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Composition of molecular organic matter pools, pigments and proteins, in Benguela upwelling and Arctic sediments

Dissertation
zur Erlangung des Doktorgrades in den Naturwissenschaften am
Fachbereich Geowissenschaften der Universität Bremen

vorgelegt von
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(Diplom Umweltwissenschaftlerin)
Bremen, November 2006

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Abstract

The major objective of this thesis was to assess the application of organic carbon degradation indices and proxies. This work focused on the joint application of the analysis of organic carbon pools, pigments and proteins, and their related degradation indices, the Chlorin Index (CI) and the amino acid-based Degradation Index (DI) that characterize the reactivity of organic material. Reactivity was defined as the availability of organic carbon to microbial degradation in sediments. Molecular carbon pools are suited to study organic carbon reactivity since organic matter degradation is associated with changing molecular composition as labile compounds are selectively depleted and refractive compounds are enriched in these pools. Hence, organic carbon availability to microorganism decreases with time.

Molecular degradation indices and proxies were applied to assess organic carbon reactivity in sediments of the Benguela upwelling system and Arctic shelf (Spitzbergen), both of which are characterized by high primary productivity. Degradation indices were compared to rates of microbial sulfate reduction as this is a dominant terminal electron acceptor process and thus represents a measure of the current availability of organic carbon to microorganisms.

Major goals of this study were the definition of time frames and potential application boundaries of molecular degradation indices as well as to explore the link between organic matter composition and carbon mineralisation. This study was part of to a multidisciplinary project that has been performed within the Research Center Ocean Margins (B2) with the aim to elucidate particulate organic matter reactivity and transformation on the Benguela continental margin. One manuscript (chapter 4) contributes to the CABANERA research program, which was designed to assess the impacts of global warming induced changes on benthic Arctic ecosystems.

The reactivity of molecular chlorin and protein pools was related to their relative time scales that were closely linked to the ability of pigment and protein matter to associate with sediment structures and to the chemical reactivity of molecules.

Organic matter composition changes on short time scales were addressed in experiments on anoxic sediment incubations. Sediments from both study areas, the Arctic and Benguela upwelling system, were enriched with fresh algae to simulate the supply of phytodetritus to the seafloor. Time course experiments showed that the Chlorin Index tracked the breakdown of macromolecular matter, which is the rate-limiting step of organic matter degradation. Conversely, the protein content and amino acid composition remained constant through the duration of the experiments. In all experiments the amount of refractive chlorin material and extent of mineralisation were proportional related. THAA content and the DI exhibited changes over longer time scales that were apparent in down core profiles of THAA and DI of both study areas. Thus it has been concluded that the CI was highly sensitive to the early stages of organic matter degradation and the DI represented later stages of organic matter decomposition. Furthermore, the extent of primary production, particle transport ways and physical protection of reactive compounds were shown to impact organic matter composition.

This knowledge was applied to two environments, the Benguela upwelling system (BUS) southeast of Africa and the Arctic shelf (Spitzbergen), to evaluate the oceanographic controls on organic carbon reactivity.

The Benguela upwelling system is distinguished by two major deposition areas of organic-rich sediments. The diatomaceous mud belt stretches close to the coast on the Namibian shelf and contains large organic carbon contents as much as 15 %. The adjacent Benguela slope is characterized by a major depocenter with carbon contents reaching to nearly 9 % of TOC. This organic-rich deposition area on the slope could be distinguished from the surrounding slope by its comparatively larger concentrations of total chlorins and THAA and consistent enhanced sulfate reduction rates. In contrast to overall highly refractive organic matter, large amounts of slightly less degraded chlorin and protein organic matter characterized the slope depocenter. With respect to the

large background of refractive organic matter, pigments represented an ancillary tool to assess more reactive organic matter. High molecular carbon concentrations and reactivity indicated a high vertical flux of fresher material to the slope depocenter, provided by a secondary upwelling zone over the upper slope. Overall, large concentrations of reactive chlorin and protein-rich organic matter fueled high sulfate reduction rates in the anoxic shelf depocenter, increased sulfate reduction rates in the slope depocenter sediments were driven by large amounts of refractory chlorin and protein carbon.

Organic matter composition and benthic mineralisation in Arctic shelf sediments (Spitzbergen) were primarily controlled by the seasonal extent of carbon supply but also its mode of deposition. Seasonal high primary production was primarily indicated by total chlorin amount and composition. Whereas high concentrations of refractory chlorin matter characterized sites of high carbon supply such as the marginal ice zone (MIZ) and Northwest coast sediments, low amounts of very fresh chlorin material reflected sites of low carbon supply, e.g. ice covered coastal sites, due to seasonal later ice retreat. Consistent with amounts, sulfate reduction rates were largest at a high supply of refractive chlorin matter. By contrast to chlorins, protein content was largest northwest and southeast of Spitzbergen and continuously decreased towards the north, thus on the track of the seasonal withdrawing sea ice. This trend and down core profiles of THAA concentration in ice covered sediments revealed that proteins reflected a later time slice of mineralisation. All in all, both molecular proxies could be applied to characterize Arctic sediments: Chlorins and the CI were suited to indicate seasonal changes of carbon supply and benthic mineralisation, and proteins provided information on longer time scales, exceeding seasonality.

Finally chlorins and THAA were employed as proxies of organic carbon fluxes. Molecular proxies were analysed in a deep sediment core on the northern Benguela slope (2000m water depth) that represented climate variations over the past 130 000 years. Chlorin contents were first used to reconstruct paleo sulfate reduction rates. Based on these rates, past fluxes of organic carbon supply and burial have been estimated. The results were in good accord with vertical flux models (e.g. by Berger et al., 1989). High rates of organic carbon burial occurred during the last glacial maximum (LGM) and were related to high accumulation of refractive organic carbon, primarily indicated by large chlorin amounts. Refractive organic carbon deposition in the LGM was most likely related to enhanced particle sedimentation and resuspension due to a lowered glacial sea level. Interglacial periods of high carbon supply were characterized by larger amounts of more labile organic matter, foremost indicated by proteins. They were attributed to result from undiluted sedimentation and probably aggregation of organic matter, thereby encapsulating reactive organic material. Thus, it was concluded that chlorin and protein organic matter pools may be used to reconstruct past carbon fluxes, as both compound classes reflect major carbon deposition modes in the study area.

Chlorins and the CI have demonstrated their versatility from initial to late stages of carbon decomposition but proteins were mainly linked to later stages of organic matter decay.

The application of molecular organic carbon pools in this study therefore contributed to improve the understanding of time scales of organic carbon degradation and might stimulate future applications of molecular proxies.

Kurzfassung

Das Ziel dieser Arbeit bestand in der Erfassung und Anwendung von Abbauindikatoren des organischen Kohlenstoffs. Den Schwerpunkt dieser Arbeit bildete die Untersuchung der Kohlenstoffreservoirs („pools“) von Pigmenten und Proteinen, sowie der Anwendung daraus abgeleiteter Abbauindikatoren, der Chlorin Index (CI) und der auf Aminosäuren basierende Degradationsindex (DI), mit denen die Reaktivität des organischen Materials charakterisiert werden kann. Reaktivität ist als die Verfügbarkeit von organischem Kohlenstoff für den mikrobiellen Abbau im Sediment definiert. Molekulare Kohlenstoffreservoirs eignen sich zur Erfassung der Reaktivität von organischem Kohlenstoff, da der Abbau von organischem Material mit einer veränderten molekularen Zusammensetzung einher geht. Während labile Komponenten im organischen Material bevorzugt abgebaut werden, steigt mit dem Abbaugrad des organischen Material der Anteil refraktärer Komponenten in den Reservoirs, somit sinkt die Verfügbarkeit von labilem Kohlenstoff.

Mit dem Ziel, die Reaktivität von organischem Kohlenstoff im Sediment zu bestimmen, wurden molekulare Abbauindikatoren und Proxies im Benguela Auftriebssystem (BUS) sowie auf dem Arktischen Schelf (Spitzbergen) eingesetzt, die durch eine hohe Primärproduktion gekennzeichnet sind. Molekulare Indikatoren wurden mit Umsatzraten der mikrobiellen Sulfatreduktion verglichen, da diese den wichtigsten terminalen Elektronenakzeptorprozeß in den untersuchten Sedimenten repräsentieren.

