $\delta^{13}C_{org}$ decreased to values comparable to the surface sediment. The mentioned change in sedimentation conditions at about 25 cm depth is marked by a decrease of $\delta^{13}C_{org}$ down to –21.2 ‰.

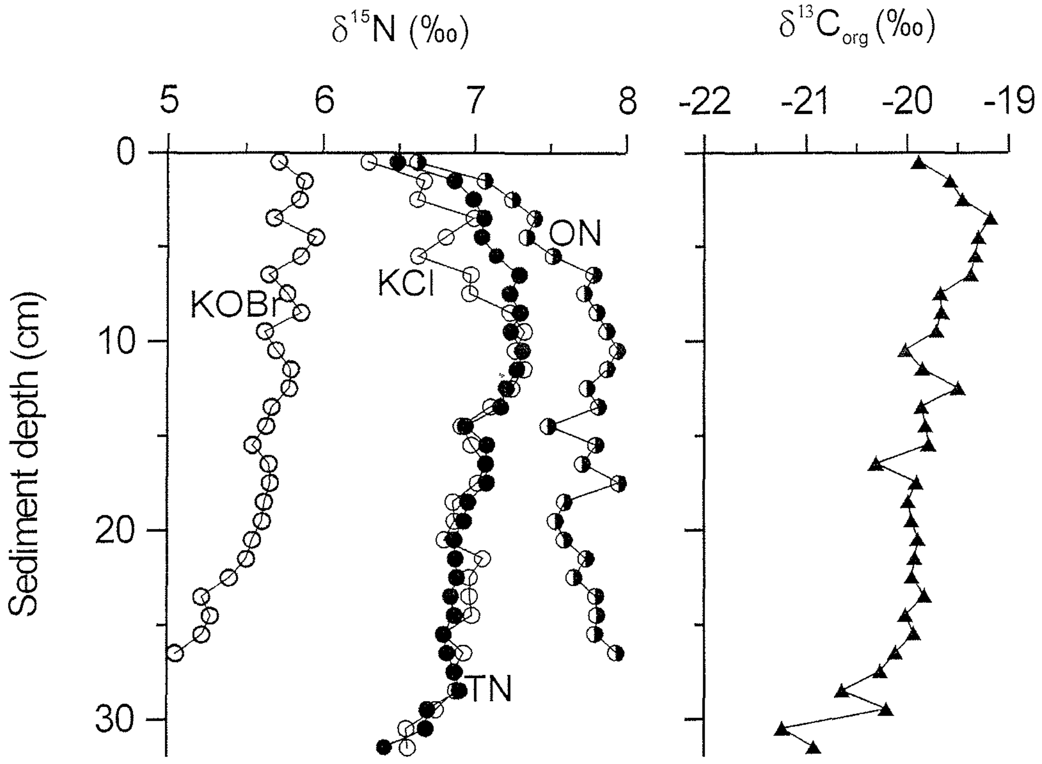

Fig. 8: Stable isotope ratios of (a)TN, $N_{KCl}$, $N_{KOBr}$ (all measured) and ON (calculated by mass balance) and of (b) organic carbon at site GeoB 4234.

## DISCUSSION

Since the sedimentary record reflects both sedimentary input and early diagenetic processes, changes in sedimentary stable isotope ratios can only be related to early diagenetic reactions if the sedimentary input was constant. This assumption was confirmed on core GeoB 4234 for at least the upper 25 cm by constant carbonate concentrations and constant porosity below the main compaction zone. Diagenetic changes in $\delta^{15}N_{TN}$ and $\delta^{13}C_{org}$ showed similarities (increase in the upper centimetres, decrease below) and dissimilarities (depth intervals of observed changes). In the following we will address the impact of oxic organic matter degradation, and of inorganic nitrogen forms on the isotopic composition of total nitrogen. Finally the different diagenetic behaviours of $\delta^{15}N$ and $\delta\,^{13}C_{org}$ will be discussed.

### Oxic degradation of organic nitrogen

It has been shown previously, that surface sediments are enriched in $^{15}N$ compared to sinking particles (Altabet and Francois, 1994; Nakatsuka et al., 1997; Sigman et al., 1999). In this study, a further increase in $\delta^{15}N_{ON}$ in the oxic zone of multicore sediments was observed (Fig. 8). This increase coincided with a decrease in ON. Similarly, incubation experiments revealed increasing $\delta^{15}N$ of particulate organic matter during degradation (Holmes et al., 1999). Oxic degradation seems to be responsible for the observed changes in $\delta^{15}N_{ON}$.

Looking at the specific processes which are responsible for these changes, the heterogeneous composition of organic matter consisting of different components with different isotopic compositions and different degradation kinetics has to be taken into consideration. A decrease of the $\delta^{15}N$ signal in sediment trap particles during sinking was explained by Nakatsuka et al. (1997) by preferential degradation of amino acids rich in $^{15}N$. A decrease of the relative proportion of amino acids was also observed during oxic degradation in sediments (Wakeham et al., 1997). However, Nakatsuka et al. (1997) stated that in contrast to degradation processes in sinking particles, organisms which are responsible for the degradation are part of the organic matter in sediments. As a consequence it is not the process of bacterial consumption of organic matter but the excretion of inorganic nitrogen by these bacteria, which causes early diagenetic changes of $\delta^{15}N_{ON}$ in the sediments.

Laboratory investigations with heterotrophic bacteria grown on monospecific substrate revealed no changes in the isotopic composition of the substrate (Macko and Estep, 1984). Instead fractionation occurred during deamination processes, favouring the formation of ammonium depleted in $^{15}N$ (Macko and Estep, 1984; Holmes et al., 1999). According to Macko et al. (1991) an increase in the TOC/ON ratio should be observed if deamination is an important process. However, since at least a part of the carbohydrates produced during deamination is consumed in the Krebs cycle, it seems to be possible to drive nitrogen fractionation by deamination without significantly changing the TOC/ON ratio.

The preferential degradation of amino acids, combined with fractionation processes during deamination, could explain the observed increase in $\delta^{15}N_{ON}$, if the excreted ammonium has a lower $\delta^{15}N$ than the average ON. The assumption that only a part (for example amino acids) of the sedimentary organic matter with constant isotopic composition was degraded and hence the isotopic ratio of the excreted ammonium ($\delta^{15}N_{NH4}$) was constant (constant release model), is mathematically expressed by equation 1 (see Appendix):

$$\text{eq. 1: } \delta^{15}N_{ON}(f) = f^{-1} \times (\delta^{15}N_{ON,\text{initial}} - \delta^{15}N_{NH4}) + \delta^{15}N_{NH4}$$

with f as the relative proportion of undegraded ON ($ON \times ON_{\text{initial}}^{-1}$).

The data of this study fit well to this equation for $\delta^{15}N_{NH4} = 5.84 \pm 0.16$ ‰ with a regression coefficient $r = 0.95$ (Fig. 9). However, this model does not take into consideration, the fact that the bacterial biomass, which is produced during the degradation processes and which is enriched in $^{15}N$, may also act as a substrate for further degradation. Intensive microbial recycling and resynthesis of organic matter was observed especially in oxic sediments (Gong and Hollander, 1997). A progressive enrichment of the substrate in $^{15}N$ as a result of microbial recycling can be described by Rayleigh fractionation (eq. 2, after Mariotti et al., 1981):

eq. 2: $\delta^{15}N_{ON}(f) = \delta^{15}N_{ON,initial} - \varepsilon \times \ln(f)$

with ε as constant fractionation factor. This approach also revealed a high regression coefficient r = –0.96 and a fractionation factor ε = 1.48 ± 0.13 ‰ (Fig. 9).

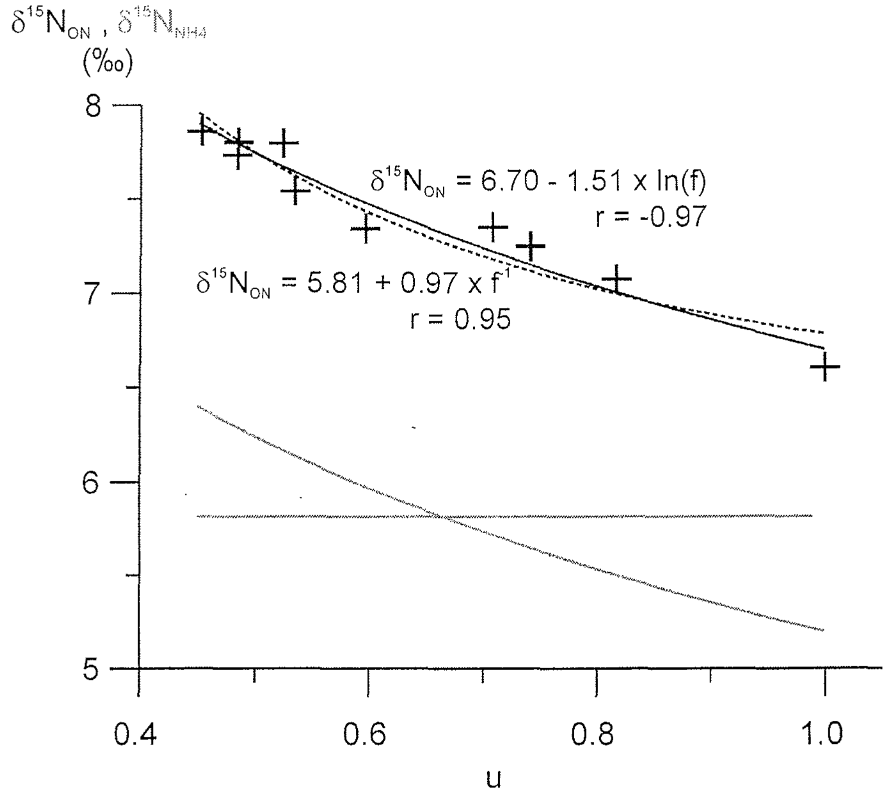

Fig. 9: Correlation for the oxic zone of $\delta^{15}N_{ON}$ against the relative amount f of undegraded ON ($ON_{initial}$ was defined as ON of the 0-1cm sample). Crosses mark the values calculated from measurements, the black lines mark the best fits (rma-regression) for the constant release model (dotted line) and the Rayleigh fractionation model (closed line). Grey lines mark the calculated isotopic composition of released ammonium (dotted: constant release model; closed: Rayleigh fractionation model). For explanations of the models see text.

The capacity of these two models to describe the natural processes in oxic early diagenesis may be proven by extrapolating the fits of the data to the chemical characteristics of the settling particles at the investigation site. A 10 month deployment of a sediment trap located near the sediment site at 28°42.49 N and 13°09.34 W at 700 m water depth revealed an average nitrogen content TN = 0.74 % and a $\delta^{15}N_{TN}$ = 3.15 ‰ (see chapter 2.2). The yearly average may be slightly higher because the two months lacking are characterised by most oligotrophic conditions and probably higher $\delta^{15}N_{TN}$. In contrast to the sedimentary investigations, the sediment trap values are assumed to reflect the organic nitrogen signal, because the organic content should be high enough to outweigh any influence of inorganic nitrogen. The reported values serve only as rough estimates of the nitrogen concentration and $\delta^{15}N_{ON}$ initially sedimentated at site GeoB 4234, since the comparability of the sources of the particulate matter in the sediment trap and in the underlying sediments is questionable (see chapter 2.2).

The fit for the Rayleigh-fractionation model yields for ON = 0.74 % an isotopic signal $\delta^{15}N_{ON} = 3.53 \pm 0.25$ ‰, which is slightly above that estimated. The calculated isotopic signal for the constant release model is much higher ($\delta^{15}N_{ON} = 5.93 \pm 0.01$ ‰). It is obvious that new organic matter of the organisms responsible for the degradation of organic matter, which is enriched in $^{15}N$, is reincorporated into the sediments and may act as well as source for subsequent degradation. The disadvantage of the constant release model is that the enrichment of degradable organic matter in $^{15}N$ during oxic diagenesis is neglected. Sigman et al. (1999) also reported an increase in $\delta^{15}N$ of labile organic matter during its degradation. However, their results did not fit to a simple Rayleigh fractionation model. Instead, they proposed Rayleigh fractionation during degradation, but different types of labile organic matter with different degradation kinetics.

Inorganic nitrogen

Assuming Rayleigh-fractionation, the instantaneous isotopic composition of released $NH_4^+$ ($\delta^{15}N_{NH4,\,inst.}$) is described by equation 3 (Mariotti et al., 1981):

eq. 3: $\delta^{15}N_{NH4,\,inst.} = \delta^{15}N_{ON}(f) - \varepsilon$

According to this model, $\delta^{15}N_{NH4}$ would be expected to increase with increasing degradation in the oxic zone (Fig. 9). The methods employed in this study were not suitable to detect such changes. However, it is unlikely that direct measurement of $\delta^{15}N$ of exchangeable ammonium or pore water nitrate could prove this hypothesis, because the oxidation of the ammonium to nitrate (nitrification) exhibits also strong isotopic fractionation (Brandes and Devol, 1997).

The concentration and isotopic composition of IN was constant in the upper 13 cm with IN = 0.0155 ± 0.0004 % and $\delta^{15}N_{IN} = 5.8 \pm 0.1$ ‰. The isotopic composition is comparable to that expected for released ammonium (Fig. 9). However, since pore water concentrations of ammonium are low in this part of the sediment, it is unlikely that this fixed ammonium is derived from authigenic early diagenetic processes. It is likely that the IN that was found in the oxic zone was derived from soils and was transported with the clay minerals into the sediments. Illite, especially, is a potential carrier of fixed ammonium (Müller, 1977). Illite was found to dominate the clay mineral composition in the adjacent area south of the Canary Islands (Hartmann et al., 1976).

Below 13 cm sediment depth, higher pore water concentrations and increasing concentrations of adsorbed ammonium coincide with an increase in fixed ammonium concentration and a decrease in its nitrogen isotope ratio ($\delta^{15}N_{KOBr}$, see Fig.8). This change is best explained by authigenic fixation of ammonium derived from anoxic organic matter degradation processes. Assuming that IN concentration and its isotopic composition in the sediment samples between 0 and 13 cm reflect the constant sedimentary signal, the isotopic composition of ammonium that was released during organic matter degradation in anoxic zones and that was additionally fixed by clay minerals may be deduced via mass balance calculations. To avoid large errors when dealing with small concentration changes this was done for the three samples at the IN maximum between 22 and 25 cm. According to this approach the stable nitrogen isotope ratio of anoxic-released ammonium was 3.6 ± 0.3 ‰. However, since we do not know the $\delta^{15}N_{ON}$ of the organic matter in the anoxic zone, we are not able to determine the magnitude of fractionation during anoxic organic matter degradation.

Total nitrogen

In most studies using sedimentary stable nitrogen isotope ratios as paleo-proxy, investigations were done on bulk sediments rather than focusing on the organic nitrogen (e.g. Rau et al., 1987; Calvert et al., 1992; Francois et al., 1992; Altabet et al., 1995; Farrell et al., 1995; Ganeshram et al., 1995; Reichart et al., 1998; Holmes et al., 1999). Müller (1977) has shown that especially in oligotrophic sediments, IN in the form of fixed ammonium may contribute up to 45% of total nitrogen content.

In this study $\delta^{15}N_{TN}$ increased less in the oxic zone than $\delta^{15}N_{ON}$ (Fig. 8). This is explained by an increasing influence of the isotopically light IN on the bulk sedimentary signal, due to decreasing ON content. The increasing concentration of IN in the suboxic zone due to fixation of ammonium generated during early diagenesis is the cause for the observed decrease of $\delta^{15}N_{TN}$ in this part of the sediments. These results show that the influence of IN on the bulk sediment has to be considered when interpreting bulk sedimentary stable nitrogen isotope ratios.

### Oxic degradation of organic carbon

Early diagenetic degradation of organic matter may be compared to principles of isotope fractionation in food webs (Saino, 1992; Nakatsuka et al., 1997). Consumers are usually enriched in $^{15}N$ and $^{13}C$ compared to their food (Wada et al., 1991). Deamination and decarboxylation processes are responsible for the observed isotope fractionation (Macko et al., 1993). According to nitrogen, these principles can explain the increase of $\delta^{15}N_{ON}$ during organic matter degradation (see discussion above). It is reasonable to assume the same principles are also responsible for early diagenetic changes of $\delta^{13}C_{org}$, resulting in an enrichment of organic matter in $^{13}C$ during its degradation. However, in most studies a decrease in sedimentary $\delta^{13}C_{org}$ was observed (e.g., Nakatsuka et al., 1995; Prahl et al., 1997; Böttcher et al., 1998). This study revealed a decrease in $\delta^{13}C_{org}$ in the oxic degradation zone below 4 cm sediment depth after an initial increase in $\delta^{13}C_{org}$ (Fig. 8).

The $\delta^{13}C_{org}$ profile can be simulated in analogy to $\delta^{15}N_{TN}$ assuming fractionation during degradation of labile organic carbon (LOC, analogue to ON) in combination with an inert fraction (refractory organic carbon, ROC, analogue to IN) which is not affected by degradation processes and is depleted in $^{13}C$ and $^{15}N$ compared to TOC and TN. The stable carbon isotope ratio of LOC ($\delta^{13}C_{LOC}$) can be calculated using the isotopic mass balance equation (Appendix) assuming a constant concentration and isotopic composition of ROC ($\delta^{13}C_{LOC}$, Fig. 10a). Describing the sedimentary food web conditions of LOC in analogy to ON with Rayleigh fractionation, a linear relationship between $\delta^{13}C_{LOC}$ and the natural logarithm of the ratio of resting LOC to initial LOC (consumption rate) is expected. Closest correlation was achieved assuming an initial relative contribution of ROC to the TOC content of 18 % (Fig. 10b,c). An estimate of the isotopic composition of ROC is not possible using this regression, since the isotope ratio of ROC ($\delta^{13}C_{ROC}$) has no impact on the calculated correlation coefficient. The fractionation factor of 4.39 ‰, which was used to calculate the change in $\delta^{13}C_{LOC}$ assuming Rayleigh fractionation, is dependent on the estimated $\delta^{13}C_{ROC}$.

We can only speculate about the nature of the hypothetical ROC which is not involved in early diagenetic degradation processes. Less intensive degradation of terrestrial organic matter compared to $^{13}C$ enriched marine organic matter has been proposed to explain negative shifts

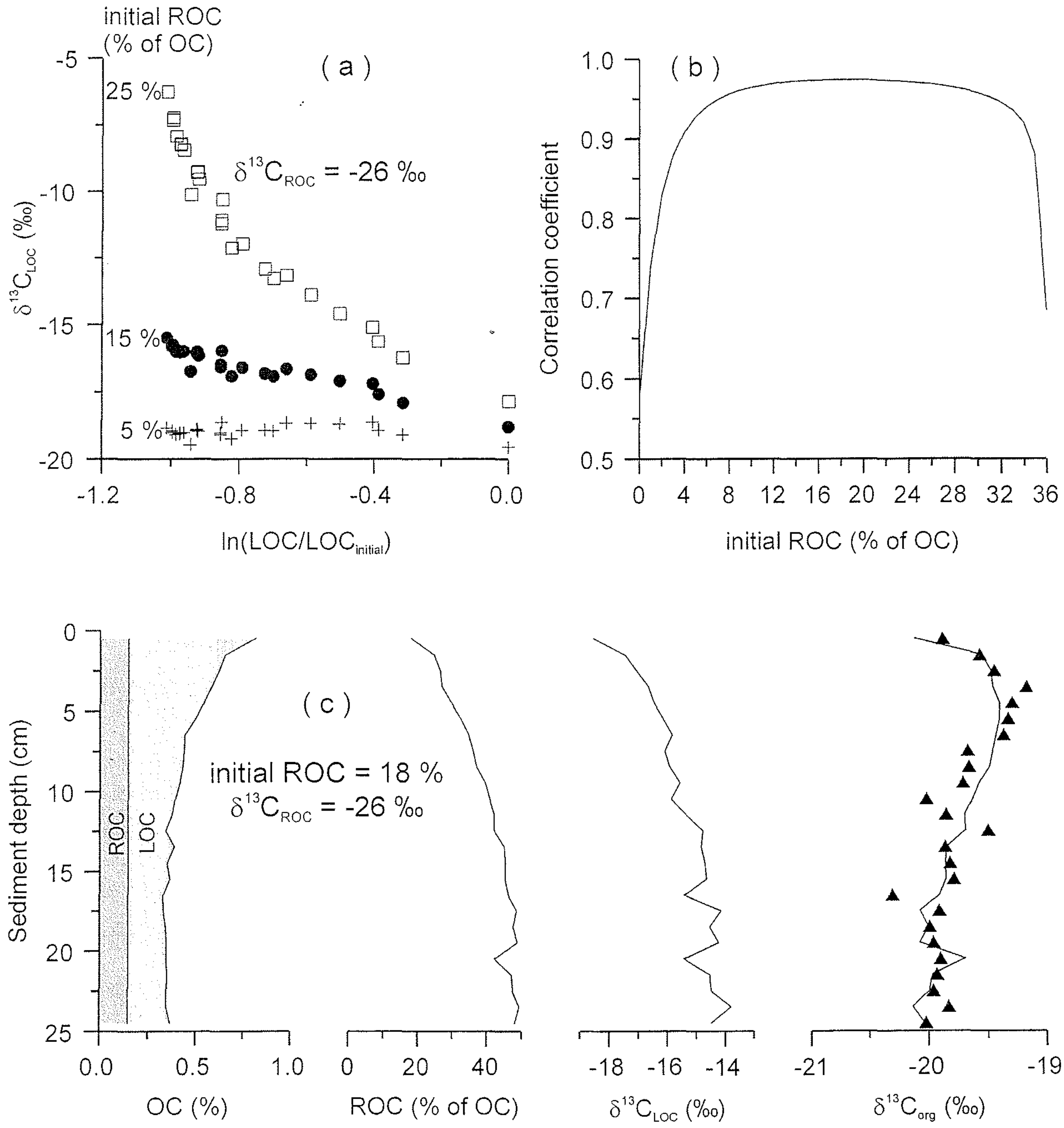

Fig. 10: a) Calculated stable carbon isotope ratio of labile organic carbon ($\delta^{13}C_{LOC}$) in dependence on ln(f) (f = $LOC/LOC_{initial}$) for different assumed initial percentages of refractory organic carbon (ROC) and b) resulting correlation coefficients calculating linear regression (supposition for Rayleigh fractionation as the cause for changes in $\delta^{13}C_{LOC}$); c) as an example we used measured TOC concentrations, an initial percentage of ROC = 18 % and $\delta^{13}C_{org}$ = –26 ‰ and assumed Rayleigh fractionation according to

$$\delta^{13}C_{LOC} = -18.82\text{ ‰} - 4.39 \times \ln(LOC/LOC_{0\text{-}1cm})$$

for modelling changes in the concentrations of ROC and LOC, of the percentages of ROC, of the isotopic compositions of LOC and of $\delta^{13}C_{org}$ (lines) and compared the latter with measured $\delta^{13}C_{org}$ values (triangles) showing a correlation with r = 0.974.

of $\delta^{13}C_{org}$ during early diagenesis (e.g. Prahl et al., 1997; Böttcher et al., 1998). Microscopic investigation and Rock-Eval pyrolysis showed that the sediments of this study are dominated by marine organic matter and yield only minor proportions of terrestrial organic matter. If we assume that terrestrial organic matter is refractory, an increase of its relative proportion with depth would be expected (Fig. 10c). However, microscopic investigation did not show a drastic increase of terrestrial organic matter with depth, which should be detected even when using it as a qualitative rather than a quantitative method. Recent investigation of continental slope sediments also revealed no preferential preservation of terrestrial organic matter (Ransom et al., 1998).

Relatively low hydrogen indices indicate intensive remineralisation of the organic matter at our study site. Remineralisation and condensation processes would result in refractory organic matter of marine origin and could explain the observed increase of AOM with depth. This observation is in agreement with the results of Zegouagh et al. (1999). These authors isolated refractory organic matter by chemical extraction of sediments south of our study site, which are also influenced by coastal upwelling. They concluded from their microscopic, chromatographic and isotopic investigations that this refractory organic matter was mainly of marine origin, produced during remineralisation and condensation processes (Zegouagh et al., 1999).

Beside terrestrial organic matter, a relative enrichment of lignins and lipids, which are also depleted in $^{13}C$, has been proposed to cause decreases in $\delta^{13}C_{org}$ (Tyson, 1995; Harvey and Macko, 1997; Böttcher et al., 1998). However, the nature and isotopic composition of refractory organic matter remains speculative, since about 80% of sedimentary organic matter is not characterisable by modern (chromatographic) methods (Wakeham et al., 1997).

The difference between early diagenetic isotopic changes in organic nitrogen, which can be explained solely by fractionation processes related to bacterial metabolism, and in organic carbon, which require additional alteration in the relative contribution of $^{13}C$-depleted refractory organic matter to be explained, is caused by the low nitrogen concentrations in the refractory organic matter. This observation is in line with the usual explanations for early diagenetic decreases in $\delta^{13}C_{org}$ due to preferential preservation of terrestrial organic matter, lignins or lipids, which have all low nitrogen contents.

The possible enrichment of sedimentary LOC in $^{13}C$ due to metabolic processes during its degradation was used to explain increasing $\delta^{13}C_{org}$ values during ageing of suspended matter (Saino, 1992). This process was disregarded in previous studies concerning early diagenetic changes in sedimentary $\delta^{13}C_{org}$. We use it in this study to explain the increase in $\delta^{13}C_{org}$ in the first few centimetres of the sediment. However, changes in the isotopic composition of settling particles in the last century may also be at least partly responsible for the observed increase. Fischer et al. (1997, 1998) explained lower $\delta^{13}C_{org}$ values in sediment traps compared to surface sediments with anthropogenic $CO_2$ release in the last decades. Since the sedimentation rate at site GeoB 4234 of the Holocene sediments estimated from oxygen isotope stratigraphy is about 8 cm/kyr (see chapter 2.5), changes in the sedimentary signal in the last century should be recognisable in the upper centimetres of the sediment, although reduced by bioturbation. In upwelling regions the effect of increased atmospheric $CO_2$ content should be small, since water column inorganic carbon content is dominated by deep water $CO_2$ content, which is not in equilibrium with the $CO_2$ partial pressure of the earths atmosphere. Our study site is influenced by seasonal upwelling mostly in the summer months (Nykjær and Van Camp, 1994). An influence of a $pCO_2$ increase on the generated $\delta^{13}C_{org}$ during the non-upwelling seasons seems possible. It remains to be investigated in a future study wether this process is quantitatively important.

## CONCLUSIONS

In our study, the observed variability of $\delta^{13}C_{org}$ and $\delta^{15}N_{TN}$ due to early diagenetic processes was less than 1 ‰. This variability is smaller than isotopic shifts caused by paleoceanographic changes that are commonly observed in sediments (e.g., Müller et al., 1994; Holmes et al., 1999). Similar processes can explain the observed early diagenetic variability of $\delta^{13}C_{org}$ and $\delta^{15}N_{TN}$.

Degradation of LOC and ON is responsible for an enrichment of these fractions in $^{13}C$ and $^{15}N$. This enrichment is comparable to general food web characteristics, which show higher $\delta^{13}C$ and $\delta^{15}N$ of the organic matter of consumers compared to their food. The enrichment in the sediments may be described by Rayleigh fractionation kinetics.

Degradation of LOC and ON is responsible as well for a relative increase in the contributions of isotopically light carbon and nitrogen fractions, which are not affected by degradation processes (ROC and IN, respectively). This process counteracts the isotopic increase due to Rayleigh fractionation. As a consequence of an increase in IN due to ammonium fixation in the suboxic part of the sediments, the influence of $\delta^{15}N_{IN}$ on $\delta^{15}N_{TN}$ increases. In contrast to $\delta^{13}C_{org}$ , no refractory fraction of organic nitrogen was needed to explain changes in $\delta^{15}N_{ON}$ by Rayleigh fractionation.

According to $\delta^{13}C_{org}$, no analytical distinction between the concentration and isotopic composition of labile and refractory organic carbon was carried out. In addition, a change in the isotopic composition of $\delta^{13}C_{org}$ in settling particles due to the atmospheric increase of $pCO_2$ during the last century may have affected the sedimentary $\delta^{13}C_{org}$ profile. As a consequence, the described processes are much better documented for $\delta^{15}N_{TN}$ than for $\delta^{13}C_{org}$.

Using sedimentary stable nitrogen and carbon isotope ratios as proxies for paleo-environmental conditions, special attention must be paid to the influence of changing early diagenetic conditions:

- Varying degrees of organic matter preservation, which is likely to occur under conditions of high variability in productivity or changing bottom water oxygenation, should result in different strengths of diagenetic isotopic shifts. For example, amino acids are reported to be preserved much better under anoxic than oxic conditions (Nguyen and Harvey, 1997), which may be important at locations with changing bottom water oxygen concentrations.
- The competition between isotopic increase during degradation of labile compounds and isotopic decrease during enrichment of resistant compounds should cause an early diagenetic enrichment of the heavier isotopes if the sediment yields low amounts of resistant compounds and vice versa. Thus, the variability of sedimentary $\delta^{15}N$ and $\delta^{13}C_{org}$ due to severe changes in the ratio of easily degradable marine organic matter with high $^{15}N/^{13}C$ content versus resistant (e.g. terrestrial) organic matter with low $^{15}N/^{13}C$ content, is assumed to increase during organic matter degradation. The uncertainty of the estimation of the isotopic composition of the marine and terrestrial end members for determination of their content in the sediments is enhanced if fractionation causes different isotopic shifts of the end members.
- Changes in concentration and isotopic composition of inorganic nitrogen may outweigh the isotopic composition of organic nitrogen in sediments poor in organic matter. The TOC/TN ratio is a recommendable tool for tracing changes in the relative importance of IN on TN in sediments low in terrestrial organic matter.
- Further investigations must be done concerning the influence of anoxic diagenesis on sedimentary stable isotope ratios. For example, the uptake of $^{15}N$-depleted ammonium and inorganic carbon by chemoautotrophic bacteria may be an additional process affecting the $\delta^{15}N$ of particulate organic matter, especially in anoxic environments (Libes and Deuser, 1988; Gong and Hollander, 1997; Holmes et al., 1999).

## ACKNOWLEDGEMENTS

Discussions with P. Müller stimulated this study especially concerning the investigation of the influence of inorganic nitrogen on the sedimentary stable nitrogen isotope ratio. Fruitful discussions with G. Fischer, H. Meggers and S. Neuer improved the study. We thank M. Segl, B. Meyer-Schack, H. Buschoff, and S. Hinrichs for their support of the laboratory work. The first author was funded by the EU (MAS3-CT96-0060).

## APPENDIX

The isotopic mass balance equation (I) is based on the principle, that neither the concentration, nor the overall isotopic composition of nitrogen respectively carbon can change in a closed system:

$$\text{(I)}: \delta^{15}N_A \times N_A = \delta^{15}N_B \times N_B + \delta^{15}N_C \times N_C$$

$$\text{for } N_A = N_B + N_C \text{ and}$$

$$^{15}N_A = {}^{15}N_B + {}^{15}N_C\ ;\ {}^{14}N_A = {}^{14}N_B + {}^{14}N_C$$

Equation (I) was adapted from Altabet and Francois (1994). $^{15}N$, $^{14}N$ and $\delta^{15}N$ may be replaced by $^{13}C$, $^{12}C$ and $\delta^{13}C$. This equation is not strictly true but it is a good approximation when dealing with small changes of isotopic composition occurring in natural systems.

The relationship between the initial amount of organic nitrogen ($ON_{initial}$), the amount of organic nitrogen which has not been degraded (ON) and the inorganic nitrogen in form of ammonium which was build up during degradation (NH4) and their isotopic compositions can be described by simple mass balance equations:

$$\text{(II)}: ON_{initial} = ON + NH4$$

$$\text{(III)}: \delta^{15}N_{ONinitial} \times ON_{initial} = \delta^{15}N_{ON} \times ON + \delta^{15}N_{NH4} \times NH4$$

Combining (II) and (III) and defining $f = ON \times ON_{initial}^{-1}$ results in (IV) which describes $\delta^{15}N_{ON}$ in dependence of f:

$$\text{(IV)}: \delta^{15}N_{ON} = \delta^{15}N_{NH4} + f^{1} \times (\delta^{15}N_{ONinitial} - \delta^{15}N_{NH4})$$

Assuming $\delta^{15}N_{NH4}$ being constant this equation describes the constant release model.

## 2.2 Manuscript 2:

# Influence of lateral particle advection and organic matter degradation on sediment accumulation and stable nitrogen isotope ratios along a productivity gradient in the Canary Islands region

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## ABSTRACT

We compare total and biogenic particle fluxes and stable nitrogen isotope ratios ($\delta^{15}N$) at three mooring sites along a productivity gradient in the Canary Islands region with surface sediment accumulation rates and sedimentary $\delta^{15}N$. Higher particle fluxes and sediment accumulation rates, and lower $\delta^{15}N$ were observed in the upwelling influenced eastern boundary region (EBC) compared to the oligotrophic sites north of Gran Canaria (ESTOC, " European Station for Time-Series in the Ocean, Canary Islands") and north of La Palma (LP). The impact of organic matter degradation and lateral particle advection on sediment accumulation was quantified with respect to the multi-year flux record at the ESTOC. Remineralisation of organic matter in the water column and at the sediment surface resulted in an organic carbon preservation of about 0.8 % and total nitrogen preservation of about 0.4 % of the estimated export production. Higher total and carbonate fluxes and accumulation rates in the lower traps and surface sediment compared to the upper traps indicated that at least 50 % of the particulate matter at the ESTOC was derived from allochthonous sources. Low $\delta^{15}N$ values in the lower traps of the ESTOC and LP point to a source region influenced by coastal upwelling. We conclude from this study that the reconstruction of export production or nutrient regimes from sedimentary records in regions with strong productivity gradients might be biased due to the mixture of particles originating from autochthonous and allochthonous sources. This could result in an imprint of high productivity signatures on sedimentation processes in oligotrophic regions.

## INTRODUCTION

The export of biogenic particles from the euphotic zone into the deep ocean and their burial in the sediments, the so-called biological pump, is an important constituent of the marine carbon and nutrient cycle that also affects the atmospheric $CO_2$ content and climate (Berger and Keir, 1984). Marine sediments act as a long-term sink for biogenic particles. Quantity as well as the biogeochemical characteristics of particles settling to the sea floor are related to the environmental conditions during their generation and may be used to trace past environmental and productivity conditions ("paleoproxies", see Fischer and Wefer, 1999, for an overview).

During settling and sedimentation, biogenic particle flux is affected by early diagenetic processes like biologically mediated organic matter degradation, and carbonate and opal dissolution. These processes result not only in a decrease of particle flux with water depth

(Martin et al., 1987) but also in the alteration of the sedimentary biogeochemical signal. For instance, preferential degradation of nitrogen enriched organic compounds is responsible for an increase of C/N ratios during organic matter degradation (Tyson, 1995). A 5 ‰ higher $\delta^{15}N$ signal in deep-sea sediments compared to sinking particles has been attributed to isotope fractionation during early diagenesis (Altabet and Francois, 1994).

The investigation of the early diagenetic alteration of geochemical and biological properties during sinking and sedimentation and the implication for their use as paleoproxies has been a major topic of recent research (e.g. Wakeham et al., 1997; Fagel et al., 1999). However, crucial to the investigation of the role of marine sediments as long-term sinks of major elements of the global biogeochemical cycle is quantification of the impact of early diagenetic processes on biogenic fluxes through the comparison of particle fluxes in sediment traps and accumulation rates in surface sediments. In a few recent studies, this promising approach was applied focusing on organic carbon and carbonate preservation (Lyle et al., 1992; Fischer and Wefer, 1996; Khripounoff et al., 1998; Ziveri et al., 1999).

In addition to early diagenesis, lateral particle transport may affect sedimentary fluxes. Especially in proximity to continental margins, transport of sinking particles by lateral advection or the transport of suspended matter in the mid- and bottom nepheloid layer may have a major impact on sedimentation (Lampitt et al., 1995; Neuer et al., 1997b; Antia et al., 1999; Heussner et al., 1999). Furthermore, turbulent kinetic eddy dispersion (Siegel and Deuser, 1997) may result in additional particle sources if the catchment areas of sediment traps include distinct source regions. This has major implications not only for the interpretation of sediment trap results, but also for sediments: if the quantity as well as the biogeochemical properties of sinking particles from different source areas are variable, lateral transport should affect both sediment accumulation and its biogeochemical signature.

In this study we compare fluxes of organic carbon, nitrogen and carbonate in sediment traps and surface sediments along a productivity gradient in the Canary Islands region ranging from a coastal upwelling influenced site to the oligotrophic subtropical gyre region. Previous particle flux studies north of Gran Canaria at the ESTOC (European Station for Time-series in the Ocean, Canary Islands) indicated increasing particle flux with depth despite particle degradation during settling (Neuer et al., 1997b). Different trapping efficiencies cannot account for this flux pattern as shown by grain size analyses and $^{230}$Th flux measurements (Ratmeyer et al., 1999; Scholten et al., in press). Instead, the observed increase in particle flux with depth has to be explained by additional particle sources in the deep water column from the adjacent high productive continental margin area (Neuer et al., 1997b). Therefore, the Canary Islands region is especially well suited for the study of the impact of lateral particle advection and particle degradation on sediment accumulation.

As a geochemical proxy we investigate the stable nitrogen isotope ratios of the sinking particles and sediment surfaces. Stable nitrogen isotope ratios of particle fluxes are strongly related to nutrient availability in the euphotic zone (Altabet and Francois, 1994; Voss et al., 1996). Phytoplankton preferentially assimilates $^{14}N$, resulting in an enrichment of euphotic zone nitrate in $^{15}N$. In upwelling influenced regions progressive nutrient depletion causes an increase in $^{15}N$ of nitrate in the water column with increasing distance from the upwelling centre (Altabet and Francois, 1994). Although early diagenesis is known to affect the sedimentary stable nitrogen isotope ratio (Altabet and Francois, 1994), similar gradients have been observed in surface sediments of upwelling regions (Altabet and Francois, 1994; Holmes et al., 1999; Hebbeln et al., 2000). The impact of lateral particle advection on sedimentary geochemical properties may thus be recorded by stable nitrogen isotope ratios.

## INVESTIGATION AREA AND SAMPLING SITES

The Canary Islands are situated in the eastern part of the subtropical North Atlantic between 100-600 km west of the NW African coast (Fig. 1a). The islands are of volcanic origin and rise from the deep-sea plain in more than 3,000 m water depth. The two easternmost islands, Lanzarote and Fuerteventura are located contiguous to the continental slope of NW Africa. The shelf width at this part of the African coast is between 30 and 100 km.

The Canary Current, as part of the eastern boundary current system, is characterised by a southward flow over the continental shelf and slope (Fig. 1a) with speeds of about 25 to 50 cm $s^{-1}$ (Stramma and Siedler, 1988; Mittelstaedt, 1991). It shows seasonal variability with stronger currents between the eastern islands and the continental slope in summer and west of the islands in winter (Stramma and Siedler, 1988). Deep-water currents in the investigation area are less intense. The general flow in the eastern subtropical Atlantic in the depth range 1200 m to the bottom is directed southward (Saunders, 1982). However, north of the Canary Islands a persistent southward deep-water flow could not be detected by either moored current meters or geostrophic current determinations (T. Müller, personal communication).

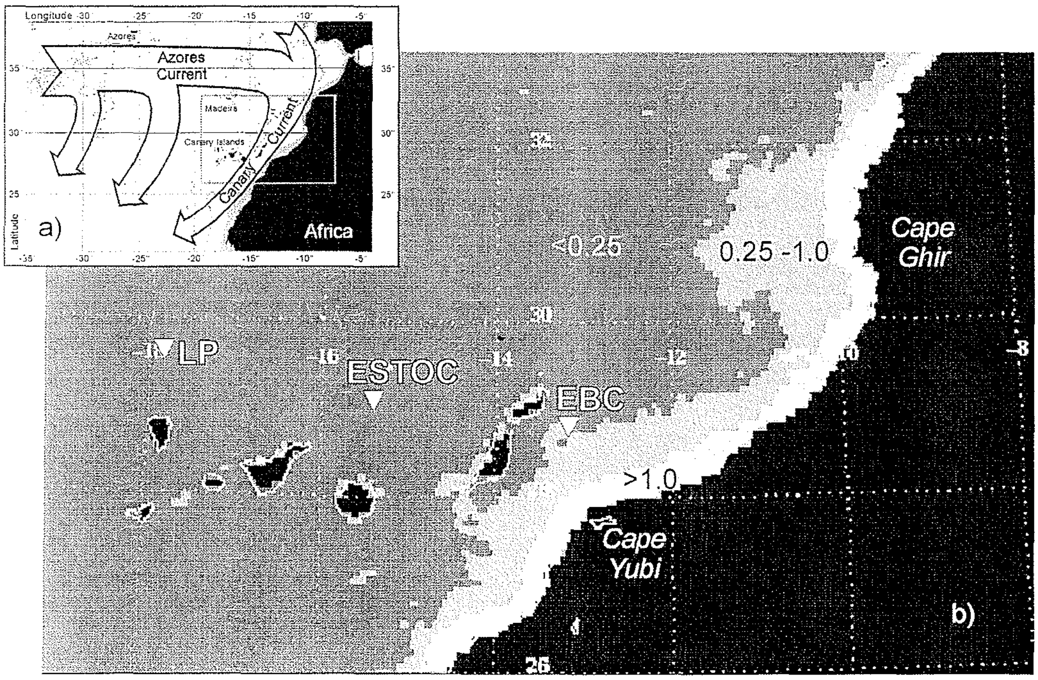

Fig. 1: a) Topography and main geostrophic transport in the warm water sphere of the subtropical East Atlantic (modified after Siedler and Onken, 1996). Thin lines indicate the 3000 m depth contour, grey shaded areas indicate the continental shelf (200 m depth contour). b) Surface pigment concentration (mg $m^{-3}$) in the Canary Islands region as observed by SeaWiFS (bin of 18 individual images from the HCAN ground station in ULPGC for 1998). The image dates are more or less evenly spaced out throughout 1998 and represent reasonably clear-sky conditions over the Canary Islands and Cape Ghir. Investigation sites with trap moorings and sediment sampling are marked with triangles.

Seasonal along-shore upwelling is observed along the NW African coast mainly in summer as a coastal band about 50-70 km wide (Mittelstaedt, 1983; Nykjær and Van Camp, 1994) while further offshore oligotrophic subtropical gyre conditions prevail (Fig. 1b). However, filaments of several hundred km length at Cape Ghir, located to the north-east, and Cape Yubi, located to the south-east of the Canary Islands, can be observed frequently (Van Camp et al., 1991). These are characterised by higher pigment concentrations compared with ambient waters (Fig. 1b), indicative of higher productivity at these sites. Upwelling filaments act as offshore transport mechanisms for nutrients and plankton (Rodríguez et al., 1999) and may thus affect sedimentation at offshore sites. The Cape Ghir filament, situated upstream of the Canary Islands, was identified as a potential source of laterally advected particles in deeper water layers at the ESTOC which is located 100 km north of Gran Canaria and about 500 km west of the African coast (Neuer et al., 1997b; Davenport et al., 1999).