Die zentrale Aufgabe dieser Studie war die Ermittlung der Zeitskalen und Einschränkungen hinsichtlich der Anwendungsmöglichkeiten molekularer Abbauindikatoren und die Erfassung der Zusammenhänge zwischen Zusammensetzung und Mineralisierungsraten des organischen Materials. Diese Arbeit trägt zu einem multidiziplinären Projekt im Rahmen des Foschungszentrums Ozeanränder bei, dessen Ziel die Aufklärung von Reaktivität und Prozessen zur Umsetzung des partikulären organischen Materials auf dem Kontinentalhang vor Namibia war. Eines der Manuskripte (Kapitel 4) trägt weiterhin zu dem Projekt CABANERA bei, das die Auswirkung der globalen Erderwärmung auf benthische Ökosysteme in der Arktis untersucht.

Die Reaktivität der molekularer Kohlenstoff Pools wurde auf unterschiedlichen Zeitskalen bestimmt, auf denen Pigmente und Proteine agieren. Diese wurden vor allem von der chemischen Reaktivität sowie dem Assoziationsvermögen des molekularen Materials mit Sedimentstrukturen bestimmt.

Änderungen in der molekularen Zusammensetzung während der frühen Abbauphase von organischem Material wurden mittels anoxischer Sedimentinkubationen erforscht. Hierzu wurden Sedimente aus beiden Untersuchungsgebieten mit Algenmaterial angereichert, um einen frischen Eintrag von Phytodetritus in das Sediment zu simulieren. Dieser Ansatz hat gezeigt, daß ausschließlich der Chlorin Index in der Lage war, die Zersetzung von makromolekularem Material zu identifizieren, welches der geschwindigkeitsbestimmende Schritt zum Abbau des organischen Materials durch Sedimentbakterien ist. Proteingehalt und -komposition während der Experimente blieben indes unverändert. Der Gehalt an refraktivem Chlorinmaterial und die Höhe der Mineralisierungsrate waren einander proportional. Anhand von Sedimentprofilen aus beiden Untersuchungsgebieten konnte geschlossen werden, daß Proteine und der DI längere Zeitskalen für den Abbaus von organischem Material repräsentieren.

Es wurde gezeigt, daß der CI ein Indikator ist, der empfindlich während der frühen Abbauphase reagiert und der DI vorwiegend den längerfristigen Abbau von organischem Material charakterisiert. Einen starken Einfluß auf die molekulare Zusammensetzung organischen Materials üben weiterhin die Höhe der Primärproduktion, Partikeltransportwege und physikalische Schutzmechanismen aus.

Diese Erkenntnisse wurden angewandt, um Kontrollfaktoren der Reaktiviät des Kohlenstoffs in den untersuchten Arbeitsgebieten zu ermitteln.

Das Benguela Auftriebssystem (BUS) läßt sich in zwei Regionen mit kohlenstoffreichen Sedimentablagerungen unterteilen. Eine diatomeenreiche Facies (mudbelt) mit bis zu 15% organischem Kohlenstoff auf dem namibianischen Schelf, sowie ein weiteres Ablagerungszentrum auf dem namibianischen Kontinentalhang (~9% organischer Kohlenstoffgehalt). Das Ablagerungszentrum auf dem Hang konnte durch seine auffallend hohen Chlorin- und Proteingehalte sowie deutlich erhöhter Sulfatereduktionsraten von der Umgebung unterschieden werden. Das molekulare Material war weiterhin etwas weniger abgebaut als in anderen Hangsedimenten vergleichbarer Wassertiefe. Anteile labilen Materials wurden auch durch Pigmentanalyse ermittelt. Diese Ergebnisse ließen auf einen vertikalen Eintrag frischeren Materials aus der Primärproduktion einer sekundären Auftriebsregion über dem äußeren Benguela Schelf schließen. Hohe Mineralisierungsraten auf dem Schelf wurden durch einen hohen Gehalt an reaktivem Material angetrieben, während erhöhte Umsatzraten auf dem Hang von großen Mengen refraktären Materials gespeist wurden.

Die Zusammensetzung des organischen Material und benthische Mineralisierungsraten in Schelfsedimenten der Arktis (Spitzbergen) wurden vorwiegend durch den saisonalen Eintrag des organischen Kohlenstoffs und durch die vorherrschenden Ablagerungsprozesse bestimmt. Die Saisonalität der Primärproduktion wurde besonders durch Gehalt und Zusammensetzung der Chlorine reflektiert. Hohe Gehalte refraktären Chlorinmaterials wurden in Regionen hoher Kohlenstoffzufuhr beobachtet, z.B. im Bereich der Eisränder und Nordwestküste Spitzbergens, während geringe Konzentrationen von hochreaktivem, labilen Chlorinmaterial überwiegend eisbedeckte Sedimente charakterisierten, die durch eine geringere Materialzufuhr gekennzeichnet waren. Höhere Sulfatreduktionsraten traten im Zusammenhang mit einer hohen Materialzufuhr z.B. an der Eisrandzone (MIZ) auf, aber waren geringer bei niedrigen Chloringehalten. Die nordwärtsgerichtete kontinuierliche Abnahme der Proteine in der Sedimentoberfläche und veränderte Proteingehalte in Tiefenprofilen in den eisbedeckten Regionen ließen auf einen späteren

Proteinabbau schließen. Beide Kohlenstoffkomponenten konnten somit zur Charakterisierung der Produktivität in der Arktis herangezogen werden.

Chlorine und Proteine wurden schließlich genutzt, um Mineralisierungsraten der mikrobiellen Sulfatreduktion im Zeitrahmen der letzten Glaziale / Interglaziale (~ 130 000 Jahre) und Flußraten von organischem Kohlenstoff zu rekonstruieren. Die Ergebnisse waren in guter Übereinstimmung mit vertikalen Flußmodellen (Berger et al., 1989). Dabei wurde eine außergewöhnlich hohe Erhaltung des organischen Kohlenstoffs während des letzten glazialen Maximums (LGM) ermittelt, dessen Sediment durch hohe Konzentrationen refraktären Chlorinmaterials charaktisiert wurde. Der Erhalt chlorinreichen Materials wurde auf erhöhte Sedimentakkummulation und Partikelresuspension, potenziell durch einen gesenkten Meeresspiegel während des LGM, zurückgeführt. Zwischeneiszeitlich erhöhte Produktivität wurde durch vergleichsweise frischeres Material, vor allem angezeigt durch Proteine, charakterisiert. Labile Proteinkomponenten wurden offensichtlich in Aggregaten aus sedimentärem und bakteriellem refraktivem Material eingeschlossen und blieben erhalten. Folglich sind Chlorine und Proteine für die Rekonstruktion von Paläokohlenstoffflüssen einsetzbar, da sie die primären Ablagerungsprozesse im untersuchten Gebiet reflektieren.

Chlorine und der Chlorin Index konnten in dieser Arbeit als vielseitige Indikatoren zur Charakterisierung kurz- bis langfristiger Abbauprozesse gezeigt werden. Beide molekulare Indikatoren haben zu einem besseren Verständnis hinsichtlich der Zeitskalen des Abbaus von organischem Material sowie zur Quantifizierung gegenwärtiger und vergangener Kohlenstoffflüsse erheblich beitragen. Die Ergebnisse dieser Studie geben somit einen Anreiz für zukünftige Anwendungen molekularer Indikatoren.

Chapter 1

Introduction

The organic carbon cycle

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Regional description:

The Benguela Upwelling System

The Arctic Shelf (Spitzbergen)

Introduction

The organic carbon cycle

The global carbon cycle can be divided into two compartments, a biological sub cycle and a geological cycle (Tissot and Welte 1984, Fig.1.1). The major part of global carbon is fixed in sedimentary rocks. The geological cycle therefore represents the major carbon reservoir, exceeding that of the biological cycle by several orders of magnitude holding $6.4 \cdot 10^{15}$ t C compared to $3 \cdot 10^{12}$ t C. The biological cycle begins with the photosynthesis of CO_2 to organic material (primary production) at the ocean surface that removes atmospheric carbon dioxide. Subsequent to organic matter deposition it ends with metabolic or chemical oxidation of detrital biomass back to carbon dioxide. Thus, organic matter mineralisation in surface sediment represents a leak between both cycles where a fraction of CO_2 can escape before it gets finally buried. At the point where organic matter is incorporated into sediments the geological cycle begins, leading to formation of fossil material (gas, coal, graphite) that could leave the cycle through erosion and subsequent reoxidation of rocks to carbon dioxide.