The Canary Islands have a major influence on local current and productivity features south of the Canary Islands (Arístegui et al., 1997). However, the islands exert little influence on the sedimentation patterns investigated in this work, since our sites are located upstream of the islands (Fig. 1). The easternmost islands Lanzarote and Fuerteventura act as a barrier for coastal waters spreading offshore and thus prevent any direct impact of coastal upwelling on the ESTOC.

Table 1: Location, water depth, collection period, sample intervals and trap depths of the particle trap deployments at EBC, the ESTOC, and LP

| Station | Latitude (N) | Longitude (W) | Water depth (m) | Designation | Collection period | | Sample interval (days) | Trap depth (km) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Start | End | | upper | middle | lower |
| ESTOC | 29°08 | 15°27 | 3610 | CI1 | 25.11.91 | 25.09.92 | 15.25 | — | 0.9 | 3.0 |
| | | | | CI2 | 01.10.92 | 09.04.93 | 9.5 | — | 0.9 | 3.0 |
| | | | | CI3 | 12.04.93 | 07.06.94 | 21[a] | — | 0.8[b] | 3.0 |
| | | | | CI4 | 09.06.94 | 02.09.94 | 8.5 | — | 0.8 | 3.0 |
| | | | | CI5 | 05.09.94 | 12.11.95 | 22[c] | — | 0.8 | — |
| | | | | CI6 | 17.11.95 | 01.12.96 | 20 | 0.5 | 0.75 | 3.0 |
| | | | | CI7 | 23.12.96 | 14.09.97 | 14 | 0.5 | 0.75 | 3.0 |
| EBC | 28°43 | 13°09 | 996 | EBC2-1 | 02.01.97 | 01.09.97 | 14[d] | — | 0.7 | — |
| LP | 29°46 | 17°57 | 4327 | LP1 | 06.01.97 | 01.09.97 | 14 | — | 0.9 | 3.8 |

[a] interval of first cup 11 days
[b] failed after 6th cup
[c] interval of first cup 19 days
[d] interval of first cup 4 days

Table 2: Location, water depth and core length of sediment sampling at EBC, the ESTOC, and LP (Fischer et al., 1997; Wefer et al., 1997)

| Station | GeoB-Nr. | Cruise | Device | Latitude (N) | Longitude (W) | Water depth (m) | Core length (cm) |
|---|---|---|---|---|---|---|---|
| EBC | 4234-1 | M37/1 | multicore | 28°53.4 | 13°13.6 | 1360 | 32 |
| | 4240-2 | M37/1 | gravity core | 28°53.3 | 13°13.5 | 1358 | 688 |
| ESTOC | 4301-1 | M38/1 | multicore | 29°09.0 | 15°30.0 | 3614 | 10 |
| | 4241-11 | M37/1 | gravity core | 29°10.0 | 15°27.1 | 3609 | 374 |
| LP | 4242-4 | M37/1 | boxcore | 29°40.9 | 17°53.4 | 4292 | 33 |
| | 4242-5 | M37/1 | gravity core | 29°40.5 | 17°53.3 | 4286 | 488 |

The mooring sites investigated in this study include the time series station ESTOC, an upwelling influenced station between Lanzarote/Fuertventura and the African shelf (EBC, Eastern Boundary Current) and a station located north of La Palma (LP) in the oligotrophic gyre region (Fig. 1b, Table 1). Higher productivity at the upwelling influenced site EBC is indicated by higher surface water pigment concentrations compared to the ESTOC and LP (Fig. 1b). Additional information on the sediments are given in Table 2.

## METHODS

Particle flux and sediment accumulation rates were studied with moored sediment traps and surface sediments along the described transect (Fig. 1b). Particle trap results at the time-series station ESTOC (CI1-CI4) have been published elsewhere (Neuer et al., 1997b). In this study we present yearly averaged data of a time-series from November 1991 to September 1997 (CI1-CI7). Trap samples at EBC and LP were analysed from the start of their deployment in January 1997 to September 1997 (Table 1).

We used 20 cup particle traps of the Kiel type (sampling area 0.5 $m^2$) with varying deployment lengths and sampling intervals (Table 1). The sampling cups of the particle traps were filled with a high density solution (40 ‰; supra pure NaCl) and were poisoned before and after deployment with mercury chloride. Samples were omitted if fish remains were detected during sampling treatment. The < 1 mm size-fraction was freeze dried and weighed before homogenisation to determine total flux (sampling and preparation after Fischer and Wefer, 1991).

Sampling of surface sediments was conducted using either a multicorer or a boxcorer (Table 2). Gravity cores at each site were used for stratigraphic purposes. Sediments collected with a multicorer were sampled at intervals of 1 cm; boxcores and gravity cores were sampled every 3 cm and 5 cm, respectively. Samples were homogenised after freeze-drying.

We followed Weber et al. (1997) for porosity and dry bulk density (DBD) determinations using dry weight and wet weight of discrete sediment samples with a small modification: total volume was either directly determined using syringes (boxcore samples) or calculated with an average grain density (multicore samples). According to error propagation, precision for porosity was 1.5 % and for DBD 0.016 g $cm^{-3}$.

We used a CHN-analyser (Heraeus) for elemental analysis of sediment and trap samples. Particulate carbon (PC) and nitrogen (PN) were measured on non-acidified samples while organic carbon (POC) was measured on acidified samples. Analytical standard deviation calculated for repeated measurements was 1.6 % (relative) for carbon and 2.0 % (relative) for nitrogen concentration. Carbonate content was calculated assuming that calcium carbonate was the only carbonate-bearing mineral (eq. 1):

eq. 1: Carbonate = (PC – POC) × 8.333

The stable nitrogen isotope ratio of PN was measured on non-acidified samples. Samples were combusted at 1050°C in a NC 2500 Elemental Analyzer (CE Instruments), that was directly interfaced with a Finnigan MAT Delta Plus mass spectrometer. Nitrogen isotope ratios are reported with reference to air nitrogen (eq. 2):

eq. 2: $\delta^{15}N$ (‰) = $((^{15}N/^{14}N_{sample}) / (^{15}N/^{14}N_{air}) - 1) \times 1000$

Long term standard deviation from repeated measurements was < 0.2 ‰. Average $\delta^{15}N$ of sediment trap time-series are presented as means weighted against nitrogen fluxes.

Gravity cores were additionally sampled for the analysis of oxygen isotopes of the calcite tests of planktonic foraminifera for stratigraphic purposes. About 20 species of *Globigerina bulloides* were picked from wet sieved samples (> 125 µm). Samples were analysed using a Finnigan MAT 251 mass spectrometer coupled with a Finnigan automated carbonate device in Bremen. Precision for repeated measurements was about ± 0.07 ‰. The laboratory standard was calibrated to PDB using the international standards NBS 18, 19, and 20.

In order to obtain an age model which is needed for sedimentation and accumulation rate calculations, oxygen isotope curves were correlated against SPECMAP (Martinson et al., 1987) using Analyserie (Paillard et al., 1996). For correction of sediment loss during coring of the gravity cores, a composite depth was determined by fitting porosity profiles (Fig. 2) as well as carbonate and POC profiles (not shown) of undisturbed multicorer or boxcorer sediments to the corresponding profiles of the upper part of the gravity cores. A slight disturbance of the surface sediments was observed in the boxcore at LP. However, we consider the impact on the calculation of sedimentation rates negligible. Tie points for calculation of average Holocene sedimentation rates are the Younger Dryas event (11 kyear, Bard et al., 1987) at 100 ± 10 cm composite depth at EBC, and stage 2.2 (19 kyear) at 51 ± 10 cm and 28 ± 5 cm composite depth at the ESTOC and at LP, respectively (Fig. 2). Ages of the tie points were confirmed by $^{14}C$ age determination on *G. bulloides* (EBC) and *G. ruber* (white) (ESTOC, LP) (Henderiks et al., submitted). Local sedimentation rates (SR) in the upper cm of the multicorer and boxcorer samples were derived from average sedimentation rates corrected for compaction after Berner (1980) assuming that changes in porosity are only caused by compaction. Sediment accumulation rate SAR was derived after equation 3:

eq. 3: SAR = SR × DBD

Carbonate, POC and PN accumulation rates were calculated by multiplying SAR with the respective sedimentary concentrations.

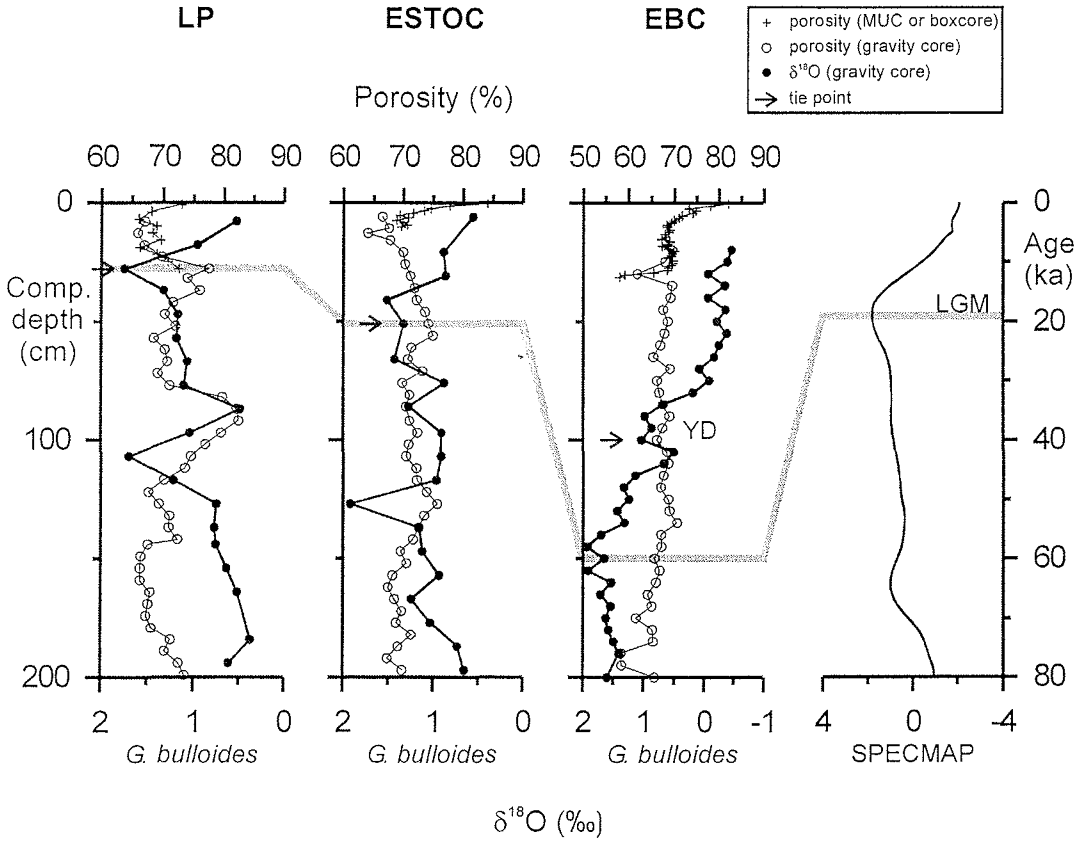

Fig. 2: Planktonic foraminifer oxygen isotope variations in gravity cores of EBC, the ESTOC and LP against composite depth. Composite depth was derived by fitting porosity changes in surface sediments to porosity changes in the upper parts of the gravity cores. Turbidite sections at gravity cores GeoB 4241 (ESTOC) and GeoB 4242 (LP) have been omitted. Oxygen isotope variations are correlated to the age dated SPECMAP record (Martinson et al., 1987).

## RESULTS

### Water column particle fluxes and $\delta^{15}N$

In this study, we focus on time-integrated fluxes in order to compare water column particle fluxes with sedimentary accumulation rates. A comprehensive discussion of the seasonal variability of flux data and stable nitrogen isotope ratios in relation to nutrient conditions and productivity will be presented elsewhere (Neuer et al., submitted). Time series data are available at http://www.pangaea.de/home/tfreudenthal/.

Average fluxes and $\delta^{15}N$ were calculated for the upwelling influenced EBC and for the oligotrophic ESTOC and LP for the duration of their deployment from the beginning of January to the beginning of September of 1997 (Table 3). The phytoplankton biomass gradient was observed in the SeaWiFS-satellite derived composite pigment concentration map (Fig. 1), with high pigment concentrations at the upwelling influenced near-coastal area (EBC) and low pigment concentration further offshore (ESTOC, LP). This gradient was matched by higher fluxes of biogenic particles at the EBC compared to the upper traps of the ESTOC and LP. The stable nitrogen isotope ratio in the upper traps showed an increase between the upwelling influenced site EBC (3.1 ‰) and the oligotrophic sites ESTOC and LP (4.2 and 5.5 ‰, respectively).

Table 3: Average fluxes and stable nitrogen isotope composition at EBC, the ESTOC and LP, January 6, 1997 - September 15, 1997

| Station | Depth (km) | Flux ($g/m^2year$) | | | | $\delta^{15}N$ (‰) |
|---|---|---|---|---|---|---|
| | | total | POC | Carbonate | PN | |
| EBC | 0.7 | 26.9 | 1.40 | 8.5 | 0.2 | 3.1 |
| ESTOC | 0.5 | 7.4 | 0.80 | 3.6 | 0.12 | 4.2 |
| | 0.75 | 6.3 | 0.52 | 3.8 | 0.07 | * |
| | 3.0 | 10.9 | 0.52 | 6.0 | 0.06 | 2.0 |
| LP | 0.9 | 7.3 | 0.74 | 3.7 | 0.09 | 5.5 |
| | 3.7 | 13.4 | 0.59 | 7.7 | 0.07 | 2.2 |

* data not available

Fluxes and changes in flux with depth were very similar at the ESTOC and further offshore at station LP. At both sites, total and carbonate fluxes were about two times higher in the lower trap while no change in POC and PN could be detected, as previously described for the ESTOC (Neuer et al., 1997b). $\delta^{15}N$ was more than 2 ‰ lower in the deep traps of the ESTOC and LP compared to the upper traps.

We have calculated annual averages of particle fluxes and $\delta^{15}N$ in different years at the ESTOC (Table 4) in order to assess their interannual variability. Depending on the duration of the trap series experiments, values represent averages between either summer or autumn of one year and summer or autumn of the next year. When possible, we calculated both the year beginning in summer and autumn in order to evaluate the sensitivity of annual fluxes on the selected start of the year. Differences were below 10 %, reflecting the stronger contribution of the high winter flux, in comparison to summer and autumn, regarding the yearly averaged flux.

Table 4: Yearly fluxes and stable nitrogen isotope composition at the ESTOC between 1991 and 1997. Note that flux averages in 800 and 3000 m water depths are both based on 5-year records, but include different years (1994-1995 in 800 m water depth only, 1993-1994 in 3000 m water depth only).

| Depth (m) | Time | Flux ($g/m^2year$) | | | | $\delta^{15}N$ (‰) |
|---|---|---|---|---|---|---|
| | | total | POC | Carbonate | PN | |
| 500 | 11/95-11/96 | 8.7 | 0.90 | 4.4 | 0.17 | 4.4 |
| | 9/96-9/97 | 6.8 | 0.76 | 3.2 | 0.12 | 4.0 |
| | **average** | **7.7** | **0.83** | **3.8** | **0.14** | **4.2** |
| 800 | 11/91-11/92 | 6.5 | 0.48 | 2.3 | 0.07 | 5.2 |
| | 8/92-8/93 | 11.1 | 0.86 | 5.3 | 0.13 | 4.1 |
| | 9/94-9/95 | 7.7 | 0.67 | 3.8 | 0.11 | 5.5 |
| | 11/95-11/96 | 7.7 | 0.72 | 4.5 | 0.11 | 4.8 |
| | 9/96-9/97 | 5.1 | 0.44 | 3.1 | 0.06 | * |
| | **average** | **7.6 ± 2.2** | **0.63 ± 0.17** | **3.8 ± 1.2** | **0.10 ± 0.03** | **4.9 ± 0.6** |
| 3000 | 11/91-11/92 | 17.3 | 0.81 | 7.8 | 0.09 | 2.9 |
| | 8/92-8/93 | 21.1 | 0.86 | 10.6 | 0.11 | 2.9 |
| | 9/93-9/94 | 15.8 | 0.86 | 8.9 | 0.10 | * |
| | 11/95-1196 | 16.4 | 0.62 | 8.6 | 0.06 | 2.5 |
| | 9/96-9/97 | 11.0 | 0.47 | 6.1 | 0.06 | 2.2 |
| | **average** | **16.3 ± 3.6** | **0.72 ± 0.17** | **8.4 ± 1.6** | **0.08 ± 0.03** | **2.6 ± 0.3** |

* data not available

During all years highest fluxes were observed in the lower trap. The interannual variability of fluxes was considerable, up to a factor of two both in the middle and lower traps. A decrease in particle fluxes between the upper and middle trap was observed during 1996 and 1997, with the exception of carbonate. The carbonate flux did not show strong variations. The average $\delta^{15}N$ at the upper and middle trap depths ranged between 4 and 5.5 ‰. In 1996, an increase in $\delta^{15}N$ between the upper and the middle trap was observed. In contrast to the changes between the upper and the middle trap, total and carbonate fluxes increased more than two-fold between the middle and the lower trap. POC flux at the lower trap was higher than POC flux at the middle trap in 1991/1992. In the other years POC flux was fairly similar in both traps. PN flux was comparable in the middle and lower trap in all years except 1995/1996, where a drastic decrease was observed. The yearly average $\delta^{15}N$ in the deep trap was about 2.2 ‰ lower compared to the middle trap.

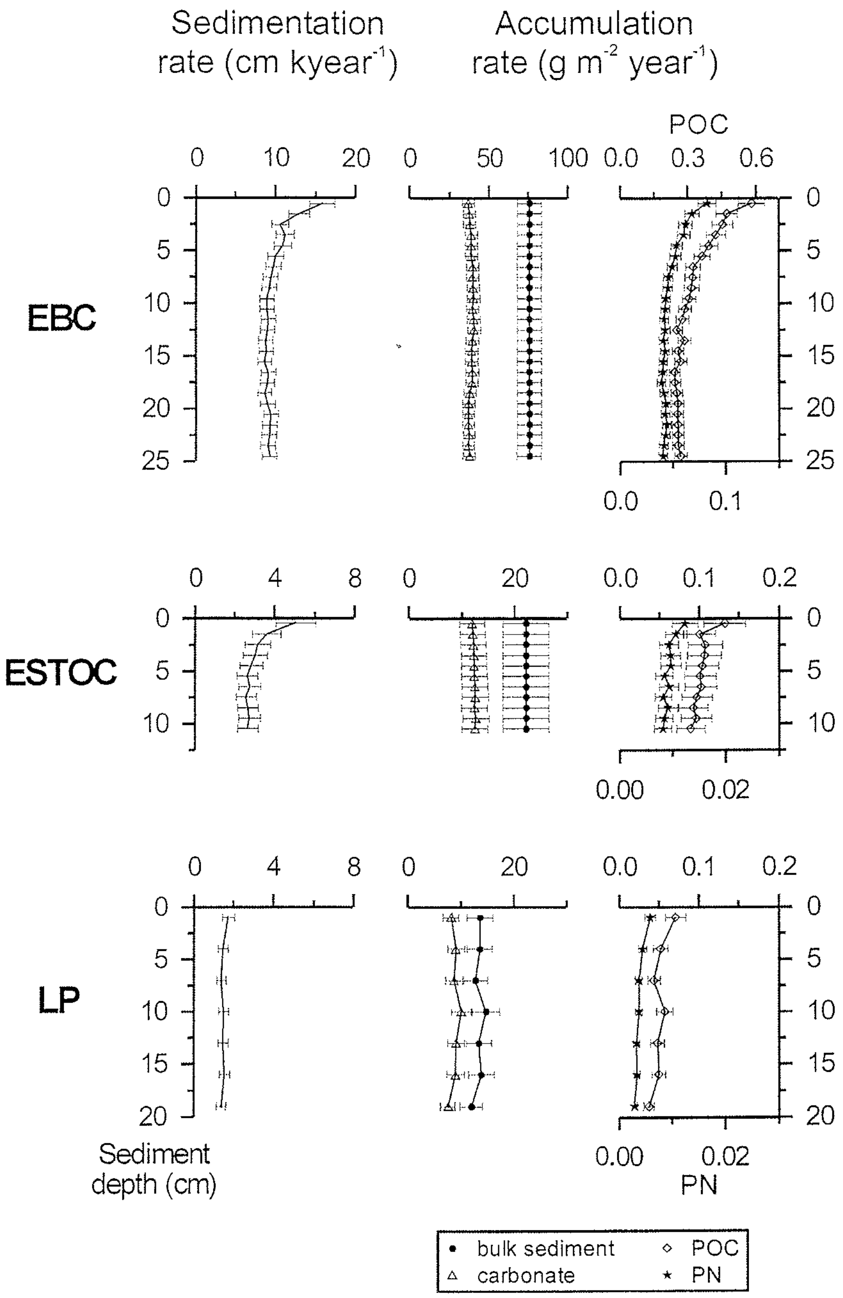

Fig. 3: Sedimentation rates, accumulation rates of bulk sediment, carbonate, POC and PN at surface sediments of EBC, the ESTOC and LP. Error bars represent estimated uncertainties in the depth of tie-points (see methods section).

## Sedimentary accumulation rates and $\delta^{15}N$

Average Holocene sedimentation rates based on planktonic foraminiferal oxygen isotope stratigraphy were highest at EBC (9.1 cm kyear$^{-1}$) and were lower at the ESTOC (2.7 cm kyear$^{-1}$) and LP (1.5 cm kyear$^{-1}$). Based on the assumption of constant bulk sediment accumulation rates, compaction results in a decrease in local sedimentation rate at each station with depth (Fig. 3). Bulk accumulation rates were highest at EBC (70 g m$^{-2}$ year$^{-1}$) and lower at the ESTOC (22 g $m^{-2}$ $year^{-1}$) and LP (13 g $m^{-2}$ $year^{-1}$). Similarly, carbonate accumulation rates were nearly constant in the upper cm at each station and showed a decrease from EBC (34 g $m^{-2}$ $year^{-1}$) to ESTOC (12 g $m^{-2}$ $year^{-1}$) and LP (9 g $m^{-2}$ $year^{-1}$). POC and PN accumulation rates decreased at all three stations in the upper 3 to 10 cm with sediment depth due to remineralisation of organic matter. POC accumulation rates both at the sediment surface and below the upper cm of main organic matter degradation were highest at EBC (0.53 and 0.24 g $m^{-2}$ $year^{-1}$, respectively) and lower at the ESTOC (0.13 and 0.09 g $m^{-2}$ $year^{-1}$, respectively) and LP (0.07 and 0.05 g $m^{-2}$ $year^{-1}$, respectively). Similar decreases were observed for PN. Surface sediment $\delta^{15}N$ showed an increase from the near coast EBC (6.49 ‰) to the oligotrophic sites ESTOC (6.74 ‰) and LP (7.14 ‰).

## DISCUSSION

Total flux at the upper traps of the oligotrophic ESTOC and LP was 5 – 11 g $m^{-2}$ $year^{-1}$, which is in the range of 5 to 17 g $m^{-2}$ $year^{-1}$ reported for other oligotrophic regions of the North Atlantic Ocean (Khripounoff et al., 1998 and references therein). The variability observed in the different studies is likely related both to spatial and interannual variability of export productivity or lithogenic inputs. Interannual variability in particle fluxes within a factor of two, comparable to our results at the ESTOC, have been observed in the oligotrophic Sargasso Sea (Deuser et al., 1995).

At the upwelling influenced EBC, flux of biogenic components (carbonate, POC) were about two-fold higher compared to the oligotrophic ESTOC and LP in 1997, matching the higher productivity at this site (Davenport et al., submitted). However, total flux at EBC was about three-fold higher compared to total fluxes at the ESTOC and LP, due to the non-carbonate fraction. Lithogenic particles transported as dust are the main component of the non-carbonate fraction in the Canary Islands region (Neuer et al., 1997b; Ratmeyer et al., 1999). Higher fluxes at EBC compared to the ESTOC and LP thus reflect both higher productivity as well as dust input in the near coastal region.

In upwelling areas sinking particles are depleted in $^{15}N$ due to preferential assimilation of $^{14}N$, while in oligotrophic areas complete assimilation of euphotic zone nitrate results in no net fractionation (Altabet and Francois, 1994). This relationship is documented by lower average $\delta^{15}N$ of sinking particles at the upwelling influenced EBC compared to the oligotrophic ESTOC and LP in comparable water depths (Table 3). This observation is in contrast to measurements of stable nitrogen isotope ratio measurements of suspended matter in the euphotic zone, where mostly higher $\delta^{15}N$ values were recorded in the upwelling region off Morocco in contrast to the oligotrophic subtropical gyre region (Waser et al., 2000).

The stable nitrogen isotope ratio of nitrate ($\delta^{15}NO_3^-$) in subsurface and deep waters is about 5 - 6 ‰ in most parts of the world oceans (Liu and Kaplan, 1989). A second possible nitrogen source is atmospheric nitrogen with a $\delta^{15}N$ of 0 ‰ which can be fixed by cyanobacteria in oligotrophic seas (Carpenter et al., 1997). Since at the ESTOC yearly averaged $\delta^{15}N$ was not below 4 ‰ in particles collected by the upper traps, we conclude that nitrogen fixation may maximally account for 20 - 30% of the new nitrogen input into the euphotic zone and may be responsible for some of the variability observed in the yearly averaged $\delta^{15}N$.

The productivity, inferred from satellite derived pigment concentrations (Fig. 1) and productivity data based on satellite derived pigment values (Davenport et al., submitted), thus is clearly matched in the upper water column by higher particle fluxes and lower $\delta^{15}N$ at the upwelling influenced EBC compared to the oligotrophic ESTOC and LP sites. How is this signal transported to the sediments? In the following sections, we will discuss the impact of lateral particle advection and particle degradation on particle fluxes and $\delta^{15}N$.

### Lateral particle advection

The multi-year particle flux observation in this study shows that a factor of 1.9 to 2.7 higher particle fluxes at the lower trap are a typical feature at the ESTOC. Higher particle fluxes observed at the lower trap at the ESTOC in combination with coarser grain sizes of the lithogenic matter compared to observations at the middle trap were explained by additional particle sources due to lateral particle advection (Neuer et al., 1997b; Ratmeyer et al., 1999). Not only the lower trap of the ESTOC but also the lower trap of LP appears to be affected by additional particle fluxes due to lateral advection. Comparison of particle fluxes in the water column with surface sediment accumulation rates can provide further indication for the impact of lateral particle advection on local sedimentation (Fig. 4a).

At EBC fluxes of more than threefold higher were found in the sediments compared to the sediment trap. This can be explained by the proximity of the EBC station to the continental shelf. Findings of Fütterer (1983) suggest that the continental slope off NW Africa between 1000 and 2000 m water depth is the depocentre for particles originating from the continental shelf. Repeated resuspension of particulate matter on the shelf and downslope mass transport promoted by the steep gradient in topography along the continental slope were supposed as causes for this particle export (Fütterer, 1983; Biscaye and Anderson, 1994).

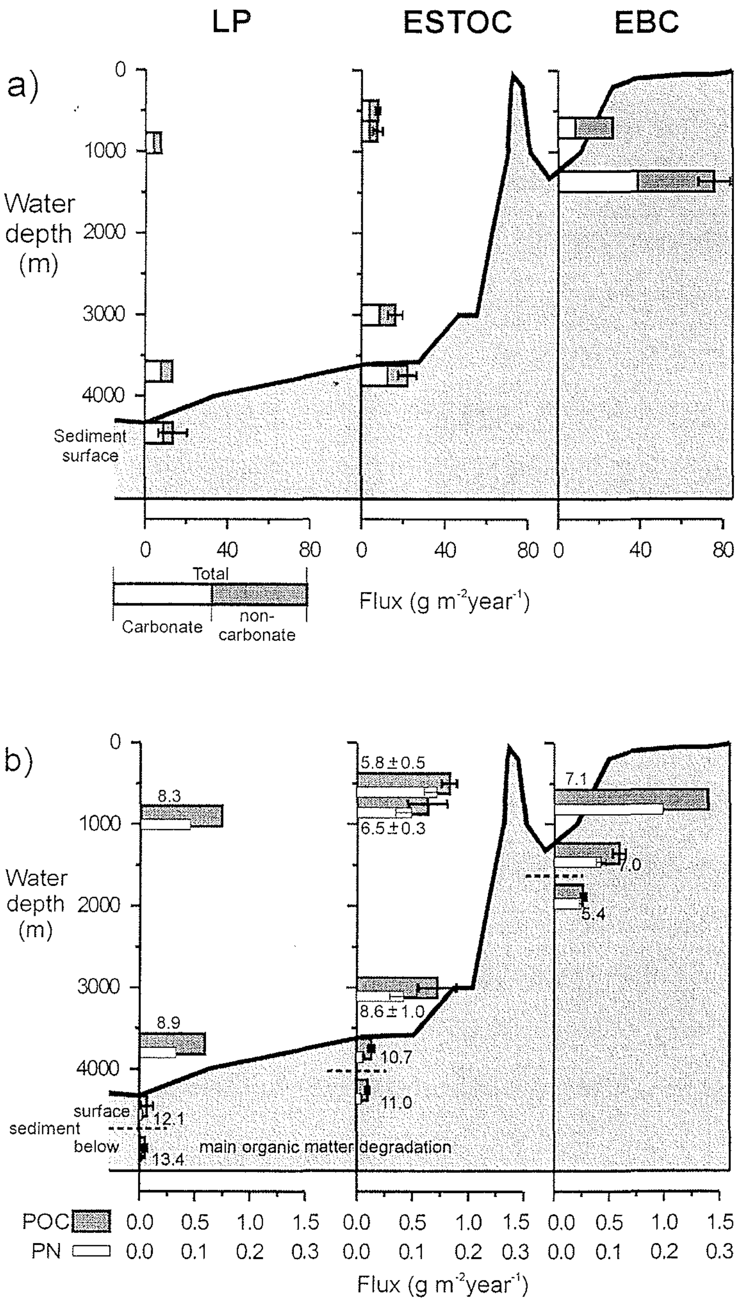

Fig. 4: a) Fluxes in the water column and accumulation rates in surface sediments along the investigated transect of total particulate matter, carbonate and (by subtraction) of the non-carbonate fraction. b) Comparison of fluxes and accumulation rates of POC, PN (bars) and of POC/PN weight ratios (numbers on bars) in the water column and surface sediments along the investigated transect. Fluxes in the water column at the ESTOC indicate average, minimum and maximum of the two-year record (upper trap) and average ± standard deviation of the five-year record (middle and lower trap). Fluxes in the water column at EBC and LP represent integrated fluxes of the 9-month record in 1997. Error bars shown for accumulation rates in sediments indicate the estimated uncertainty of calculated sedimentation rates.

Accumulation rates of bulk sediment and carbonate in the sediments of the ESTOC and LP are comparable with fluxes measured in the lower traps. The correspondence is remarkable considering the different timeframes regarded (traps: 1 to 5 years; sediments: average of several hundreds of years) and considering the uncertainties of estimation of sedimentary accumulation rates (e.g. assumption of constant sedimentation rates during the last 19,000 years). However, in contrast to the differences in sediment accumulation, at least during 1997 no higher fluxes were measured at the ESTOC compared to LP. This may indicate that the similarity of fluxes at the ESTOC and LP in 1997 was a rather unusual phenomenon. In addition we have to consider bottom nepheloid sediment transport (e.g. Lampitt et al., 1995), which does not affect sedimentation at the lower traps but which may affect sediment accumulation at both stations in different magnitudes.

Comparison of total particle fluxes in the upper and middle with the lower trap at the ESTOC indicates that at least 50 % of the sedimenting particles in the lower trap and probably in the surface sediments were supplied from allochthonous sources. This is a minimum estimate since particle degradation is not considered. On the other hand this estimate might be biased due to different trapping efficiencies of the middle and lower trap. A similar estimate based on $^{230}$Th trapping efficiency-corrected particle fluxes during trap deployments CI1 and CI2 (Scholten et al., in press) resulted in at least 30 % of particles derived from allochthonous sources at 3000 m water depth. Additional allochthonous sediment supply by bottom nepheloid layer transport is likely but cannot be discerned in this study.

Particulate matter degradation

For the upper and middle traps at the ESTOC, the influence of lateral advection of particles from remote high productivity sites seems to be negligible. Between these two trap depths carbonate flux did not change in 1996 and 1997 while total flux decreased slightly, demonstrating the dominant influence of organic matter degradation on changes of fluxes in this depth interval (Fig. 4b).

Organic matter degradation is also important when comparing fluxes between the middle and lower trap depths at the ESTOC and LP. This is shown by an increase of the POC/PN ratio (Fig. 4b), likely due to preferential degradation of nitrogen rich compounds (Tyson, 1995). Despite degradation, organic carbon fluxes between the middle and lower traps did not differ much, in some years an increase was even observed. As discussed in the previous section, this must be explained by lateral particle transport affecting the lower trap.

Strongest changes in organic carbon and nitrogen fluxes were observed between the lower traps and the upper centimetre of the underlying sediments. Long exposure to the oxygenated deep water and to benthic fauna at the sediment/water interface results in the most pronounced degradation of organic matter (Cole et al., 1987). Within the upper 10 - 15 cm of the sediments a further decrease of organic carbon and nitrogen flux was observed.

The impact of sedimentary degradation processes on organic carbon and nitrogen fluxes may be quantified by comparing fluxes in sediment traps and accumulation rates of the underlying sediments if the following assumptions hold true:

1. The observed particle fluxes in the sediment traps are typical for the last several hundreds to thousands of years integrated in the surface sediments. The late Holocene that is represented in the surface sediments seems to be a rather stable period with respect to climate and productivity off Morocco (Marret and Turon, 1994). However, interannual variability of particle fluxes within a factor two has to be taken into account (Deuser et al., 1995; this study). Thus, quantification of preservation requires relatively long-term observations of particle fluxes such as available at the ESTOC.

2. Trapping efficiencies of the sediment traps are known. Scholten et al. (in press) estimated $^{230}$Th trapping efficiencies of about 10 and 20 % in the middle and lower traps at the ESTOC. However, $^{230}$Th-corrected total fluxes as well as biogenic fluxes resulted in higher fluxes at the oligotrophic ESTOC than in the temperate NE Atlantic (Scholten et al., in press). These results contradict observations of higher productivity in the temperate ocean compared to the oligotrophic subtropical gyre region (Longhurst et al., 1995). It is therefore questionable if the trapping efficiency correction according to the $^{230}$Th-method is valid for the ESTOC. We therefore assume 100 % trapping efficiency at the lower trap, which might cause overestimation of organic matter preservation if trapping efficiencies are lower.

3. The sources of trapped particles and surface sediments are comparable. Due to the strong impact of lateral advection on particle fluxes, only a comparison of particle fluxes of the lower trap at the ESTOC with surface sediment accumulation rates appears justified. A possible impact of bottom nepheloid layer transport is neglected.

Overall, about 14 % of organic carbon and 11 % of nitrogen collected by the lower trap resisted degradation on and in the sediments at the ESTOC. This preservation rate is high compared to other open ocean sites, where 1.8 - 7.5 % organic carbon preservation was observed (Lyle et al., 1992; Fischer and Wefer, 1996; Khripounoff et al., 1998).

We can estimate the particle export at 100 m water depth (including both autochthonous and allochthonous particle sources) corresponding to the observed organic carbon and nitrogen fluxes at 3000 m water depth by applying the power function proposed by Martin et al. (1987) which describes typical depth related organic matter remineralisation rates in the water for open ocean conditions. The validity of this power function in the eastern subtropical Atlantic was recently confirmed by Khripounoff et al. (1998). The export production corresponding to the particle flux at 3000 m water depth at the ESTOC was 13.4 g C $m^{-2}$ $year^{-1}$ and 2.4 g N $m^{-2}$ $year^{-1}$ according to this approach. Accordingly, about 0.75 % POC and 0.38 % PN is buried in the sediments.

In addition to organic matter degradation, carbonate dissolution has to be considered for the interpretation of depth related changes in particle flux. The calcite lysocline depth is situated well below 4000 m in the Atlantic Ocean (Broecker and Takahashi, 1978). Sprengel et al. (in press) observed no modification of the coccolith carbonate flux between the middle and lower trap at the ESTOC in 1996. Aragonite dissolution would cause only a minor loss of carbonate since aragonitic pteropods contribute to less then 5 % of total carbonate in the upper trap of the ESTOC (H.M., unpublished data). The surface sediments at the ESTOC, EBC and LP did show rather constant carbonate concentrations and accumulation rates. Therefore we assume that carbonate dissolution is of only minor importance in the investigation area.

### Influence of organic matter degradation and lateral particle advection on $\delta^{15}N$

Early diagenetic reactions related to organic matter degradation may cause isotopic fractionation (e.g. Macko et al., 1993) and are probably responsible for 4-5 ‰ higher $\delta^{15}N$ values in surface sediments compared to the isotopic ratio of the export production that are observed in deep-sea regions (Francois et al., 1997). At the ESTOC, a slight increase of $\delta^{15}N$ between the upper and middle trap was observed in 1996, while organic carbon and nitrogen fluxes decreased. Strongest decreases of organic matter fluxes were observed between the lower traps and the sediment surface. They were accompanied by strongest increases of $\delta^{15}N$ by about 4-5 ‰ (Fig. 5). A further increase due to degradation of organic matter in the upper 10 cm of surface sediments was observed at EBC (chapter 2.1). Increases of organic matter $\delta^{15}N$ during remineralisation have previously been reported from culture experiments (Macko and Estep, 1984; Holmes et al., 1999), peat (Macko et al., 1991), suspended matter (Saino and Hattori, 1987), and in marine sediments (Sigman et al., 1999; this study [see chapter 2.1]).

The increase in marine sediments was explained by deamination and excretion of $^{15}$N depleted ammonium (Holmes et al., 1999; this study [see chapter 2.1]).

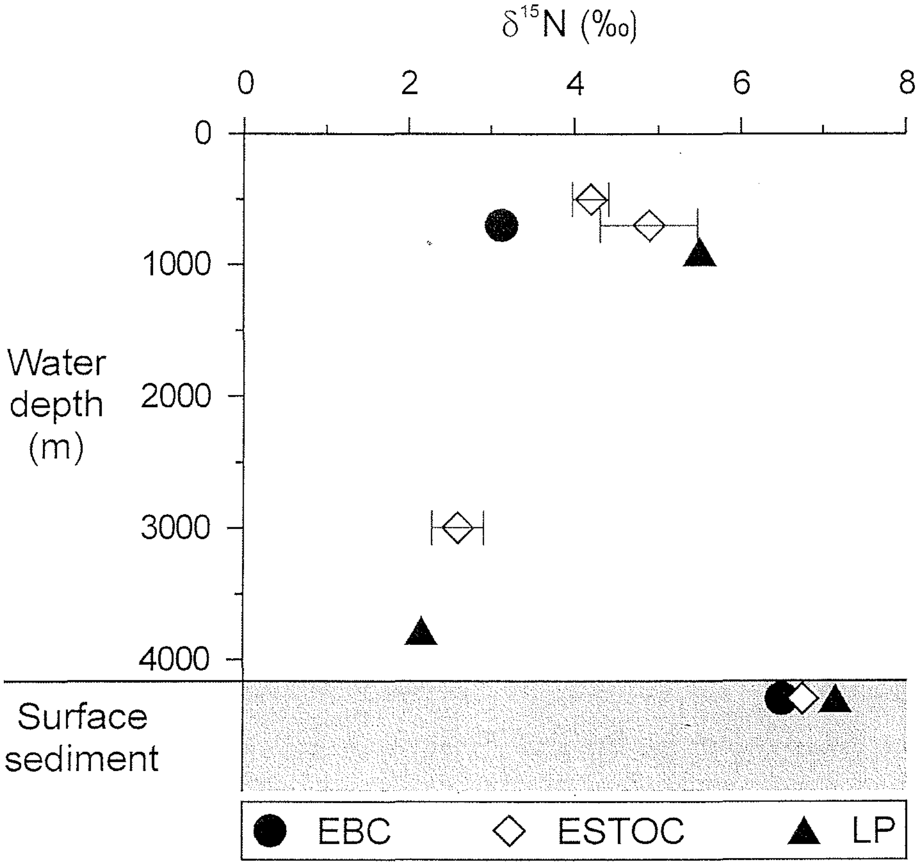

Fig. 5: Stable nitrogen isotope ratios of sinking particles and sediment surfaces. Averages of the same time intervals as in Fig. 4 are presented.

Sediment trap studies frequently showed a decrease in $\delta^{15}$N of sinking particles with depth (Altabet et al., 1991; Voss et al., 1996; Nakatsuka et al., 1997), as was observed in this study at the ESTOC and LP between the middle and the lower trap. Preferential degradation of $^{15}$N-enriched organic compounds or bacterial uptake of $^{15}$N depleted ammonium were suggested as possible causes of this decrease (Nakatsuka et al., 1997; Holmes et al., 1999). However, if early diagenetic reactions were responsible for this decrease, the different early diagenetic behaviour of stable nitrogen isotopes in sinking particulate matter in the upper water column and surface sediments needs to be explained. Moreover, other studies on sinking particles showed that this decrease is not of general significance (Wu et al., 1999; T.F., unpublished data) and thus the local settings need to be taken into consideration.

In addition to diagenetic alterations, an influence of laterally advected particles with low $\delta^{15}$N on sedimentation at the lower trap could explain the observed relative depletion in $^{15}$N at the ESTOC and LP. We can infer on the part of the nitrogen flux at the lower trap of the ESTOC, that is derived from autochthonous sources ($N_{autoch}$), by extrapolating the nitrogen flux at the middle or upper trap to the expected flux at 3000 m water depth using the power function proposed by Martin et al. (1987). Assuming that the $\delta^{15}N$ of sinking particulate matter at 500 to 800 m water depth represents the $\delta^{15}N$ of the autochthonous particles at 3000 m water depth ($\delta^{15}N_{autoch} = \delta^{15}N_{500/800}$) we can calculate the amount of allochthonous particles transported by lateral advection ($N_{alloch}$) and their $\delta^{15}N$ ($\delta^{15}N_{alloch}$) using the yearly averaged nitrogen flux at 3000 m ($N_{3000}$) and isotopic composition ($\delta^{15}N_{3000}$) for different years according to Equations 4 and 5:

eq. 4: $N_{alloch} = N_{3000} - N_{autoch}$

eq. 5: $\delta^{15}N_{alloch} = (\delta^{15}N_{3000} \times N_{3000} - \delta^{15}N_{autoch} \times N_{autoch}) \times N_{alloch}^{-1}$

This approach suggests a relative proportion of allochthonous nitrogen of 50 – 75 % and a $\delta^{15}N_{alloch}$ of 1 – 2 ‰ at the ESTOC. This is only a rough estimate since any impact of diagenetic alterations on stable nitrogen isotope ratios was neglected.

The upwelling region off Morocco is believed to be the source of the allochthonous particles at the lower trap of the ESTOC (Neuer et al., 1997b; Davenport et al., 1999). As shown at the upwelling influenced EBC, sinking particles derived from coastal upwelling are depleted in $^{15}N$. Particulate nitrogen may be even more depleted in $^{15}N$ near the upwelling centres assuming an isotopic ratio of upwelled nitrate of 5 ‰ and a fractionation factor of 5 – 9 ‰ (Altabet and Francois, 1994). Thus, lateral advection of $^{15}N$ depleted particles seems to be a reasonable explanation for the low $\delta^{15}N$ values at the lower traps of the ESTOC and LP.

The difference between the $\delta^{15}N$ in the upper traps and sediment surfaces of about 2 ‰ at the ESTOC and LP is low compared to the 4-5 ‰ diagenetic offset that is typical for the open ocean (Altabet and Francois, 1994; Francois et al., 1997). The isotope ratio of the sediment surface at LP may even be overestimated since a slight disturbance of the sediment surface occurred during coring at this site. Francois et al. (1997) reported for surface sediments of oligotrophic open ocean sites $\delta^{15}N$ values of about 9 ‰. The much lower surface sediment values of 6.7 and 7.1 ‰ at the ESTOC and LP, respectively, are a further indicator for the influence of lateral advection of upwelling derived particles with low $\delta^{15}N$ at these sites. In addition, lateral advection and the accompanying eutrophic overprint on oligotrophic sedimentation can explain the smaller contrast of $\delta^{15}N$ values between the upwelling influenced site EBC and the oligotrophic sites ESTOC and LP in sediment surfaces (0.25 -

0.65 ‰) compared to the isotopic signatures in sinking particles in the upper traps at the same sites (1 - 2.5 ‰).

General implications

Several studies have confirmed the importance of lateral particle transport at continental margin sites (Lampitt et al., 1995; Antia et al., 1999; Heussner et al., 1999). According to Siegel's concept, lateral input of additional particles is not restricted to areas with strong, persistent currents. Quasi-random mesoscale eddy motion results in an increase of the source area of particles at a single point with increasing water depth (Siegel and Deuser, 1997). This increase has no impact on the magnitude and composition of particle flux if the spatial distribution of productivity is constant. However, an overprint of particle fluxes in areas of low productivity by particles from highly productive areas must be considered for areas with strong productivity gradients. Thus, the impact of lateral particle advection is especially important in those regions where strong productivity gradients exist.

A synthesis of the impact of lateral particle advection on sedimentary geochemical properties as derived from the study of $\delta^{15}N$ and accumulation rates in the Canary Islands region is presented in Figure 6. Highest production occurs under upwelling conditions on the African shelf. Resuspension and offshore particle transport result in very low accumulation of upwelling-derived particles on the shelf and high sedimentation on the slope between about 1000 and 2000 m water depth (Fütterer, 1983). A smaller part of these upwelling derived particles accumulates off the continental slope in the abyssal plain. However, since autochthonous production in these regions is low, upwelling derived particles may contribute to more than 50 % of total sediment accumulation. This high input will likely influence accumulation rates and sedimentological geochemical characteristics as shown by the stable nitrogen isotope ratio. Under these circumstances quantitative approaches estimating productivity variations by sedimentary organic carbon fluxes or nutrient availability by sedimentary stable nitrogen isotope ratios may have to be reconsidered in regions with strong productivity gradients like those imposed by continental margins (compare Holmes et al., 1999; Sarnthein et al., 1992).

In addition to lateral advection, organic matter degradation has a strong impact both on the magnitude of sediment accumulation and the geochemical composition. However, despite lateral advection and early diagenesis, the productivity gradient is still matched by higher

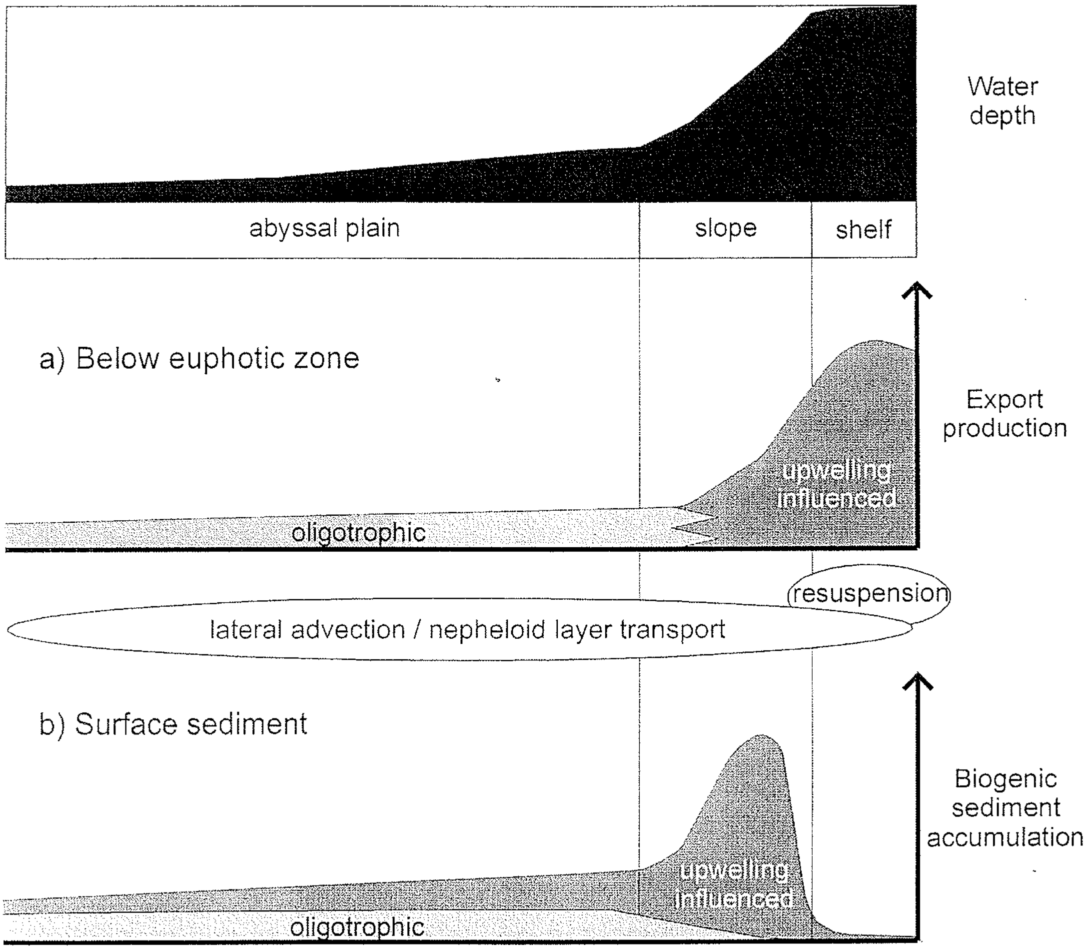

Fig. 6: Schematic presentation of productivity and sediment accumulation as influenced by shelf sediment resuspension and lateral transport of particulate matter off NW Africa along a productivity gradient including coastal upwelling and offshore oligotrophic conditions.

accumulation rates and lower $\delta^{15}N$ at the sediment surface of the upwelling influenced EBC compared to the oligotrophic ESTOC and LP. Thus, sedimentary organic matter accumulation and stable nitrogen isotope ratios may be used for a qualitative reconstruction of productivity variations and nutrient conditions in the Canary Islands region.

## CONCLUSION

The productivity gradient in the Canary Islands region is mirrored both in upper sediment traps and in surface sediments by higher particle fluxes and lower $\delta^{15}N$ at the upwelling-influenced site EBC compared to the oligotrophic sites ESTOC and LP. Thus, a qualitative estimation of productivity changes and nutrient availability by estimation of biogenic fluxes and stable nitrogen isotope ratios in sediments appears to be feasible. However, during settling and sedimentation the primary flux signal is overprinted by diagenetic processes as well as by lateral transport of particles, either due to downslope transport or due to lateral advection. Remineralisation of organic matter is responsible for a decrease of organic carbon and nitrogen fluxes and an overall increase in particulate $\delta^{15}N$. Less than 1 % of the organic export production is preserved in the sediments. The lateral transport of particles originating from the coastal high productivity region results in a coastal imprint on the sedimentation rates of the oligotrophic deep-sea area in the Canary Islands region. Thus, accumulation rates in sediments underlying oligotrophic waters are higher and $\delta^{15}N$ values are lower than would be expected from upper water column characteristics. Under these circumstances, quantitative approaches estimating productivity variations by sedimentary organic carbon fluxes or nutrient availability by sedimentary stable nitrogen isotope ratios may have to be reconsidered especially in regions with strong productivity gradients like continental margins.

## ACKNOWLEDGEMENTS

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## 2.3 Manuscript 3:

# Surface water properties recorded on the seafloor of the Canary Islands region through the distribution of geochemical and micropaleontological parameters

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## ABSTRACT

The Canary Islands region occupies a key position with respect to biogeochemical cycles, with the zonal transition from oligotrophic to nutrient-rich waters and the contribution of Saharan dust to the particle flux. We present the distribution of paleoceanographically significant geochemical proxies (TOC, carbonate, $\delta^{15}N$, $\delta^{13}C_{org}$, C/N-ratio) and micropaleontological parameters (diatoms, dinoflagellates, foraminifera, pteropods), within 80 surface sediment samples in order to characterise the influence of coastally upwelled water on the domain of the subtropical gyre. Thus, we characterise these geochemical and micropaleontological parameters as proxies for environmental conditions that can then be used for paleoceanographic reconstructions of past climatic cycles.

The data from the surface sediment analyses mirror the high biomass gradient from the coast to the open ocean, as observed by satellite data of surface chlorophyll or SST. The distribution of total dinoflagellate cysts, the planktic foraminifera species *Globigerina bulloides*, the diatom resting spore *Chaetoceros spp.* and the TOC coincided well with the areas of strong filament production off Cape Ghir and Cape Jubi, while the warm-water planktic foraminifera *Globigerinoides ruber* (white), the diatom *Nitzschia spp.* and the $\delta^{15}N$-values showed the opposite trend. Factor analyses on the planktic foraminifera species distribution indicate 3 major assemblages in the Canary Islands region which are representing the present surface water conditions from the upwelling influenced region via a mixing area towards the subtropical gyre.

## INTRODUCTION

Upwelling regions are of strong importance for the global $CO_2$-budget, since on the one hand they are $CO_2$-source areas through the upwelling of water masses which are enriched in dissolved inorganic carbon (carbonate/ physical pump) and on the other hand they act as $CO_2$-sinks through organic carbon production and resulting burial of organic carbon in the underlying sediments (biological pump) (Broecker, 1982; Berger, 1982; Berger and Keir, 1984; Berger and Wefer, 1990). Upwelling areas (coastal and open-ocean) are the source of more than 80 % of the present-day oceans new production, whereas the coastal upwelling itself account for more than 10 % (Brink et al., 1995). During the process of upwelling, cold and nutrient-rich subsurface water is brought to the surface. The nutrients provided by upwelling promote the growth of phytoplankton that forms the basis of the marine food chain. Consequently, most of the major fisheries areas of the world are situated in regions where strong upwelling occurs. This is also the case alongshore the NW African coast near the Canary Islands were intensive fishery activities took place (compare with Rodriguez et al. 1999).

Coastal upwelling is the response of the shelf waters to the alongshore wind stress (Mittelstaedt, 1991) and the strength and persistence of upwelling off NW Africa is coupled with the seasonal variation of the trade winds, which itself is coupled with the meridional shift of the Azores High. During summer the Azores High is situated northernmost and the boundary of the trade winds is located between 32°N and 20°N. In winter the Azores High is in its southernmost position with trade wind boundaries between 25°N and 10°N. Thus, upwelling is strong throughout the year between 25°N and 20°N, while north of 25°N, in the research area of the Canary Islands, upwelling occurs only in summer (Speth et al., 1978; Mittelstaedt, 1991; Hernández-Guerra and Nykjaer, 1997).

Upwelling and its main impact on the marine environment are usually restricted to the waters over the shelf and the upper slope region (Mittelstaedt, 1991). However, remarkable features in the satellite pictures of the research area off NW Africa are filaments of upwelled waters extending into the open ocean. The most striking feature for NW Africa is the giant filament off Cape Blanc, where cool and pigment-rich waters extend several hundred kilometres offshore (van Camp et al., 1991; Nykjaer and van Camp, 1994). Smaller filaments are also found north of this region in the area of the Canary Islands region at Cape Ghir (Hagen et al., 1996; Head et al., 1996) and Cape Jubi (Arístegui et al., 1994; Barton, 1998) (Fig. 1). In addition to this, unusual heating patterns are found in the shadow zone of winds and currents south of Cape Ghir (van Camp et al., 1991, Mittelstaedt, 1991) and south of the Canary Islands where current flow perturbation lead to eddy formation (Arístegui et al., 1994, 1997).

Large gradients of temperature and chlorophyll concentrations at the sea surface which could influence also the underlying sediments make upwelling areas particularly well suited for a combination of satellite, sedimentological and geochemical observations. The research area is located within the eastern part of the N-Atlantic subtropical gyre. The zonal current at the Azores at the northern boundary of the subtropical gyre is followed by anticyclonic flow turning to the south in three current bands; a first east of the Mid-Atlantic Ridge, a second in the Central Canary Basin and a third in the Canary Current close to the eastern boundary off NW-Africa (Stramma and Siedler, 1988). Along the coast, where the upwelling zone off NW Africa is restricted to a coastal band of about 50-70 km width, upwelling and related currents interact with the Canary Current (Mittelstaedt, 1991).

Stronger upwelling processes and associated higher productivity has often been proposed to explain lower atmospheric $CO_2$-contents during the last glacial periods (e.g. Sarnthein et al., 1988). Variations in atmospheric $CO_2$ in the Quaternary are well known from ice core studies and the glacial to interglacial $CO_2$ changes were a strong amplifier of climate variability (Neftel et al., 1982; Barnola et al., 1983; Lorius et al., 1990). The NW African upwelling area has often been cited as the type-example of the glacial high productivity (Sarnthein et al., 1988). Recently Bertrand et al. (1996) and Guichard et al. (1997, 1999) documented in the NW Africa upwelling system, that stronger productivity in glacial periods could even co-exist with stronger productivity in interglacial periods depending on the local hydrographical situation. Accordingly, the detailed assessment of regional ecosystems as sources or sinks of carbon and their quantitative $CO_2$-contributions to the global carbon cycle has to be worked out in future. Surface sediment studies are the first step and the basis for actualistic approaches for understanding the present-day conditions and, thus, to get a key for understanding the past climatic variations.

Major questions of this and following studies (compare with chapters 2.4 and 2.5) were therefore: 1.) How is the present day oceanographic condition reflected in the surface sediment? 2.) Which season is responsible for the determination of the surface sediment composition? 3.) Could the knowledge about the connection between present oceanographic condition and the sedimentology act as an actualistic tool to decipher the past?

Within this study we will compare monthly or annual SST and chlorophyll satellite data of the years 1997 and 1998 with the distribution of various proxies within the underlying sediments to understand to what extent a special season is determinant for the surface sediment record.

A good overview about sediment components most widely used as proxies for estimating upwelling intensity and productivity of surface water masses is listed within Brink et al. (1995). The use of these proxies in paleoceanography is described in detail in Fischer and Wefer (1999). In this study we will concentrate on the contents of total organic carbon (TOC), nitrogen and carbonate, the stable isotope ratio of the organic carbon ($\delta^{13}C_{org}$), nitrogen stable isotopes from bulk samples ($\delta^{15}N$) and changes in the assemblages of floral and faunal organisms (diatoms including key-species, dinoflagellates, foraminifera (planktic foraminifera including key-species), pteropods). All mentioned proxies undergo changes during the transport through the water column, at the seafloor or within the sediments, a major source of interference with productivity reconstruction (Jahnke and Shimmield, 1995). However, preservation and other changes rarely affect different components in the same fashion and therefore the multiproxy-approach will be the best method to gain a better understanding of upwelling in the Canary Islands region. Nevertheless, mechanisms affecting the various proxies will also be discussed in this study.

## MATERIAL AND METHODS

80 surface sediment samples (taken with multicorer and giant boxcorer) were recovered during 5 cruises with RV "Meteor" (M 37/1, M 38/1, M 42/4, M 45/5) and RV "Victor Hensen" (VH 96/1) from 1996 to 1999 (Neuer et al., 1997a, in press.; Wefer et al., 1997, 1999a; Fischer et al., 1998) (Fig. 1, Tab. 1).

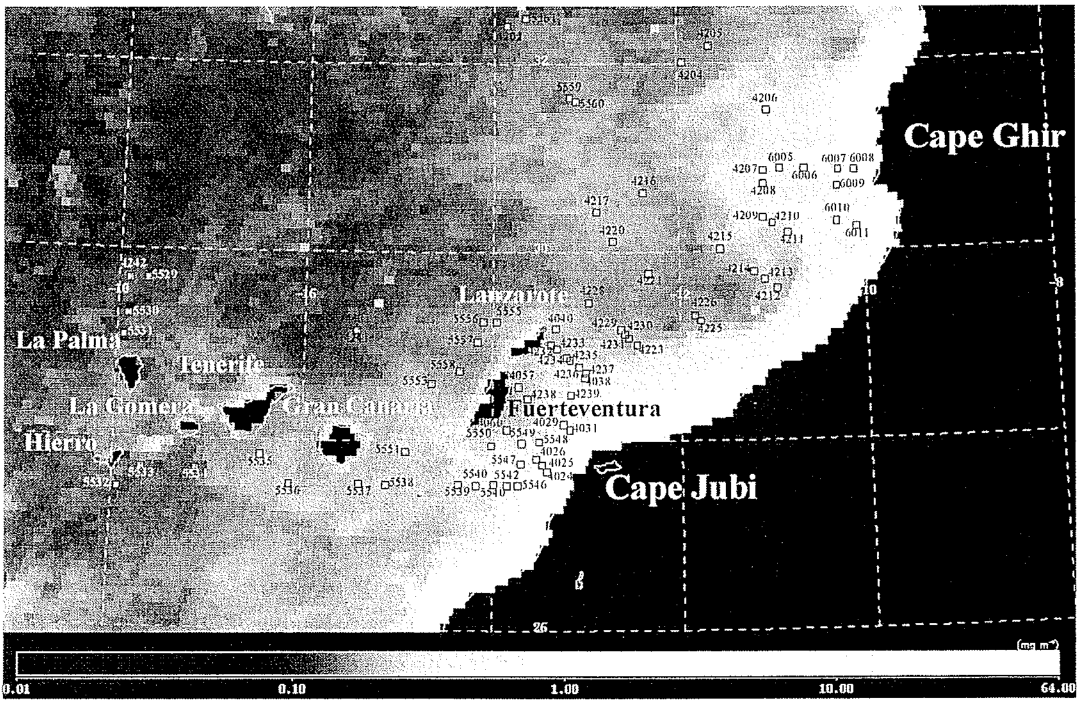

Fig. 1: Annual mean chlorophyll concentration in the Canary Islands region as observed by SeaWIFS. Data provided by the SeaWIFS Project, NASA/Goddard Space Flight Center. Squares represent surface sediment sites which have been investigated in this study.

As an actualistic approach surface sediment investigations of geochemical parameters and microfossils were performed to describe the spatial variability of these parameters. Various geochemical parameters (e.g. TOC, carbonate, nitrogen and $\delta^{15}N$) that are known from previous research as good upwelling indicators have been used (e.g. Müller et al., 1983; Brink et al, 1995; Hebbeln et al., 2000). Upwelling is also reflected in the micropaleontology and is characterised by a dominance of special diatom species (Abrantes, 1988; Bárcena and Abrantes, 1998; Abrantes and Moita, 1999), a dominance of special planktic foraminifera

Table 1: List of surface samples used in this study. Referred are cruise identifications and the analyses performed for each sample.

| Core GeoB | Latitude (°N) | Longitude (°W) | Water-Depth (m) | Device | Cruise | Geo-chemistry | oraminifera/ Pteropoda | Diatoms | Dino-flagellates |
|---|---|---|---|---|---|---|---|---|---|
| **4024-3** | 27°40.7 | 13°25.9 | 95 | GBC | VH 96/1 | x | x | x | |
| **4025-2** | 27°44.9 | 13°29.2 | 496 | GBC | VH 96/1 | x | x | x | |
| **4026-1** | 27°48.5 | 13°32.6 | 990 | GBC | VH 96/1 | x | x | x | |
| **4029-2** | 28°10.8 | 13°15.8 | 680 | GBC | VH 96/1 | x | x | x | |
| **4031-1** | 28°07.7 | 13°11.3 | 100 | GBC | VH 96/1 | x | x | x | |
| **4038-2** | 28°40.6 | 13°02.2 | 695 | GBC | VH 96/1 | x | x | x | |
| **4040-2** | 29°11.6 | 13°20.1 | 1000 | GBC | VH 96/1 | x | x | x | |
| **4057-2** | 28°35.0 | 13°44.1 | 1000 | GBC | VH 96/1 | x | x | x | |
| **4060-2** | 28°07.5 | 13°50.9 | 1000 | GBC | VH 96/1 | x | x | x | |
| **4202-1** | 32°28.6 | 13°39.8 | 4289 | GBC | M37/1 | x | x | x | x |
| **4204-1** | 32°01.1 | 11°56.7 | 3213 | GBC | M37/1 | x | x | x | x |
| **4205-1** | 32°10.9 | 11°38.9 | 3272 | GBC | M37/1 | x | x | x | x |
| **4206-2** | 31°30.0 | 11°01.3 | 1855 | GBC | M37/1 | x | x | x | x |
| **4207-1** | 30°51.8 | 11°04.3 | 2123 | GBC | M37/1 | x | x | x | x |
| **4208-1** | 30°42.8 | 11°04.7 | 2724 | GBC | M37/1 | x | x | x | |
| **4209-1** | 30°21.4 | 11°05.0 | 2150 | GBC | M37/1 | x | x | x | x |
| **4210-2** | 30°18.0 | 10°58.8 | 1959 | MUC | M37/1 | x | x | x | |
| **4211-1** | 30°11.6 | 10°49.3 | 1773 | MUC | M37/1 | x | x | x | x |
| **4212-3** | 29°36.2 | 10°57.0 | 1256 | MUC | M37/1 | x | x | x | x |
| **4213-1** | 29°41.8 | 11°04.7 | 1547 | MUC | M37/1 | x | x | x | |
| **4214-3** | 29°46.9 | 11°11.8 | 1788 | MUC | M37/1 | x | x | x | x |
| **4215-1** | 30°02.2 | 11°33.2 | 2106 | MUC | M37/1 | x | x | x | x |
| **4216-2** | 30°37.9 | 12°23.8 | 2325 | MUC | M37/1 | x | x | x | |
| **4217-1** | 30°26.1 | 12°53.7 | 2504 | MUC | M37/1 | x | x | x | |
| **4220-2** | 30°06.9 | 12°43.4 | 404 | GBC | M37/1 | x | x | | |
| **4221-2** | 29°46.5 | 12°20.3 | 1826 | MUC | M37/1 | | | | x |
| **4223-1** | 29°01.1 | 12°28.0 | 777 | MUC | M37/1 | x | x | x | x |
| **4225-3** | 29°16.5 | 11°46.9 | 1281 | MUC | M37/1 | x | x | x | |
| **4226-1** | 29°19.2 | 11°50.0 | 1400 | MUC | M37/1 | x | x | x | |
| **4227-1** | 29°46.1 | 12°20.2 | 1826 | MUC | M37/1 | x | x | x | |
| **4228-1** | 29°28.2 | 12°59.4 | 1633 | MUC | M37/1 | x | x | x | x |
| **4229-2** | 29°10.9 | 12°38.3 | 1422 | MUC | M37/1 | x | x | x | |
| **4230-1** | 29°07.7 | 12°35.8 | 1316 | MUC | M37/1 | x | x | x | |
| **4231-2** | 29°05.2 | 12°33.1 | 1197 | MUC | M37/1 | x | x | x | |
| **4232-1** | 29°01.3 | 13°23.2 | 1161 | MUC | M37/1 | x | x | x | |
| **4233-2** | 28°58.5 | 13°19.8 | 1303 | MUC | M37/1 | x | x | x | |
| **4234-1** | 28°53.4 | 13°13.6 | 1360 | MUC | M37/1 | x | x | x | |
| **4235-1** | 28°51.4 | 13°11.4 | 1247 | MUC | M37/1 | x | x | x | |
| **4236-2** | 28°47.0 | 13°05.7 | 1030 | MUC | M37/1 | x | x | x | |
| **4237-1** | 28°43.7 | 13°01.0 | 800 | MUC | M37/1 | x | x | x | x |
| **4238-2** | 28°27.1 | 13°38.1 | 1185 | MUC | M37/1 | x | x | x | |
| **4239-1** | 28°29.6 | 13°10.8 | 881 | MUC | M37/1 | x | x | x | x |
| **4241-5** | 29°10.0 | 15°27.2 | 3610 | GBC | M37/1 | | | | x |
| **4242-4** | 29°40.9 | 17°53.4 | 4292 | GBC | M37/1 | x | x | | |
| **4301-1** | 29°10.0 | 15°27.2 | 3610 | MUC | M38/1 | x | x | x | |

| Core GeoB | Latitude (°N) | Longitude (°W) | Water-Depth (m) | Device | Cruise | Geo-chemistry | oraminifera/ Pteropoda | Diatoms | Dino-flagellates |
|---|---|---|---|---|---|---|---|---|---|
| **5529-1** | 29°41.4 | 17°41.9 | 4166 | MUC | M42/4 | x | x | x | |
| **5530-3** | 29°18.2 | 17°53.8 | 3985 | MUC | M42/4 | x | x | | |
| **5531-1** | 29°04.8 | 17°55.5 | 3301 | MUC | M42/4 | x | x | | |
| **5532-2** | 27°28.3 | 17°56.0 | 3150 | MUC | M42/4 | x | x | | |
| **5533-1** | 27°40.9 | 17°41.6 | 3251 | MUC | M42/4 | x | x | | |
| **5534-2** | 27°40.7 | 17°07.8 | 2832 | MUC | M42/4 | x | x | | |
| **5535-1** | 27°50.6 | 16°27.2 | 2690 | MUC | M42/4 | x | x | | |
| **5536-3** | 27°32.2 | 16°08.1 | 3456 | MUC | M42/4 | x | x | | |
| **5537-2** | 27°32.1 | 15°24.1 | 2362 | MUC | M42/4 | x | x | | |
| **5538-2** | 27°32.2 | 15°07.0 | 2537 | MUC | M42/4 | x | x | | |
| **5539-2** | 27°32.2 | 14°21.3 | 2202 | MUC | M42/4 | x | x | | |
| **5540-3** | 27°32.1 | 14°10.5 | 2035 | MUC | M42/4 | x | x | | |
| **5541-2** | 27°32.2 | 13°59.7 | 1748 | MUC | M42/4 | x | x | | |
| **5542-3** | 27°32.2 | 13°50.8 | 1431 | MUC | M42/4 | x | x | | |
| **5546-3** | 27°32.2 | 13°44.2 | 1071 | MUC | M42/4 | x | x | | |
| **5547-2** | 27°45.6 | 13°42.6 | 1310 | MUC | M42/4 | x | x | | |
| **5548-3** | 27°59.5 | 13°31.1 | 1162 | MUC | M42/4 | x | x | | |
| **5549-2** | 27°58.7 | 13°41.7 | 1454 | MUC | M42/4 | x | x | | |
| **5550-3** | 27°57.1 | 14°00.9 | 1738 | MUC | M42/4 | x | x | | |
| **5551-2** | 27°52.6 | 14°54.9 | 1885 | MUC | M42/4 | x | x | | |
| **5553-2** | 28°36.6 | 14°38.7 | 3397 | MUC | M42/4 | x | x | | |
| **5555-2** | 29°16.0 | 13°57.4 | 2837 | MUC | M42/4 | x | x | | |
| **5556-3** | 29°15.9 | 14°06.6 | 3170 | MUC | M42/4 | x | x | | |
| **5557-2** | 29°02.7 | 14°09.9 | 2949 | MUC | M42/4 | x | x | | |
| **5558-2** | 28°44.7 | 14°21.2 | 2471 | MUC | M42/4 | x | x | | |
| **5559-1** | 31°38.7 | 13°11.2 | 3178 | MUC | M42/4 | x | x | | |
| **5560-2** | 31°36.6 | 13°07.1 | 3944 | MUC | M42/4 | x | x | | |
| **5561-1** | 32°42.2 | 12°56.1 | 3500 | MUC | M42/4 | x | x | | |
| **6005-1** | 30°52.8 | 10°53.8 | 1781 | MUC | M45/5 | x | x | | |
| **6006-2** | 30°52.1 | 10°37.8 | 1275 | MUC | M45/5 | x | x | | |
| **6007-1** | 30°51.1 | 10°16.0 | 899 | MUC | M45/5 | x | x | | |
| **6008-2** | 30°50.7 | 10°05.9 | 355 | MUC | M45/5 | x | x | | |
| **6009-1** | 30°40.9 | 10°16.5 | 579 | MUC | M45/5 | x | x | | |
| **6010-1** | 30°15.0 | 10°05.0 | 406 | MUC | M45/5 | x | x | | |
| **6011-2** | 30°18.9 | 10°17.3 | 993 | MUC | M45/5 | x | x | | |

species (Bé and Tolderlund, 1971; Thiede, 1971, 1975; Hilbrecht, 1996) and certain dinoflagellate cysts (Zonnefeld, 1997; Targarona et al., 1999), a decrease in pteropods (Thiede, 1975; Ganssen and Lutze, 1982), and a high standing stock of benthic foraminifera (Lutze, 1980; Lutze and Coulbourn, 1984). With respect to the various micropaleontological proxies, different numbers of samples have been investigated for species composition in this study.

The regional distribution of all investigated parameters were plotted using the PC-program OceanDataView (Schlitzer, 2000). The gridding method uses a variable grid with increased resolution and smaller averaging length scales in the upwelling-influenced positions where most sampled sites are situated.

## Geochemical analyses

Prior to the geochemical analyses, sediment samples were freeze-dried and homogenized. Total carbon (TC) and total nitrogen (TN) were measured on non-acidified samples while TOC was measured on acidified samples using a CHN-Analyzer (Haereus). Analytical standard deviation calculated for repeated measurements was 1.6 % for carbon and 2.0 % for nitrogen concentration. Carbonate content was calculated assuming that calcium carbonate was the only carbonate-bearing mineral ($CaCO_3$ = (TC – TOC) * 8.33). The carbon/nitrogen-ratio (C/N ratio) represents the weight ratio of organic carbon and total nitrogen.

For the measurement of $\delta^{15}N$ and $\delta^{13}C_{org}$, sediment samples were combusted at 1050 °C in a NC 2500 Elemental Analyzer (CE Instruments). The $\delta^{15}N$ and $\delta^{13}C$ of the gas thus formed was measured using a Finnigan MAT delta plus mass spectrometer. The stable nitrogen isotope ratio of TN was measured on non-decalcified samples. Nitrogen isotope ratios are reported with reference to air nitrogen ($\delta^{15}N$ (‰) = $((^{15}N/^{14}N_{sample}) / (^{15}N/^{14}N_{air}) - 1) * 1000$). $\delta^{13}C_{org}$ samples of METEOR cruises M 37/1, M 38/1 and VH 96/1 were decalcified with 1M HCl and washed with pure water. Samples from METEOR cruises M 42/4 and M 45/5 were decalcified with 6M HCl in silver boats. However, no significant differences of the $\delta^{13}C_{org}$ using the two decalcification methods have been observed (Rühlemann, 1996). For carbon isotope measurements we used a working standard (Burgbrohl $CO_2$ gas), which has been calibrated with NBS 18, 19, and 20 standards against PDB. Precision calculated from repeated measurements on laboratory sediment standard was about ± 0.1 ‰ for $\delta^{13}C_{org}$ and ± 0.2 ‰ for $\delta^{15}N$.

## Micropaleontological analyses

### *Diatoms*

The presence of diatoms, for a preliminary view, was investigated by the analysis of a smear-slide prepared for each sample. For quantitative analysis, 2 $cm^3$ of fresh sediment was taken from each sample, weighed, dried, weighed again and cleaned according to the method of Fenner (1982). Slides were prepared using the evaporation tray method of Battarbee (1973), and mounted with Permount medium. These slides were examined under a Nikon Labophot 2 microscope equipped with DIC (Differential Interference Contrast) and using 10 x eyepieces and 100 x objectives. Diatoms, silicoflagellates, radiolariens, dinoflagellates (Actyniscus) and phytoliths were counted in three of the four slides prepared from each sample following Abrantes et al. (1994). The considered siliceous microfossils were counted in 100 randomly selected fields of view per slide. Absolute abundances are expressed as number of valves per g of dry sediment (valv./g). The relative abundance of diatom species was determined for each sample following the counting procedures of Schrader and Schuette (1968). In general, for each sample about 300 specimens were identified and raw counts were then converted to percent abundance. In samples containing very few diatoms, the number of specimen counted was usually not higher than 200 or even 100.

*Planktic and benthic foraminifera and pteropods*

Sediment samples for coarse fraction analyses were freeze-dried, weighed, and washed on a sieve with 63 µm mesh size. After splitting in further subfractions, the coarse fraction >125 µm was splitted into aliquots of at least 300-500 particles and quantified. Planktic foraminifera species and various other particles including benthic foraminifera and pteropods have been identified within the coarse fraction (>125 µm) with a light microscope. Absolute abundances are expressed as specimen per g of dry sediment (spec./g).

As an indicator for carbonate preservation the number of fragmented planktic foraminifera species were counted and expressed as percentages of the total number of planktic foraminifera (Thunell, 1976).

The good correlation of SST and micropaleontology data within surface sediments was firstly and successfully used by Imbrie and Kipp (1971) and Kipp (1976) for a reconstruction of the past SST changes in sediment cores by using factor analyses and transfer functions. Accordingly, we have used factor analyses to combine planktic foraminifera species in assemblages to compare these with the present-day satellite-derived SST and chlorophyll concentration of the region. Since two species (*Globigerina bulloides* and *Globigerinoides ruber* (white-variety)) are dominating the Canary Islands region surface sediments, we have used the natural logarithm of the percentages of each planktic foraminifera species to get species assemblages.

The taxonomy follows Hemleben et al. (1989) with the exception that we have named the species *Neogloboquadrina pachyderma* dextral *Neogloboquadrina incompta* following Cifelli (1961) and Meggers and Baumann (1997). In addition, we have differentiated *N. incompta* in species with 4 and with >4.5 chambers. Since species of the *Globorotalia menardii* group are very rare in the surface sediments of the Canary Islands region they were grouped together.

Factor analyses were calculated with the program package CAPFAC (Imbrie and Kipp, 1971).

### *Dinoflagellates*

For counting of total dinoflagellate cysts 1.5-2 g of dried sediment sample was treated with 10 % HCl for carbonate removal. Subsequently, 38 % HF was added and the samples were agitated for two hours. The acid was decanted and the residue was sieved through a 20 µm sieve. The residue remaining on the sieve was transferred to a glass tube and centrifuged. From the glass-tube, the residue was transferred to a reaction vessel with a 0.5 ml scale interval and concentrated to a 1 ml volume. From this vessel, with a pipette, 50 µl of homogenised residue were placed on a slide, embedded with glycerine jelly, and sealed with paraffin wax. The whole slides were counted using a microscope and the counts were expressed qualitatively in cysts per g dry sediment.

### Satellite data

Pflaumann et al. (1996) have already discussed in detail the importance of densely spaced SST data for surface sediment calibration needed especially in regions with a strong thermal gradient in the surface waters. By comparing satellite SST data of the years 1997 and 1998 with the climatological atlas (Levitus and Boyer, 1994) off NW Africa in the coastal upwelling area it is obvious that significant local temperature features like the Cape Jubi filament were not resolved by the 1° * 1° grid of Levitus and Boyer (1994). Consequently, SST has been computed from Advanced Very High Resolution Radar (AVHRR) radiances operational since 1981 for the years 1997 and 1998. Data are mapped into an equal-angle projection of 9 km resolution. Pigment concentration of the year 1997 is derived from the Sea-viewing Wide Field-of-view Sensor (SeaWIFS). SeaWIFS was launched in August 1997 and is a multi-channel scanning spectrometer, which observes the ocean surface in 8 spectral bands with the same 9 km resolution as AVHRR. The satellite derived hydrographical data were used for correlations with sedimentological proxies.

## RESULTS

### Geochemical results

The geochemical parameters shown here are TOC and carbonate content, carbon/nitrogen ratio, the nitrogen stable isotope signal of the bulk sediment ($\delta^{15}N$) and the stable carbon isotope signal of the organic fraction of the sediment ($\delta^{13}C_{org}$).

The TOC content within the Canary Islands surface sediments ranges from 0.34 % to 1.87

% (Fig. 2A). The spatial variability of TOC content shows a zonal gradient with highest values off the capes and low values in the open ocean. Highest TOC contents are recognised at Cape Ghir (1.87 % at site GeoB 6007-1), while Cape Jubi shows contents up to 1.55 % at site GeoB 5546-3. The lowest values (<0.6 %) are found north of La Palma and in the near shore sites GeoB 4024-3 or GeoB 4220-2.

Since the use of TOC as an indicator for productivity requires a major marine derived source of the organic carbon, the C/N-ratio was also determined (Fig 2B). The C/N-ratios are usually used to characterise the organic material within sediments in terms of terrigenous and marine components. In the whole research area C/N-ratios are between 6.3 and 14 that is in the range of marine organic carbon. Lowest values are found off Cape Ghir. However, a gradient from values of about 8 at sites GeoB 6007-1 and GeoB 6008-2 nearest to Cape Ghir towards ratios of 6.3 at site GeoB 4211-1 is obvious. Highest C/N-ratios between 11 and 12 are analysed north of La Palma at site GeoB 4242-4 (12.06) and GeoB 5531-1 (11.24). One C/N-ratio at GeoB 4220-2 is outstanding with a value of 13.95.

The spatial variability of the $\delta^{15}N$ as a nutrient indicator shows a distribution inverse to the TOC content, thus, lowest $\delta^{15}N$-values are measured off the capes (Fig. 2C). Cape Ghir is characterised by the lowest $\delta^{15}N$-values. From site GeoB 6007-1 to GeoB 6010-1 values ranges between 4.59 and 5.17 ‰. Cape Jubi shows also light $\delta^{15}N$-values at sites GeoB 4025-2 (5.23 ‰), GeoB 5546-3 (5.40 ‰) and GeoB 5547-2 (5.44 ‰). Highest $\delta^{15}N$-values are found in offshore positions such as GeoB 4242-4 north of La Palma (7.14 ‰), GeoB 4204-2 (6.99 ‰) and GeoB 5533-1 (6.97 ‰) east of Hierro. Overall the $\delta^{15}N$-values increase from east to west along the productivity gradient. However, different to the TOC distribution, a NNE-SSW-belt with light values is evident from seamounts positions north of the Canary Islands (e.g. GeoB 5561-1 (5.92 ‰)) via an area west Fuerteventura/Lanzarote (e.g. GeoB 5558-2 (5.58 ‰)) towards an area south of Tenerife and Gran Canaria (e.g. GeoB 5535-1 (5.48 ‰) or GeoB 5536-3 (5.94 ‰)).

The $\delta^{13}C_{org}$ is as the C/N-ratio another useful proxy to determine the ratio between terrigenous and marine derived organic matter. Values range between –21.16 ‰ at GeoB 5531-1 north of La Palma and –19.55 ‰ at GeoB 5555-2 west of Lanzarote typical for marine organic matter (compare with Wagner and Dupont, 1999). From the $\delta^{13}C_{org}$-dataset not only a strong zonal gradient is visible, but a meridional gradient is also obvious (Fig. 2D). Heaviest values are found in the area off Cape Jubi with a decrease towards the north pointing to a relative increase of terrigenous organic matter towards Cape Ghir.

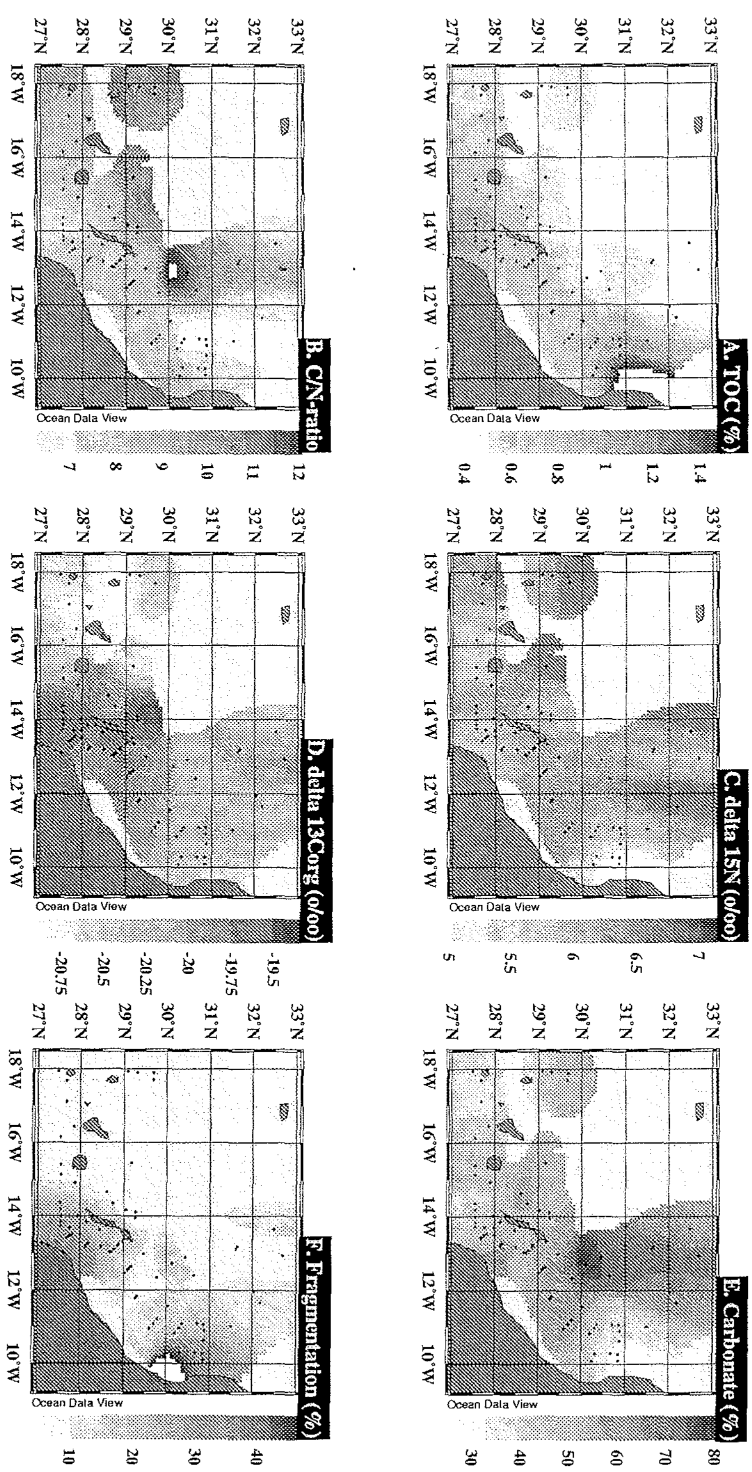

Fig. 2: Spatial distribution of geochemical parameters in the surface sediments from the Canary Islands region (A: Total organic carbon (TOC) in %; B: Carbon/nitrogen-ratio (C/N-ratio); C: $\delta^{15}N$ of the bulk sediment in ‰; D: $\delta^{13}C$ of the organic fraction in ‰; E: Carbonate content in %; F: Fragments of planktic foraminifera in % of the total number of planktic foraminifera).