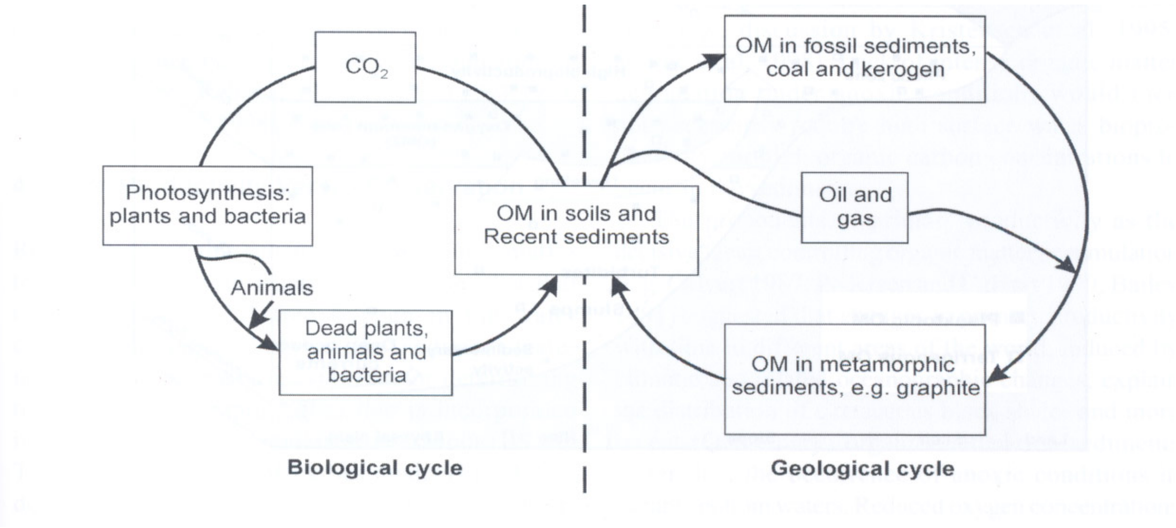

Fig.1 Carbon Cycle by Tissot and Welte (1984)

Generally the in and out fluxes of individual carbon reservoirs are balanced (Tissot and Welte 1984). However, burning of fossil fuels since the industrial revolution has created an increased carbon flux from the huge geological to the comparatively small atmospheric reservoir that result in severely increased atmospheric carbon dioxide concentrations and a global warming of the Earth' climate (Houghton et al., 2001).

From the ocean's surface to the seafloor

Phytoplankton photosynthesis accounts for 95% of the global oceanic primary production (Killops and Killops, 1993). As photosynthetic productivity depends on the availability of light and nutrients, its spatial extent varies on a global scale. Total annual primary production has been estimated in the range of $30\text{-}50 \cdot 10^9$ tons of carbon (Berger et al., 1989; Hedges and Keil, 1995). Zones of particular high oceanic carbon fixation occur on continental margins (several hundred g C_{org} m^{-2} y^{-1}) as primary productivity is associated with nutrient-rich waters such as at the polar fronts or at coastal upwelling areas (see Seiter et al., 2004, Fig.1.2). Marine phytoplankton productivity along with physical transfer processes account for the partitioning of CO_2 between ocean and atmosphere (Broecker and Peng, 1982), therefore, the rates at which carbon is cycled through the ocean and the factors that may bias the rates of transfer are important with respect to atmospheric levels of anthrophogenic produced CO_2 (Jahnke, 1996; Jahnke et al., 1990).

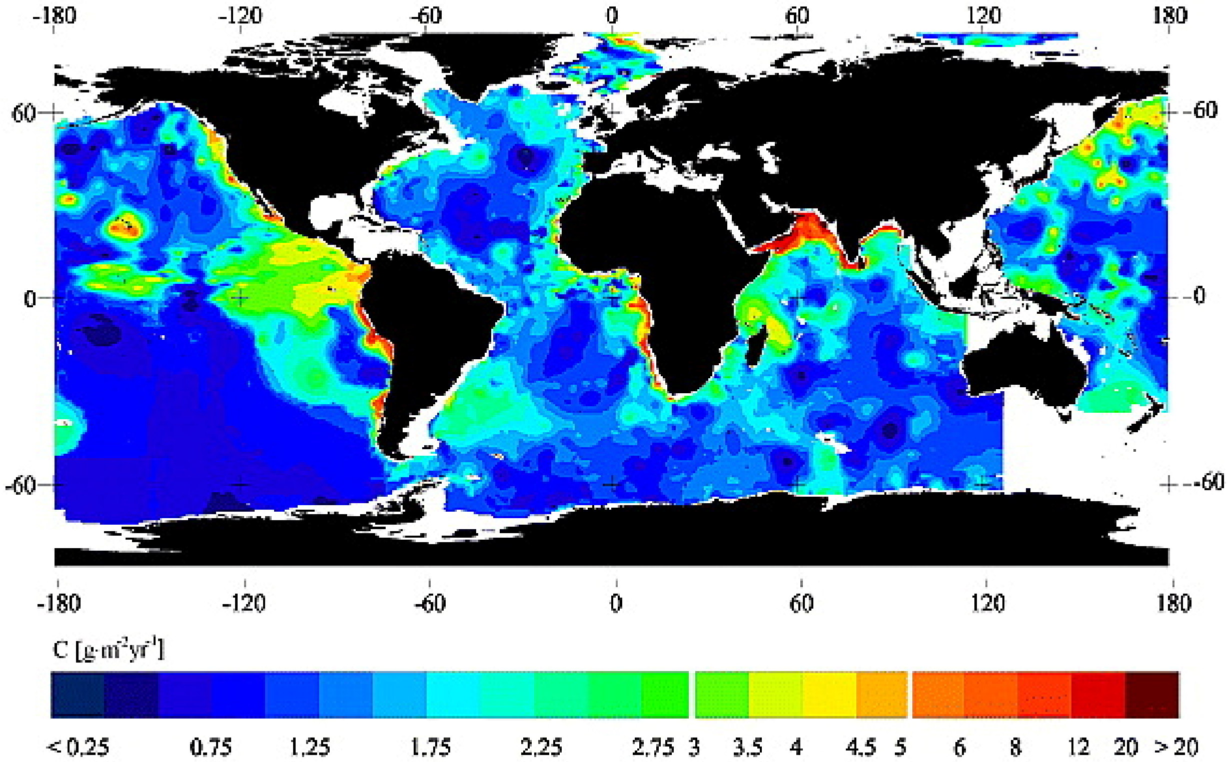

Fig.1.2 Global distribution of minimum particulate organic carbon flux (g C m^{-2} y^{-1}) as calculated from global *in situ* dissolved oxygen uptake (DOU), taken from Seiter et al. (2004)

At the ocean surface CO_2 is converted into organic matter by primary producers. As organic matter sinks, it is in parts oxidised and microbially degraded, releasing initially fixed carbon back to waters as CO_2 (Broecker and Peng, 1993). A fraction of organic matter escapes rapid recycling within the mixed layer and is exported into deeper water and to the sediment (Berger and Keir, 1984). The efficiency of this “biological pump” is controlled by the magnitude of primary production: of the organic matter produced at the ocean surface only a very small portion reaches the underlying seafloor and is ultimately buried, generally this fraction depends upon primary production rate and water column depth (Müller and Süß, 1979). Below the productive euphotic zone organic matter export production decreases rapidly and will be largely remineralized when entering the benthic boundary layer (Fig. 1.3 according to Rullkötter, 2006).