To interpret the distribution of carbonate bearing organisms and access organic particle dilution within the surface sediment, we also need information on sediments carbonate content (Fig. 2E). The carbonate content is, in contrast to the TOC, low off the capes. Overall, the carbonate content ranges from values of 24.91 % at site GeoB 6008-2 off Cape Ghir towards 87.11 % at site GeoB 4220-2. Lowest values are evident near shore in the areas of both capes and south of the Canary Islands nearby Hierro (e.g. at site GeoB 5533-1). At the latter position also high numbers of volcanic ash grains are present within the sediments (not shown).

The fragmentation index of planktic foraminifera species helps to detect areas where carbonate dissolution takes place (Fig. 2F). The percentages of fragments within the planktic foraminifera assemblages range from 4.0 % at GeoB 4217-1 to 65.5 % at GeoB 6010-1 off Cape Ghir. Overall, the highest percentages of fragmented planktic foraminifera tests are found in the areas off the capes pointing to stronger carbonate dissolution at these sites.

### Micropaleontological results

In this section percentages of the >63 µm-fraction, the numbers of planktic and benthic foraminifera, diatoms, dinoflagellate and pteropods (expressed as valves, cysts and specimen per g dry sediment) of the investigated surface sediments will be shown.

The >63 µm fraction values are useful to detect allochthonous particles within the sample set, because turbidites, shelf–influenced samples and dilution by non-biogenic particles could be detected (Fig. 3G). The >63 µm fraction ranges from 0.8 % at GeoB 6008-1 off Cape Ghir towards highest values at GeoB 4220-2 (78.9 %), GeoB 4031-1 (88.5 %) and GeoB 4024-3 (94.1 %). These shelf samples are also characterised by high carbonate contents (see above). High numbers of shelf-derived carbonate particles like fragments of molluscs, bryozoans and corals are evident in the shelf samples GeoB 4024-3 and GeoB 4031-1. These samples have not to be considered for correlations with surface water SST and chlorophyll since the geochemical/micropaleontological characteristics are masked by the dilution of allochthonous particles. The sample GeoB 4220-2 is taken from the Conception Bank Seamount north of the Canary Islands in a water-depth of 400 m and like the shelf samples contains high amounts of molluscs- and coral fragments. Disregarding all these samples, the region off Cape Ghir and Cape Jubi is characterised by fine-grained sediments, whereas the offshore positions contain increased amounts of coarse fraction.

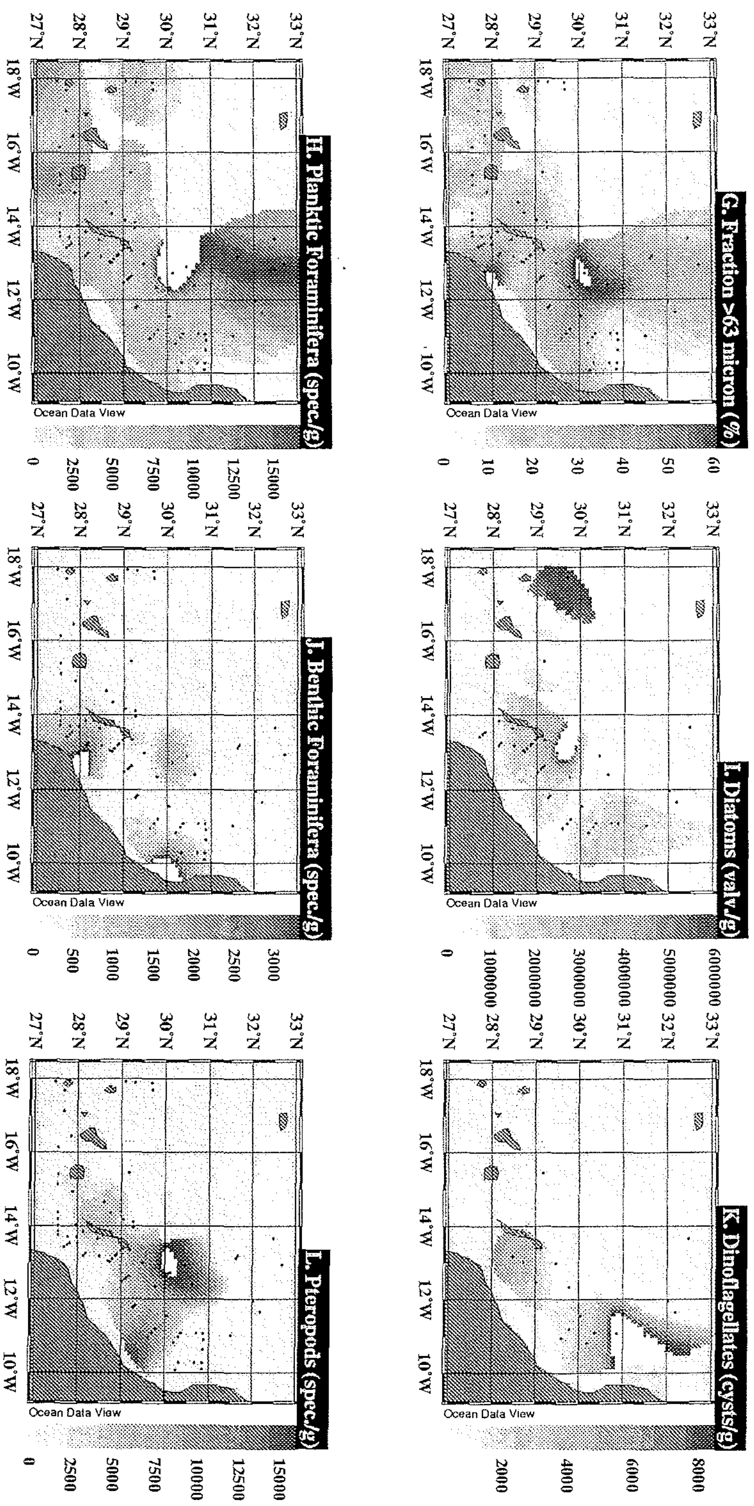

Fig. 3: Spatial distribution of micropaleontological parameters in surface sediments from the Canary Islands region (G: Fraction >63 µm in %; H: planktic foraminifera in specimen per g dry sediment; I: diatoms in valves per g dry sediment; J: benthic foraminifera in specimen per g dry sediment; K: dinoflagellates in cysts per g dry sediment; L: pteropods in specimen per g dry sediment).

The planktic foraminifera content ranges from values of 84 spec./g at GeoB 6008-1 off Cape Ghir to values of >16,000 spec./g at GeoB 5560-2 and mimics the >63 μm size distribution (Fig. 3H). An outstanding high value of >30,000 spec./g is again obvious at the shallow-water seamount position at GeoB 4220-2. Highest contents are recognised north of Lanzarote, south of Gran Canaria and south of Hierro.

Diatom concentration are highest in two samples, one at site GeoB 4228-1 ($11.1*10^6$ valv./g) north of Lanzarote and another north of La Palma in site GeoB 5529-1 ($6.0*10^6$ valv./g) (Fig. 3I). No diatoms are found at sites GeoB 4029-2, GeoB 4060-1 and GeoB 4231-2 and at the above mentioned shelf positions GeoB 4024-3 and 4031-1. However, a significant decrease in the amount of diatoms from $3.2 *10^6$ valv./g (GeoB 4207-1) to $0.2*10^6$ valv./g (GeoB 4217-1) can be observed within the surface sediments possibly reflecting the filament extension off Cape Ghir.

The spatial distribution of benthic foraminifera shows two clear maxima off Cape Ghir and Cape Jubi (Fig. 3J). Maximal contents are recognised in site GeoB 6010-1 (7,100 spec./g) and site GeoB 4025-2 (4,300 spec./g) for Cape Ghir and Cape Jubi respectively. Benthic foraminifera are absent at site GeoB 5558-2 and rare north of La Palma (<20 spec./g).

A similar distribution pattern in spite of the lower sample resolution is seen in the dinoflagellate cyst distribution (Fig. 3K). Highest numbers of dinoflagellates cysts are recognised off Cape Ghir in site GeoB 4207-1 (13,000 cysts/g) and lowest numbers were observed north of Gran Canaria at site GeoB 4241-5 (192 cysts/g). Samples closest to the Cape Ghir are dominated by *Lingulodinium machaerophorum*, *Gymnodinium spp* and *Protoperidinium spp*. These dinoflagellate cysts are usually found in high productivity and upwelling regions (e.g. Dale and Fjellså, 1994). A detailed description of the species distribution is given by Targarona et al. (1999).

Pteropods consist of aragonite that is easily dissolved in the water column or within the surface sediments. Thus, there is a good negative correlation between the occurrence of pteropod tests and fragmented planktic foraminifera (see above) (Fig. 3L). Highest numbers are observed in a distinct region between the two capes with contents up to 12,300 spec./g in site GeoB 4212-3. The seamount sample GeoB 4220-2 again shows the highest content (19,000 spec./g) due to its low water-depth, less carbonate dissolution and the distance to the upwelling centre. The samples north of La Palma and off the capes are barren of pteropods.

### Planktic foraminifera and diatom species results

Due to the best sample resolution we have chosen four species from two organism groups, the diatoms as a representative of the phytoplankton and the planktic foraminifera as a representative of the zooplankton to show how the species composition of this two groups mirror the productivity gradient in the Canary Islands region.

The distribution of *Chaetoceros spp.* resting spores shows highest relative abundances (>50 %) off Cape Ghir at sites GeoB 4208-1 (62.1 %) and GeoB 4207-1 (52.2 %) (Fig.4M). Lowest contents are recognised at site GeoB 4223-2 (3.4 %). The Cape Jubi filament is not mirrored probably due to the fact that only a few samples are counted for diatoms in this area. Another maximum in relative abundances of *Chaetoceros spp.* is located north of La Palma at site GeoB 5529-1 (34.9 %).

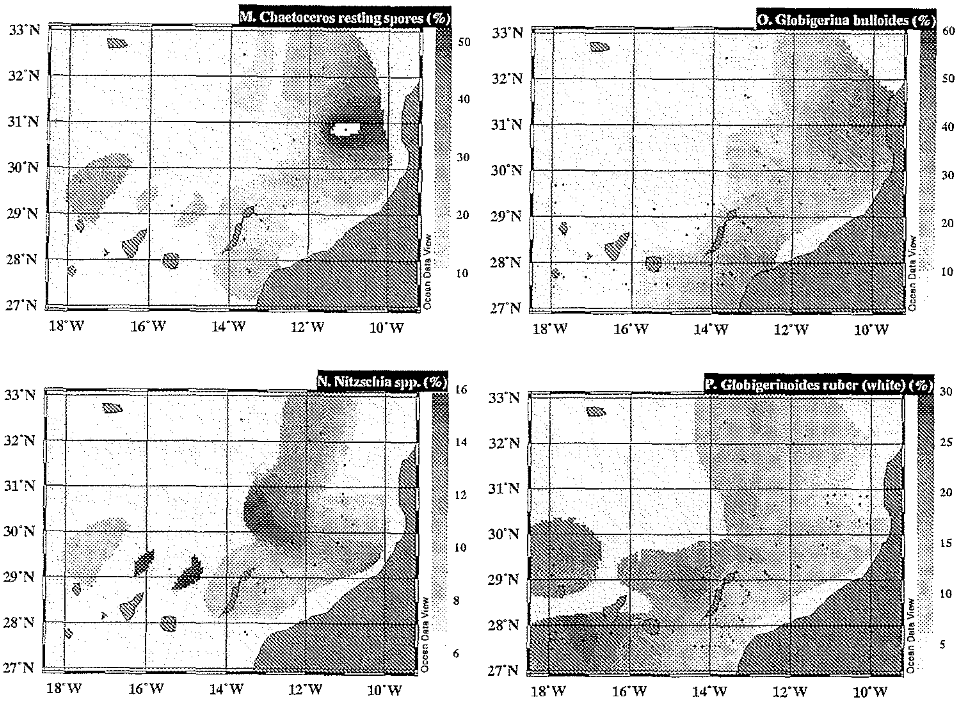

Fig. 4: Spatial distribution of the relative abundances of diatom and planktic foraminifera species in surface sediments from the Canary Islands region (M: Diatom *Chaetoceros spp.* resting spores in %; N: Diatom *Nitzschia spp.* in %; O: Planktic foraminifera *Globigerina bulloides* in %; Planktic foraminifera *Globigerinoides ruber* (white-variety) in %).

An opposite trend is shown by the relative abundances of *Nitzschia spp.* (Fig 4N). This species shows lowest relative abundances in the area nearby Cape Ghir (e.g. site GeoB 4207-1 with 5.7 %) and higher abundances in a belt 60 nm offshore (e.g. site GeoB 4227-1 (15.2 %) and GeoB 4217-1 (15.2 %)). The maximum relative abundance is reached north of Gran Canaria at site GeoB 4301-1 (15.8 %).

In the planktic foraminifera datasets high relative abundances of *G. bulloides* are obvious at both capes with maxima at site GeoB 6008-2 (61.4 %) for Cape Ghir and at site GeoB 5546-3 (46.3 %) for Cape Jubi (Fig. 4O). High relative abundances are also evident in the two shelf samples GeoB 4031-1 (60.0%) and GeoB 4024-3 (55.9%) which both are situated in the Cape Jubi domain. Intermediate relative abundances of *G. bulloides* (20 to 30 %) are present between the two capes east of the Canary Islands. Offshore we find the lowest relative abundances of *G. bulloides* at site GeoB 5533-1 (1.5 %) east of Hierro and GeoB 5530-13 (1.5 %) north of La Palma. In both cases, north and south of the Canary Islands, a strong zonal decrease from the capes towards the subtropical gyre is reflected.

The second investigated planktic foraminifera *G. ruber* (white) shows a spatial distribution opposite to *G. bulloides* (Fig. 4P), with maximum relative abundances in the open ocean south of the Canary Islands (29.6 % at site GeoB 5534-2) and north of the Canary Islands (33.8 % at site GeoB 5558-2). Minima are obvious in both cape regions, at site GeoB 6008-2 (2.5 %) off Cape Ghir and at site GeoB 5546-3 (7.6 %) off Cape Jubi. Low relative abundances of *G. ruber* (white) are also found in the shelf samples GeoB 4031-1 (2.0 %) and GeoB 4024-3 (5.9 %) nearby Cape Jubi.

### Planktic foraminifera factor analyses

A Q-mode principal component analysis including 78 surface sediment samples and 25 planktic foraminifera taxa/groups from the Canary Islands region was calculated in order to combine 25 planktic foraminifera species into factors. 3 factors explain 94.2 % of the total variance (Tab. 2). The model provides high communality values (>0.83) for all samples except the site GeoB 4024-3 with a communality value of 0.65.

Factor 1 (Fig. 5Q) explains 32.0 % of the total variance and is mainly determined by *Globigerina falconensis*, *G. ruber* (white), *Globigerinoides ruber* (pink) and *Globigerinita glutinata* (Tab. 2). *G. bulloides* is anticorrelated to this assemblage. This factor is called the "warm-water factor" and represents the water masses of the subtropical gyre. The spatial distribution of the varimax-rotated Q-mode principal component scores (Fig. 5Q) is similar to the distribution of the relative abundance of *G. ruber* (white) (Fig. 4P). Highest scores are obvious north of La Palma at site GeoB 5531-1 (0.83) and south and east of Hierro at sites GeoB 5532-2 and GeoB 5533-1 (both 0.81). Lowest scores are present in a coastal band from Cape Ghir to Cape Jubi.

Factor 2 (Fig. 5R) explains 31.2 % of the total variance and is dominated by *G. bulloides*. Next to this species *N. incompta*, *Globorotalia inflata* and *Turborotalita quinqueloba* are represented in this "upwelling/filament factor" (Tab. 2). The geographic distribution of the factor scores in the surface sediment samples indicate highest scores exclusively off Cape Ghir and Cape Jubi. Sites GeoB 6009-1 (-0.78) and GeoB 6010-1 (-0.77) are representing Cape Ghir and sites GeoB 5546-3 (-0.77) and GeoB 4029-2 (-0.73) Cape Jubi. Lowest scores are present north of La Palma at site GeoB 5529-1 with a value of –0.30.

Factor 3 (Fig. 5S) is filling in the gap between highest scores of factor 2 at the capes and highest scores of factor 1 far offshore. Factor 3 explains 31.0 % of the total variance and is dominated by an assemblage consisting out of *Globigerinella siphonifera*, *G. bulloides*, *Turborotalia humilis*, *Globigerinella calida* and *Pulleniatina obliquiloculata* (Tab. 2). This factor is called the "mixing factor". Its spatial distribution of factor scores shows highest values east of the Canary Islands. The length-axis of the Canary Islands Fuerteventura and Lanzarote is in its NE-SW direction a direct boundary to factor 1. Highest scores of factor 3 are obvious in site GeoB 4232-1 (0.82) and lowest scores off Cape Ghir and Cape Jubi (e.g. in site GeoB 6009-1 (0.28) or GeoB 5542-3 (0.33)).

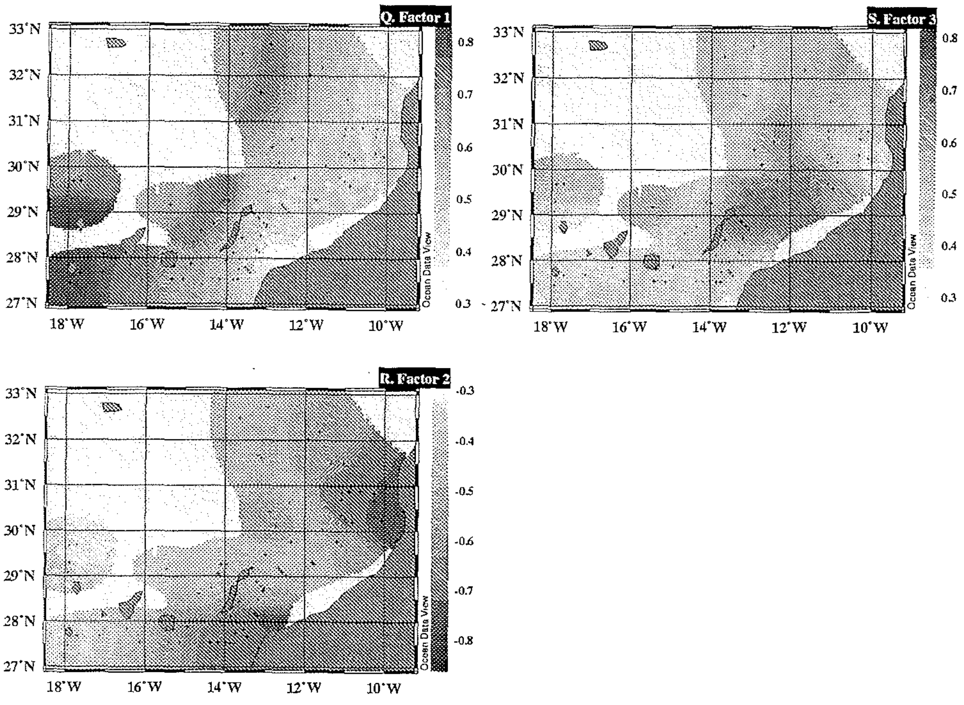

Fig. 5: Spatial distribution of factor scores derived from a factor analyses on the planktic foraminifera assemblage in surface sediments from the Canary Islands region (Q: Factor 1 "warm-water factor"; R: Factor 2 "upwelling/filament factor"; S: Factor 3 "mixing factor").

Table 2: Factor loadings of the 3 factors as determined from factor analyses of the relative abundances of the planktic foraminfera in the Canary Island region. The relevant species are marked in bold.

| **Species** | **Factor 1** | **Factor 2** | **Factor 3** |
|---|---|---|---|
| *G. bulloides* | **-0.33** | **-0.766** | **0.341** |
| *G. falconensis* | **0.451** | -0.106 | -0.172 |
| *T. quinqueloba* | 0.11 | **-0.258** | -0.141 |
| *T. humilis* | 0.243 | 0.137 | **0.327** |
| *G. rubescens* | **0.371** | -0.166 | -0.055 |
| *G. calida* | 0.042 | -0.043 | **0.285** |
| *G. siphonifera* | -0.096 | 0.144 | **0.487** |
| *G. ruber* pink | 0.135 | 0.01 | 0.031 |
| *G. ruber* white | **0.412** | -0.01 | 0.246 |
| *G. sacculifer* | 0.138 | 0.029 | **0.302** |
| *G. conglobatus* | -0.071 | 0.087 | 0.227 |
| *G. tenellus* | 0.146 | -0.022 | 0.097 |
| *O. universa* | 0.071 | -0.077 | 0.038 |
| *N. dutertrei* | 0.038 | 0.044 | 0.089 |
| *N. pachyderma* | -0.016 | -0.162 | -0.055 |
| *N. incompta* | 0.123 | **-0.301** | -0.097 |
| *N. incompta* (>4 chambers) | 0.177 | -0.149 | -0.052 |
| *P. obliquiloculata* | 0.03 | 0.015 | **0.252** |
| *G. glutinata* | **0.331** | -0.034 | 0.141 |
| *G. hirsuta* | 0.135 | 0.016 | -0.005 |
| *G. theyeri* | -0.037 | -0.034 | 0.019 |
| *G. crassaformis* | -0.078 | 0.084 | 0.248 |
| *G. inflata* | 0.122 | **-0.294** | 0.007 |
| *G. truncatulinoides* | 0.155 | -0.098 | 0.025 |
| *G. scitula* | 0.083 | 0.063 | 0.147 |

## DISCUSSION

The coastal upwelling processes along the Moroccan coast are more pronounced around capes, which are sites of filament production. These filaments are exporting substantial biomass into the oligotrophic portions of the N Atlantic gyre and are likely to superimpose their signal on the sediments. Most parameters within the surface sediments correspond well to this surface water phytoplankton biomass as recorded by historic satellite derived pigment data (van Camp et al., 1991; Davenport et al., 1999). Decreases of surface water phytoplankton biomass with increasing distance to the upwelling area were matched by the surface sediment distribution of key-species of diatoms and planktic foraminifera, by decreasing dinoflagellate cyst contents, increasing $\delta^{15}N$, decreasing TOC and increasing carbonate contents.

To compare satellite derived temperature and pigment chlorophyll data of surface waters of single years (here 1997 and 1998) with the geochemical and micropaleontological record of the underlying sediments several processes (displacement processes, dust input and preservation) that influence and alter the surface sediment composition have to be considered.

### Displacement processes

One important factor determining the surface sediment is the effect of bioturbation at the seafloor that leads to a mixing of the sediment. The mixed layer in the Atlantic is about 2 to 12 cm thick depending on the organic carbon flux (Trauth et al., 1997). Consequently, a long-term averaging of the geochemical and micropaleontological characteristics of the surface sediments is produced for thousands of years. We have to keep in mind that a comparison between the present hydrographical conditions (SST and chlorophyll content) and proxies within the sediment will therefore never produce ideal correlations. However, since the Holocene is known to show relatively stable climatic conditions during the last 6000 years as well in the marine environment (e.g. Sarnthein et al., 1982; Marret and Turon, 1994) as in the terrestrial environment (e.g. Lamb et al., 1989; Cheddadi et al., 1998) a comparison of the surface sediment composition to the present hydrography seems to be reasonable.

Next to bioturbation turbidity currents at the seafloor and lateral advection within the intermediate and the deep nepheloid layers could transport allochthonous material to the site of interest. A strong influence of turbidity currents is known to occur at the submarine slopes of the western Canary Islands (Weaver and Thomson, 1993; Wynn et al., 2000). However, the effect of turbidity current influence is nearly negligible in the investigated sediments, since the core description shortly after recovery did not indicate a strong turbidity influence (Neuer et al., 1997a, in press.; Wefer et al., 1997, 1999a; Fischer et al., 1998). Much more complicated to detect is the influence of lateral advection processes within the surface sediments. Sinking velocities of empty tests of planktic foraminifera are in the order of hundreds of meters per day (Fok-Pun and Komar, 1983; Takahashi and Bé, 1984) leading to deposition within days or weeks in water-depths ranging from 90 m to 4200 m. In this time a lateral transport of the sinking tests occurs which could lead to differences between living and sedimented assemblages of planktic foraminifera. This effect is much more pronounced within the diatom or the calcareous nannoplankton groups, since these organisms are mostly much smaller and thus have slower sinking speeds (Berger, 1976). North of the Canary Islands impact of upwelling derived particles on the offshore sedimentation was shown in sediment trap studies and by a comparison of biogenic fluxes in sediment traps and surface sediments (Neuer et al, 1997b; Ratmeyer et al, 1999; chapter 2.2 of this study). Accordingly, lateral advection influences not only the continental slope sedimentation, but has also a strong impact on the sediment accumulation and the geochemical signature in the open ocean. However, most of the investigated proxies in this study indicate in their spatial distribution a well-established gradient from the upwelling-influenced coastal area towards the subtropical gyre domain. This points to the fact that in spite of strong lateral advection north of the Canary Islands the E-W productivity contrast is only smoothed within the surface sediments (Figs. 2-5).

### Dust input

TOC is a major component in both carbonate and silicate shelled marine organisms and therefore is a frequently used productivity proxy. However, the Canary Islands region is affected by repeated events of atmospheric dust that bring terrigenous organic particles into the marine sediments. Therefore, to use TOC as a marine productivity proxy the marine and the terrigenous fraction have to be distinguished (Müller et al., 1983; Meyers, 1994; Wagner and Dupont, 1999). C/N-ratios and $\delta^{13}C_{org}$-values in the research area are in the range of marine organic carbon indicating that the TOC is being mainly of marine origin (Fig. 2B/D). However, input of atmospheric dust to the Canary Islands region is well known from satellite pictures, from dust collector investigations, and from surface sediment analysis (Koopmann, 1981; Coude-Gaussen et al., 1987; Hooghiemstra, 1988; Bergametti et al., 1989). Along the transect from the upwelling-influenced site GeoB 4234-1 via a position north of Gran Canaria (GeoB 4301-1) to a site north of La Palma (GeoB 4242-4) the terrigenous component decrease only slightly from 50 % near shore, 45 % at the intermediate site to 40 % north of La Palma in the subtropical gyre system (data based on the sum of carbonate, TOC and TN contents shown in this study and Freudenthal unpublished opal data (<1.5 % for each of the three sites)). The estimate that approximately half of the sediment is composed of terrigenous particles mainly derived from dust input with a slightly increase towards offshore is also confirmed by the sediment trap data of the same three sites (Neuer et al., submitted). If we assume that the terrigenous input is relatively constant in the Canary Islands region, then the lower C/N-ratios and higher $\delta^{13}C_{org}$-values confirm the TOC indication of strongest productivity off the capes (Fig. 2).

### Preservation and diagenetic processes

Terrigenous particles, carbonate and opal followed by organic material are the major components of marine sediments, as so, preservation of this components is of major importance for the interpretation of marine sediments.

Pteropods are the most susceptible group for carbonate dissolution. They are rare to absent in surface sediments within the main filament area off the capes that are also the areas with lowest carbonate contents and highest fragmentation of the planktic foraminifera (Figs. 2, 3). It appears reasonable to relate the rareness and absence of aragonitic pteropod tests and the higher fragmentation of planktic foraminifera to the local formation of a more carbonate-dissolving bottom and pore water, such as derived from increased degradation of organic matter at the seafloor. In the filament area the aragonite compensation depth (ACD) rises up to a water-depth of 355 m off Cape Ghir and 1300 m off Cape Jubi as determined from the spatial distribution of aragonite (pteropod) free surface sediments. Offshore, in the domain of the subtropical gyre, the ACD is located much deeper in 3,200 m water-depth. This is in agreement with findings of Ganssen and Lutze (1982), who documented an ACD-rising from 3,100 m to 400 m water-depth in the higher productivity zone off Cape Blanc at 20°N. Thus, carbonate preservation proxies can be used as indirect indicators of the surface water properties, since high productivity produces high contents of TOC in the underlying sediments, and thus, high $pCO_2$ within the sediments may be responsible for complete aragonite dissolution and slight calcite dissolution. However, no preferential dissolution of susceptible planktic foraminifera species is observed either near shore or offshore. This is confirmed by the occurrence of the same species in seasonal plankton tows and sediment trap time-series (Abrantes et al., submitted; Meggers unpublished data).

The dissolution patterns of siliceous components within sediments are much more complicated. Siliceous particles are easily dissolved within the upper part of the water column with higher SST and lower dissolved silicate concentration (Berger, 1976) and the global average preservation ratio between production and burial of biogenic silica is only at about 3 % (Tréguer et al., 1995). In the research area silicate dissolution has a strong influence on the diatom distribution since some of the investigated surface samples are barren of diatoms.

The preservation of TOC is also strongly dependent on the water-depth in which particles were finally sedimented, since a strong decay of TOC occurred during the settling through the water-column (Suess, 1980; Martin et al., 1987). This raises one important question; is the strong zonal gradient in TOC concentration reflecting the primary signal of surface water productivity or the increasing water-depths towards the open ocean? A general decrease of TOC concentration with water-depth is observed (Fig. 6). Both, increased preservation and higher supply of organic matter at the upwelling influenced sites could explain this relationship. However, it is obvious that especially sediment samples between the two capes (in the "mixing zone" defined by the planktic foraminifera assemblage of factor 3 (Fig. 5)) reveal relative low TOC concentrations despite of shallow water-depths. This observation is in correspondence with relative low productivity indicated by lower chlorophyll concentration compared to the filament areas off the capes (Fig. 1). Therefore we conclude that the variability in organic matter supply and not the water-depth related organic matter preservation is responsible for the observed spatial TOC distribution.

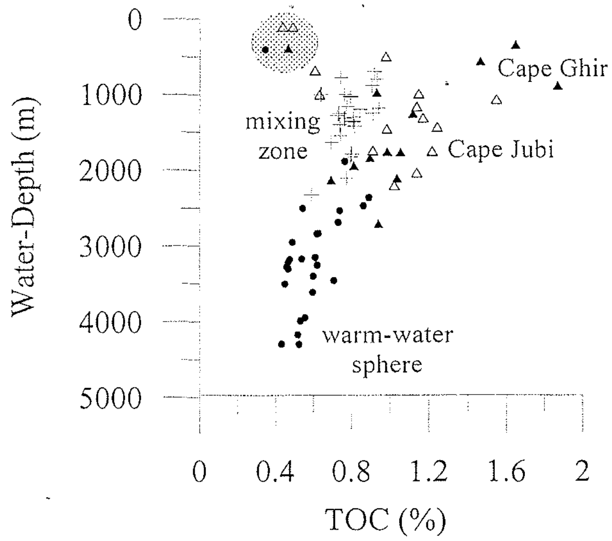

Fig. 6: Correlation of total organic carbon content (TOC) to the water-depth. The three major domains in the research area as derived from the planktic foraminifera factor analyses were shown with different signatures (triangles for the capes which are influenced by upwelling and filament production (filled: Cape Ghir; not filled: Cape Jubi), crosses for the mixing area and dots for the warm-water sphere of the subtropical open ocean). The shadded area is indicating four samples which are characterized by "unusal" conditions (GeoB 4024-3 and GeoB 4031-1 (shelf area); GeoB 6010-1 (turbidite influence), GeoB 4220-2 (seamount position).

Correlation of geochemical and micropaleontological parameters to the present oceanographic conditions

By comparing surface sediment proxies with the SST and chlorophyll concentration of the years 1997 and 1998, it can be established to what extent a particular season (winter-bloom, upwelling season, filament building season) is represented in the accumulation at the seafloor of the Canary Islands region. In spite of all mentioned restrictions (see above) good correlation coefficients were obvious for the relative abundance of planktic foraminifera species *G. bulloides* and *G. ruber* (white) to the satellite SST data (Fig. 7). A negative correlation is obvious between the planktic foraminifera *G. bulloides* and the SST, while *G. ruber* (white) is showing a positive correlation (Fig. 7). Maximum abundances of *G. bulloides*

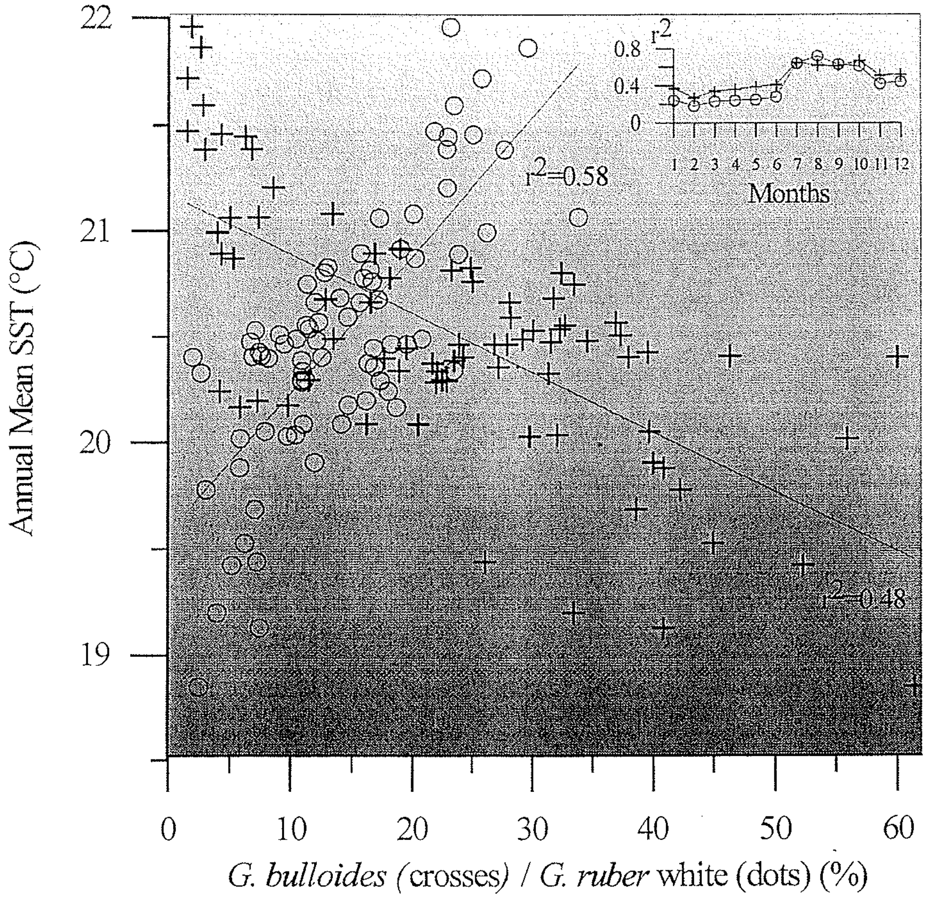

Fig. 7: Correlation of the relative abundances of planktic foraminifera species *Globigerina bulloides* (+) and *Globigerinoides ruber* (white-variety) (o) to the annual mean SST of the years 1997 and 1998 in the Canary Islands region. The correlation coefficients ($r^2$) of the relative abundances of both species over the monthly average SST from January to December are also shown with best correlations of both species in summer months.

in the upwelling region is in agreement with the oxygen isotope data of *G. bulloides* off NW Africa showing surface $\delta^{18}O$ values consistent with temperatures from the upwelling season (Ganssen, 1983; Ganssen and Sarnthein, 1983). Also within the geochemical parameters a relatively good correlation with surface water properties (SST and chlorophyll) is indicated. The TOC is positively correlated to the content of chlorophyll, whereas a negative correlation to the SST is less obvious (Fig. 8).

In most of the investigated proxies the spatial surface distribution indicate the E-W productivity gradient. Also the $\delta^{15}N$ is increasing from the areas off Cape Ghir and Cape Jubi towards the open ocean reflecting the decreasing availability of nutrients in the surface waters (Fig. 2C). Results from shallow traps of the sediment trap transect north of the Canary Islands reflect also the strong gradient from light to heavy values of $\delta^{15}N$ from an upwelling-

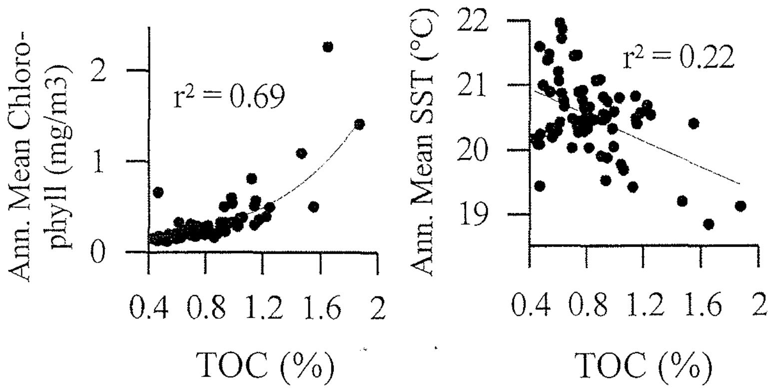

Fig. 8: Correlation of the total organic carbon content (TOC) in surface sediments to the annual mean chlorophyll of the year 1998 and the annual mean SST of the years 1997 and 1998.

influenced site towards the subtropical gyre (see chapter 2.2). This indicates that the $\delta^{15}N$ from surface sediments could be interpreted as a good proxy for Holocene nutrient availability in surface waters. Having this in mind, a clearly marked offshore NNE-SSW-belt within the surface sediments with again $\delta^{15}N$-values <6 ‰ could also reflect higher nutrient availability. If we are looking in detail to the sites with “anomalous” light $\delta^{15}N$ values far offshore, we recognise that the northernmost samples are taken on or nearby seamounts. These topographic features are known to introduce anticyclonic eddies and associated higher nutrient availability in the surface waters (Genin and Boehlert, 1985; Dower et al., 1992; Odate and Furuya, 1998). Uplifted isotherms under the euphotic zones are often associated with higher nutrient contents and deeper chlorophyll maximum with relatively high chlorophyll concentration that are not detectable with satellites, but are possible causes for a significant lower $\delta^{15}N$ in the underlying surface sediment. The sites west of the Canary Islands Fuerteventura and Lanzarote that are also characterised by light $\delta^{15}N$ values are known to be temporal affected by the Cape Jubi filament (Davenport et al., 1999) or by episodic west coast upwelling (Hernández-Guerra et al., 1993; Johnson and Stevens, 2000). Another area showing light $\delta^{15}N$ values in the surface sediments is situated south of the Canary Islands (Fig. 2C). This minimum in $\delta^{15}N$ could be best explained by the islands induced eddy formation which is known to occur mainly in the current shadow of the islands (Arístegui et al., 1994; 1997). Episodically occurring anti-cyclonic eddies could result here in a temporal higher nutrient availability. However, we could not exclude the effects of diagenesis for all of the mentioned sites (compare with Altabet and Francois, 1994; Holmes et al., 1999). Despite of this possible causes for the lighter $\delta^{15}N$ values in the NNE-SSW belt, the other proxies for higher surface water productivity like the relative abundances of *G. bulloides*, the TOC content as well as the numbers of benthic foraminifera did not correspond to the $\delta^{15}N$, and thus did not confirm the speculations about the causes of lighter $\delta^{15}N$. Possible future investigations using e.g. an increased spatial resolution of the diatom assemblage or other proxies could bring new insights to this topic.

Factor analyses implications

The factors defined from the planktic foraminifera assemblages are mirroring the oceanographic conditions in the region (Fig. 5).

The "warm-water factor" (factor 1) is representing a planktic foraminifera assemblage that is known to be associated to higher SST. The most obvious species that is determining this factor is *G. ruber* (white). But also the second important species *G. falconensis* is known to have a distinct preference for physical conditions in subtropical regions with highest abundances in summer (Bé and Tolderlund, 1971; Hilbrecht, 1996). The worldwide relationship of relative abundance and SST of *G. glutinata* as the third important species of factor 1 resembles those of *G. bulloides* (Thiede, 1975; Hilbrecht, 1996). However, *G. glutinata* is most abundant in higher latitudes and adjacent to upwelling zones and may occur in a late stage of the bloom succession and at the margins of productive areas (Hilbrecht, 1996). Thus, relative abundances of *G. glutinata* in the Canary Islands region show some inverse correlation with relative abundances of *G. bulloides* (compare also with Bé and Hudson (1977)). Hilbrecht (1996) suggest that different feeding strategies related to the upwelling phytoplankton bloom succession (compare with Armstrong et al., 1987) may explain why both species are related to productive environments, but occupy different zones. Overall, factor 1 shows good correlation to the annual mean SST, especially to summer SST (Fig. 9).

All species of the "upwelling/filament factor" (factor 2) (*G. bulloides*, *N. incompta*, *G. inflata* and *T. quinqueloba*) are well known to reflect colder SST conditions (Bé and Tolderlund, 1971; Thiede, 1975; Bé, 1977). This is in agreement with the annual mean SST from the research area (Fig. 9). When looking to the most important species of this factor, *G. bulloides*, it is striking that the best correlation coefficient (>0.7) to SST is obvious for August, which is known to be the month with strongest upwelling (Fig. 7) (van Camp et al., 1991; Davenport et al., 1999). In other upwelling regions like the Benguela upwelling *G. bulloides* is present together with *N. incompta* in the highly productive intermediate zone

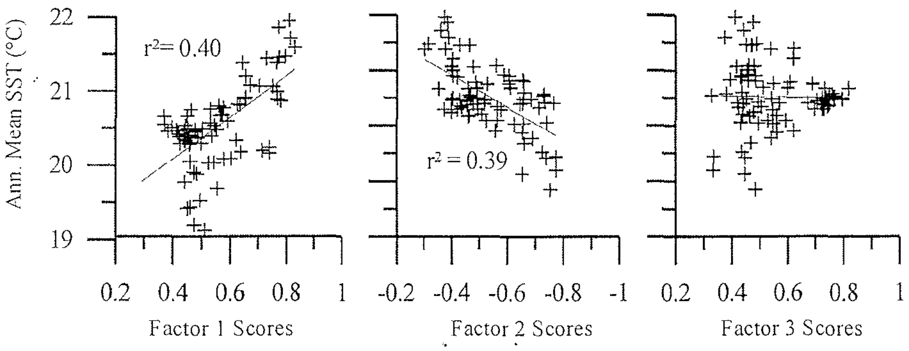

Fig. 9: Correlation of the factor scores derived from a factor analyses on the relative abundances of 25 species/groups of planktic foraminifera from surface sediments of the Canary Islands region to the annual mean SST derived from AVHRR data of the years 1997 and 1998.

between the oligotrophic and the upwelling waters (Giraudeau, 1993), while the upwelling itself is mainly reflected by high numbers of *Neogloboquadrina pachyderma*, *N. incompta* and *T. quinqueloba* (Giraudeau and Rogers, 1994). Since upwelling of North Atlantic Central Water off NW Africa is restricted to an area of 50-70 km width on the shelf (Mittelstaedt, 1991), we have unfortunately investigated only few samples directly influenced by upwelling. However, these samples reveal the same assemblage and are calculated within the same factor as the filament samples. Therefore the name "upwelling/filament factor" for factor 2 seems to be reasonable.

The factor 3 assemblage is a mixture of planktic foraminifera species that are known to be associated to warmer conditions with a tolerance to a temporal increase in productivity (like *P. obliquiloculata* and *G. siphonifera*) and species which have a preference for high productivity (like *G. bulloides*). *G. siphonifera* is known to be abundant in the subtropical province, but is also associated to upwelling regions and boundary currents (Bé, 1977). *P. obliquiloculata*, which also shows some relations to productive water masses (Hilbrecht, 1996), together with *G. sacculifer* are frequently encountered in the subtropical province, but normally belong to the tropical province (Bé, 1977). The "mixing factor" assemblage is present in an oceanographic realm that is characterised by essentially other conditions than found off the capes or in the open ocean. Mittelstaedt (1991) for instance shows that SE of Cape Ghir, within the Bay of Agadir, which is part of the spatial distribution of factor 3, the seas are generally calm during strong northerly trade winds, because this area is sheltered by the Atlas mountains, which therefore also prevent strong upwelling.

Between Cape Ghir and Cape Jubi and the warm-water sphere in the "battlefield" between the two major regimes/factors "upwelling/filament" and "warm-water", an upwelling influence occurred during summer and fall while oligotrophic open ocean conditions prevail during winter and spring. While "upwelling-fingerprints" could be recognised during the whole year within the open ocean off the capes due to a more or less annual stability of the filament structure, the extent of the filaments were most pronounced during the summer months reaching also the region between Cape Ghir and Cape Jubi (Davenport et al., 1999). Multiple regressions show a relatively good correlation between factors 1 (positive correlation) and 2 (negative correlation) to the annual mean SST (Fig. 9). No correlation is obvious in comparing the "mixing factor" scores to the annual mean SST (Fig. 9).

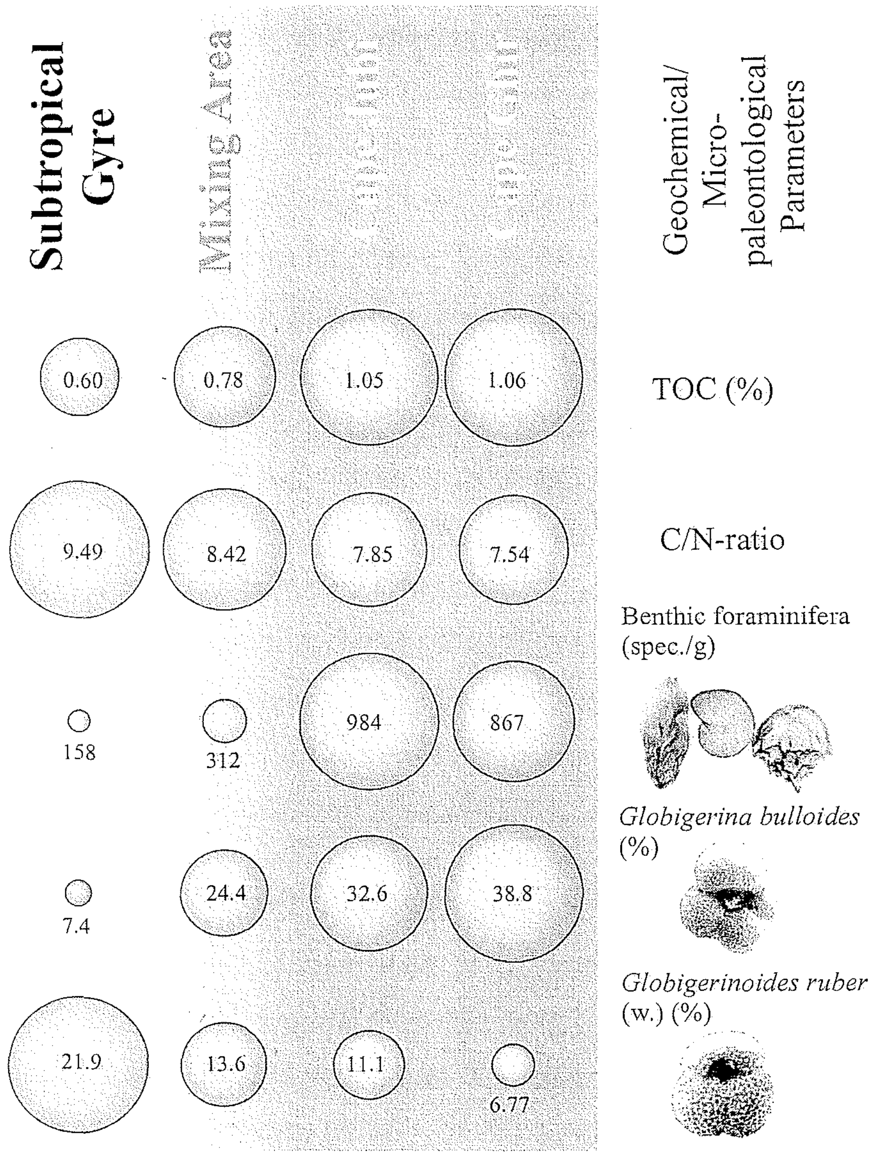

Fig. 10: Schematic summary of the 3 domains in the research area of the Canary Islands region (the subtropical gyre, the filament areas off Cape Jubi and Cape Ghir and a mixing zone which is seasonally influenced by the two other areas) indicating in all parameters a well established zonal productivity gradient. The domains are derived from the planktic foraminifera factor analyses and contents or percentages are mean values for each area.

## CONCLUSIONS

Geochemical and microfossil data from surface sediments of the Canary Islands region mirror the high biomass and SST-gradient from the coast towards the oligotrophic subtropical gyre, as observed by satellite data (Fig. 10). Despite of strong influence of lateral advection in sediment traps in the region, the surface sediment is reflecting the strong contrast between the upwelling influenced area and the subtropical gyre. Lateral advection seems to be only a mechanism that is smoothing the present productivity gradient within the surface sediment. TOC decrease, C/N-ratio increase, decreasing numbers of benthic foraminifera or dinoflagellates and decreasing relative abundances of *G. bulloides* and *Chaetoceros* spp. and the opposite for *G. ruber* (white) are typical representatives of several valuable proxies mirroring the E-W-productivity gradient. Factor analyses of the planktic foraminifera assemblage indicate three major factors in the Canary Islands region. A "warm-water factor" which is comparable to the subtropical water masses of the oligotrophic ocean, an "upwelling/filament factor" which is clearly reflecting the recent filament positions and a third "mixing-factor" which is determined by mixing the first and the second together in an area between Cape Ghir and Cape Jubi. Multiple regressions show a good correlation between chlorophyll concentration and the TOC content and between SST and the planktic foraminifera factor loadings (for factor 1 and 2).

Overall, the multiproxy approach used in this study is reflecting the present day conditions in many details (e.g. islands-generated eddies in the shadow of the Canary Islands, a mixing zone between the capes and the subtropical gyre domain). The signals within the surface sediments are therefore good averages of the present day oceanographic conditions and could be used within paleoceanographic reconstructions in future.

## ACKNOWLEDGEMENTS

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European Union MAST programme through the CANIGO project, grant number MAS3-CT96-0060.

## 2.4 Manuscript 4:

### Glacial-interglacial variability of particle accumulation in the Canary Basin: A time-slice approach (abridged version)

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## ABSTRACT

Particle supply and sediment accumulation in the Canary Basin are strongly modified by seasonal coastal upwelling and dust input from the Sahara. Along an E-W depth profile and fertility gradient north of the Canary Islands, we demonstrate an increase in total mass accumulation rates from a low of 1-2 g $cm^{-2}$ $ka^{-1}$ in the outer oceanic domain to 6-12 g $cm^{-2}$ $ka^{-1}$ closer to the Moroccan shelf in Holocene sediments. During the Last Glacial Maximum (LGM, oxygen isotopic event 2.2), a steeper gradient was found with 2 to 4 times higher mass accumulation rates at the near-shore sites. Total mass accumulation rates during the Last Interglacial Climax (LIC, isotopic event 5.5) and end of the Penultimate Glaciation (ePG, isotopic event 6.2) resemble Holocene values, with lowered near-shore maxima of 3 and 4 g $cm^{-2}$ $ka^{-1}$, respectively. During these two time-slices, accumulation rates were significantly lowered at the site east of the island Lanzarote (1.5-2 g $cm^{-2}$ $ka^{-1}$), in contrast to the Holocene and LGM.

Analyses of separate sediment components show that total organic carbon, total carbonate, lithogenic and diatom accumulation rates were generally enhanced during glacial times, especially during the LGM. In contrast, glacial accumulation rates of biogenic carbonate particles (coccoliths and planktic foraminifera shells) remained constant or were lowered with respect to interglacial time periods at the site closest to the Moroccan shelf, despite a doubling of bulk carbonate accumulation. This could indicate lowered supply from the productive euphotic zone or a latitudinal, offshore shift of the main sedimentary depocentre. However, enhanced carbonate dissolution could by itself account for this decrease in biogenic carbonate accumulation. Increased glacial input of detrital carbonate, derived from the exposed Moroccan shelf, appears to be responsible for the overall enhanced carbonate accumulation at the same sites, east of Lanzarote.

## SUMMARY

In this study, accumulation rates of bulk sediments, lithogenic matter and separate biogenic components are quantified in order to reconstruct the temporal variability of marine productivity and aeolian supply in the northern Canary Islands region. Five sediment cores were selected, including two near-shore sites influenced by coastal upwelling (sites GeoB 4223 and GeoB 4240), two deep-sea sites in the oligotrophic subtropical gyre region (sites GeoB 4241 and GeoB 4242) and one site located within the transitional zone from the eutrophic coastal upwelling and the oligotrophic subtropical gyre region (site GeoB 4216) (Fig. 1). Accumulation rates at the different sites were compared at four time-periods corresponding to the Holocene, the Last Glacial Maximum (LGM, including oxygen isotopic event 2.2), the Last Interglacial Climax (LIC, including oxygen isotopic event 5.5), and the end of the Penultimate Glaciation (ePG, including oxygen isotopic event 6.2).

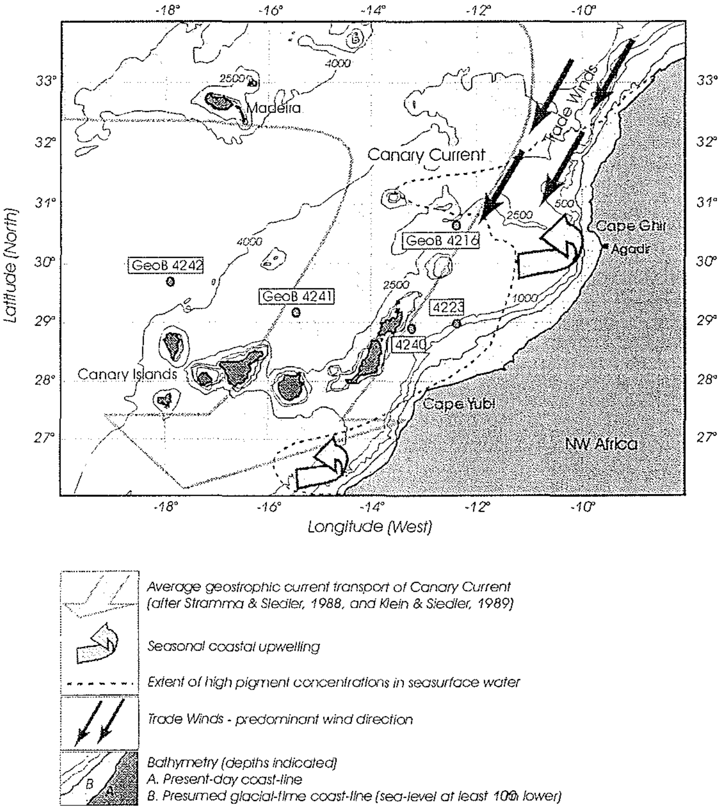

Fig. 1: Map of the Canary Islands region, showing the locations of gravity cores used in this study. Main oceanographic and atmospheric circulation patterns are indicated (after Mittelstaedt, 1983; Stramma and Siedler, 1988; Klein and Siedler, 1989; Nykjær and Van Camp, 1994). Note the speckled area, depicting the area above 100 m water depth today and presumed exposed shelf during glacial sea level lows.

Oxygen isotope stratigraphy (correlation with SPECMAP) and $^{14}$C AMS dating were used to estimate average sedimentation rates for these time-slices at each investigated site. Bulk mass accumulation rates (MAR) were calculated using average linear sedimentation rates and dry bulk density. Accumulation rates of separate sediment components (organic carbon (TOC), total carbonate, planktic foraminifera, pteropods, coccoliths and diatoms) were determined by multiplying their concentration with the bulk MAR. Lithogenic particulate matter was estimated as the non-carbonate fraction corrected for TOC. Fragmentation of planktic foraminifera and corrosion of placoliths of the coccolithophore *Emiliania huxleyi* were taken as an indicator of (biogenic) carbonate dissolution.

Mass accumulation rates reveal a strong E-W decrease from the near-shore sites to the deep-sea sites during the Holocene (Fig. 2). This gradient is even steeper during the LGM due to enhanced accumulation rates especially at the near-shore sites influenced by coastal upwelling and at the transitional site. During the LIC and ePG the regional gradient and glacial-interglacial variability is not as pronounced. However, we have no data for this time period at site GeoB 4223, since the gravity core at this site did not recover sediments beyond isotopic stage 5.2. The other continental slope site (GeoB 4240) shows low accumulation rates for the LIC and the ePG, which are comparable to values at the deep-sea sites. Preliminary stratigraphies of other sediment cores in the vicinity of site GeoB 4240 indicate that extreme low accumulation rates during oxygen isotopic stages 6 and 5 are not typical for the continental slope region, and may be an artefact of the sedimentation rates calculated for a condensed section at this site (Freudenthal, unpublished data). Similar to bulk accumulation rates, maximum accumulation of TOC, carbonate and lithogenic matter was observed at the continental slope sites, with overall highest accumulation rates during the LGM.

Despite maximum bulk carbonate accumulation rates at site GeoB 4223 during the LGM, the accumulation of calcareous microfossils (foraminifera, coccoliths, pteropods) was significantly lowered compared to the Holocene, at this time. With the exception of site GeoB 4223, where no diatoms were preserved, maximum diatom accumulation rates were observed during glacial times with highest values at sites GeoB 4216 and GeoB 4240 during the LGM (Fig. 2).

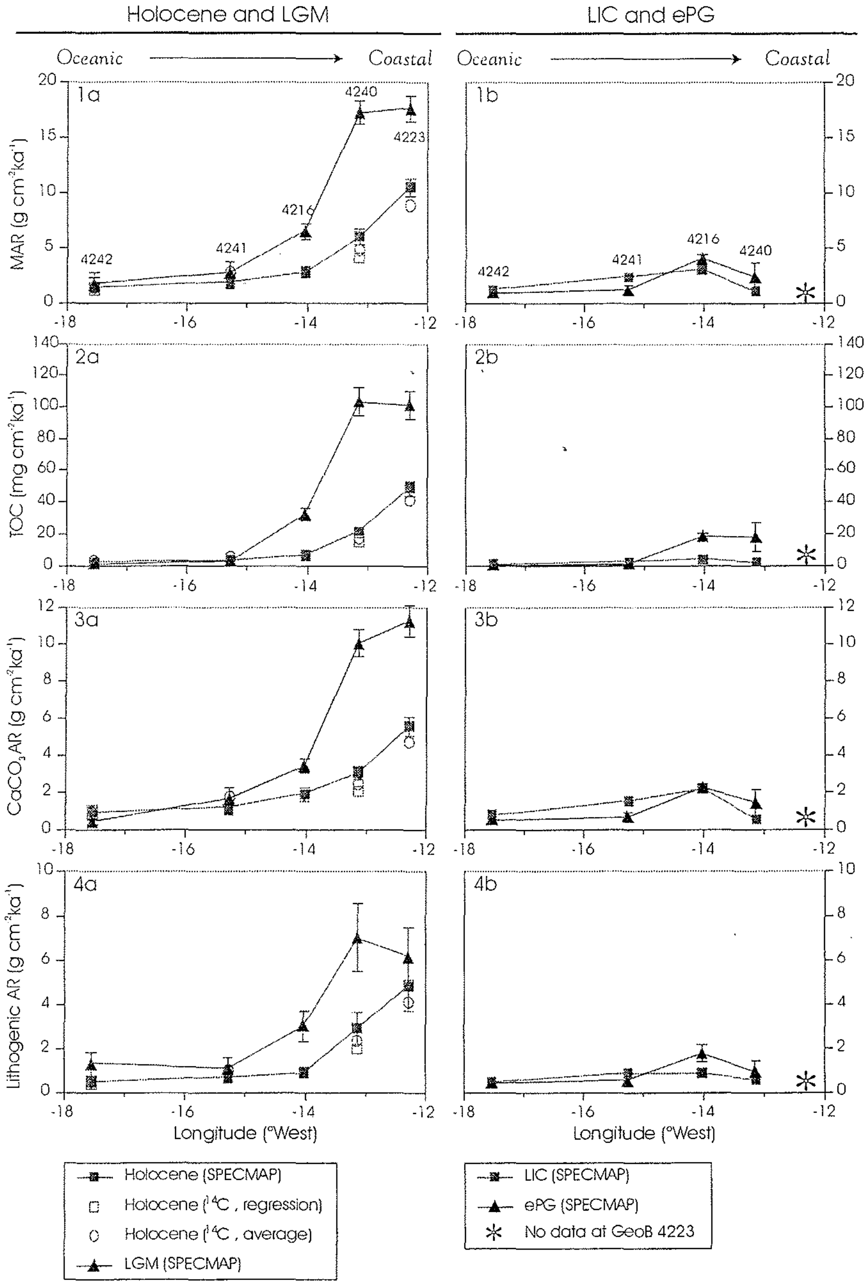

Fig. 2.: Average bulk accumulation rates and accumulation of separate sediment components for a) Holocene and Last Glacial Maximum and b) Last Interglacial Climax and end of Penultimate Glaciation time-slices along the E-W transect north of the Canary Islands. Vertical error bars represent 2$\sigma$-ranges of the total cumulative errors:

1. Bulk sediment accumulation rates, in g $cm^{-2}$ $ka^{-1}$
2. Total organic carbon (TOC) accumulation rates, in mg $cm^{-2}$ $ka^{-1}$
3. Bulk carbonate accumulation rates, in g $cm^{-2}$ $ka^{-1}$
4. Bulk lithogenic accumulation rates, in g $cm^{-2}$ $ka^{-1}$; note that this reflects the non-carbonate fraction corrected for TOC content. Biogenic opal was not excluded from these calculations which is believed to be only a minor sediment constituent in wt.%.

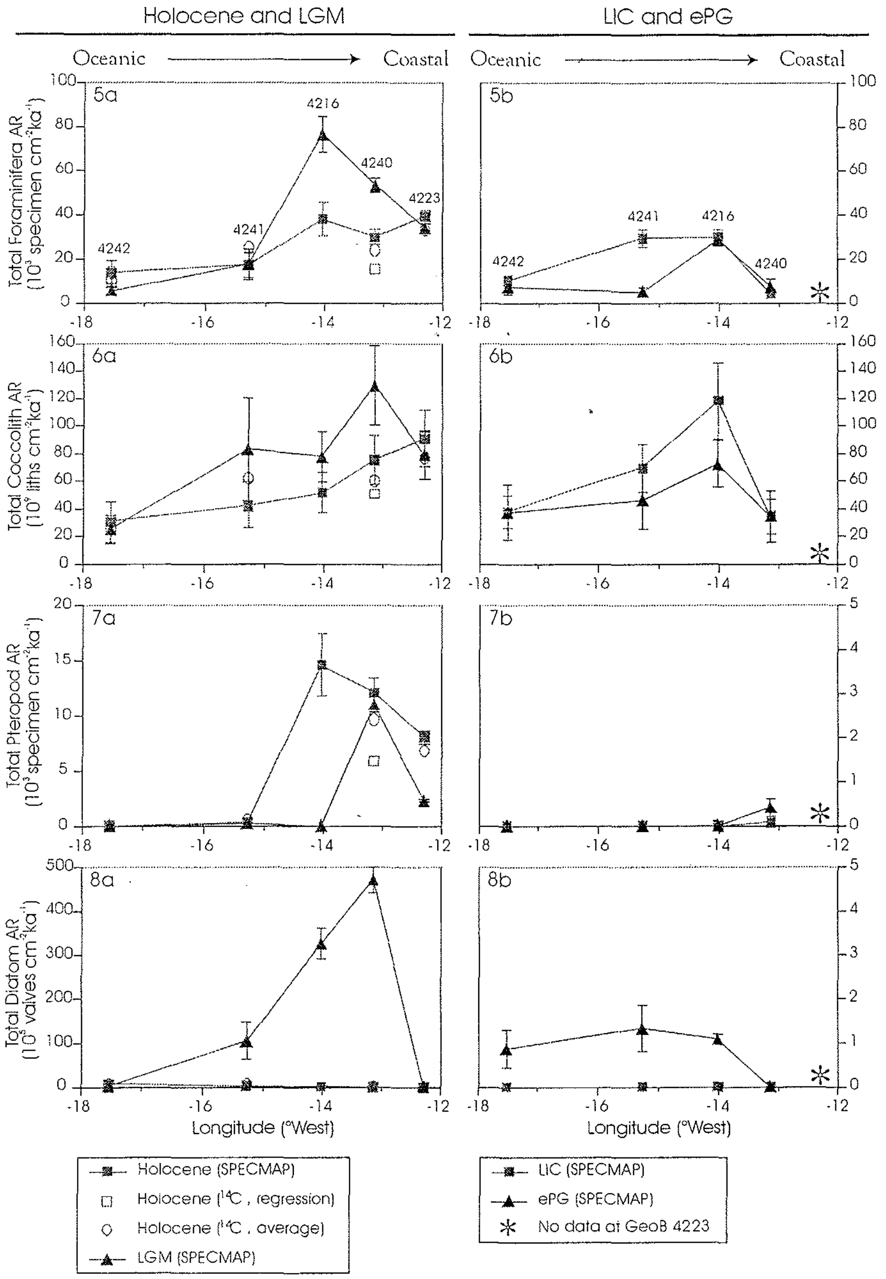

Fig. 2 (continued):

5. Total planktonic foraminifera (biogenic calcite) accumulation rates, in $10^3$ specimen $cm^{-2}$ $ka^{-1}$
6. Total coccolith (biogenic calcite) accumulation rates, in $10^9$ liths $cm^{-2}$ $ka^{-1}$
7. Total pteropod (biogenic aragonite) accumulation rates, in specimen $cm^{-2}$ $ka^{-1}$
8. Total diatom (biogenic opal) accumulation rates, in $10^5$ specimen $cm^{-2}$ $ka^{-1}$; note the change in vertical scale between a) and b). LGM values are two orders of magnitude higher than other time-slices.

The observed glacial-interglacial variability in bulk sediment accumulation and its separate components may be explained by a combination of factors: a) Enhanced productivity as a response to stronger trade winds led to the higher accumulation of total organic carbon and diatoms during glacial time-slices. b) Increased glacial carbonate dissolution (Fig. 3) was responsible for lowered biogenic carbonate particle accumulation (foraminifera and coccoliths). c) Investigation of the fine fraction (not shown) revealed that the accumulation of detrital carbonate particles at the continental slope sites was enhanced during glacial times.

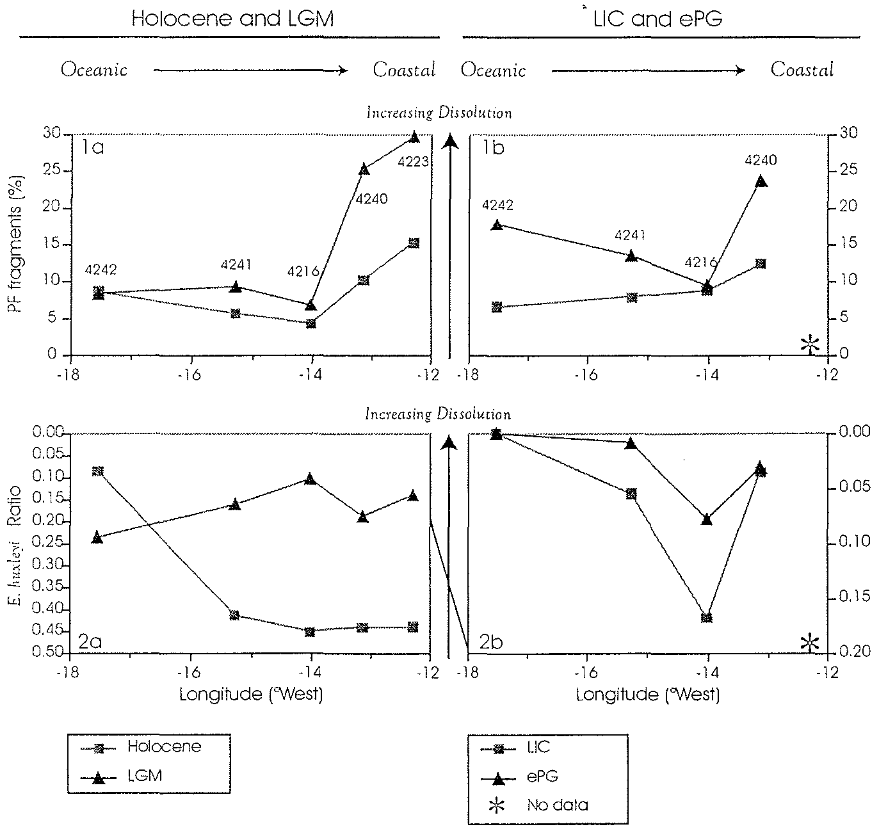

Fig. 3.: Biogenic carbonate dissolution indices for a) Holocene and Last Glacial Maximum and b) Last Interglacial Climax and end of Penultimate Glaciation time-slices along the E-W transect north of the Canary Islands:

1. Planktic foraminifera fragmentation index, in percent. Percentages of broken planktic foraminifera with a loss <50 %. Increase in biogenic carbonate dissolution indicated by vertical arrow.
2. *Emiliana huxleyi* coccolith preservation index, based on the ratio between well-preserved and corroded placoliths. Increase in biogenic carbonate dissolution indicated by vertical arrow.

Erosion of Pleistocene shelf sediments during sea-level low stand is probably the cause of higher carbonate accumulation at these sites. d) In addition to erosion of shelf sediments, increased supply of aeolian dust associated with stronger trade winds is expected to have been responsible for the glacial increase of lithogenic accumulation rates at all investigated sites.

This interpretation is in good agreement with "classical" studies describing the northern NW African upwelling and trade wind system (e.g. Sarnthein et al., 1982). However, this multi-proxy time-slice approach revealed that proxies for paleoproductivity are strongly influenced by their degree of preservation and processes of reworking on a regional scale.

## 2.5 Manuscript 5:

# Upwelling intensity and filament activity off Morocco during the last 250,000 years

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submitted to Deep-Sea Research Part II

Content Page

## ABSTRACT

The high productive upwelling area off Morocco is part of one of the four major Trade Wind driven continental margin upwelling zones of the world oceans. While coastal upwelling occurs mostly on the shelf, biogenic particles derived from upwelling are deposited mostly at the upper continental slope. Nutrient rich coastal water is transported by the Cape Ghir filament at 30°N up to several hundreds of kilometres offshore. Both upwelling intensity and filament activity are dependent on the strength of the summer trades. This study is aimed to reconstruct changes in Trade Wind intensity over the last 250,000 years by the analysis of the productivity signal contained in the sedimentary biogenic particles of the continental slope and beneath the Cape Ghir filament. Detailed geochemical and geophysical analyses (TOC, carbonate, C/N, $\delta^{13}C_{org}$, $\delta^{15}N$, $\delta^{13}C$ of benthic foraminifera, $\delta^{18}O$ of benthic and planktic foraminifera, magnetic susceptibility) have been carried out at two sites on the upper continental slope and one site located further offshore influenced by the Cape Ghir filament. A second offshore site south of the filament was analysed (TOC, magnetic susceptibility) in order to distinguish the productivity signal related to the filament from the general offshore variability. Higher productivity during glacial times was observed at all four sites. However, the variability of productivity during glacial times was remarkably different at the filament-influenced site compared to the upwelling influenced continental slope sites. While the productivity record at the continental slope is strongly influenced by zonal shifts of the upwelling area due to sea-level changes, the filament-influenced site is highly sensitive to changes in Trade Wind intensity. Time series analyses indicate precessional forcing of the Trades. An impact of sea-level changes on the sedimentary productivity record has to be considered at all continental margins characterised by a broad shelf.

## INTRODUCTION

Near-shore upwelling of nutrient enriched subthermocline waters and their offshore transport by filaments result in high rates of primary production and fixation of carbon. Upwelling regions play thus an important role in global carbon cycling. Changes in upwelling intensity and consequent changes in primary productivity have been proposed to explain part of the changes of climate sensitive atmospheric $CO_2$ concentrations on glacial-interglacial time-scales (Sarnthein et al., 1987). Both upwelling intensity and the formation and extension of filaments (in the following named filament activity) are dependent on regional climate, especially on the strength and duration of long-shore blowing winds (Speth et al., 1978;

Lutjeharms and Meeuwis, 1987; McCreary et al., 1991; Strub et al., 1991; Nykjær and Van Camp, 1994). Thus, detection of past productivity variations in upwelling regions was used to infer on changes in past wind circulation (Müller et al., 1983; Hughen et al., 1996).

Because a part of the biological production in the euphotic zone is exported to the sea floor, information about past productivity variations are stored in marine sediments. Both, magnitude and biogeochemical composition of biogenic particle fluxes are related to the productivity conditions in the upwelling region. A variety of micropaleontological and geochemical methods have been developed to reconstruct past variations in export production and variations in water mass characteristics like sea surface temperature, salinity, or nutrient availability that depend on upwelling intensity. A comprehensive overview about the use of these methods in paleoceanography was given by Wefer et al. (1999a).

The influence of sea-level changes on the sedimentary productivity record was only recently discussed and is poorly understood (Guichard et al., 1999; Martinez et al., 1999; Bertrand et al., 2000). During the last glacial maximum (LGM) sea-level was about 120 m lower compared to present day conditions (Fairbanks, 1989). The impact of this drop in sea-level has to be considered especially in coastal regions with a broad and shallow shelf area, as it is the case off NW Africa. At present, upwelling occurs mostly on the shelf (Mittelstaedt, 1991). A retreat of the coastline towards the edge of the shelf during times of low sea-level forces an offshore movement of the upwelling centre towards the continental slope. Thus, changes in the sedimentary productivity record might be induced by changes in the upwelling intensity and/or by changes in the distance of the investigation site to the upwelling centre. Additionally, lateral particle transport and nutrient dynamics may have changed during times of low sea-level compared to present conditions (Fütterer, 1983; Bertrand et al., 2000). Separating the impact of sea-level changes from wind-induced changes in upwelling intensity is the requirement for the use of sedimentary paleoproductivity records as paleoclimatic archives. This is hardly possible when only one site is investigated as representative for the whole upwelling system as done in most previous studies.

In this study we investigate, how productivity variations over the last 250,000 years are preserved in marine sediments off Morocco (NW Africa). We try to distinguish between the influence of sea-level changes and variations in Trade Wind intensity on the sedimentary paleoproductivity record, by investigating four different sites (Fig. 1). Two sites are located at the continental slope near to the coastal upwelling area. The other two sites are located further offshore, one of them off Cape Ghir, a region of intensive filament activity at present. We show that the climatic signal is strongly overprinted by the impact of sea-level variations at the coastal upwelling influenced sites. The filament-influenced site is highly sensitive to climatic induced changes in productivity during glacial times. The summer NE Trade Wind circulation that controls upwelling activity and filament intensity off Morocco, seems to be strongly controlled by precessional forcing mechanisms.

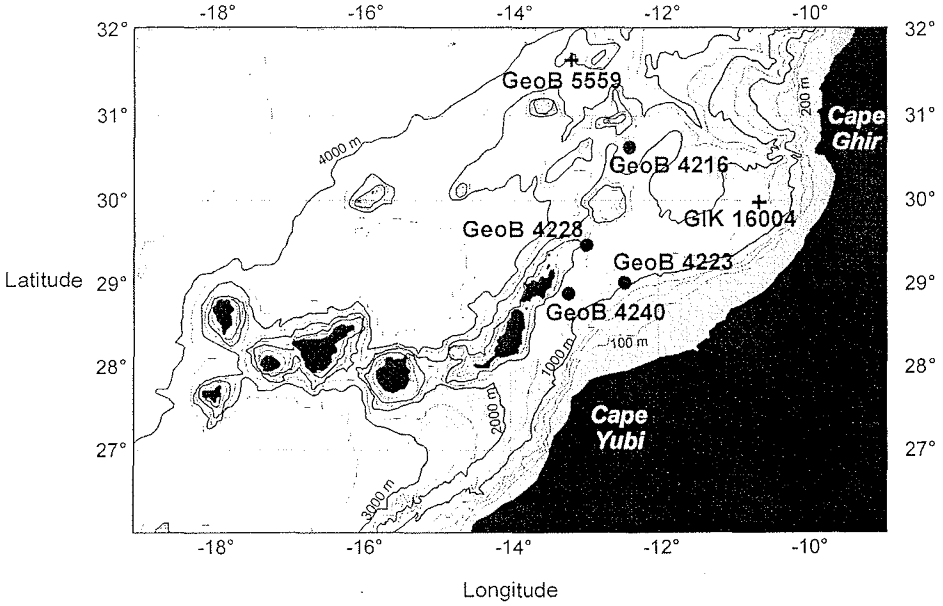

Fig. 1. Bathymetric map showing the investigation area off Morocco. Circles indicate the positions of sites investigated in this study. Further sites discussed in this study are marked with crosses. The main area of higher pigment concentrations related to coastal upwelling and the Cape Ghir filament, based on an 18 days stack of SeaWiFS images in 1998 (see chapter 2.2, Fig. 1), is shaded.

## PRESENT-DAY CLIMATE AND OCEANOGRAPHY OFF NW AFRICA

The NE Trade Wind belt is the prevailing wind system off NW Africa. Seasonal variations are caused by the latitudinal shift of the subtropical high-pressure system currently known as the Azores High and of the tropical deep-pressure system related to the Inter-Tropical Convergence Zone. During the boreal winter, the Trade Wind belt is mainly located between 10 and 25°N. During boreal summer, Trade Winds blow prevalently between 20 and 32°N.

The main direction of the Trade Winds along the NW African coast is long-shore, thus generating upwelling of cold and nutrient rich waters along this coast. According to the seasonal migration of the Trade Wind belt, summer and fall are the seasons of strongest upwelling off Morocco. Upwelling is observed in a coastal band about 50 km wide mainly on the continental shelf (Van Camp et al., 1991). The shelf has a width of 30-100 km. Water depth on the shelf is mainly below 100 m (Fig. 1).

The main current off NW Africa is the southward-directed Canary Current that is associated with the coastal upwelling (Mittelstaedt, 1991). The interaction of the Canary Current, coastal upwelling and morphological features of coast and continental shelf leads to the development of meanders that carry cold and nutrient rich coastal waters in filament form into the warm subtropical gyre region (Johnson and Stevens, 2000). One of the most prominent filaments off Morocco is located west of Cape Ghir and reaches occasionally several hundred kilometres offshore (Van Camp et al., 1991; Nykjær and Van Camp, 1994; Hagen et al., 1996). The filament activity is similar to coastal upwelling dependent on the strength and duration of the Trade Winds, although a 3-month phase lag was observed between the onset of the maximum Trade Winds in summer and the time of most intense upwelling off Cape Ghir (Nykjær and Van Camp, 1994). High pigment concentrations indicating high productivity are observed both in filaments and the coastal upwelling zone (Van Camp et al., 1991; Davenport et al., 1999) (Fig. 1).

The preservation of the productivity signal in the sediments is largely dependent on the bottom water mass characteristics, especially on their oxygen concentration. The water mass stratification and oxygenation off NW Africa was reviewed by Sarnthein et al. (1982). Below the Subtropical water, the North Atlantic Central Water (100 - 600 m), the Mediterranean Outflow Water (MOW, centred at about 1200 m), and the North Atlantic Deep Water (NADW, below 2000 m) are the characteristic water masses in the investigation area. In some cases an influence of a derivative of Antarctic Intermediate Water (500 - 1000 m) was observed north of the Canary Islands that was carried above the continental slope by the pole ward undercurrent (Mittelstaedt, 1991; Müller et al., 1999). All water masses are well oxygenated at present day conditions.

## MATERIALS AND METHODS

The four sediment cores investigated in this study were recovered during Meteor cruise M37/1 in December 1996 (Wefer et al., 1997). Two sites are located at the continental slope (GeoB 4223, GeoB 4240), and two are located further offshore (GeoB 4216, GeoB 4228) (Fig. 1; Table 1). Upwelling occurs mostly on the shelf. However, most biogenic fluxes derived from the upwelling are deposited at the continental slope between 1000 and 1500 m, due to strong hydrodynamic processes, which occur on the shelf (Fütterer, 1983). Therefore, we consider the continental slope sites as upwelling influenced sites. Site GeoB 4216 is located west of Cape Ghir and may thus be influenced by the Cape Ghir filament. At present, the filament reaches only occasionally far enough offshore to influence this site. At the surface sediments no significant impact of the Cape Ghir filament on sedimentation at this site was observed (Meggers et al., this issue). However, we expect a significant impact during times of increased Trade Winds and stronger filament activity in the past. We selected site GeoB 4228 as offshore reference site for comparison with site GeoB 4216 in order to be able to distinguish the filament signal and the offshore "background" signal of organic matter sedimentation.

Table 1: Location, water depth, and length of investigated gravity and piston cores

| Site | Device | Latitude (°N) | Longitude (°W) | Water depth (m) | Core recovery (cm) |
|---|---|---|---|---|---|
| GeoB 4216 | gravity corer | 30°38 | 12°24 | 2324 | 1117 |
| GeoB 4223 | gravity corer | 29°01 | 12°28 | 775 | 779 |
| GeoB 4228 | piston corer | 29°29 | 12°59 | 1638 | 1188 |
| GeoB 4240 | gravity corer | 28°53 | 13°14 | 1358 | 688 |

Core descriptions

Opening and visual description of the sediment cores was conducted on board (Fischer et al., 1997; Wefer et al., 1997), besides of core GeoB 4240 that was opened at the University of Bremen. Sediments consist mainly of light brownish or olive green undisturbed nannofossil ooze. At cores GeoB 4216 and GeoB 4228 a volcanic ash layer was identified at 768 cm and 693 cm sediment depth, respectively. A second ash layer was identified at 1098 cm sediment depth in core GeoB 4216 and at 997 cm sediment depth in core GeoB 4228. The ash-layers were used for stratigraphic correlation of cores GeoB 4216 and GeoB 4228. Two sand layers containing biogenic coarse-grained carbonates at about 160 cm and 485 cm sediment depth of 4.5 and 3 cm thickness, respectively, were observed in core GeoB 4228. We interpret them as turbidites. At core GeoB 4240 three sand layers of 1 – 1.5 cm thickness containing volcanic material were observed at 172 cm, 178 cm, and 182 cm sediment depth.

Geophysical and geochemical properties

Magnetic susceptibility was measured in 1 cm steps using a GEOTEK Multi Sensor Core Logger. Geochemical analysis was conducted with a sample spacing of 5 cm. Analysis of TOC, carbonate, C/N, $\delta^{15}N$, and $\delta^{13}C_{org}$ was conducted on freeze-dried and homogenised sediment samples. For the measurement of carbon concentrations, samples were placed in ceramic crucibles and analysed using a LECO CS-244 determinator. TOC was measured after treatment of sediment with 6M HCl and heating at 80°C. A small loss of acid soluble organic carbon through the walls of the crucibles (< 0.1 wt. %) was negligible compared to the observed variability of TOC concentrations. Carbonate concentrations were calculated from the total carbon content (TC), measured on untreated samples as $CaCO_3 = (TC - TOC) \times 8.333$. We calculated TOC and carbonate concentrations on salt free basis, using wet weight and dry weight determinations for calculation of pore water content and assuming a salinity of 35 ‰. Precision of TOC and carbonate analysis was better than 3 and 2 %, respectively.

For the analysis of C/N ratio, $\delta^{15}N$, and $\delta^{13}C_{org}$ samples were placed in tin boats and combusted at 1050°C in an NC 2500 Elemental Analyzer (CE Instruments). The $\delta^{15}N$ and $\delta^{13}C$ of the gas thus formed was measured using a Finnigan MAT delta plus mass spectrometer. The ratio of $^{12}C$ to $^{14}N$ was used for calculation of the C/N ratio after calibration against a laboratory sediment standard. The $\delta^{15}N$ of sediments from cores GeoB 4223 and GeoB 4240 was measured on untreated sediment samples. Due to the low nitrogen concentrations at large parts of core GeoB 4216, we determined $\delta^{15}N$ at this site after decalcifying with 1M HCl and washing with deionised water. The $\delta^{15}N$ of decalcified samples correlated well with $\delta^{15}N$ of untreated samples at sites GeoB 4223 and GeoB 4240 ($r^2 = 0.75$; $n = 286$) with decalcified samples being in average 0.11 ‰ lighter compared to untreated samples. $\delta^{13}C_{org}$ and C/N ratios were measured on decalcified samples.

The stable oxygen ($\delta^{18}O$) and carbon ($\delta^{13}C$) isotope ratios of benthic and planktic foraminifera were analysed using a Finnigan MAT 251 mass spectrometer with an automated carbonate preparation device at the University of Bremen. Each measurement has been performed on 10 to 15 individual shells of the planktic foraminifer *Globigerina bulloides* (200 – 250 µm) and on 3 to 6 shells of the epibenthic foraminifer *Cibicidoides wuellerstorfi* at sites GeoB 4216 and GeoB 4240. Due to the low abundance of *C. wuellerstorfi* we used the endobenthic foraminifer *Uvigerina peregrina* at site GeoB 4223. The isotopic composition of the shells was measured on the $CO_2$ gas released after treatment of the shells with phosphoric acid at a constant temperature of 75°C.