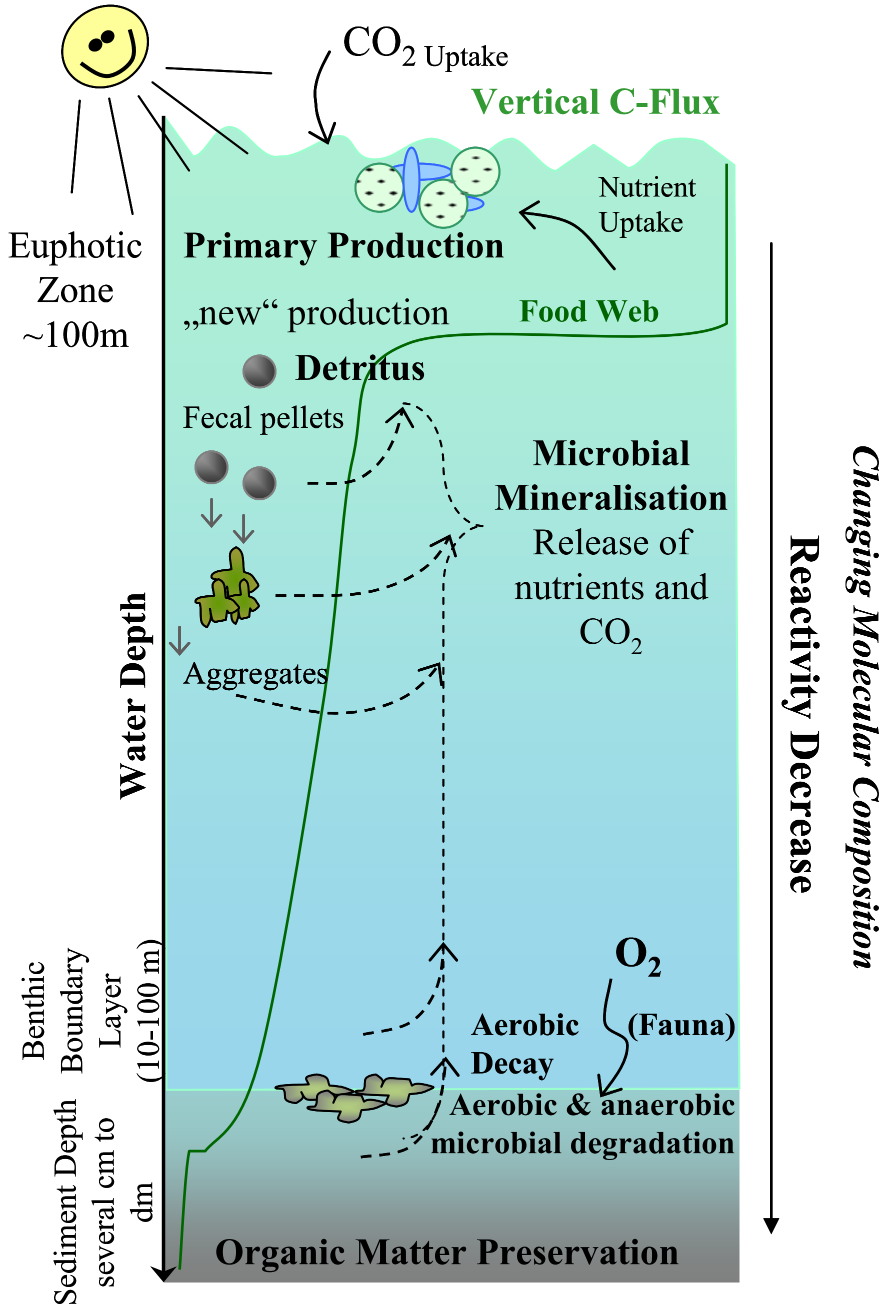

Fig.1.3 Scheme of the vertical organic matter flux from primary production at the ocean surface to deposition on the seafloor, aerobic and anaerobic microbial mineralisation and subsequent burial of organic carbon (modified after Rullkötter, 2006).

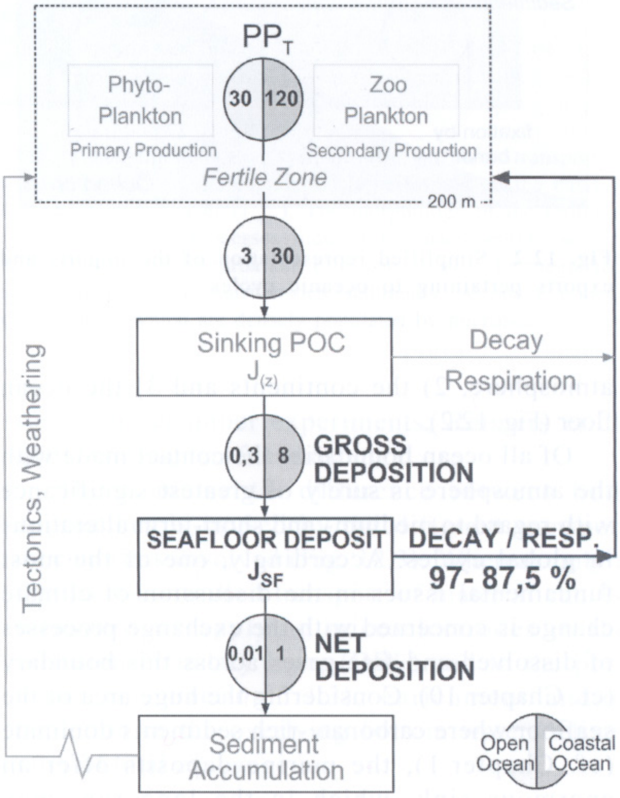

Fig.1.4 Scheme of the particulate organic carbon cycle in the ocean according to Berger et al., 1989. Carbon fluxes are given in g C m^{-2} y^{-1}. Filled semicircles represent the coastal ocean, open semicircles the open ocean area. (taken from Zabel and Hensen, 2006)

At the sediment water interface and upper sediment layer organic matter mineralisation continues at several carbon oxidation pathways and even extends to deep sub seafloor sediments, the so-called deep biosphere (Parkes et al., 1994; D'Hondt et al., 2004). However, major carbon degradation and incorporation into the sediment takes place within the surface mixed layer and mineralisation rates decrease as sediment depth increases. Some 25 to 50 % of sinking organic matter may reach the seafloor in coastal seas but only ~ 1% reaches deep-sea sediments (Suess, 1980). The fraction of supplied organic carbon that escapes from microbial mineralisation will be preserved and finally buried in sediments (Fig.1.4). Burial of initially deposited organic matter is positively linked to the rate of deposition and constitutes approximately 5-20 % in shelf sediments (Henrichs and Reeburgh, 1987) in contrast to 1 to 0.01 % of surface primary productivity that was reported of being buried in the deep sea (Berger et al., 1989(a), see Fig.1.4).

Continental margin systems (<2000m water depth) contribute to 10-15 % of the global primary production and may be responsible for > 40 % of organic carbon sequestration in the ocean (Muller-Karger et al., 2005); they represent a significant sink of atmospheric carbon dioxide.

Diagenetic status of sinking OM

The transition from the biosphere to the geosphere is not clearly defined as the transformation of biogenic matter already begins after the decay of living organisms (Rullkötter, 2006). Sinking organic matter is subject to extensive degradation due to microbial remineralisation and heterotrophic consumption (>99 %), both altering the molecular composition of organic matter, thus its reactivity, during transit to the deep-sea floor (Wakeham and Lee, 1993). Consistent with increased transformation of organic matter composition its molecular characterizable fraction (composed of pigments, lipids, amino acids, carbohydrates) is reduced from 80 % (fresh OM) at the ocean surface to < 20 % in altered sediments (Wakeham et al., 1997). Progressive changes of organic matter structure and chemical composition are a result of selective degradation as labile compounds get preferably depleted, and refractory compounds become selectively enriched during diagenesis (Wakeham et al., 1997; Cowie and Hedges, 1994). The reactivity of organic material is defined by its lability towards enzymatic decay (Dauwe et al., 1999). Moreover, the degradation state of organic material determines its availability to microbial mineralisation. Therefore, there should be a clear link between the degradation state - molecular composition, packaging, and the ambient oxidant concentration – and the reactivity or susceptibility of organic matter to further microbial decomposition.

Controls of organic matter degradation and reactivity

Reactivity of organic matter (its availability to microbial mineralisation) can be described as a function of the depositional environment and sediment packaging, organic carbon composition and amount.

Factors that control the degradation time of organic matter during transit in the water column are the water depth, the sinking velocity of particles that can be severely enhanced through transit by fecal pellets ("fecal pellet express" e.g. in the deep ocean) and high organic matter sedimentation rates, that decrease particle residence and thus oxygen exposure times (Rullkötter et al., 1987; Müller and Süß, 1979; Betzer et al., 1984; Hartnett et al., 1998). Rate and extent of organic carbon mineralisation mainly depend on the availability of electron acceptors in sediments – in particular oxygen- (Canfield et al., 1993; Canfield, 1994), concentration and source of the metabolisable pool of organic matter and its degradation state (Berner 1980, 1989; Westrich and Berner, 1984; Hedges et al., 1988), sediment mixing and physical protection of organic carbon e.g. by adsorption on sediment particles or association with the sediment matrix (Keil et al., 1994; Mayer, 1994; Ransom et al., 1998).

Which of these controls exerts the greatest influence on organic matter preservation represents a major challenge of biogeochemical research. Two principal approaches have been discussed concerning organic carbon preservation. Deposition of high organic carbon amounts in marine sediments has been ascribed to an oxygen-free (euxinic) water column (stagnant basin or Black Sea model) by DeMaison and Moore (1980). In contrast high primary productivity and associated high particle sedimentation was proposed as the decisive factor that controls organic matter accumulation (Pedersen and Calvert, 1990; Bailey, 1991). The productivity model is based on high-productivity areas of the ocean (e.g. upwelling areas) where reduced oxic or anoxic conditions result from large amounts of decaying biomass that settle on the seafloor, enhancing oxygen consumption in water column and sediments. It has been demonstrated that high organic matter sedimentation rates promote the burial of organic carbon as a result of shortened oxygen exposure time (Canfield et al., 1993; Hartnett et al., 1998; Devol and Hartnett, 2001).