For all stable oxygen and carbon isotope measurements we used a working standard (Burgbrohl $CO_2$ gas), which has been calibrated with NBS 18, 19, and 20 standards against PDB. For the stable nitrogen isotope measurements 99.996 % pure tank $N_2$ was used as working standard. It was calibrated against air using IAEA standards N-1 and N-2. Analytical standard deviation is about ± 0.05 ‰ for $\delta^{13}C$ and ± 0.07 ‰ for $\delta^{18}O$ of carbonate shells. Precision calculated from repeated measurements on a laboratory sediment standard was about ± 0.1 ‰ for $\delta^{13}C_{org}$, ± 0.2 ‰ for $\delta^{15}N$, and ± 0.5 for the C/N ratio.

The geophysical and geochemical parameters were completely analysed at the upwelling influenced sites GeoB 4223 and GeoB 4240 and at the filament influenced site GeoB 4216. For the analysis of the offshore organic background sedimentation at site GeoB 4228 we focussed on the analysis of TOC and on magnetic susceptibility for stratigraphic comparison.

## RESULTS

### Stratigraphy

Age control at sites GeoB 4216, GeoB 4223, and GeoB 4240 was obtained by correlating the $\delta^{18}O$ records with the SPECMAP stack (Imbrie et al., 1984) (Fig. 2). For this purpose the planktic $\delta^{18}O$ records were used, since they have been measured with high resolution at all three sites using the same species (*G. bulloides*). Although the SPECMAP stack was obtained using $\delta^{18}O$ records of rather low resolution the validity of the initial age model (Imbrie et al., 1984) was confirmed by various independent tests (Martinson et al., 1987; Raymo, 1997). In our study, the major transitions, stadials and interstadials could be easily identified in all three cores, besides of oxygen isotope event 3.0. More detailed time control of the events surrounding the last Termination was obtained by correlating planktic $\delta^{18}O$ records of the upper parts of the three cores with the planktic $\delta^{18}O$ record from core SU81-18 that has been dated by $^{14}C$ -AMS in great detail and that is located north of our investigation area off Portugal (Bard et al., 1989). We converted the $^{14}C$ ages into calendar ages using the program CALIB 4.1 (Stuiver and Braziunas, 1993) and the INTCAL98 dataset for marine carbonates (Stuiver et al., 1998). Ages between the tie points were obtained by linear interpolation.

Strong time coherence in the variability of magnetic susceptibility is recognised at all three sites when applying the age models to the magnetic susceptibility records in cores GeoB 4216, GeoB 4223, and GeoB 4240 (Fig. 3). Age control of GeoB 4228, where no oxygen isotope data are available, was obtained by correlating magnetic susceptibility with the age-dated magnetic susceptibility profile of core GeoB 4216.

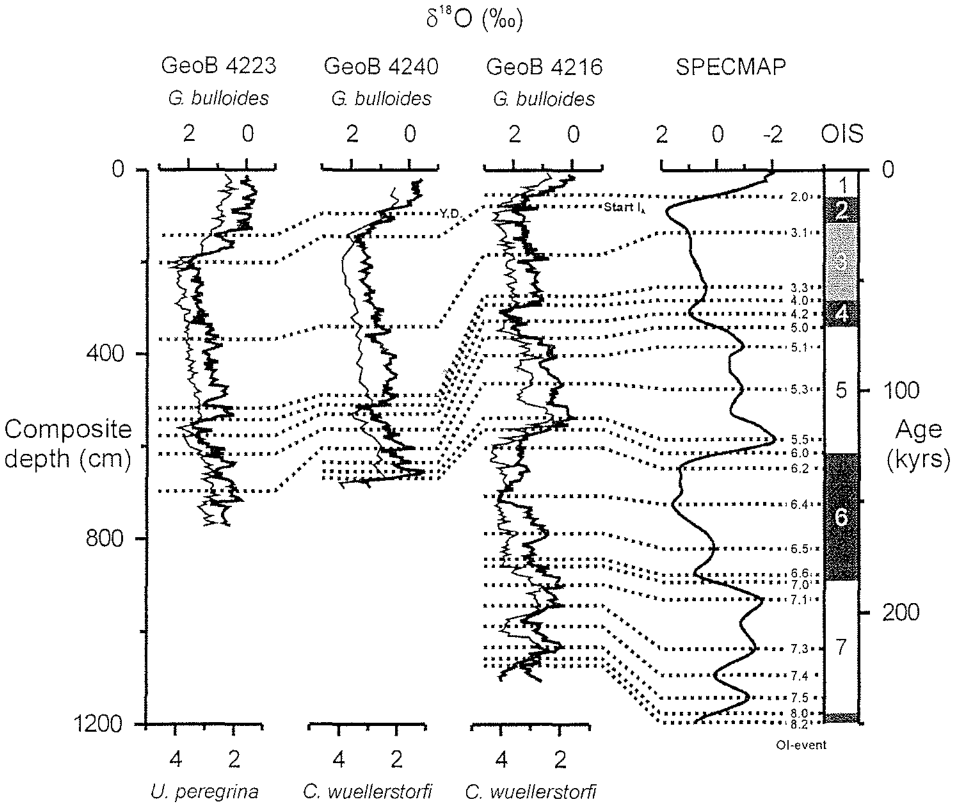

Fig. 2. Depth records of planktic (bold line) and benthic (thin line) oxygen isotope ratios of cores GeoB 4223, GeoB 4240 and GeoB 4216 compared to the SPECMAP stack (Imbrie et al., 1984). Composite depth includes core depth and estimated sediment loss during coring (5 to 17 cm, Henderiks et al., submitted). Correlations of the planktic records with the SPECMAP stack are indicated by dotted lines. In addition, events during the last termination used as tie points are indicated (Y.D.: Younger Dryas; Start $I_A$: Start of Termination I). The right bar indicate oxygen isotope stages (OIS), with glacial stages in dark grey and interglacial stages in white. Although OIS 3 is an interglacial stage per definition, it is shaded in light grey, due to its strong glacial climatic character (compare Sarnthein et al., 1987).

Several $^{14}C$ measurements on *G. bulloides* and on mixed planktic foraminifera samples of cores GeoB 4223 and GeoB 4240 (Henderiks et al., submitted) confirmed our age models (Fig.4a). However, three samples around the oxygen isotope event 3.1 yielded different results: While one measurement on *G. bulloides* confirmed our age model, two mixed samples were about 4 ka older. The reason for the strong differences in the $^{14}C$ ages of monospecific and mixed samples is not clear (see for discussion Henderiks et al., submitted).

Higher average sedimentation rates were observed at the near-coastal sites GeoB 4223 and GeoB 4240 (average 8.7 and 5.2 cm/ka, respectively) compared to the open ocean sites GeoB 4216 and GeoB 4228 (average 4.3 and 4.0 cm/ka, respectively) (Fig. 4a and b). Sedimentation rates were higher during glacial times than during interglacial times at all four sites. Unusual sedimentation rates below 2 cm/ka during oxygen isotope stage (OIS) 5 at site GeoB 4240 may be explained by sediment winnowing during the last interglacial.

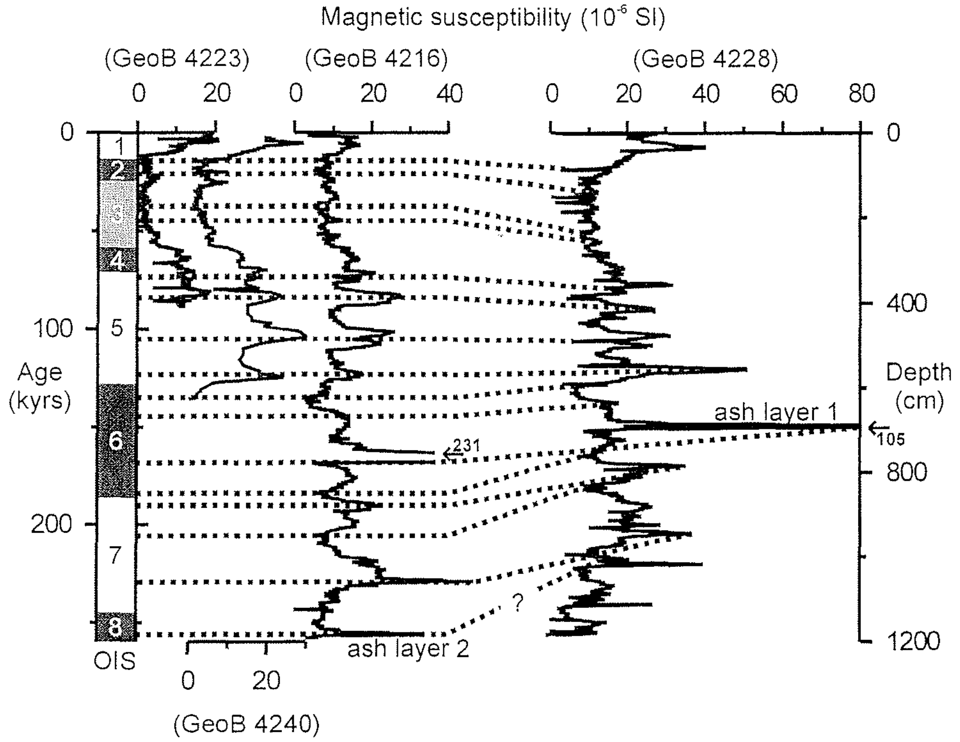

Fig. 3. Magnetic susceptibility of core GeoB 4228 and correlation with magnetic susceptibility of cores GeoB 4216, GeoB 4223, and GeoB 4240. Numbers at arrows indicate maximal magnetic susceptibility at ash layer 1 that was used for stratigraphic correlation.

## Geochemical results at the offshore sites GeoB 4216 (filament influenced) and GeoB 4228 (not influenced)

The records of different geochemical proxies related to productivity at the Cape Ghir filament influenced site GeoB 4216 are shown in Figure 5. TOC concentrations are generally low (mostly < 0.2 %) during interglacial OISs 1, 5, and 7. During glacial OISs 2, 3, 4, 6, and 8 concentrations are generally higher (0.2 – 0.8 %) and show a strong variability. Distinct TOC peaks named P1 to P10 were observed at 15 (Termination I), 24, 32, 43, 63, 128 (Termination II), 152, 178, 224 (substadial 7.4), and 242 (Termination III) ka BP (Fig. 5). While Terminations I + II are characterised by strongest TOC peaks, the peak at Termination III is much less pronounced. Site GeoB 4228 as a reference site for offshore conditions with less influence of the Cape Ghir filament, shows similar to site GeoB 4216 higher TOC concentrations during glacial times (Fig. 5). However, with the exception of a distinct peak during Termination II, the variability during glacial times is strongly reduced compared to site GeoB 4216.

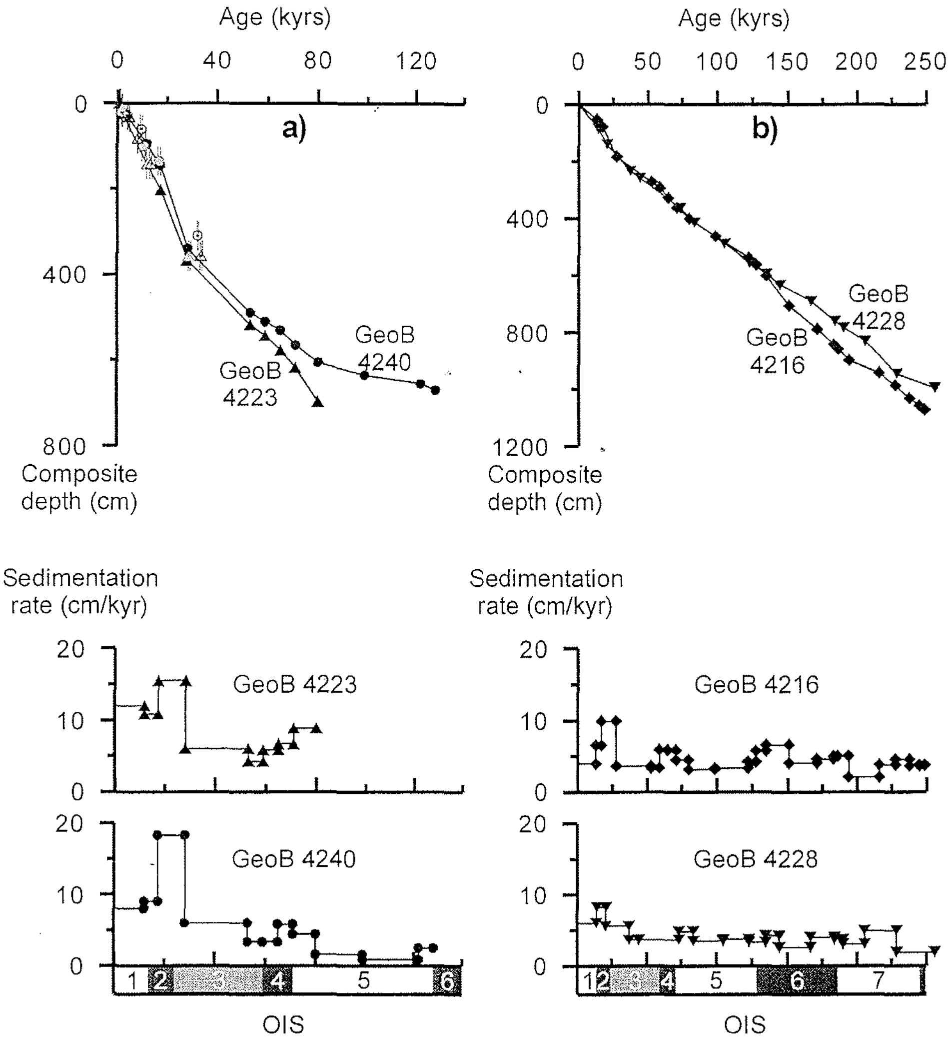

Fig. 4. Age-depth plots and sedimentation rate estimates for a) the near-coastal stations GeoB 4223 and GeoB 4240 and b) the offshore stations GeoB 4216 and GeoB 4228. Black symbols indicate tie points derived from oxygen isotope stratigraphy (cores GeoB 4216, GeoB 4223, GeoB 4240) or from correlation of susceptibility (core GeoB 4228). Grey symbols indicate $^{14}C$ ages on monospecific *G. bulloides* samples. Open symbols indicate $^{14}C$ AMS ages of mixed planktic foraminifera samples. $^{14}C$ AMS ages were calibrated to calendar years BP and are given as $2\sigma$-ranges (95% confidence limit) (see Henderiks et al., submitted).

Maxima in TOC concentration in core GeoB 4216 are accompanied by synchronous changes in other geochemical proxies related to productivity: carbonate concentrations vary between 25% and 80% and generally are low during TOC maxima. C/N ratios vary between 4 and 8 with glacial OISs 2, end of 3, 6 and 8 yielding generally higher values. Distinct TOC peaks are accompanied by local maxima of C/N. $\delta^{13}C_{org}$ varies between –23.6 and –19.9 ‰. The record shows a long-term decrease between OISs 5 and 1 by about 1 ‰. Values of $\delta^{15}N$ vary between 4.5 and 7.8 ‰. Values of $\delta^{13}C$ of *C. wuellerstorfi* vary between –0.2 and 1.1 ‰. Local minima of $\delta^{13}C_{org}$, $\delta^{15}N$ and $\delta^{13}C$ of *C. wuellerstorfi* coincide with TOC maxima.

The interpretation of none of these proxies is unequivocal. However, the strong time coincidence of variations suggests a common cause for this variability that will be discussed later.

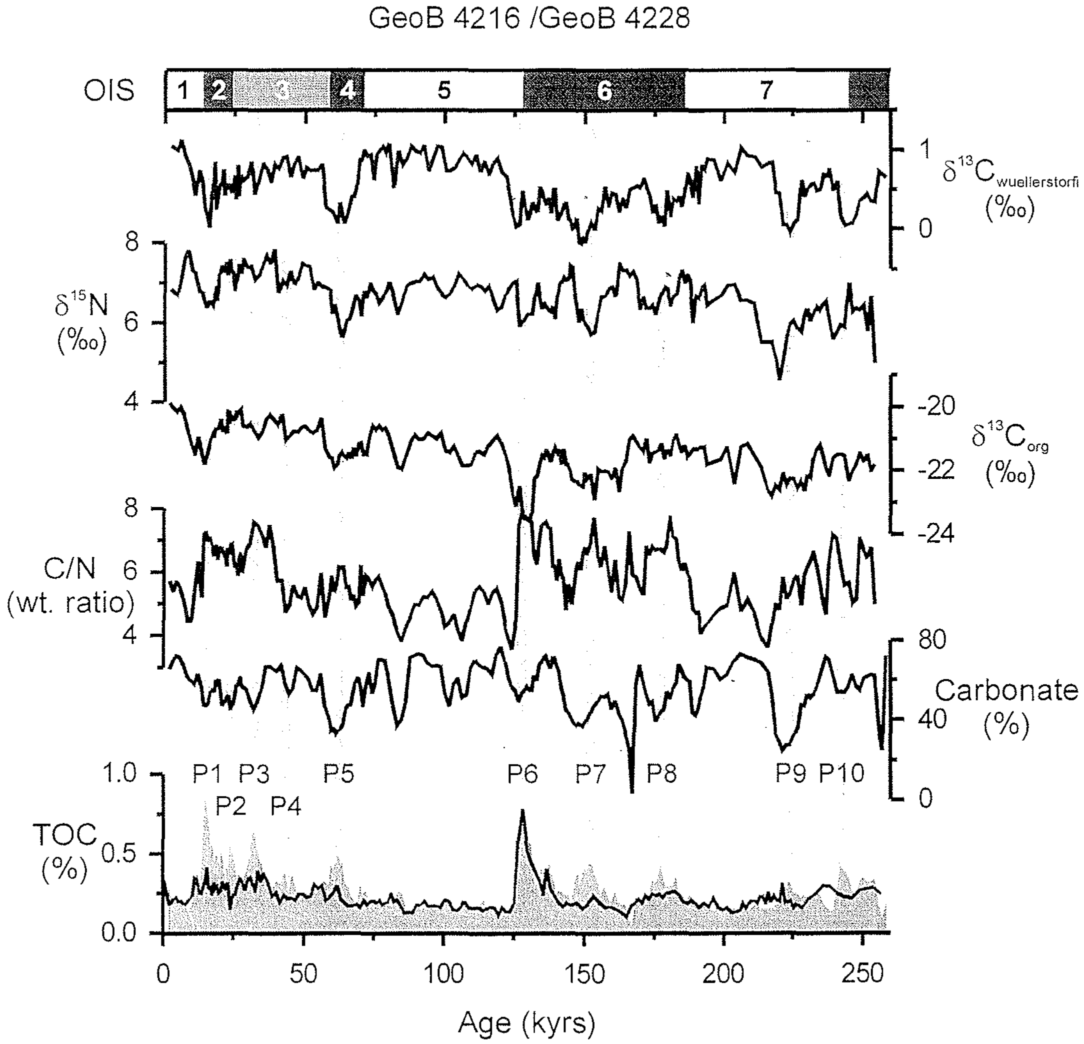

Fig. 5. Geochemical properties in core GeoB 4216 and TOC concentration in core GeoB 4228. TOC concentrations in cores GeoB 4216 and GeoB 4228 are indicated by grey shading and black line, respectively. Grey bars indicate distinct TOC peaks in core GeoB 4216.

Geochemical results at the near-coastal sites GeoB 4223 and GeoB 4240 (upwelling influenced)

TOC concentrations at GeoB 4223 and GeoB 4240 (0.25 - 1.2 %) are higher compared to the offshore stations (Fig. 6 and Fig. 7). The general pattern observed in the offshore stations with higher TOC concentrations during glacial times is also observed in the near-coastal stations. Despite of this similarity remarkable differences were identified: The early Holocene

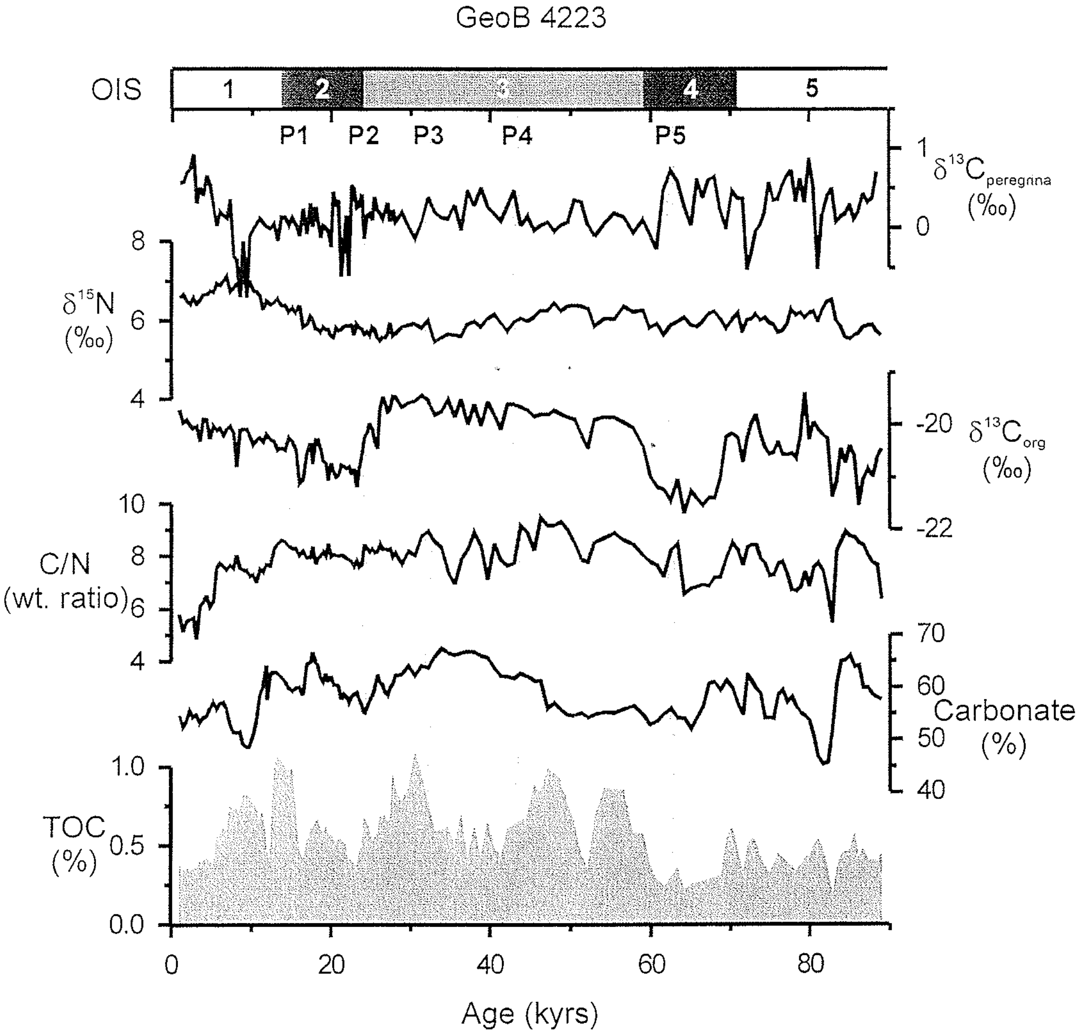

Fig. 6. Geochemical properties in core GeoB 4223. Times of TOC peaks in core GeoB 4216 are indicated for comparison by grey bars.

(OIS 1) is characterised in GeoB 4223 by high TOC concentrations up to 0.8 % and OIS 4 exhibits low TOC concentrations at both sites. While TOC peaks P1, P3, and P6 identified in GeoB 4216 coincide with TOC maxima in GeoB 4223 and GeoB 4240, this seems not to be the case for peaks P2, P4, and P5.

At the near-coastal stations, both carbonate concentrations and C/N ratios are high during glacial OISs 2, late 3, and 6. These are time intervals with high TOC concentrations. The $\delta^{13}C_{org}$ values are low (about –21 ‰) during OISs 2, 4, and 6. During interglacial times they range between –20.5 and –19.5 ‰. The $\delta^{15}N$ values are lowest (about 6 ‰) during OISs 2, late 3, and 6. During interglacial times they are slightly higher with a maximum in the middle Holocene (up to 7.5 ‰). The benthic $\delta^{13}C$ of GeoB 4240 (*C. wuellerstorfi*) ranges between

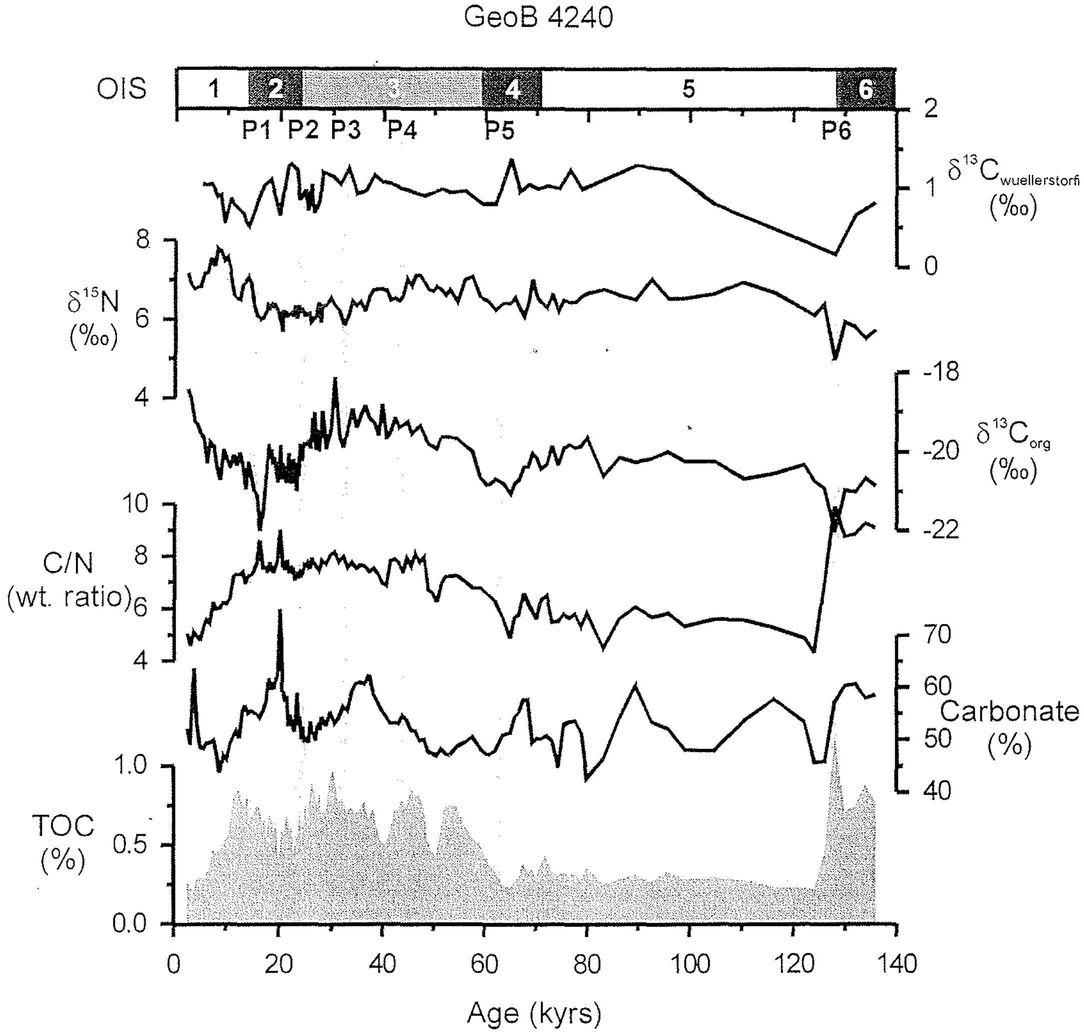

Fig. 7. Geochemical properties in core GeoB 4240. Times of TOC peaks in core GeoB 4216 are indicated for comparison by grey bars.

0.5 and 1.4 ‰ with lowest values during OISs 1/2 and 6. The benthic $\delta^{13}C$ of GeoB 4223 (*U. peregrina*) ranges between –0.9 and 0.9 ‰. Times of higher TOC concentrations (OIS 3 to early OIS 1) are coincident with generally lower benthic $\delta^{13}C$ values at site GeoB 4223.

## DISCUSSION

Productivity variations in the upwelling area off NW Africa between 13°N and 32°N during glacial-interglacial cycles have been investigated by various methods using micropaleontological and geochemical proxies (Müller et al., 1983; Sarnthein et al., 1987; Marret and Turon, 1994; Martinez et al., 1996; Guichard et al., 1999; Abrantes, 2000). Besides sites located at 20°N (Harris et al., 1996; Guichard et al., 1997; Martinez et al., 1999) commonly increased upwelling was observed during glacial OISs 2, 3, 4, and 6 relative to interglacial OISs 1 and 5. These findings are corroborated by generally higher TOC concentrations and higher sedimentation rates during glacial times observed in this study at all four investigated sites.

Despite of this overall similarity, remarkable differences were observed between the different sites in this study. The highest variability in TOC concentrations was observed at site GeoB 4216. In contrast to core GeoB 4216 the near-shore stations GeoB 4223 and GeoB 4240 show comparably low TOC concentrations during OIS 4. While TOC peaks coincide with minima of carbonate, $\delta^{13}C_{org}$, $\delta^{15}N$, and $\delta^{13}C_{benthic}$ at site GeoB 4216, this observation is not generally true for sites GeoB 4223 and GeoB 4240. These differences point to a rather complex sedimentation pattern in the investigation area.

The differences between the productivity records of sites GeoB 4216 and GeoB 4228 may be explained by the high influence of the Cape Ghir filament during glacial times at site GeoB 4216. This interpretation is supported by investigations of surface sediments in the investigation area: although lateral particle transport and early diagenesis result in a smoothing of the geochemical productivity signal in the sediments (see chapter 2.2), even meso-scale features like the Cape Ghir are reflected in the sediments by proxies related to productivity and nutrient conditions, like TOC concentration and $\delta^{15}N$ (see chapter 2.3).

If the variations in the productivity record are climatically induced, at least the productivity records of upwelling influenced sites GeoB 4223 and GeoB 4240 should co-vary with the record of site GeoB 4216, since both upwelling intensity and filament activity are dependent on the strength and duration of the Trade Winds. In the following we discuss, why this co-variation is not seen in the sediments. First the possible alteration or masking of the marine productivity records by early diagenesis and terrestrial sediment supply is evaluated. Then we discuss the locally varying impact of sea level and climatic induced changes on the sedimentary record of the various geochemical productivity indicators.

### Early diagenesis

The remineralisation of organic matter in sinking particles and in the sediments has a major impact on sedimentary TOC concentrations, on C/N ratios, and the stable nitrogen and carbon isotope ratios (Tyson, 1995). Organic matter degradation in marine sediments causes an increase of $pCO_2$ in pore waters that may result in carbonate dissolution even in sediments located above the water column carbonate lysocline (Jahnke et al., 1994; Milliman et al., 1999). Thus changes in organic matter preservation would cause synchronous changes in organic geochemical proxies and carbonate concentrations as observed in GeoB 4216.

Reduced bottom water oxygenation as indicated by lower $\delta^{13}C$ of epibenthic foraminifera, due to a decrease of NADW formation especially during terminations, could account for enhanced organic matter preservation (Sarnthein and Tiedemann, 1990; Sarnthein et al., 1994). Oxygen concentrations off Portugal at similar water depths compared to this study may have dropped from recently 5-6 µM/l to less than 0.5 µM/l during distinct intervals of OISs 2 and 3 (Baas et al., 1998). Site GeoB 4216 (2300 m water depth) is influenced by NADW, while sites GeoB 4223 (770 m), GeoB 4240 (1360 m), and GeoB 4228 (1600 m) are situated in the depth range of the MOW. Changes of organic matter preservation at site GeoB 4216 due to changes of NADW production could therefore explain the differences in the organic geochemical profiles at this site compared to the MOW influenced sites. However, the upwelling influenced site GIK 12392, located at 25°N at 2575 m water depth, should have experienced similar bottom water oxygenation variations as site GeoB 4216, although the variability of TOC concentrations resembles those of GeoB 4228 and GeoB 4240 with high concentrations during OISs 2,3, and 6 and low concentrations during OISs 1,4, and 5 (Müller and Suess, 1979). We therefore conclude that not regional changes in organic matter preservation caused by changes in bottom water oxygenation but local changes in organic matter supply are responsible for the observed variability. Similarly, Martinez et al. (1996) concluded from an integrated study of organic and inorganic productivity proxies at an upwelling influenced site south of our investigation area at 25°N that these proxies reflect primarily changes in their supply despite of the severe impact of early diagenesis.

### Terrestrial organic matter supply versus marine productivity

In many studies the sedimentary organic carbon has been proven to be a highly valuable and reliable productivity indicator in high productive continental margin areas if the impact of terrestrial organic matter was of minor importance (see review by Rühlemann et al., 1999).

Terrestrial particles are mainly transported to the northern Canary basin as dust while river transport is of minor importance in this area adjacent to the semi-arid to arid NW African continent. Typical carbonate variations in the North Atlantic with low concentrations during glacial times and cold periods of interglacial times, as are observed at the offshore site GeoB 4216, have been related to dilution by increased dust supply (Bacon, 1984; Francois et al., 1990; Matthewson et al., 1995). Dissolution has a minor impact on carbonate variability at site GeoB 4216 (chapter 2.4). At the near-coastal sites GeoB 4223 and GeoB 4240 high carbonate concentrations during OISs 2 and 4 may be explained either by upwelling influenced biogenic carbonate production that exceeds increased dust supply during glacial times, or by increased detritical carbonate sedimentation (chapter 2.4).

Dust consists mainly of lithogenic components but also of smaller amounts of biogenic components containing terrestrial organic matter. Thus, the question arises, if the observed variability of TOC concentrations at site GeoB 4216, which is coincident with increased dust supply indicated by low carbonate concentrations, may be explained by terrestrial organic matter sedimentation?

Sedimentary C/N ratios and $\delta^{13}C_{org}$ values are widely used to distinguish between marine and terrestrial organic matter. Typical terrigenous C/N ratios are greater than 20, whereas marine ratios range from 5 to 10 (Tyson, 1995). However, the analysis of sedimentary C/N ratios allows only rough estimates of the relative contribution of terrestrial organic matter, due to preferential degradation of nitrogen enriched organic compounds and the influence of inorganic nitrogen on sedimentary C/N ratios. $\delta^{13}C_{org}$ may be used for quantification if the influence of C4–plant material can be neglected and if the different isotope ratios of the marine and terrestrial end members are known (Wagner and Dupont, 1999). Pollen investigations indicate that terrestrial organic matter sedimentation in the northern Canary Basin is dominated by C3–plants from the Mediterranean realm (Hooghiemstra et al., 1992). C3–plants reveal low $\delta^{13}C_{org}$ values between –25.5 to –29.3 ‰ with an average of –27 ‰ (Tyson, 1995). A single measurement on dust sampled in the vicinity of the Canary Islands resulted in a terrestrial $\delta^{13}C_{org}$ of –25 ‰ (T.F., unpublished data). The stable carbon isotope ratio of marine organic matter of low and middle latitudes range typically from –18.5 to –21.5 ‰ (Sackett, 1986). Part of the variability of the marine $\delta^{13}C_{org}$ signature may be explained by varying $pCO_2$ due to glacial/interglacial changes in the atmospheric $CO_2$ content or in upwelling intensity (Rau et al., 1989; Müller et al., 1994).

In our study C/N ratios between 4 and 10 and $\delta^{13}C_{org}$ values between –23.5 and –19 ‰ indicate a general dominance of marine organic matter in the sediments. This interpretation is supported by microscopic investigations of the organic matter in sediments off NW Africa (Martinez et al., 1999; see also chapter 2.1 in this study). The variability observed in $\delta^{13}C_{org}$, may be attributed both to variations in the terrestrial organic matter supply and to changes in the productivity conditions related to upwelling activity and filament intensity. These factors are likely to cohere since both are dependent on the intensity of the Trade Winds.

A high sensitivity of $\delta^{15}N$ to a varying nutrient supply was shown in various upwelling regions of the world ocean (Altabet and Francois, 1994; Holmes et al., 1998; Hebbeln et al., 2000). According to preferential assimilation of $^{14}NO_3^-$ and Rayleigh fractionation kinetics, an increased supply of unutilised nitrate causes lower $\delta^{15}N$ values of the marine organic matter (Altabet and Francois, 1994). Other possible factors influencing the sedimentary $\delta^{15}N$ seem to be of minor importance. Changes in the $\delta^{15}N$ of nitrate due to changes in the global nutrient cycling should affect all investigated sites in the same manner (Altabet and Curry, 1989; Kienast, 2000). A significant impact of $^{15}N$ depleted inorganic nitrogen in organic poor sediments of the investigation area would result contrary to our observations in low sedimentary $\delta^{15}N$ with low TOC concentrations and low C/N ratios (chapter 2.1).

In some cases, $^{15}N$ depleted sedimentary stable nitrogen isotope ratios were also used as an indicator of terrestrial organic matter (Sweeney and Kaplan, 1980; Mariotti et al., 1984). Thus, similar to $\delta^{13}C_{org}$ the variability of sedimentary $\delta^{15}N$ may be attributed both to variations in the terrestrial organic matter supply and to changes in the productivity conditions. However, $\delta^{15}N$ is less sensitive to variations in terrestrial organic matter, since marine organic matter yields much higher nitrogen concentrations. Regarding the general dominance of marine organic matter in the sediments of our investigation area, we interpret variations of $\delta^{15}N$ as indicator of nutrient supply related to variations in upwelling intensity and filament transport. Increased nutrient supply was responsible for increased productivity as shown by low $\delta^{15}N$ and high TOC concentrations at OISs 2 and 3 in the upwelling influenced sites GeoB 4223 and GeoB 4240, and a general coincidence of $\delta^{15}N$ minima and TOC maxima at the offshore site GeoB 4216 during glacial periods.

We conclude that variations in TOC concentrations reflect the variability in marine productivity. The much higher variability observed at the offshore site GeoB 4216 compared to site GeoB 4228 indicate that local productivity processes (and not dust supply, which should have similar signals in both offshore sites) related to the Cap Ghir filament are documented in TOC concentrations of core GeoB 4216.

Additional evidence for the interpretation of TOC concentrations at core GeoB 4216 as marine productivity signal reflecting filament activity is provided by the analysis of the gradient in $\delta^{18}O$ of planktic foraminifera between site GeoB 4216 and the upwelling influenced sites GeoB 4223 and GeoB 4240 (Fig.8). This gradient is independent of organic matter degradation or terrestrial sediment supply. The $\delta^{18}O$ is dependent on the global variability of the hydrological cycle that is documented in sea-level variations, and is further dependent on the local surface water density (e.g. Billups and Schrag, 2000). The water density is a function of salinity and temperature. A strong density gradient exists between coastal upwelled and offshore subtropical gyre surface waters partly due to changes in salinity induced by evaporation (Hagen et al., 1996). The density gradient between the filament influenced site GeoB 4216 and the upwelling influenced sites GeoB 4223 and GeoB 4240 should be small if upwelled water is transported by the Cape Ghir filament offshore to site GeoB 4216, and should be stronger if the filament is weak and does not reach this site. Examination of the $\delta^{18}O$ gradient reveals lowest gradients between the end of OISs 3 and 2 where highest TOC concentrations at GeoB 4216 and thus strongest filament activity was observed (Fig. 8), supporting the interpretation of TOC variability at site GeoB 4216 as filament signal.

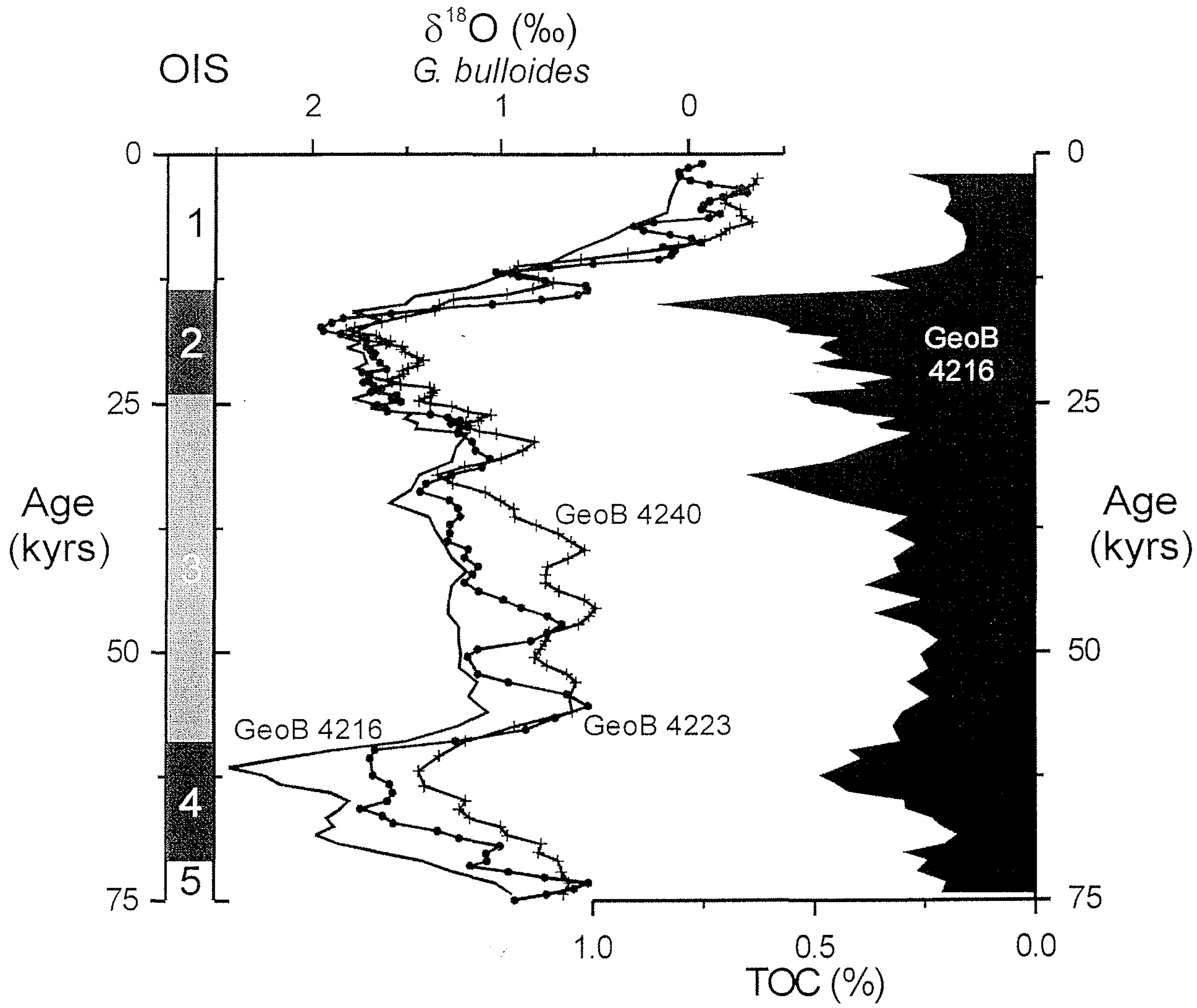

Fig. 8. Comparison of smoothed $\delta^{18}O$ of *G. bulloides* (5 point least square smoothing using the program AnalySeries; Paillard et al., 1996) at the upwelling influenced sites GeoB 4223 and GeoB 4240 and at the filament influenced site GeoB 4216 as related to TOC variations at site GeoB 4216.

Influence of sea-level changes and Trade Winds on the productivity signal

Productivity variations related to coastal upwelling and to the Cape Ghir filament depend on the strength of the NE Trade Wind system in the investigation area. If the regional climate would be the only factor influencing the sedimentary productivity record, variations in productivity proxies should co-vary at the coastal upwelling influenced sites GeoB 4223 and GeoB 4240, and at the filament influenced site GeoB 4216. As already pointed out, this is not the case. Another factor with different regional impact on the different investigation sites is needed to explain the observed dissimilarity. Sea-level changes could be an important additional factor. Three major processes have to be considered:

1. Sea-level changes are responsible for zonal shifts of the centres of upwelling and filament activity. During glacial times lowered sea level caused a shift of the shoreline and the upwelling centre towards the shelf edge that is towards the investigations sites (compare Guichard et al., 1999).

2. Sea-level changes should have an impact on the nutrient content of upwelled waters. During interglacial times, when upwelling is centred on the shelf, upwelled waters have been in contact with the sea floor of the shelf, where much of the nutrient regeneration occurs. This contact was less important during glacial times when much less flooded shelf area existed (Bertrand et al., 2000).

3. Most of the particle production on the shelf is deposited in the upper part of the continental slope during interglacial sea level high stand conditions. During glacial times, when the shelf was much narrower, different modes of lateral particle transport and deposition on the continental shelf and slope area may have been active (Fütterer, 1983). Erosion of shelf sediments during glacial low sea level could explain increased detritical particle sedimentation on the slope (chapter 2.4).

Calculation of power spectra may help to distinguish the climatically induced variability of the productivity records from the sea-level induced variability. Sea-level changes are mainly reflected by the benthic and planktic $\delta^{18}O$ records. The power spectra of the $\delta^{18}O$ records are dominated by variances at orbital periodicity related to eccentricity and obliquity (T = 100 ka and 41 ka, respectively) and to minor amounts related to precession (T = 23 ka). The dominance of the obliquity signal is seen at all three sites GeoB 4216, GeoB 4223, and GeoB 4240 (Fig. 9). The eccentricity is only detected at site GeoB 4216 depending on the length of the time series.

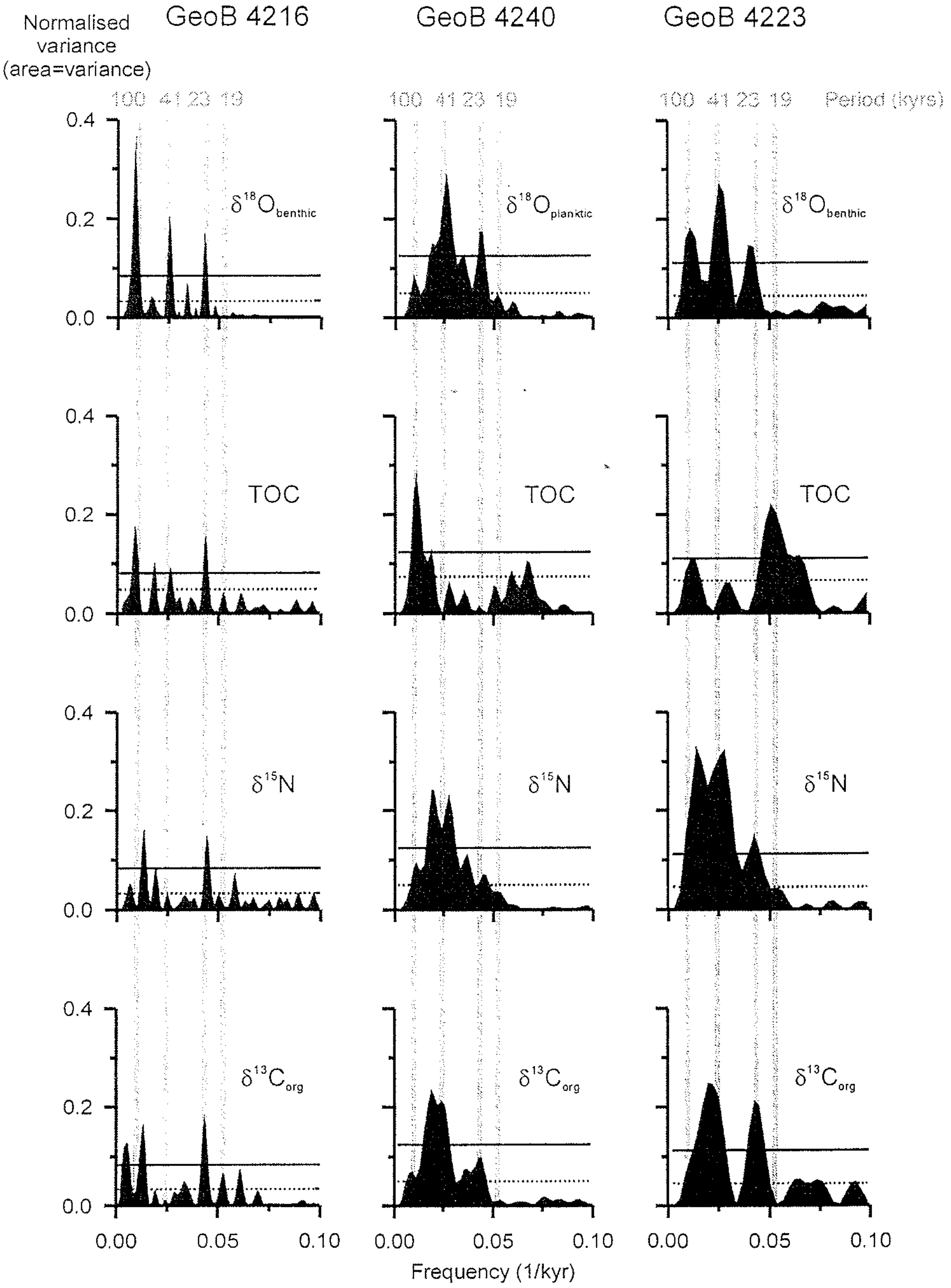

Fig. 9. Power spectra of $\delta^{18}O$, TOC concentrations, $\delta^{15}N$, and $\delta^{13}C_{org}$ in cores GeoB 4216, GeoB 4223, and GeoB 4240. Spectra were calculated from harmonic analyses of each parameter after Schulz (1994) without time-interpolation (6 dB bandwidth [site GeoB 4216: 0.005 $ka^{-1}$; site GeoB 4240: 0.009 $ka^{-1}$; site GeoB 4223: 0.014 $ka^{-1}$]; significance level $\alpha = 0.01$; linear trend subtracted) Horizontal lines indicate critical levels for Siegel test (Siegel, 1980) (dotted line) and Fisher test (Fisher, 1929). Grey bars mark Milankovitch frequencies.

TOC, $\delta^{15}N$ and $\delta^{13}C_{org}$ profiles at site GeoB 4216 are characterised by a higher relative variance at the precessional frequency. While the obliquity signal is still significant with regard to TOC, it is not detected at the $\delta^{15}N$ and $\delta^{13}C_{org}$ profiles. Sea-level changes seem to have a minor impact on the accumulation of organic matter and its geochemical signature at this site. Instead, frequency analyses indicate a strong precessional forcing on productivity.

At the upwelling influenced sites GeoB 4223 and GeoB 4240 a strong obliquity component is observed both at the $\delta^{15}N$ and $\delta^{13}C_{org}$ profiles, which indicates an impact of sea-level changes on these proxies at the near-coastal sites. Low $\delta^{15}N$ and $\delta^{13}C_{org}$ values were observed during OISs 2, 3 (low $\delta^{15}N$ but high $\delta^{13}C_{org}$), 4, and 6 that is during times of low sea level. With respect to $\delta^{15}N$, the impact of sea level is best explained by a lateral shift of the upwelling centre towards the investigation sites during lowered sea level. A decrease of sedimentary $\delta^{15}N$ towards the upwelling centre due to increased concentrations of upwelled nitrate and preferential assimilation of $^{14}NO_3^-$, is a general feature observed in upwelling systems (e.g. Altabet and Francois, 1994; Hebbeln et al., 2000; Holmes et al., 1998; Meggers et al., this issue). The coincident decrease of $\delta^{13}C_{org}$ may be explained in analogy by increased concentrations of $CO_2$ due to the shift of the upwelling centre towards the investigation sites. Next to the obliquity signal indicating the impact of sea-level changes, precessional forcing is still recognised at the TOC, $\delta^{15}N$ and $\delta^{13}C_{org}$ profiles of core GeoB 4223. No indication of precessional forcing on productivity was found at site GeoB 4240. The strong sensitivity of sites GeoB 4223 and GeoB 4240 to longitudinal shifts of the coastal upwelling in combination with the impact of changing nutrient concentrations of the upwelled waters and changing shelf and slope deposition patterns, all related to sea-level changes, can explain the differences in the productivity records of core GeoB 4216 on the one hand and of cores GeoB 4223 and GeoB 4240 on the other hand. We assume that upwelling intensity and filament activity are controlled by the same precessional forcing mechanism. However this forcing mechanism is masked at the near-coastal sites by the dominant impact of sea-level changes on the productivity signal. In contrast, site GeoB 4216 seem to be a highly sensitive recorder of productivity variations related to Cape Ghir filament intensity and thus related to NE Trade Wind strength.

Analysis of grain sizes of the terrigenous fraction and pollen at two nearby stations (site GeoB 5559 and site GIK 16004, see Fig. 1 for locations) support the interpretation of a relationship between Trade Winds and productivity variations at site GeoB 4216 (Fig. 10). Major TOC peaks in core GeoB 4216 coincide with the exception of a peak at about 33 ka with maxima in median grain sizes indicating increased wind strength at site GeoB 5559 (Moreno et al., submitted). Peaks in the abundance of *pinus* pollen at site GIK 16004, which originate from the Mediterranean vegetation belt and can be used as a Trade Wind indicator

(Hooghiemstra et al., 1992; Dupont, 1999), coincide with TOC peaks in core GeoB 4216. Thus, productivity variations at site GeoB 4216 together with grain sizes at site GeoB 5559 and pollen at site GIK16004 are indicative for a precessional forcing of summer Trade Winds off NW Africa.

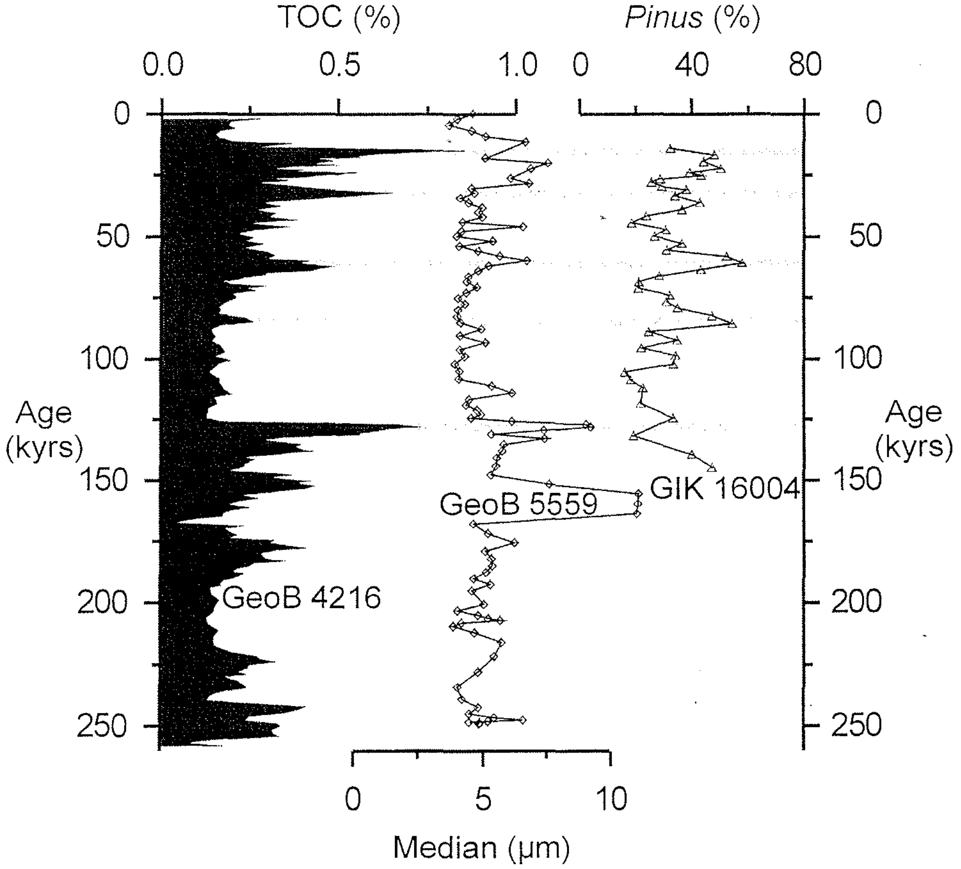

Fig. 10. Comparison of TOC variability at the filament-influenced site GeoB 4216 with grain size variations (Moreno et al., submitted) and Trade Wind indicating percentages of *pinus* pollen (Hooghiemstra et al., 1992) in nearby sediment cores.

## CONCLUSIONS

Despite of early diagenesis and lateral particle transport, sedimentary geochemical properties reflect mainly productivity gradients in the investigation area adjacent to the upwelling area off Morocco, allowing at least a qualitative reconstruction of productivity variations in the late Quaternary. The productivity records at the four sites investigated in this study showed both similarities and differences. The observed general pattern, of higher marine productivity during glacial times is similar at all four sites. However, detailed examination of the records revealed strong differences in the variability of productivity during glacial times indicating different forcing mechanisms.

Two different processes were identified that influence the productivity record: global sea-level changes control the distance of the investigation site to the upwelling zone, while the strength of summer NE Trades is determinant for the upwelling intensity. The impact of sea-level changes strongly overprints the regional climatic signal at the continental slope sites. In contrast the productivity record of a further offshore-located site that is influenced by the upwelling related Cape Ghir filament, is highly sensitive to changes in Trade Wind intensity. Summer Trade Wind intensity off NW Africa seems to be related to precessional forcing mechanisms.

This study shows that a careful selection of the investigation site is needed for the investigation of paleointensity of coastal upwelling. A dominance of sea-level changes on the productivity record largely overprinting the paleoclimatic signal has to be considered at all continental margins that are characterised by a broad shelf.

## ACKNOWLEDGEMENTS

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# 3. CONCLUSIONS

This PhD thesis entitled *Reconstruction of productivity gradients in the Canary Islands region off Morocco by means of sediments and sinking particles* was carried out in the context of the EU-project CANIGO (Canary Islands Azores Gibraltar Observations) off NW Africa combining particle trap and sedimentary investigations. Geochemical proxies were applied to trace productivity variations in space and time. The studies conducted may be listed in three general parts:

I. As a methodological component of this thesis, the processes responsible for early diagenetic changes of stable nitrogen and carbon isotope ratios in marine sediments were investigated in order to improve the knowledge and the possible pitfalls of their use as paleo-proxies (chapter 2.1).

II. Present regional productivity gradients were reconstructed in sinking particles and surface sediments in order to evaluate the potential of the applied productivity proxies to reconstruct past productivity changes in the investigation area (chapters 2.2 and 2.3).

III. The evaluated proxies were used for reconstruction of past productivity variations in the investigation area in relation to climate change. For this purpose, both the accumulation of biogenic compounds in time-slices (chapter 2.4) and the variability of geochemical properties along time-series (chapter 2.5) were investigated in different sediment cores.

In the following, the main results of these parts will be summarised. The summary will be concluded by a brief outlook.

## 3.1 Early diagenetic fractionation of stable nitrogen and carbon isotopes

In the study investigating the impact of early diagenetic processes on the isotopic ratio of different nitrogen fractions in marine sediments, two main processes were identified that potentially influence the isotopic composition of nitrogen and carbon isotope ratios of the organic matter:

1.: Benthic heterotrophic organisms responsible for the remineralisation of sedimentary organic matter excrete inorganic nitrogen and carbon (dissolved $NH_4^+$ and $CO_2$) depleted in $^{15}N$ and $^{13}C$ with respect to the organic source and build up new organic matter enriched in $^{15}N$ and $^{13}C$.

2.: Preferential degradation of organic compounds with isotopic compositions different from the bulk sedimentary organic matter caused isotopic fractionation.

While the first process seemed to dominate changes in the nitrogen isotopic ratio of the organic matter in sediments of the investigation area, both processes compete with respect to stable carbon isotopes. This diverging behaviour can be explained by low nitrogen concentrations of the refractory organic matter. Inorganic nitrogen (mainly $NH_4^+$ fixed between the lattices of clay minerals) is depleted in $^{15}N$. The relative increase of inorganic nitrogen during remineralisation of organic nitrogen tends to counteract the metabolic increase of sedimentary $\delta^{15}N$.

## 3.2 Reconstruction of present productivity gradients in sinking particles and surface sediments

Three sediment trap moorings were placed along a productivity gradient in the northern Canary Islands region. The productivity gradient which is documented by the photosynthetic pigment concentrations as observed by satellites was reflected in the biogenic fluxes and their stable nitrogen isotopic composition in the upper few hundreds of meters. However, the primary flux signal was altered during settling of the particles and in the sediments. Less than 1% of the exported organic matter flux was preserved in the sediments due to remineralisation in the water column and in surface sediments. Concomitantly, the $\delta^{15}N$ of the sinking particles increased. In addition to organic matter remineralisation, the lateral transport of biogenic particles strongly affected sedimentary fluxes and lead to a eutrophic overprint on the oligotrophic flux signal at deep-sea sites up to 800 km offshore from the coastal upwelling margin.

Investigations of particle accumulation and micropaleontological and geochemical properties of surface sediments revealed that despite of particle degradation and lateral transport, productivity gradients in the Canary Islands region were matched in surface sediments. Although the gradients were smoothed, a qualitative reconstruction of productivity gradients by the investigation of sediments was possible. Even mesoscale features like the Cape Ghir filament were reflected by the productivity proxies in the surface sediments. The impact of terrestrial dust derived from the African continent seemed to be of minor importance with respect to the organic matter accumulation as indicated by C/N ratios and the stable carbon isotopes of the organic matter.

### 3.3 Reconstruction of past productivity variations

Past productivity variations off Morocco were investigated in sediment cores of six investigation sites. Two of them were located on the continental slope close to the high-productive upwelling area (sites GeoB 4223 and GeoB 4240), two sites were situated further offshore (sites GeoB 4216 and GeoB 4228), one of them influenced by the Cape Ghir filament (site GeoB 4216), and two cores belonged to the oligotrophic subtropical gyre region (sites GeoB 4241 and GeoB 4242). Productivity variations were investigated both by means of biogenic accumulation rates in time-slices and by changes of geochemical properties along time-series. Both approaches revealed higher productivity during glacial times at the upwelling and filament influenced sites, while little changes were observed at the oligotrophic sites.

The interpretation of the productivity records at the upwelling influenced continental slope sites with respect to changes of the regional climate was impeded by the strong impact of sea-level changes, carbonate dissolution, and dilution by detrital biogenic sedimentation. At one of these sites (GeoB 4240) extremely low sediment accumulation rates, typical of "oceanic" conditions, were encountered during oxygen isotopic stage 5 which indicated a local perturbation of sedimentation. Comparison of the productivity record at the filament influenced site (GeoB 4216) with proxies related to atmospheric circulation (pollen, grain-size of lithogenic matter) showed that this location was uniquely suited to reflect variations in trade wind intensity especially during glacial times. Time series analyses indicated precessional forcing of summer Trade Winds off NW Morocco.

### 3.4 Outlook

As already outlined in the general introduction, the interest in the reconstruction of productivity gradients off NW Africa lies in its potential implications for climate research. In addition to the reconstruction of climate variability, the regional quantification of $CO_2$ sources and sinks as components of the global carbon cycle is an important step for a better understanding of climate change.

For future research, an increase in the time-resolution and more precise dating (e.g. by carrying out additional $^{14}C$ AMS dating) are needed in order to investigate if episodic and short term-events (like for example N-Atlantic cooling related to ice-berg discharges or to perturbations in the zonal Atlantic heat transport) may cause or may be triggered by subtropical climate variations. Due to the variety of processes influencing the accumulation of biogenic particles in the marine sediments (climate induced productivity variations, sea-level changes and related local displacements of upwelling cells, erosion, particle degradation, sediment winnowing and focussing) high spatial resolution is needed for the regional assessment of their role as a carbon sink. It was shown in chapter 2.5 that fast scanning methods like the Multi Sensor Core Logging method can provide useful data for stratigraphic correlation of additional sediment cores of the Canary Islands region with the dated cores presented in this study. Thus, age models and geochemical analyses in combination with core-logging data of all 72 sediment cores taken off Morocco and in the vicinity of the Canary Islands may provide the basis for quantitative estimates of the regional sediment accumulation off NW Africa.

# 4. LITERATURE

Abrantes, F., 1988. Diatom assemblages as upwelling indicators in surface sediments in Portugal. Mar. Geol., 85: 15-39.

Abrantes, F., 2000. 200,000 yr diatom records from Atlantic upwelling sites reveal maximum productivity during LGM and a shift in phytoplankton community structure at 185,000 yr. EPSL, 176(1): 7-16.

Abrantes, F. and Moita, M.T., 1999. Water column and recent sediment data on diatoms and coccolithophorids, off Portugal, confirm sediment record of upwelling events. Oceanologica Acta. 22(1): 67-84.

Abrantes, F., Sprengel, C., Bollmann, J., Palma, S., Nave, S., Meggers, H. and Henderiks, J., submitted. Flux of organisms along an East-West transect at 29°N in the Canary Island region. Deep-Sea Res. II.

Abrantes, F., Winn, K. and Sarnthein, M., 1994. Late Quaternary paleoproductivity variations in the NE and Equatorial Atlantic: diatom and $C_{org}$ evidence. In: R. Zahn, T.F. Pedersen, M.A. Kaminski and L. Labeyrie (Editors), Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change. NATO ASI Series, Vol.1(17), Springer, pp. 425-439.

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 Res., 35: 535-554.

Altabet, M.A. and Curry, W.B., 1989. Testing models of past ocean chemistry using foraminifera $^{15}$N /$^{14}$N. Global Biogeochem. Cycles, 3(2): 107-119.

Altabet, M.A. and Francois, R., 1994. Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization. Global Biogeochem. Cycles, 8(1): 103-116.

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, 354: 136-139.

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

Antia, A.N., von Bodungen, B. and Peinert, R., 1999. Particle flux across the mid-European Continental Margin. Deep-Sea Res. I, 46(12): 1999-2024.

Arístegui, J., Sangrá, P., Hernández-León, S., Cantón, M., Hernández-Guerra, A. and Kerling, J.L., 1994. Island-induced eddies in the Canary Islands. Deep-Sea Res. I, 41(10): 1509-1525.

Arístegui, J., Tett, P., Hernandez-Guerra, A., Basterretxea, G., Montero, M.F., Wild, K., Sangrá, P., Hernández-León, S., Cantón, M., Garcia-Braun, J.A., Pacheco, M. and Barton, E.D., 1997. The influence of island-generated eddies on chlorophyll distribution: a study of mesoscale variation around Gran Canaria. Deep-Sea Res. I, 44(1): 71-96.

Armstrong, D.A., Mitchell-Innes, B.A., Verheye-Dua, F., Waldron, H. and Hutchings, L., 1987. Physical and biological features across an upwelling front in the southern Benguela. In: A.I.L. Payne, J.A. Gulland, K.H. Brink, (Editors), The Benguela and Comparable Ecosystems. South African Journal of Marine Sciences 5, pp. 171-190.

Baas, J.H., Schönfeld, J. and Zahn, R., 1998. Mid-depth oxygen drawdown during Heinrich events: evidence from benthic foraminiferal community structure, trace-fossil tiering, and benthic $\delta^{13}$C at the Portuguese Margin. Mar. Geol., 152(1-3): 25-55.

Bacon, M.P., 1984. Glacial to interglacial changes in carbonate and clay sedimentation in the Atlantic Ocean estimated from $^{230}$Th measurements. Isotope Geoscience, 2: 97-111.

Bárcena, M.A. and Abrantes, F., 1998. Evidence of a high-productivity area off the coast of Málaga from studies of diatoms in surface sediments. Mar. Micropal., 35: 91-103.

Bard, E., Arnold, M., Maurice, P., Duprat, J., Moyes, J. and Duplessy, J.C., 1987. Retreat velocity of the North Atlantic polar front during the last deglaciation determined by $^{14}$C accelerator mass spectrometry. Nature, 328: 791-794.

Bard, E., Fairbanks, R., Arnold, M., Maurice, P., Duprat, J., Moyes, J. and Duplessy, J.-C., 1989. Sea-level estimates during the last deglaciation based on $\delta^{18}$O and accelerator mass spectrometry $^{14}$C ages measured in *Globigerina bulloides*. Quat. Res., 31: 381-391.

Barnola, J.M., Raynaud, D., Korotkevich, Y.S. and Lorius, C., 1987. Vostok ice core provides 160,000-year record of atmospheric $CO_2$. Nature, 329: 408-414.

Barnola, J.M., Raynaud, D., Neftel, A. and Oeschger, H., 1983. Comparisons of $CO_2$ measurements by two laboratories on air bubbles in polar ice. Nature, 303: 410-413.

Barton, E.D., 1998. Eastern boundary of the North Atlantic: Northwest Africa and Iberia. In: A.R. Robinson and K.H. Brink (Editors), The Global Coastal Ocean - Regional Studies and Synthesis. The Sea, ideas and observations on progress in the study of the seas. John Wiley, New York, pp. 633-657.

Barton, E.D., Arístegui, J., Tett, P., Cantón, M., García-Braun, J., Hernandez-Leon, S., Nykjaer, L., Almeida, C., Almunia, J., Ballesteros, S., Basterretxea, G., Escánez, J., García-Weill, Hernández-Guerra, A., López-Laatzen, F., Molina, R., Montero, M.F., Navarro-Pérez, E., Rodríguez, J.M., van Lenning, K., Vélez, H. and Wild, K., 1998. The transition zone of the Canary Current upwelling region. Prog. Oceanogr., 41: 455-504.

Battarbee, R., 1973. A new method for estimating absolute microfossil numbers with special reference to diatoms. Limnol. Oceanogr., 18: 647-653.

Bé, A.W.H., 1977. An ecological, zoogeographic and taxonomic review of recent planktonic foraminifera. In: A.T.S. Ramsey (Editor), Oceanic Micropaleontology. Academic Press, London, pp.1-100.

Bé, A.W.H. and Hutson, W.H., 1977. Ecology of planktonic foraminifera and biogeographic patterns of life and fossil assemblages in the Indian Ocean. Micropal., 23: 369-414.

Bé, A.W.H. and Tolderlund, D.S., 1971. Distribution and ecology of living planktonic foraminifera in surface waters of the Atlantic and Indian Oceans. In: B.M Funnell, W.R. Riedel (Editors), Micropaleontology of Oceans. Cambridge University Press, London: pp. 105-149.

Bergametti, G., Gomes, L., Coude-Gaussen, G., Rognon, P. and Le Coustumer, M.-N., 1989. African dust observed over Canary Islands: Source-regions identification and transport pattern for some summer situations. J. Geophys. Res., 94: 14855-14864.

Berger, W.H., 1976. Biogenous deep sea sediments: Production, preservation and interpretation. In: J.P. Riley, R. Chester (Editors), Chemical Oceanography. Academic Press, London, New York, San Francisco, pp. 265-389.

Berger, W.H., 1982. Increase of carbon dioxide in the atmosphere during deglaciation, the coral reef hypothesis. Naturwissenschaften, 69: 87-88.

Berger, W.H. and Keir, R.S., 1984. Glacial-Holocene changes in atmospheric $CO_2$ and the deep-sea record. In: J.E. Hansen and T. Takahashi (Editors), Climate Processes and Climate Sensitivity. Geophysical Monographs. American Geophysical Union, Washington, DC, pp. 337-351.

Berger, W.H. and Wefer, G., 1990. Export production: seasonality and intermittency, and paleoceanographic implications. Palaeogeography, Palaeoclimatology, Palaeoecology, 89: 245-254.

Berner, R.A., 1980. Early Diagenesis - A Theoretical Approach. Princeton Series in Geochemistry. Princeton University Press, Princeton, N.J., 241 pp.

Bertrand, P., Pedersen, T.F., Martinez, P., Calvert, S. and Shimmield, 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.

Bertrand, P., Shimmield, G., Martinez, P., Grousset, F., Jorissen, F., Paterne, M., Pujol, C., Bouloubassi, I., Buat Menard, P., Peypouquet, J.-P., Beaufort, L., Sicre, M.-A., Lallier-Verges, E., Foster, J., Ternois, Y. and the other participants of the Sedorqua Program, 1996. The glacial ocean productivity hypothesis: the importance of regional temporal and spatial studies. Mar. Geol., 130(1-2): 1-9.

Billups, K., Schrag, D.P., 2000. Surface ocean density gradients during the Last Glacial Maximum. Paleoceanogr., 15(1): 110-123.

Biscaye, P.E. and Anderson, R.F., 1994. Fluxes of particulate matter on the slope of the southern Middle Atlantic Bight: SEEP-II. Deep-Sea Res. II, 41(2/3): 459-509.

Boatman, C.D. and Murray, J.W., 1982. Modeling exchangeable $NH_4^+$ adsorption in marine sediments: Process and controls of adsorption. Limnol. Oceanogr., 27: 99-110.

Böttcher, M.E., Oelschläger, B., Höpner, T., Brumsack, H.-J. and Rullkötter J., 1998. Sulfate reduction related to the early diagenetic degradation of organic matter and "black spot" formation in tidal sandflats of the German Wadden Sea (southern North Sea): stable isotope ($^{13}C$, $^{34}S$, $^{18}O$) and other geochemical results. Org. Geochem., 29: 1517-1530.

Brandes, J.A. and Devol, A.H., 1997. Isotopic fractionation of oxygen and nitrogen in coastal marine sediments. Geochim. Cosmochim. Acta, 61: 1793-1801.

Brink, K.H., Abrantes, F., Bernal, P.A., Dugdale, R.C., Estrada, M., Hutchings, L., Jahnke, R.A., Müller, P.J. and Smith, R.L., 1995. Group report: How do coastal upwelling systems operate as integrated physical, chemical, and biological systems and influence the geological record? The role of physical processes in defining the spatial structures of biological and chemical variables. In: C.P. Summerhayes, K.C. Emeis, M.V. Angel, R.L. Smith, B. Zeitschel (Editors), Upwelling in the Ocean: Modern Processes and Ancient Records. John Wiley and Sons Ltd., New York, pp. 103-124.

Broecker, W.S., 1982. Ocean chemistry during glacial time. Geochim. Cosmochim. Acta, 46: 1689-1705.

Broecker, W.S. and Henderson, G.M., 1998. The sequence of events surrounding Termination II and their implications for the cause of glacial-interglacial $CO_2$ changes. Paleoceanogr., 13(4): 352-364.

Broecker, W.S. and Peng, T.H., 1982. Tracers in the Sea. Eldigo Press, 692 pp.

Broecker, W.S. and Takahashi, T., 1978. The relationship between lysocline depth and in situ carbonate ion concentration. Deep-Sea Res., 25: 65-95.

Burkhardt, S., Riebesell, U. and Zondervan, I., 1999. Effects of growth rate, $CO_2$ concentration, and cell size on the stable carbon isotope fractionation in marine phytoplankton. Geochim. Cosmochim. Acta, 63(22): 3729-3741.

Calvert, S.E., Nielsen, B. and Fontugne, M.R., 1992. Evidence from nitrogen isotope ratios for enhanced productivity during formation of eastern Mediterranean sapropels. Nature, 359: 223-225.

Carpenter, E.J., Harvey, H.R., Fry, B. and Capone, D.G., 1997. Biogeochemical tracers of the marine cyanobacterium *Trichodesmium*. Deep-Sea Res. I, 44(1): 27-38.

Cifelli, R., 1961. *Globigerina incompta*, a new species of pelagic foraminifera from the North Atlantic. Cushman Foundation Foraminiferal Research, Contributions, 12: 83-86.

Cheddadi, R., Lamb, H.F. Guiot, J. and van der Kaars, S., 1998. Holocene climatic change in Morocco: a quantitative reconstruction from pollen data. Climate Dynamics, 14: 883-890.

Cole, J.J., Honjo, S. and Erez, J., 1987. Benthic decomposition of organic matter at a deep-water site in the Panama Basin. Nature, 327: 703-704.

Coude-Gaussen, G., Rognon, P., Bergametti, G., Gomes, L. Strauss, B., Gros, J.M. and Le Coustumer, M.N., 1987. Saharan dust on Fuerteventura Island (Canaries): Chemical and mineralogical characteristics, air mass trajectories, and probable sources. J. Geophys. Res., 92: 9753-9771.

Cowie, G.L. and Hedges, J.I., 1991. Organic carbon and nitrogen geochemistry of Black Sea surface sediments from stations spanning the oxic:anoxic boundary. In: E. Izdar, J.W. Murray (Editors), Black Sea Oceanography. Kluwer, pp. 343-349.

Dale, B. and Fjellså, A., 1994. Dinoflagellate cysts as productivity indicators: state of the art, potential and limits. In: R. Zahn, T.F. Pedersen, M.A. Kaminski and L. Labeyrie (Editors), Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change. NATO ASI Series, Vol.1(17), Springer, pp. 521-537.

Davenport, R., Neuer, S., Helmke, P., Perez-Marrero, J., Llinas, O. and Wefer, G., submitted. Primary production in the northern Canary Islands region as inferred from SeaWiFS Imagery. Deep-Sea Res. II.

Davenport, R., Neuer, S., Hernández-Guerra, A., Rueda, M.J., Llinas, O., Fischer, G. and Wefer, G., 1999. Seasonal and interannual pigment concentration in the Canary Islands region from CZCS data and comparison with observations from the ESTOC. Int. J. Remote Sensing, 20(7): 1419-1433.

de Lange, G.J., van Os, B., Pruysers, P.A., Middelburg, J.J., Castradori, D., van Santvoort, P., Müller, P.J., Eggenkamp, H. and Prahl, F.G., 1994. Possible early diagenetic alteration of palaeo proxies. In: R. Zahn, T.F. Pedersen, M.A. Kaminski and L. Labeyrie (Editors), Carbon Cycling in the Glacial Ocean: Constraints on the Ocean's Role in Global Change. NATO ASI Series, Vol.1(17), Springer, pp. 225-258.

Despois, J. and Raynal, R., 1967. Géographie de l'Afrique du Nord-Ouest. Bibliothèque Scientifique. Payoz, Paris, 570 pp.

Deuser, W.G., Jickels, T.D., King, P. and Commeau, J.A., 1995. Decadal and annual changes in biogenic opal and carbonate fluxes to the deep Sargasso Sea. Deep-Sea Res. I, 42(11/12): 1923-1932.

Dower, J., Freeland, H. and Juniper, K., 1992. A strong biological response to oceanic flow past Cobb Seamount. Deep-Sea Res. I, 39(7-8): 1139-1145.

Dupont, L.M., 1999. Pollen and spores in marine sediments from the East Atlantic. A view from the ocean into the African continent. In: G. Fischer, G. Wefer (Editors), Use of Proxies in Paleoceanography: Examples from the South Atlantic. Springer-Verlag, Berlin Heidelberg, pp. 523-546.

Emerson, S., 1985. Organic carbon preservation in marine sediments. In: E.T. Sundquist and W.S. Broecker (Editors), The Carbon Cycle and Atmospheric $CO_2$: Natural Variations Archaen to Present. Geophysical Monographs. American Geophysical Union, Washington DC, pp. 78-87.

Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J. and Boutefeu, A., 1977. Methode rapide de chacacterisation des roches-mere, de leur potential petrolier et de leur degre d'evolution. Revue del Institute Francais Petrole, 32: 23-42.

Fagel, N., André, L. and Dehairs, F., 1999. Advective excess Ba transport as shown from sediment and trap geochemical signatures. Geochim. Cosmochim. Acta, 63(16): 2353-2367.

Fairbanks, R.G., 1989. A 17,000 year glacio-eustatic sea level record: influence of glacial melting rates on the Younger Dryas event and deep-ocean circulation. Nature, 342: 637-642.

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.

Fenner, J., 1982. Diatoms in the Eocene and Oligocene sediments off NW Africa, their stratigraphic and paleogeographic occurrences. Ph.D. Thesis, University of Kiel.

Fischer, G., Wefer, G., (Eds.), 1999. Use of proxies in paleoceanography: Examples from the South Atlantic. Springer Verlag, Berlin, Heidelberg, 735 pp.

Fischer, G. and Wefer, G., 1991. Sampling, preparation and analysis of marine particulate matter. In: D.C. Hurd and D.W. Spencer (Editors), The Analysis and Characterisation of Marine Particles. Geophys. Monogr., pp. 391-397.

Fischer, G. and Wefer, G., 1996. Long-term observations of particle fluxes in the Eastern Atlantic: Seasonality, changes of flux with depth and comparison with the sediment record. In: G. Wefer, W.H. Berger, G. Siedler and D.J. Webb (Editors), The South Atlantic: Present and Past Circulation. Springer Verlag, Berlin Heidelberg, pp. 325-344.

Fischer, G. and Wefer, G. (Editors), 1999. Use of proxies in paleoceanography. Examples from the South Atlantic. Springer, Berlin, 735 pp.

Fischer, G., Behr, H.D., Berkenheger, I., Budziak, D., Dierssen, H., Dittert, N., von Dobeneck, T., Fabian, K., Gerhardt, S., Hespenheide, B., Höppner, R., Karwath, B., Lambers, K., von Lom-Keil, H., Ochsenhirt, W.-T., Panteleit, B., Pierro, H., Ratmeyer, V., Romero, O., Rosiak, U., Rühlemann, C., Ruhland, G., Scholz, M., Sydow, U., Vidal, L., Wolff, T. and Zatloukal, N, 1997. Report and preliminary results of Meteor-cruise M 38/1, Las Palmas - Recife, 25.1. - 1.3.1997. Berichte, 94. Fachbereich Geowissenschaften, Universität Bremen, Bremen, 178 pp.

Fischer, G., Müller, P. J. and Wefer, G., 1998. Latitudinal $\delta^{13}C_{org}$ variations in sinking matter and sediments from the South Atlantic: effects of anthropogenic $CO_2$ and implications for paleo-$PCO_2$ reconstructions. J. Mar. Systems, 17: 471-495.

Fischer, G., Schneider, R., Müller, P. J. and Wefer, G., 1997. Anthropogenic $CO_2$ in Southern Ocean surface waters: evidence from stable organic carbon isotopes. Terra Nova, 9: 153-157.

Fisher, R.A., 1929. Tests of significance in harmonic analysis. Proceedings of the Royal Society of London, Series A 125, 54-59.

Fok-Pun, L. and Komar, P.D., 1983. Settling velocities of planktonic foraminifera: Density variations and shape effects. J. Foraminiferal Res., 13: 60-68.

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 $\delta^{15}N$. Paleoceanogr., 7: 589-606.

Francois, R., Altabet, M.A. and Sigman, D., 1996. Bulk sediment $\delta^{15}N$ as a tool in paleoceanography. V. M. Goldschmidt Conference, March 31 - April 4, 1996, Heidelberg, Germany, Journal of Conference Abstracts, 1(1): 177.

Francois, R., Altabet, M.A., Yu, E.-F., 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 $CO_2$ concentrations during the last glacial period. Nature, 389: 929-935.

Francois, R., Bacon, M.P. and Suman, D.O., 1990. Thorium 230 profiling in deep-sea sediments: high-resolution records of flux and dissolution of carbonate in the equatorial Atlantic during the last 24,000 years. Paleoceanogr., 5: 761-787.

Fütterer, D.K., 1983. The modern upwelling record off northwest Africa. In: J. Thiede and E. Suess (Editors), Coastal Upwelling. Its sediment record. Part B: Sedimentary records of ancient coastal upwelling. NATO Conference Series, Series IV:Marine Science 10b, Plenum Press, New York, London, pp. 105-121.

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, 376: 755-758.

Ganssen, G., 1983. Dokumentation von küstennahem Auftrieb anhand stabiler Isotope in rezenten Foraminiferen vor Nordwest-Afrika. „Meteor“ Forschungs-Ergebnisse Reihe C, 37: 1-46.

Ganssen, G. and Lutze, G.F., 1982. The aragonite compensation depth at the northeastern Atlantic continental margin. „Meteor“ Forschungs-Ergebnisse Reihe C, 36: 57-59.

Ganssen, G. and Sarnthein, M., 1983. Stable isotope composition of foraminifers: The surface and bottom water record of coastal upwelling. In: E. Suess, J. Thiede (Editors), Coastal Upwelling. Its sediment record. Part A: Responses of the sedimentary regime to present coastal upwelling. NATO Conference Series, Series IV: Marine Science 10a, Plenum Press, New York and London, pp. 99-121.

Gasse, F. and Fontes, J.C., 1992. Climatic changes in northwest Africa during the last deglaciation (16-7 ka BP). In: E. Bard and W.S. Broecker (Editors), The Last Deglaciation: Absolute and Radiocarbon Chronologies. NATO ASI Series, Series I: Global Environmental Change. Springer-Verlag, Berlin Heidelberg, pp. 295-325.

Genin, A. and Boehlert, G.W., 1985. Dynamics of temperature and chlorophyll structures above a seamount: an oceanic experiment. J. Mar. Res., 43(4): 907-924.

Giraudeau, J., 1993. Planktonic foraminferal assemblages in surface sediments from the southwest African continental margin. Mar. Geol., 110: 47-62.

Giraudeau, J. and Rogers, J., 1994. Phytoplankton biomass and sea-surface temperature estimates from sea-bed distribution of nannofossils and planktonic foraminifera in the Benguela upwelling system. Micropal., 40(3): 275-285.

Gong, C. and Hollander, D.J., 1997. Differential contribution of bacteria to sedimentary organic matter in oxic and anoxic environments, Santa Monica Basin, California. Org. Geochem., 26: 545-563.