Aerobic and microbial degradation may be reduced by physical protection of labile organic matter through sorption onto surfaces of sinking particles during export to the seafloor or at incorporation into the sediment (Keil et al., 1994). Chlorin-rich organic matter (from phytoplankton) has a demonstrated high surface reactivity and also amino acids were shown to sorb to mineral and sediment surfaces (Satterberg et al., 2003; Henrichs and Sugai, 1993). Labile material may also be protected when incorporated into small spaces of mineral matrices not accessible to exoenzymes that perform hydrolytic breakdown of macromolecular matter. In conclusion, circumstances of organic matter deposition vary and several combined factors may control carbon preservation.

Carbon oxidation pathways

Most of the settling organic detritus which represents a compilation of complex macromolecular compounds is completely mineralised to CO_2. As prokaryote organisms are not capable to take up particles and molecules larger than 600 daltons (Weiss et al., 1991) the first step of organic matter mineralisation is the hydrolytic breakdown of macromolecules through extracellular enzymes that are produced by bacteria. At the same time this is the rate-limiting step of the subsequent sequence of mineralisation processes, because cleaved monomer compounds do not accumulate, but are rapidly metabolized in sediments (Arnosti, 2004).

Table 1.1 Pathways of organic carbon oxidation and their standard energy yields per mol organic carbon (according to Jørgensen 2000)

Pathway	**Reaction**	**$\Delta G°$ ($kJ\ mol^{-1}$)**
Aerobic respiration	$CH_2O + O_2 \rightarrow CO_2 + H_2O$	-479
Denitrification	$5\ CH_2O + 4\ NO_3^- \rightarrow 2N_2 + 4\ HCO_3^- + CO_2 + 3\ H_2O$	-453
Mn(IV) reduction	$CH_2O + 3CO_2 + H_2O + 2MnO_2 \rightarrow 2Mn_2^+ + 4\ HCO_3^-$	-349
Fe (III) reduction	$CH_2O + 7CO_2 + 4Fe(OH)_3 \rightarrow 4\ Fe^{2+} + 8\ HCO_3^- + 3\ H_2O$	-114
Sulfate reduction	$4\ CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$	-77
Methanogenesis	$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$	-28
Fermentation	$CH_3CH_2COH + H_2O \rightarrow CH_3COO- + HCO_3^- + 3H_2 + H^+$	10

The complete mineralisation of organic carbon to CO_2 in sediments is mediated by a successive sequence of carbon oxidation processes where different inorganic acceptors are reduced and become depleted with depth as follows:

$O_2 \rightarrow NO_3^- \rightarrow Mn(IV) \rightarrow Fe(III) \rightarrow SO_4^{2-}$ (Fröhlich et al., 1979)

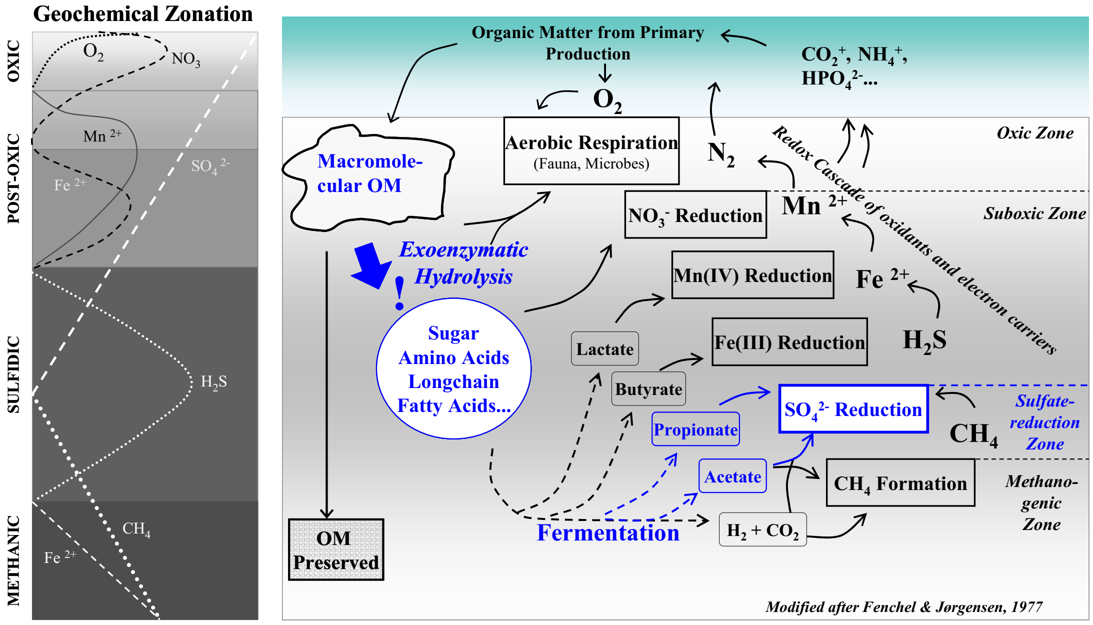

Fig.1.5 Scheme of organic carbon oxidation pathways, their vertical geochemical zonation and consumption of oxidant (After Fenchel and Jørgensen 1977, in Jørgensen 2006; modified after Kasten et al., 2003)

This redox cascade corresponds to a decrease in the free energy available by respiration with the different electron acceptors (Tab.1.1). Electron acceptors with highest energy yields are usually preferred and due to the limited availability of utilizable oxidants, a vertical zonation of carbon oxidation pathways is observed in sediments that may spatially overlap depending on substrate availability (Fig.1.5) (Jakobsen and Postma, 1999; Kostka et al., 1999; Jørgensen, 2006).

Aerobic respiration is the most energetic process that yields the largest free energy (-479 kJ mol^{-1}). The oxic layer may extend down to several cm as oxygen penetration depth increases with water depth in slope and deep-sea sediments, however is limited to only mm to cm on the shelf or may be even absent at high organic matter input such as on the Benguela shelf (Wenzhöfer and Glud, 2002; Fig.1.5, Jørgensen et al., 2005; Bailey, 1991). Subsequent to aerobic respiration, denitrification of carbon molecules occurs in the suboxic zone. In contrast to these most energetic processes, metal and sulfate reducing bacteria depend on the activity of fermenting bacteria that decompose higher molecular weight compounds (e.g. sugars, amino acids etc.). Fermentation products then serve as electron donors for i.e. bacterial sulfate reduction. Below the sulfate reduction zone CO_2 is the only available electron acceptor and methane remains as the terminal product of organic matter degradation (Fig.1.5).

Consistent with the overwhelming part of buried organic carbon being stored in shelf (82%) and continental slope sediments (16%), the relative amount of aerobic and anaerobic mineralisation of organic matter is also strongly related to the distance to the ocean margins (Wollast, 1998; Jørgensen and Kasten, 2006). Sulfate reduction predominates overall organic carbon mineralisation in sediments underlying highly-productive or oxygen-depleted coastal waters such as the Chilean upwelling area and the Black Sea, where the fraction mineralised by SRR accounted for almost 80% or even total mineralisation (Tab.1.2). In other shelf sediments anoxic sulfate reduction represents ~ 25-50% of organic carbon mineralisation (Jørgensen, 1982). With increasing water depth and lowered organic matter supply the relative importance of sulfate reduction drops below 1% down the continental slope and becomes less significant in deep-sea sediments to the benefit of oxic respiration and suboxic processes such as nitrate, manganese and iron reduction.

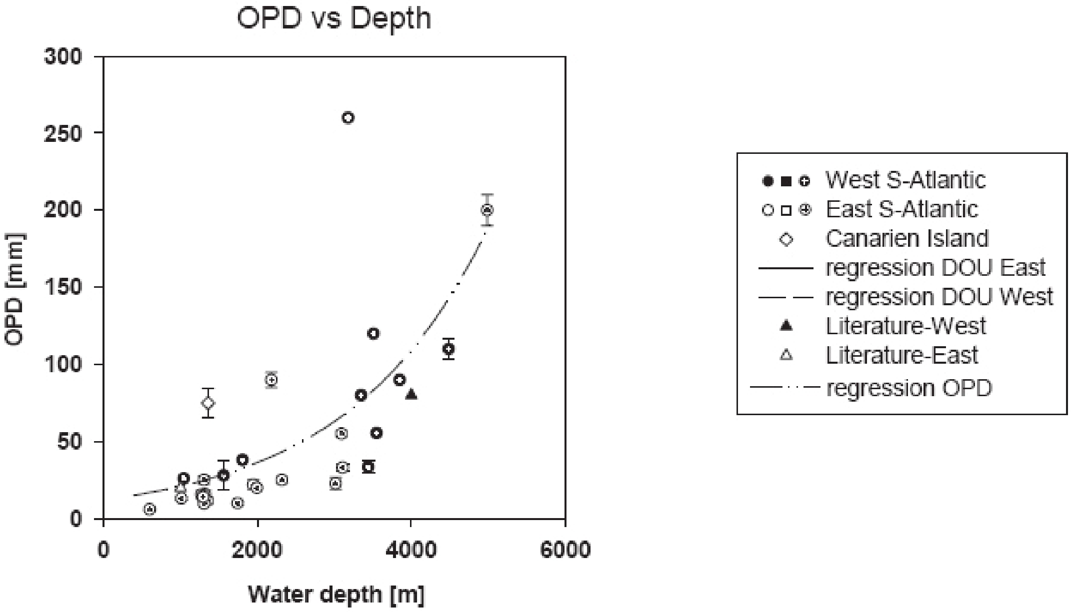

Fig.1.6 Oxygen penetration depth, OPD, as a function of water depth: OPD exponentially increases with water depth. In sediments <2000m of the South Atlantic OPD is approximately 2-3cm. (Taken from Wenzhöfer and Glud, 2002)

Tab.1.2 Quantitative importance of sulfate reduction to the mineralisation of deposited organic material. (According to Jørgensen and Kasten, 2006)

Location	**Water Depth** [m]	**Rate of C_{org} degradation** [mmol m^{-2} d^{-1}]	**C_{org} mineralised by sulfate reduction**	**Reference**
Cape Lookout Bight	9	114	75 %	Crill and Martens (1987)
Chilean shelf	34-122	10	56 - 79 %	Thamdrup and Canfield (1996)
Baltic Sea	16	9.8	44 %	Jørgensen (1996)
Gulf of Maine	50-300	10.7	43 %	Christensen (1989)
St. Lawrence Estuary	335	10	26 %	Edenborn et al., (1987)
E. South Atlantic (Benguela upwelling region)	850-3000	0.28-3.1	9 - 40 %	Ferdelman et al., (1999)
Eastern tropical Pacific	3760	0.5	0.05% *	D'Hondt et al. (2004) Jahnke (1996)
Black Sea, anoxic	130-1176	1.30-2.86	~ 100 %	Jørgensen (2004)

**modeled rate*

Degradability (availability) of organic matter

The degradability of organic material declines with sediment depth along with microbial mineralisation. The progressive decrease of organic carbon reactivity is often described by the multi-G model (Berner, 1980; Westrich and Berner, 1984). During decomposition the most biologically labile compounds of organic biomass will be preferably decomposed, leaving more refractory organic compounds behind. These more refractive compounds may degrade as well, but on a slower time scale. This decrease can be considered as the result of a number of different carbon pools that decay each with its own degradation characteristics and are consecutively depleted at exponential rates as diagenesis proceeds. Westrich and Berner (1984) demonstrated in sediments where sulfate reduction is the prevailing carbon oxidation process that measured rates of sulfate reduction reflect the actual rate of organic carbon turnover, and thus represent a direct measure of the current availability (reactivity) of organic matter to microbial degradation. Accordingly, sulfate reduction rates depend on both, the concentration and the quality of available organic matter. The overall rate of organic carbon oxidation by sulfate reduction is thus the sum of the rates of decomposition (k_iG_i, with k_i representing the first order rate constant and G_i the concentration of organic carbon of a specific degradability):

$$DG/dt = -(k_1G_1 + k_2G_2 + k_3G_3 + ...) \qquad (1.1)$$

Organic carbon pools and molecular composition

Organic tissue is composed of a variety of molecules with very different properties and reactivities (Wakeham et al., 1997). Labile compounds of organic matter mixtures such as pigments, selected lipids or hydrolysable amino acids get preferently degraded and removed from the total organic carbon pool as diagenesis progresses (Cowie and Hedges, 1994; Lee et al., 2000) and have been used to track organic matter degradation. For example preferential enzymatic degradation of amino acids relative to bulk organic matter causes the relative proportion of amino acid nitrogen (%AA-N, hereafter expressed as relative proportion of total hydrolysable amino acids to TN, THAA-%N and as part of TOC, THAA-%C) to decline from 75-90% in fresh plankton to 40-50% in sinking aggregates and further to 10-30% in sedimentary organic matter (Lee, 1988).

Preferably lost (pigments, proteins, lipids) and preserved (lignin) compounds are thus more suitable indicators of organic matter degradation than bulk chemical properties as i.e. the elemental C/N ratio. C/N values are often used to determine organic matter maturity as preferential utilization of nitrogen increases this ratio from low values (C/N 5-7) that indicate fresh material. Bulk organic matter composition provides mechanistic information rather than of organic matter availability, because C/N ratios also include the large proportion of uncharacterized material in the sediments. They moreover lack the ability to clearly separate between terrestrial and marine carbon sources (Cowie and Hedges, 1994).

We will focus on two of the more labile classes of organic matter in marine sedimentary material, pigments and proteins. They constitute a major fraction of the characterized carbon in marine particulate matter and therefore represent useful indicators of organic matter degradation (Lee et al., 2000). Biomarkers that are either selectively lost or preserved during diagenesis have often very specific degradation pathways that complicate a clear separation of preferential breakdown and variable input. As biomarker molecules usually occur in trace quantities they hardly represent important energy sources for heterotrophic organisms (Dauwe and Middelburg, 1998).

The degradation of bulk organic matter results in systematic changes of the molecular composition of amino acids. Principal component analysis of mol percentage contribution of amino acids was used to establish a protein-based Degradation Index (DI) developed by Dauwe and Middelburg (1998) and Dauwe et al. (1999) that ranked changes of individual acids to a general pattern. Amino acids associated with structural compounds (e.g. diatom cell wall) such as glycine, serine and threonine are enriched upon progressive degradation, whereas amino acids contained in cell plasma (phenylalanine, glutamic acid and tyrosine) become selectively depleted. The amino-acid based DI by Dauwe et al. (1999) varies from –2.2 to 1.5. DI values of 1-1.5 identify more labile sources such as phytoplankton and bacteria, between –0.3-1 in coastal and ocean margin sediments with values <-1 for very refractive organic matter in deep-sea sediments. The DI was shown to be consistent with other protein-based degradation indicators such as the relative abundance of non-protein amino acids, γ-aminobutyric acid (GABA) and β-alanine (BALA) that usually increase during diagenesis. Consequently the ratio between the protein precursor (e.g. aspartate) and the non-protein degradation product (e.g. β-alanine) is decreased (Cowie and Hedges, 1992 and 1994).

Probable mechanisms for the preservation of labile organic matter such as proteins may include sorptive attachment to sediment surfaces (Keil et al., 1994), and sorption in the small pores of minerals (Mayer, 1994), where bio molecules may be protected from enzymatic hydrolysis. These possibilities must be considered if the DI is interpreted. Moreover, the estimation of the total protein pool by measurement of total hydrolysable amino acids (THAA) may not accurately reflect all protein available for microbial degradation (Pantoja and Lee, 2003) as some amino acids are bound in physical matrices (e.g. diatom walls, see Fig.1.7) or biominerals that may not be released during acid hydrolysis (Ingalls et al., 2003).

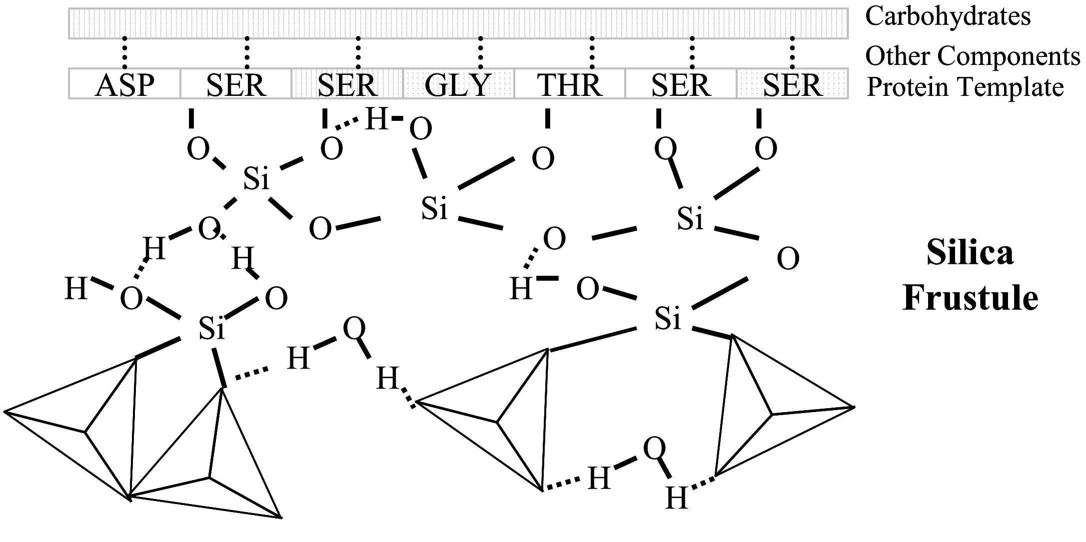

Fig.1.7 Structural model of the diatom cell wall with incorporated amino acids according to Lobel et al.,1996 and Hecky et al., 1973.