Grasshoff, K., Ehrhardt, M. and Kremling, K., 1983. Methods of sea water analysis. Verlag Chemie, pp. 419.

Guichard, S., Jorissen, F., Bertrand, P., Gervais, A., Martinez, P., Peypouquet, J.-P., Pujol C. and Vergnaud-Grazzini, C., 1997. Foraminifères benthiques et paléoproductivité: réflections sur une carotte de l´upwelling (NW african). Comptes Rendus de l'Académie des Sciences - Series IIA - Earth and Planetary Science, 325 : 65-70.

Guichard, S., Jorissen, F. and Peypouquet, J.-P., 1999. Late Quaternary benthic foraminiferal records testifying lateral variability of the Cape Blanc upwelling signal. Comptes Rendus de l'Académie des Sciences - Series IIA - Earth and Planetary Science, 329 : 295-301.

Hagen, E., Zulicke, C. and Feistel, R., 1996. Near-surface structures in the Cape Ghir filament off Morocco. Oceanol. Acta, 19(6): 557-598.

Harris, P.G., Zhao, M., Rosell-Melé, A., Tiedemann, R., Sarnthein, M. and Maxwell, J.R., 1996. Chlorin accumulation rate as a proxy for Quaternary marine primary productivity. Nature, 383: 63-65.

Hartmann, M., Müller, P.J., Suess, E. and van der Weijden, C.H., 1976. Chemistry of Late Quaternary sediments and their interstitial waters from the NW African continental margin. "Meteor" Forschungs-Ergebnisse, Reihe C 24: 1-67.

Harvey, H.R. and Macko, S.A., 1997. Kinetics of phytoplankton decay during simulated sedimentation: changes in lipids under oxic and anoxic conditions. Org. Geochem., 27: 129-140.

Head, E.J.H., Harrison, W.G., Irwin, B.I., Horne, E.P.W. and Li, W.K.W., 1996. Plankton dynamics and carbon flux in an area of upwelling off the coast of Morocco. Deep-Sea Res. I, 43(11-12): 1713-1738.

Hebbeln, D., Marchant, M., Freudenthal, T. and Wefer, G., 2000. Surface sediment distribution along the Chilean continental slope related to upwelling and productivity. Mar. Geol., 164(3-4): 119-137.

Hemleben, C., Spindler, M. and Anderson, O.R., 1989. Modern Planktonic Foraminifera. Springer-Verlag, Berlin, 363 pp.

Henderiks, J., Freudenthal, T., Meggers, H., Abrantes, F., Nave, Silvia, Salqueiro, E., Freitas, P., Bollmann, J. and Thierstein, H.R., (submitted). Glacial-interglacial variability of particle accumulation in the Canary Basin: A time-slice approach. Deep-Sea Res. II.

Hernández-Guerra, A, Arístegui, J., Cantón, M. and Nykjaer, L., 1993. Phytoplankton pigment patterns in the Canary Islands area as determined using Coastal Zone Colour Scanner data. Internat. J. Remote Sensing, 14: 1431-1437.

Hernández-Guerra, A. and Nykjaer, L., 1997. Sea surface temperature variability off northwest Africa: 1981-1989. Internat. J. Remote Sensing, 18(12): 2539-2558.

Heussner, S., De-Madton, X.D., Radakovitch, O., Beaufort, L., Biscaye, P.E., Carbonne, J., Delsaut, N., Etcheber, H. and Monaco, A., 1999. Spatial and temporal patterns of downward particle fluxes on the continental slope of the Bay of Biscay (northeastern Atlantic). Deep-Sea Res. II, 46(10): 2101-2146.

Hilbrecht, H., 1996. Extant planktic foraminifera and the physical environment in the Atlantic and Indian Oceans. Mitteilungen aus dem Geologischen Institut der Eidgen. Technischen Hochschule und der Universität Zürich, Neue Folge, 300, Zürich, 99 pp.

Holmes, M.E., Eichner, C., Struck, U. and Wefer, G., 1999. Reconstruction of surface ocean nutrient utilization using stable nitrogen isotopes in sinking particles and sediments. In: G. Fischer and G. Wefer (Editors), The use of Proxies in Paleoceanography: Examples from the South Atlantic. Springer, pp. 447-468.

Holmes, M.E., Müller, P.J., Schneider, R.R., Segl, M. and Wefer, G., 1998. Spatial variations in euphotic zone nitrate utilization based on $\delta^{15}N$ in surface sediments. Geo-Marine Letters, 18: 58-65.

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 $^{15}N/^{14}N$ ratios. Paleoceanogr., 12(4): 604-616.

Hooghiemstra, H., 1988. Palynological records from northwest African marine sediments: a general outline of the interpretation of the pollen signal. Phil. Trans. Royal Society London, 318: 431-449.

Hooghiemstra, H., Stalling, H., Agwu, C.O.C. and Dupont, L.M., 1992. Vegetational and climatic changes at the northern fringe of the Sahara 250,000 - 5000 years BP: evidence from 4 marine pollen records located between Portugal and the Canary Islands. Review of Paleobotany and Palynology, 74: 1-53.

Hughen, K.A., Overpeck, J.T., Peterson, L.C. and Trumbore, S., 1996. Rapid climatic changes in the tropical Atlantic region during the last deglaciation. Nature, 380: 51-54.

Imbrie, J. and Kipp, N.G., 1971. A new micropaleontological method for quantitative paleoclimatology: Application to a late Pleistocene Caribbean core. In: K.K. Turekian (Editor), The Late Cenozoic Glacial Ages. Yale University Press, New Haven, pp. 71-181.

Imbrie, J. Hays, J.D., Martinson, D.G., McIntyre, A., Mix, A.C., Morley, J.J., Pisias, N.G., Prell, W.L. and Shackleton, N.J.., 1984. The orbital theory of Pleistocene climate: support from a revised chronology of the marine d18O record. In: A.L. Berger, J. Imbrie, J.Hays, G. Kukla, B. Saltzman (Editors), Milankovitch and Climate: Understanding the Response to Astronomical Forcing. D. Reidel Publishing Company, Dordrecht, pp. 269-305.

Jahnke, R.A. and Shimmield, G.B., 1995. Particle flux and its conversion to the sediment record: coastal upwelling systems. In: C.P. Summerhayes, K.C. Emeis, M.V. Angel, R.L. Smith, B. Zeitschel (Editors), Upwelling in the Ocean: Modern Processes and Ancient Records. John Wiley and Sons Ltd., New York, pp. 83-100.

Jahnke, R.A., Craven, D.B. and Gaillard, J.-F., 1994. The influence of organic matter diagenesis on $CaCO_3$ dissolution at the deep-sea floor. Geochim. Cosmochim. Acta, 58(13): 2799-2809.

Johnson, J. and Stevens, I., 2000. A fine resolution model of the eastern North Atlantic between the Azores, the Canary Islands and the Gibraltar Strait. Deep-Sea Res. I, 47(5): 875-899.

Karlin, R., Lyle, M. and Zahn, R., 1992. Carbonate variations in the northeast Pacific during the late Quaternary. Paleoceanogr., 7(1): 43-61.

Keeling, C.D., Whorf, T.P., Wong, C.S. and Bellagay, R.D., 1985. The concentration of atmospheric carbon dioxide at Ocean Weather Station P from 1969 to 1981. J. Geophys. Res., 90(D6): 10511-10528.

Keeney, D.R. and Nelson, D.W., 1982. Nitrogen - inorganic forms. In: A.L. Page, R.H. Miller and D.R. Keeney (Editors), Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties. Agronomy Monograph No. 9, Madison, pp. 643-698.

Khripounoff, A., Vangriesheim, A. and Crassous, P., 1998. Vertical and temporal variations of particle fluxes in the deep tropical Atlantic. Deep-Sea Res. I, 45(2-3): 193-216.

Kienast, M., 2000. Unchanged nitrogen isotopic composition of organic matter in the South China Sea during the last climatic cycle: Global implications. Paleoceanogr., 15(2): 244-253.

Kipp, N.G., 1976. New transfer function for estimating past sea-surface conditions from sea-bed distribution of planktonic foraminiferal assemblàges in the North Atlantic. Geological Society of America, Memoir 145.

Klein, B. and Siedler, G., 1989. On the origin of the Azores Current. J. Geophys. Res., 94 (C5): 6159-6168.

Knoll, M., Lenz, B., Lopez Laatzen, F., Müller, T.J. and Siedler, G., submitted. The eastern boundary current system between the Canary Islands and the African coast. Deep-Sea Res. II.

Koopmann, B., 1981. Sedimentation von Saharastaub im subtropischen Nordatlantik während der letzten 25.000 Jahre. „Meteor“ Forschungs-Ergebnisse Reihe C, 35: 23-59.

Lamb, H.F., Eicher, U. and Switsur, V.R., 1989. An 18,000-year record of vegetation, lake-level and climatic change from Tigalmamine, Middle Atlas, Morocco. J. Biogeography, 16: 65-74.

Lampitt, R.S., Raine, R.C.T., Billett, D.S.M. and Rice, A.L., 1995. Material supply to the European continental slope: a budget based on benthic oxygen demand and organic supply. Deep-Sea Res. I, 42(11/12): 1865-1880.

Letolle, R., 1980. Nitrogen-15 in the natural environment. In: P. Fritz and J.C. Fontes (Editors), Handbook of environmental isotope geochemistry. Elsevier, Amsterdam, pp. 407-434.

Levitus, S. and Boyer, T. 1994. World Ocean Atlas 1994. Volume 4; Temperature. NOAA Atlas NESDIS 4, NOAA Washington DC, USA.

Libes, S.M. and Deuser, W.G., 1988. The isotopic geochemistry of particulate nitrogen in the Peru Upwelling Area and the Gulf of Maine. Deep-Sea Res., 35: 517-533.

Lisitzin, A.P., 1972. Sedimentation in the world oceans. SEPM Special Publications, 17: 1-218.

Littke, R., Baker, D.R. and Rullkötter, J., 1997. Deposition of petroleum source rocks. In: D.H. Welte, B. Horsfield and D.R. Baker (Editors), Petroleum and Basin Evolution. Springer, pp. 271-334.

Liu, K.-K. and Kaplan, I.R., 1989. The eastern tropical Pacific as a source of $^{15}$N-enriched nitrate in seawater off southern California. Limnol. Oceanogr., 34(5): 820-830.

Liu, K.-K., Su, M.-J., Hsueh, C.-R. and Gong, G.-C., 1996. The nitrogen isotopic composition of nitrate in the Kuroshio Water northeast of Taiwan: evidence for nitrogen fixation as a source of isotopically light nitrate. Mar. Chem., 54: 273-292.

Longhurst, A., Sathyendranath, S., Platt, T. and Caverhill, C., 1995. An estimate of global primary production in the ocean from satellite radiometer data. J. Plankton Res., 17: 1245-1271.

Lorius, C., Jouzel, J., Raynaud, D., Hansen, J. and Le Treut, H. 1990. The ice-core record: climate sensitivity and future greenhouse warming. Nature, 347: 139-145.

Lückge, A., Boussafir, M., Lallier-Vergés, E. and Littke, R., 1996. Comparative study of organic matter preservation in immature sediments along the continental margin of Peru and Oman. Part I: Results of petrographic and bulk geochemical data. Org. Geochem., 24: 437-451.

Lutjeharms, J.R.E. and Meeuwis, J.M., 1987. The extent and variability of south-east Atlantic upwelling. In: A.I.L. Payne, J.A. Gulland, K.H. Brink (Editors), The Benguela and Comparable Ecosystems. South African Journal of Marine Science, pp. 51-62.

Lutze, G.F., 1980. Depth distribution of benthic foraminifera on the continental margin off NW Africa. „Meteor" Forschungs-Ergebnisse Reihe C, 32: 31-80.

Lutze, G.F. and Coulbourn, W.T., 1984. Recent benthic foraminifera from the continental margin of Northwest Africa: Community structure and distribution. Mar. Micropal., 8: 361-401.

Lyle, M., Zahn, R., Prahl, F., Dymond, J., Collier, R., Pisias, N. and Suess, E., 1992. Paleoproductivity and carbon burial across the California Current: the multitracers transect, 42°N. Paleoceanogr., 7(3): 251-272.

Macko, S.A. and Estep, M.L.F., 1984. Microbial alteration of stable nitrogen and carbon isotopic compositions of organic matter. Org. Geochem., 6: 787-790.

Macko, S.A., Engel, M.H., Hartley, G., Hatcher, P., Helleur, R., Jackmann, P. and Silfer, J., 1991. Isotopic compositions of individual carbohydrates as indicators of early diagenesis of organic matter in peat. Chem. Geol., 93: 147-161.

Macko, S.A., Engel, M.H. and Parker, P.L., 1993. Early diagenesis of organic matter in sediments. Assessment of mechanisms and preservation by the use of isotopic molecular approaches. In: M.H. Engel and S.A. Macko (Editors), Organic Geochemistry. Olenum Press, New York, pp. 211-224.

Macko, S.A., Fogel, M.L., Hare, P.E. and Hoering, T.C., 1987. Isotopic fractionation of nitrogen and carbon in the synthesis of amino acids by microorganisms. Chem. Geol., 65: 79-92.

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 Soil, 62: 413-430.

Mariotti, A., Lancelot, C. and Billen, G., 1984. Natural isotopic composition of nitrogen as a tracer of origin for suspended organic matter in the Scheldt estuary. Geochim. Cosmochim. Acta, 48: 549-555.

Marret, F. and Turon, J.-L., 1994. Paleohydrology and paleoclimatology off Northwest Africa during the last glacial-interglacial transition and the Holocene: Palynological evidences. Mar. Geol., 118: 107-117.

Martin, J.H., Knauer, G.A., Karl, D.M. and Broenkow, W.W., 1987. VERTEX: carbon cycling in the northeast Pacific. Deep-Sea Res., 34(2): 267-285.

Martinez, P., Bertrand, P., Bouloubassi, I., Bareille, G., Shimmield, G., Vautravers, B., Grousset, F., Guichard, S., Ternoys, Y. and Sicre, M.-A., 1996. An integrated view of inorganic and organic biogeochemical indicators of paleoproductivity changes in a coastal upwelling area. Org. Geochem., 24: 411-420.

Martinez, P., Bertrand, P., Shimmield, G.B., Cochrane, K., Jorissen, F.J., Foster, J., Dignan, M., 1999. Upwelling intensity and ocean productivity changes off Cape Blanc (northwest Africa) during the last 70,000 years: geochemical and micropalaeontological evidence. Mar. Geol., 158(1-4): 57-74.

Martinson, D.G., Pisias, N.G., Hays, J.D., Imbrie, J., Moore, T.C.Jr. 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. Quat. Res., 27: 1-29.

Matthewson, A.P., Shimmield, G.B., Kroon, D. and Fallick, A.E., 1995. A 300 kyr high-resolution aridity record of the North African continent. Paleoceanogr., 10(3): 677-692.

Mayer, L.M., 1994. Surface area control of organic carbon accumulation in continental shelf sediments. Geochim. Cosmochim. Acta, 58: 1271-1284.

McCreary, J.P., Fukamachi, Y. and Kundu, P.K., 1991. A numerical investigation of jets and eddies near an eastern ocean boundary. J. Geophys. Res., 96(C2): 2515-2534.

Meggers, H. and Baumann, K.H. 1997. Late Pliocene/Pleistocene calcareous plankton and paleoceanography of the North Atlantic. In: H.C. Hass, M.A. Kaminski (Editors), Contributions to the Micropaleontology and Paleoceanography of the Northern North Atlantic. Grzybowski Foundation Special Publication, pp. 39-50.

Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. Chem. Geol., 114: 289-302.

Milliman, J.D., 1993. Production and accumulation of calcium carbonate in the ocean: budget of a non-steady state. Global Biogeochem. Cycles, 7(4): 927-957.

Milliman, J.D., Troy, P.J., Balch, W.M., Adams, A.K., Li, Y.-H. and Mackenzie, F.T., 1999. Biologically mediated dissolution of calcium carbonate above the chemical lysocline? Deep-Sea Res. I, 46: 1653-1669.

Mittelstaedt, E., 1983. The upwelling area off Northwest Africa - a description of phenomena related to coastal upwelling. Prog. Oceanogr., 12: 307-331.

Mittelstaedt, E., 1991. The ocean boundary along the northwest African coast: Circulation and oceanographic properties at the sea surface. Prog. Oceanogr., 26: 307-355.

Moreno, A., Targarona, J., Henderiks, J., Canals, M., Freudenthal, T. and Meggers, H., submitted. Orbital forcing of dust supply to the North Canary Basin over the last 250 kyrs. Quat. Science Rev..

Müller, A. and Opdyke, B.N., 2000. Glacial-interglacial changes in nutrient utilization and paleoproductivity in the Indonesian Throughflow sensitive Timor Trough, easternmost Indian Ocean. Paleoceanogr., 15(1): 85-94.

Müller, P.J., 1977. C/N ratios in Pacific deep-sea sediments: effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. Geochim. Cosmochim. Acta, 41: 765-776.

Müller, P.J. and Suess, E., 1979. Productivity, sedimentation rate, and sedimentary carbon content in the oceans. Deep-Sea Res., 26A: 1347-1362.

Müller, P.J., Erlenkeuser, H. and von Grafenstein, R., 1983. Glacial-interglacial cycles in oceanic productivity inferred from organic carbon contents in eastern North Atlantic sediments. In: J. Thiede and E. Suess (Editors), Coastal Upwelling. Its Sediment Record. Part B: Sedimentary Records of Ancient Coastal Upwelling. NATO Conference Series, Series IV: Marine Science 10b. Plenum Press, New York London, pp. 365-398.

Müller, P. J., Schneider, R. and Ruhland, G., 1994. Late quaternary $pCO_2$ variations in the Angola Current: evidence from organic carbon $\delta^{13}C$ and alkenone temperatures. In: R. Zahn, T.F. Pedersen, M.A. Kaminski and L. Labeyrie (Editors), Carbon Cycling in the Glacial Ocean: Constraints of the Ocean´s Role in Global Change. NATO ASI Series, Vol.1(17), Springer, pp. 343-366.

Müller, T.J., Llinas, O., López Laatzen, F., Hernandez Guerra, A., 1999. The eastern boundary current system from eulerian measurements, CANIGO Conference Las Palmas de Gran Canaria. 12 - 16 Septembre 1999. Book of Abstracts, p. 82.

Müller-Hohenstein, K. and Popp, H., 1990. Marokko: Ein islamisches Entwicklungsland mit kolonialer Vergangenheit. Länderprofile. Klett, Stuttgart, 229 pp.

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 $\delta^{15}N$, $\delta^{13}C$ and $\delta^{14}C$. Deep-Sea Res. I, 44(12): 1957-1979.

Nakatsuka, T., Watanabe, K., Handa, N., Matsumoto, E. and Wada, E., 1995. Glacial to interglacial surface nutrient variations of Bering deep basins recorded by $\delta^{13}C$ and $\delta^{15}N$ of sedimentary organic matter. Paleoceanogr., 10: 1047-1061.

Neftel, A.E., Moor, E., Oeschger, H. and Stauffer, B., 1985. Evidence from polar ice cores for the increase in atmospheric $CO_2$ in the past two centuries. Nature, 315: 45-47.

Neftel, A., Oeschger, H., Schwander, J., Stauffer, B. and Zumbrunn, R., 1982. Ice core sample atmospheric $CO_2$ content during the past 40,000 yr. Nature, 295: 220-223.

Neuer, S., Barth, H., Benabdeljelil, A., Bollmann, J., Cianca-Aguilar, A., Coca Saez de Albeniz, J., Eberwein, A., González-Davila, F., Güss, S., Klein, B., Kopiske, E., Koy, U., Loquay, K., Lorenzen, C., Luzardo-Hernández, F., Meinecke, G., Ohm, K., Plugge, R., Reuter, R., Ruhland, G., Snoussi, M. and Spiedt, A., 1997a. Report and preliminary results of FS "Victor Hensen" Cruise 96/1, Bremerhaven - Bremerhaven, 10.1.- 4.3.1996. Berichte Fachbereich Geowissenschaften, Universität Bremen 96, 76 pp.

Neuer, S., Bergenthal, M., Cianca, A., Deeken, A., Diekamp, V., Freudenthal, T., Gerdes, A., Godoy, J., Gonzáles-Davila, M., Hayn, C., Klein, T., Köster, J., Kretschmar, F., Langer, J., Maroto, L., Meggers, H., Meinecke, G., Metzler, W., Nave, S., Ratmeyer, V., Rosiak, U., Rueda, M.J., Schiebel, R., Villagarcia, M., von Oppen, C. and Waldmann, C., in press. Report and preliminary results of FS "METEOR"-Cruise M 45/5, Bremen - Las Palmas, 01.10.1999-03.11.1999. Berichte Fachbereich Geowissenschaften, Universität Bremen, in press.

Neuer, S., Ratmeyer, V., Davenport, R., Fischer, G. and Wefer, G., 1997b. 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 Res. I, 44(8): 1451-1466.

Neuer, S., Freudenthal, T., Davenport, R., Llinas, O. and Rueda, M.-J., submitted. Seasonality of surface water properties and particle flux along a productivity gradient off NW Africa. Deep-Sea Res. II.

Nguyen, R.T. and Harvey, H.R., 1997. Protein and amino acid cycling during phytoplankton decomposition in oxic and anoxic waters. Org. Geochem., 27: 115-128.

Nicholson, S.E., 1996. A review of climate dynamics and climate variability in Eastern Africa. In: T.C. Johnson and E.O. Odada (Editors), The Limnology, Climatology and Paleoclimatology of the East African Lakes. Gordon and Breach, Amsterdam, pp. 25-56.

Nykjær, L. and Van Camp, L., 1994. Seasonal and interannual variability of coastal upwelling along northwest Africa and Portugal from 1981 to 1991. J. Geophys. Res., 99(C7): 14197-14207.

Odate, T. and Furuya, K. 1998. Well-developed subsurface chlorophyll maximum near Komahashi No. 2 seamount in the summer of 1991. Deep-Sea Res. I, 45(10): 1595-1607.

Paillard, D., Labeyrie, L. and Yiou, P., 1996. Macintosh program performs time-series analysis. Eos Trans. AGU, 77: 379.

Pflaumann, U., Duprat, J., Pujol, C. and Labeyrie, L.D., 1996. SIMMAX: A modern analog technique to deduce Atlantic sea surface temperatures from planktonic foraminifera in deep-sea sediments. Paleoceanogr., 11(1): 15-35.

Prahl, F.G., de Lange, G.J., Scholten, S. and Cowie G.L. 1997. A case of post-depositional aerobic degradation of terrestrial organic matter in turbidite deposits from the Madeira Abyssal Plain. Org. Geochem., 27: 141-152.

Ransom, B., Kim, D., Kastner, M. and Wainwright, S., 1998. Organic matter preservation on continental slopes: Importance of mineralogy and surface area. Geochim. Cosmochim. Acta, 62: 1329-1345.

Ratmeyer, V., Fischer, G. and Wefer, G., 1999. Lithogenic particle fluxes and grain size distributions in the deep ocean off northwest Africa: Implications for seasonal changes of aeolian dust input and downward transport. Deep-Sea Res. I, 46(8): 1289-1337.

Rau, G.H., Arthur, M.A. and Dean, W.E., 1987. $^{15}N/^{14}N$ variations in Cretaceous Atlantic sedimentary sequences: implications for past changes in marine nitrogen biochemistry. Earth Planet. Sci. Lett., 82: 269-279.

Rau, G.H., Froelich, P.N., Takahashi, T. and Des Marais, D.J., 1991. Does sedimentary organic $\delta^{13}C$ record variations in Quaternary ocean $[CO_2(aq)]$? Paleoceanogr., 6: 657-677.

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

Raymo, M.E., 1997. The timing of major climate terminations. Paleoceanography 12 (4), 577-585.

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

Rodríguez, J.M., Hernández-León, S. and Barton, E.D., 1999. Mesoscale distribution of fish larvae in relation to an upwelling filament off Northwest Africa. Deep-Sea Res. I, 46: 1969-1984.

Romankevich, E.A., 1984. Geochemistry of OM in the Ocean. Springer, Berlin Heidelberg, New York, 334 pp.

Rühlemann, C., 1996. Akkumulation von Carbonat und organischem Kohlenstoff im tropischen Atlantik: Spätquartäre Produktivitäts-Variationen und ihre Steuerungsmechanismen. Berichte Fachbereich Geowissenschaften, Universität Bremen 84, 139 pp.

Rühlemann, C., Müller, P.J. and Schneider, R.R., 1999. Organic carbon and carbonate as paleoproductivity proxies: Examples from high and low productivity areas of the tropical Atlantic. In: G. Fischer and G. Wefer (Editors), Use of Proxies in Paleoceanography: Examples from the South Atlantic. Springer-Verlag, Berlin Heidelberg, pp. 315-344.

Sachs, J.P. and Repeta, D.J., 1999. Oligotrophy and nitrogen fixation during eastern Mediterranean sapropel events. Science, 286: 2485-2488.

Sackett, W.M., 1986. Stable carbon isotope studies on OM in the marine environment. In: P.F. Fontes, J.C. Fritz (Editors), Handbook of Environmental Isotope Geochemistry. Elsevier, Amsterdam, pp. 139-169.

Saino, T., 1992. $^{15}N$ and $^{13}C$ natural abundance in suspended particulate organic matter from a Kuroshio warm-core ring. Deep-Sea Res., 39: 347-362.

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

Sarnthein, M. and Koopmann, B., 1980. Late Quaternary Deep-Sea Record on Northwest African dust supply and wind circulation. Palaeoecology of Africa and the Surrounding Islands, 12: 239-253.

Sarnthein, M. and Tiedemann, R., 1990. Younger Dryas-style cooling events at glacial terminations I - IV at ODP site 658: associated benthic $\delta^{13}C$ anomalies constrain meltwater hypothesis. Paleoceanogr., 5(6): 1041-1055.

Sarnthein, M., Pflaumann, U., Ross, R., Tiedemann, R. and Winn, K., 1992. Transfer functions to reconstruct ocean palaeoproductivity: a comparison. In: C.P. Summerhayes, W.L. Prell and K.C. Emeis (Editors), Upwelling Systems: Evolution Since the Early Miocene. Geological Society Special Editions, pp. 411-427.

Sarnthein, M., Thiede, J., Pflaumann, U., Erlenkeuser, H., Fütterer, D., Koopmann, B., Lange, H. and Seibold, E., 1982. Atmospheric and oceanic circulation patterns off Northwest Africa during the past 25 million years. In: U. von Rad, K. Hinz, M. Sarnthein and E. Seibold (Editors), Geology of the Northwest African Continental Margin. Springer-Verlag, Berlin, Heidelberg, pp. 545-604.

Sarnthein, M., Winn, K., Duplessy, J.-C. and Fontugne, M.R., 1988. Global variations of surface ocean productivity in low and mid latitudes: influence of $CO_2$ reservoirs of the deep ocean and atmosphere during the last 21,000 years. Paleoceanogr., 3: 361-399.

Sarnthein, M. Winn, K., Jung, S.J.A., Duplessy, J.-C., Labeyrie, L., Erlenkeuser, H. and Ganssen, G., 1994. Changes in east Atlantic deepwater circulation over the last 30,000 years: Eight time slice reconstructions. Paleoceanogr., 9(2): 209-267.

Sarnthein, M., Winn, K. and Zahn, R., 1987. Paleoproductivity of oceanic upwelling and the effect on atmospheric $CO_2$ and climatic change during deglaciation times. In: W.H. Berger and L.D. Labeyrie (Editors), Abrupt Climatic Change: Evidence and Implications. NATO ASI Series. Series C: Mathematical and Physical Sciences. D. Reidel Publishing Company, pp. 311-337.

Sathyendranath, S., Longhurst, A., Caverhill, C.M. and Platt, T., 1995. Regionally and seasonally differentiated primary production in the North Atlantic. Deep-Sea Res. I, 42(10): 1773-1802.

Saunders, P.M., 1982. Circulation in the eastern North Atlantic. J. Mar. Res., 40 Suppl.: 641-657.

Schlesinger, W.H., 1991. Biogeochemistry: an analysis of global change. Academic Press, Inc., San Diego, 443 pp.

Schlitzer, R., 2000. Ocean Data View. http://www.awi-bremerhaven.de/GPH/ODV, 2000, Version 4.0.15-2000.

Schlünz, B., Schneider, R.R., Müller, P.J., Showers, W.J. and Wefer, G., 1999. Terrestrial organic carbon accumulation on the Amazon deep sea fan during the last glacial sea level low stand. Chem. Geol., 159(1-4): 263-281.

Schneider, R.R. Müller, P.J., Ruhland, G., Meinecke, G., Schmidt, H. and Wefer, G., 1996. Late Quaternary surface temperatures and productivity in the east-equatorial South Atlantic: Response to changes in trade/monsoon wind forcing and surface water advection. In: G. Wefer, W.H. Berger, G. Siedler and D. Webb (Editors), The South Atlantic: Present and Past Circulation. Springer, Berlin Heidelberg New York, pp. 527-551.

Scholten, J.C. Fietzke, J., Vogler, S., Rutgers van der Loeff, M. M., Mangini, A., Koeve, W., Waniek, J., Stoffers, P., Antia, A. and Kuss, J., in press. Trapping efficiencies of sediment traps from the deep eastern North Atlantic: The $^{230}$Th calibration. Deep-Sea Res. II.

Schrader, H., 1992. Coastal upwelling and atmospheric $CO_2$ changes over the last 400,000 years: Peru. Mar. Geol., 107: 239-247.

Schrader, H.J. and Schuette, G., 1968. Marine Diatoms. In: C. Emiliani (Editor), The Sea. 7, John Wiley and Sons, New York, pp. 1179-1231.

Siedler, G. and Onken, R., 1996. Eastern recirculation. In: W. Krauss (Editor), The Warmwatersphere of the North Atlantic Ocean. Gebrüder Bornträger, Berlin, Stuttgart, pp. 339-364.

Siegel, A.F., 1980. Testing the periodicity in a time series. J. Am. Stat. Assoc., 75: 345-348.

Siegel, D.A. and Deuser, W.G., 1997. Trajectories of sinking particles in the Sargasso Sea: modelling of statistical funnels above deep-ocean sediment traps. Deep-Sea Res. I, 44(9-10): 1519-1541.

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. Paleoceanogr., 14(2): 118-134.

Silva, J. A. and Bremner, J. M., 1966. Determination and isotope-ratio analysis of different forms of nitrogen in soil: 5. fixed ammonium. Soil Sci. Soc. Am. Proc., 30: 587-594.

Speth, P., Detlefsen, H. and Sierts, H.-W., 1978. Meteorological influence on upwelling off Northwest Africa. Deutsche Hydrographische Zeitung, 31(3): 95-104.

Sprengel, C., Baumann, K.-H. and Neuer, S., in press. Seasonal and interannual variation of coccolithophore fluxes and species composition in sediment traps north of Gran Canaria (29°N 15°W). Mar. Micropal.

Stein, R., 1991. Accumulation of organic carbon in marine sediments. Lecture Notes in Earth Sciences, 34: 1-216.

Stramma, L. and Siedler, G., 1988. Seasonal changes in the North Atlantic subtropical gyre. J. Geophys. Res., 93(C7): 8111-8118.

Strub, P.T., Korso, P.M. and Huyer, A., 1991. The nature of the cold filaments in the California Current system. J. Geophys. Res., 96(C8): 14,743-14,768.

Stuiver, M., Braziunas, T.F., 1993. Modelling atmospheric $^{14}$C influences and $^{14}$C ages of marine samples to 10,000 BC. Radiocarbon 35 (1), 137-189.

Stuiver, M., Reimer, P.J., Bard, E., Beck, J.W., Burr, G.S., Hughen, K.A., Kromer, B., McCormac, F.G., van der Plicht, J., Spurk, M., 1998. INTCAL98 radiocarbon age calibration, 24,000 cal BP. Radiocarbon 40 (3), 1041-1083.

Suess, E., 1980. Particulate organic carbon flux in the oceans; surface productivity and oxygen utilization. Nature, 288: 260-263.

Summerhayes, C.P., Milliman, J.D., Briggs, S.R., Bee, A.G. and Hogan, C., 1976. Northwest African shelf sediments: influence of climate and sedimentary processes. J. Geol., 84: 277-300.

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

Sweeney, R.E., Liu, K.K. and Kaplan, I.R., 1978. Oceanic nitrogen isotopes and their uses in determining the source of sedimentary nitrogen. In: B.W. Robinson (Editor), Stable Isotope in the Earth Science. New Zealand Department of Scientific and Industrial Research Bulletin, pp. 9-26.

Takahashi, K. and Bé, A.W.E., 1984. Planktonic foraminifera: factors controlling sinking speeds. Deep-Sea Res. I, 31: 1477-1500.

Targarona, J., Warnaar, J., Boessenkool, K.P., Brinkhuis, H. and Canals, M., 1999. Recent dinoflagellate cyst distribution in the north Canary basin, NW Africa. Grana, 38: 1-9.

ten Haven, H.L., Rullkötter, J. and Stein, R., 1989. Preliminary analysis of extractable lipids in sediments from the eastern North Atlantic (Leg 108): Comparison of a coastal upwelling area (site 658) with a nonupwelling area (site 659). In: W.F. Ruddiman, M. Sarnthein et al. (Editors), Proceedings of the Ocean Drilling Program, Scientific Results, pp. 351-360.

Tetzlaff, G. and Peters, M., 1986. Deep-sea sediments in the eastern equatorial Atlantic off the African coast and meteorological flow patterns over the Sahel. Geologische Rundschau, 75(1): 71-79.

Thiede, J., 1971. Planktonische Foraminiferen in Sedimenten vom ibero-marokkanischen Kontinentalrand. Ph.D.Thesis, Universität Kiel, 90 pp.

Thiede, J., 1975. Shell- and skeleton-producing plankton and nekton in the eastern North Atlantic Ocean. „Meteor“ Forschungs-Ergebnisse Reihe C, 20: 33-79.

Thunell, R.C., 1976. Optimum indices of calcium carbonate dissolution in deep-sea sediments. Geol., 4: 525-528.

Trauth, M.H., Sarnthein, M. and Arnold, M., 1997. Bioturbational mixing depth and carbon flux at the seafloor. Paleoceanogr., 12(3): 517-526.

Tréguer, P., Nelson, D.M., van Bennekom, A.J., DeMaster, D.J., Leynaert, A. and Quéguiner, B., 1995. The silica balance in the world ocean: A reestimate. Science, 268: 375-379.

Tyson, R.V., 1995. Sedimentary organic matter. Chapman & Hall, London, 615 pp.

Van Camp, L., Nykjær, L., Mittelstaedt, E. and Schlittenhardt, P., 1991. Upwelling and boundary circulation off Northwest Africa as depicted by infrared and visible satellite observations. Prog. Oceanogr., 26: 357-402.

Voß, M. and Struck, U., 1997. Stable nitrogen and carbon isotopes as indicator of eutrophication of the Oder river (Baltic Sea). Mar. Chem., 59: 35-49.

Voss, M., Altabet, M.A. and von Bodungen, B., 1996. $\delta^{15}N$ in sedimenting particles as indicator of euphotic-zone processes. Deep-Sea Res. I, 43(1): 33-47.

Wada, E., Mizutani H. and Minagawa, M., 1991. The use of stable isotopes for food web analysis. Critical Reviews in Food Science and Nutrition, 30: 361-371.

Wagner, T., Dupont, L., 1999. Terrestrial organic matter in marine sediments: analytical approaches and eolian-marine records of the central Equatorial Atlantic. In: G. Fischer and G. Wefer (Editors), Use of Proxies in Paleoceanography: Examples from the South Atlantic. Springer-Verlag, Berlin Heidelberg, pp. 547-574.

Wakeham, S.G., Lee, C., Hedges, J.I., Hernes, P.J. and Peterson, M.L., 1997. Molecular indicators of diagenetic status in marine organic matter. Geochim. Cosmochim. Acta, 61(24): 5363-5369.

Waser, N.A.D., Harrison, W.G., Head, E.J.H., Nielsen, B., Lutz, V.A. and Calvert, S.E., 2000. Geographic variations in the nitrogen isotope composition of surface particulate nitrogen and new production across the North Atlantic Ocean. Deep-Sea Res. I, 47(7): 1207-1226.

Weaver, P.P.E. and Thomson, J., 1993. Calculating erosion by deep-sea turbidity currents during inition and flow. Nature, 364: 136-138.

Weber, M.E., Niessen, F., Kuhn, G. and Wiedicke, M., 1997. Calibration and application of marine sedimentary physical properties using a multi-sensor core logger. Mar. Geol., 136: 151-172.

Wefer, G., Abrantes, F., Bassek, D., Bollmann, J., Bozzano, G., Diekamp, V., Dittert, L., Eberwein, A., Klump, J., Kuhlmann, H., Lindblom, S., Meggers, H., Meinecke, G., Metzler, W., Moustafa, Y., Peters, M., Ratmeyer, V., Rieß, W., Rosiak, U., Segl, M., Skoglund, S., Targarona, J., Vaqueiro, S., Waldmann, C., Wenzhöfer, F. and Zabel, M., 1997. Report and preliminary results of Meteor cruise M 37/1, Lisbon - Las Palmas, 04.12.1996 - 23.12.1996. Berichte Fachbereich Geowissenschaften, Universität Bremen, 90, 79 pp.

Wefer, G., Berger, W.H., Bijma, J. and Fischer, G., 1999a. Clues to ocean history: a brief overview of proxies. In: G. Fischer, G. Wefer (Editors), Use of Proxies in Paleoceanography: Examples from the South Atlantic. Springer-Verlag, Berlin Heidelberg, pp. 1-68.

Wefer, G., Segl, M., Bassek, D., Buhlmann, K., Deeken, A., Dehning, K., Diekamp, V., Drünert, F., Eberwein, A., Franke, P., Freudenthal, T., Geisen, M., Godoy, J., Gonzáles-Davila, M., Günther, L., Hayn, C., Henderiks, J., Irmisch, A., Jeronimo, D., Kotte, N., Kretschmar, F., Langer, J., Makaoui, A., Maroto, L., Meggers, H., Meinecke, G., Metzler, W., Moreno, A., Nave, S., Neuer, S., Nowald, N., Ratmeyer, V., Rosiak, U., Schroeter, M., Sprengel, C., Targarona, J., Thiele, J., Thierstein, H.R., von Oppen, C. and Waldmann, C., 1999b. Report and preliminary results of FS "METEOR"-Cruise M 42/4, Las Palmas - Las Palmas – Viena do Castelo, 26.09.-26.10.1998. Berichte Fachbereich Geowissenschaften, Universität Bremen, 132, 104 pp.

Wu, J., Calvert, S.E., Wong, C.S. and Whitney, F.A., 1999. Carbon and nitrogen isotopic composition of sedimenting particulate material at Station Papa in the subarctic northeast Pacific. Deep Sea Res. II, 46(11-12): 2793-2832.

Wynn, R.B., Masson, D.G., Stow, D.A.V. and Weaver, P.P.E., 2000. Turbidity current sediment waves on the submarine slopes of the western Canary Islands. Mar. Geol., 163: 185-198.

Zegouagh, Y., Derenne, S., Largeau, C., Bertrand, P., Sicre, M.-A., Saliot, A. and Rousseau B., 1999. Refractory organic matter in sediments from the North-West African upwelling system: abundance, chemical structure and origin. Org. Geochem., 30: 101-117.

Ziveri, P., Young, J.R. and van Hinte, J.E., 1999. Coccolithophore export production and accumulation rates. GeoRes. Forum, 5: 41-56.

Zonneveld, K.A.F., 1996. Palaeoclimatic and palaeo-ecologic changes in the Eastern Mediterranean and Arabian Sea regions during the last deglaciation: a palynological approach to land-sea correlation. Ph.D. Thesis, Utrecht University, Utrecht, 197 pp.

# APPENDIX

## 1. Presentations at international conferences

Freudenthal, T (1998): Organic carbon, carbonate carbon, and stable nitrogen isotopes in sediments of the Canary Basin. CANIGO Subproject 3 meeting, Januar 1998, Lanzarote (oral presentation).

Freudenthal, T., Meggers, H., Davenport, R. & Wefer, G. (1998): Productivity gradients in the Canary basin as recorded by sedimentary carbon content and foraminiferal assemblages.- CANIGO 2nd General Meeting, Januar 1998, Lisbon (poster).

Freudenthal, T., Meggers, H., Wefer, G., Wenzhöfer, F. & Henderiks, J. (1998): Sedimentary stable nitrogen isotopes in the Canary Basin: A new attempt.- Proceedings of the 6th International Conference on Paleoceanography, p. 112, August 1998, Lisbon (poster).

Freudenthal, T. (1998): What can we learn from $^{15}N$ analysis? CANIGO Subproject 3 meeting, Oktober 1998, Bremen (oral presentation)

Freudenthal, T., Neuer, S. & Wefer, G. (1999) – Nitrogen isotopes along a productivity gradient in the Canary Basin.- ASLO meeting, abstract book p. 67, Februar 1999, Santa Fe, (poster).

Freudenthal, T., Meggers, H., Davenport, R., Stevens, I., Henderiks, J. & Wefer G., (1999): Glacial/interglacial variability of filament activity and upwelling intensity in the Canary Basin.- CANIGO Final Conference, September 1999, Las Palmas (oral presentation).

Freudenthal T., et al. (1999): Overview on results of subproject 3 and possible relations to subproject.- CANIGO Subproject 1 meeting, März 1999, Toulouse (oral presentation)

Freudenthal, T., Neuer, S. & Wefer G. (1999) – Nitrogen isotopes along a productivity gradient in the Canary Basin.- JGOFS meeting, Dezember 1999, Bremen (poster).

## 2. Further publications

Hebbeln, D., Marchant, M., Freudenthal, T. and Wefer, G., 2000. Surface sediment distribution along the Chilean continental slope related to upwelling and productivity. Mar. Geol., 164(3-4): 119-137.

Moreno, A., Targarona, J., Henderiks, J., Canals, M., Freudenthal, T. and Meggers, H., submitted. Orbital forcing of dust supply to the North Canary Basin over the last 250 kyrs. Quat. Science Rev..

Neuer, S., Freudenthal, T., Davenport, R., Llinas, O. and Rueda, M.-J., submitted. Seasonality of surface water properties and particle flux along a productivity gradient off NW Africa. Deep-Sea Res. II.

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Publications of this series:

No. 1 **Wefer, G., E. Suess and cruise participants**
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(Atlantischer Sektor). 161 pages, Bremen, 1989.

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135 pages, Bremen, 1990.

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202 pages, Bremen, 1990.

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Bericht über die METEOR-Fahrt M 12/1, Kapstadt - Funchal, 13.3.1990 - 14.4.1990.
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Schwermetallspuren und geochemische Gleichgewichte zwischen Porenlösung und Sediment
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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.

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18.1. - 7.2.1991. 46 pages, Bremen, 1993.

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