So far no direct relationship between rates of microbial degradation and quality indicators based on bulk organic matter characteristics has been established. Indicators as i.e. the C/N ratio describe rather the chemical composition of organic material but lack information of the enzymatic susceptibility of macromolecular matter or possible physical protection (Arnosti, 2004). Refractive organic matter may drive high rates of carbon degradation as bacteria are able to thrive on a very small fraction made up of labile (fresh) organic matter (Arnosti and Holmer, 2003) that may be masked against a large background of highly altered organic material. Thus a quality indicator should be very specific to fresh organic matter and highly sensitive to microbial degradation to assess organic matter bioavailability.

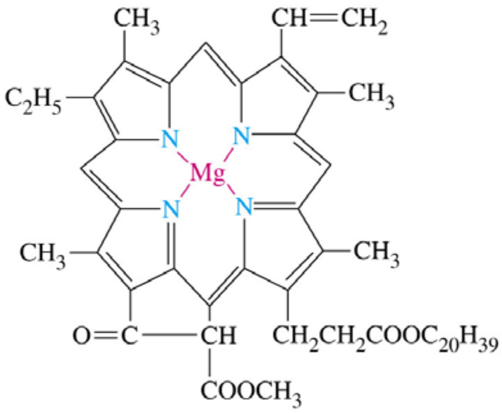

Fig.1.8 Molecular structure of chlorophyll *a*.

Chlorins, in contrast to proteins, are apparently better suited to assess the availability or freshness of organic material as they represent the immediate decay products of chlorophyll *a*, omnipresent in all photosynthetic organisms (Rowan, 1989) (Fig.1.8). Due to inherent high lability of pigments, these reactive compounds are quickly depleted during export in the water column and chlorophyll *a* thus rapidly decomposes to pheophytins (by loss of the central Mg atom), pheophorbides (loss of phytol side chain) and other chlorins (Stephens et al., 1997). Chlorins are particularly sensitive to the early stage of organic matter decay (Meckler et al., 2004) and based on the chemical lability of total chlorins (including chlorophyll *a* and all of its degradation products), Schubert et al. (2002 and 2005) have developed a degradation state indicator, the Chlorin Index (CI) that has been used to characterize organic matter composition in sediments of the Peru and Chile upwelling regions (Niggemann, 2005). Chlorins were applied to characterize present-day primary production as well as paleoproductivity (Schubert et al., 2005; Schubert et al., 1998; Harris et al., 1996), however information on its application to short time scales of organic matter degradation or in the Arctic realm affected by seasonal high productivity, if compared to the perennial high production in the Benguela upwelling system, are so far missing.

Therefore in chapter 2 of this study we will compare and discuss diagenetic controls of molecular organic matter composition, identified by the pigment- and protein-based CI and DI, in Arctic shelf and Benguela continental margin sediments. The CI and DI will be studied with respect to their significance during short- as well as medium-term organic matter degradation. Both indices will be further applied to paleoenvironmental time scales in sediments of the northern Benguela slope and discussed in chapter 5. Paleoceanographic implications from the chlorin and protein carbon pools will finally be used to introduce an early model that shows how past organic carbon fluxes may be reconstructed from molecular carbon pools (chapter 5).

The first move to a thorough understanding of organic matter composition and its potential controls has been done by the assessment of a state-of-the-art characterization of the two research areas: the highly-productive Benguela upwelling system distinguished by two major shelf and slope depocenters and the seasonal high-productive Arctic shelf. With the focus to evaluate organic matter reactivity in these regions, molecular degradation indices are compared to sulfate reduction rates, which represent the current organic carbon availability to microbial mineralisation. In chapter 3 the molecular carbon pools and their degradation state will be discussed for the Benguela depocenters, followed by a characterization of seasonal changes of organic matter composition and carbon pools in chapter 4. In the following section an overview of regional features of the Benguela upwelling system and Arctic shelf is given. Subsequent chapters 2 to 5 represent manuscripts that are planned for submission to scientific journals.

Regional description

The Benguela Upwelling System

The Benguela upwelling system (BUS) is one of the four major coastal upwelling system and located off Southwest Africa adjacent to the coasts of Namibia and South Africa. Upwelling is bordered by the Agulhas retroflection in the south and the Angola-Benguela frontal zone in the north, which are both warm water systems. Its major currents are the equatorward flowing Benguela Ocean Current (BOC) and the Benguela Coastal Current (BCC) over the Benguela shelf. Primarily driven by the intensity of trade winds, the BUS can be divided into a northern area characterized by perennial upwelling and a southern part with seasonal upwelling events.

The most intense coastal upwelling of nutrient-rich water and thus largest primary productivity is located offshore Lüderitz Bay, where high production rates of ~ 130-350 g C m^{-2} a^{-1} were measured (Mitchell-Innes et al., 2002; Behrenfeld and Falkowski, 1997). High rates of primary productivity off the Namibian coastline are also visible by high concentrations of chlorophyll *a* in surface waters that may form large filaments stretching as far as 1300 km offshore (Summerhayes et al., 1995 (a+b)) observed on satellite images (Fig.1.9). Rather than in its centre most of enhanced productivity occurs at the outer fringe of upwelling cells (Lutjeharms and Stockton, 1987).

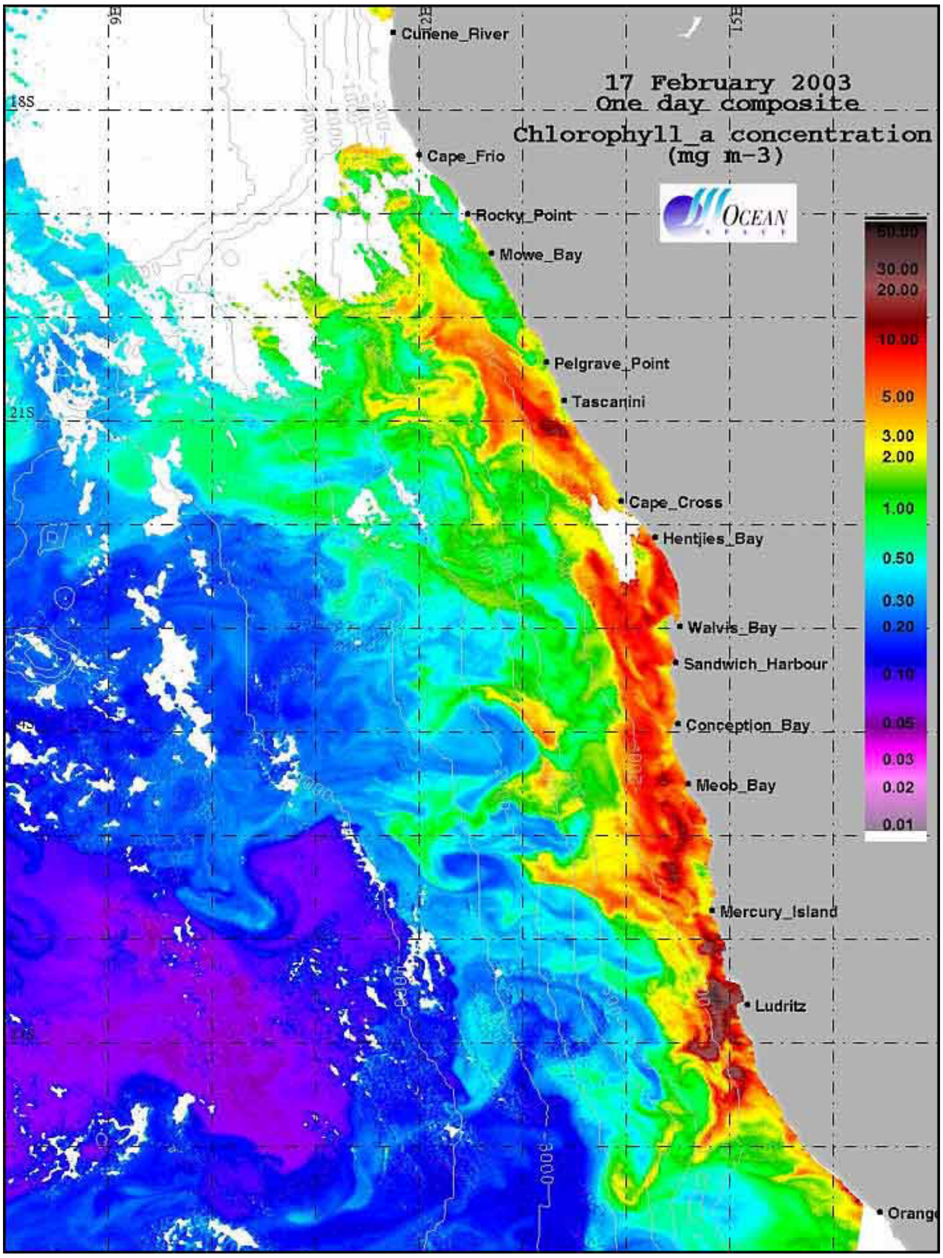

Fig.1.9 SeaWifs satellite image of ocean surface chlorophyll *a* concentration taken during the period of the cruise to Namibia in February 2003.

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The continuous upwelling strip parallel to the coast and the secondary upwelling front offshore, as indicated by eddies and filaments in surface waters correspond to the double-shelf breaks observed in the region. The incidental shelf circulation of the Benguela upwelling is characterized by a poleward flowing undercurrent and cross-shelf flow (Shannon and Nelson, 1996) (Fig.1.10). Along both fronts high accumulation of organic material (exported phytodetritus) and a widespread oxygen minimum zone (OMZ) account for the formation of two major depocenters of organic carbon, the Benguela shelf "mudbelt" (TOC of ~ 15%) and a major depocenter on the continental slope offshore Namibia (TOC ~8%) (Bremner and Willis, 1993; Bailey, 1991; Walsh et al., 1981). Thus the BUS may represent a prominent sink of atmospheric carbon dioxide and deserves closer attention with respect to the processes that control organic carbon burial in high-deposition environments.

Diagenetic controls of organic matter production, deposition, remineralisation and subsequent burial on the Benguela shelf and slope depocenter will be discussed in chapters 2 and 3.

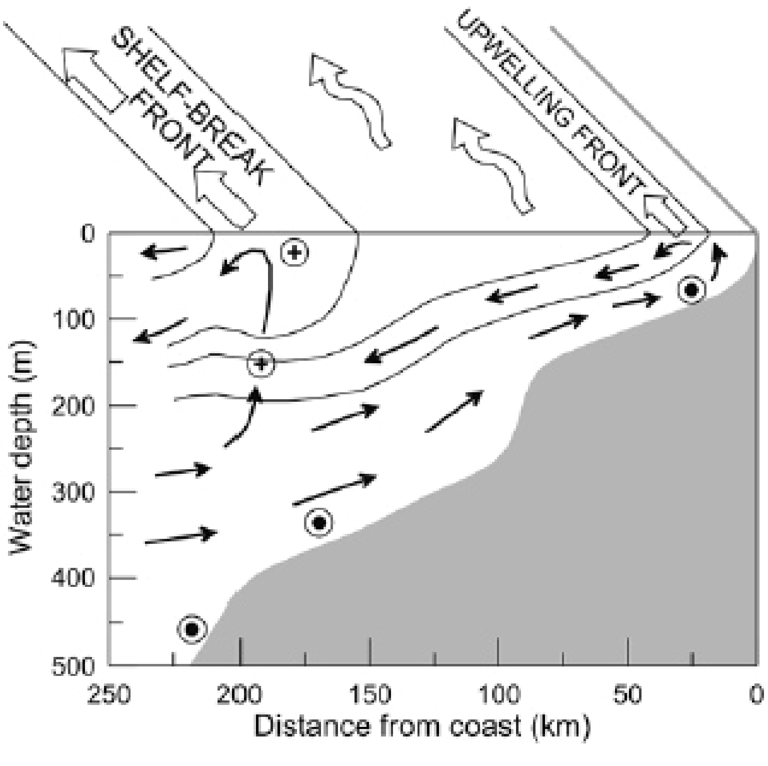

Fig.1.10 Model of the major upwelling pattern off Namibia. Shown are cross-shelf flowing water, surface currents, poleward (circle with dots) and equatorward (circle with crosses) moving undercurrents with respect to the coastal upwelling strip and the shelf-break front (taken from Mollenhauer et al., 2002, modified after Summerhayes et al., 1995)

The Arctic Shelf (Spitzbergen)

The Arctic contains the largest shelf area (>50%) of oceans worldwide that represent important regions for sea-ice production, entrapment and processing of land derived input of particulate matter (Jakobsson et al., 2003). Living conditions in the polar climate are extreme due to persistent low temperatures and restricted solar radiation (Sakshaug, 1997). Primary production thus strongly depends on the seasonal increase in light, stabilisation of the upper water layers and subsequent large phytoplankton blooms in the Barents Sea, where Spitzbergen is located (Fig.1.11), that usually occur between May and June. Annual high primary production in the Barents Sea was estimated to be as much as <20-200g C $m^{-2}y^{-1}$ and 120 g C $m^{-2}y^{-1}$ in the Barents Sea and the western Spitzbergen Shelf (Sakshaug, 2003).

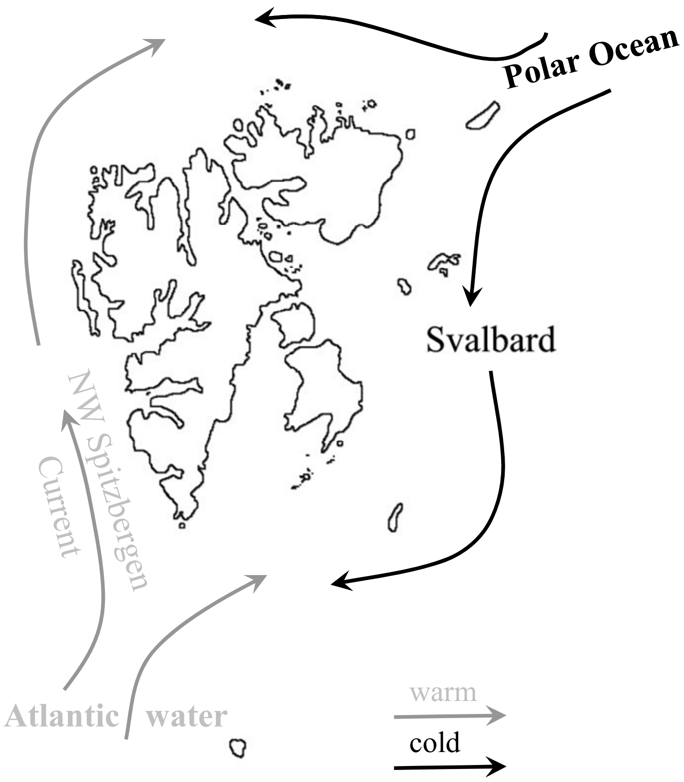

Fig.1.11 Schematic map of the major currents: South and West Spitzbergen are affected by Atlantic warm water and Northeast Spitzbergen is under the influence of cold Polar Ocean water.

The Spitzbergen archipelago is located in the transition between the Atlantic and Polar Arctic water masses. The northward flowing West Spitzbergen Current carries warm and nutrient-rich Atlantic water along the northwest coast that promotes earlier retreat of ice during spring, whereas the east coast of Spitzbergen is affected by cold polar waters carried by the East Spitzbergen Current, and hence, shorter periods of summer ice withdrawal (Hebbeln and Wefer, 1991; Falk-Petersen et al., 2000).

Sea ice is inherently important to Arctic life, as associated biological and biogeochemical processes are manifold (Fig.1.12). Sea ice controls the heat transfer at the ocean-atmosphere interface and the penetration of light into the sea, exerting major influence of sub ocean surface productivity. During winter particles and snow get deposited and embedded in ice that moreover represents a biological habitat above, beneath (e.g. zooplankton) and within the ice (ice algae) as well as in its melt water region, the marginal ice zone (MIZ), due to the summer stratification and high primary productivity related with the ice edge. Benthic communities in sediments beneath low (ice covered) as well as highly productive (ice margin, open water) regions depend on the seasonal variable export flux of organic carbon and thus a strong benthic-pelagic coupling exists in the Arctic (Jakobsson et al., 2004). To what extent the composition (≈availability) of seasonally supplied organic matter at the different shelf processes may affect the extent of benthic mineralisation and relative contribution of carbon oxidation pathways will be surveyed in chapter 4.

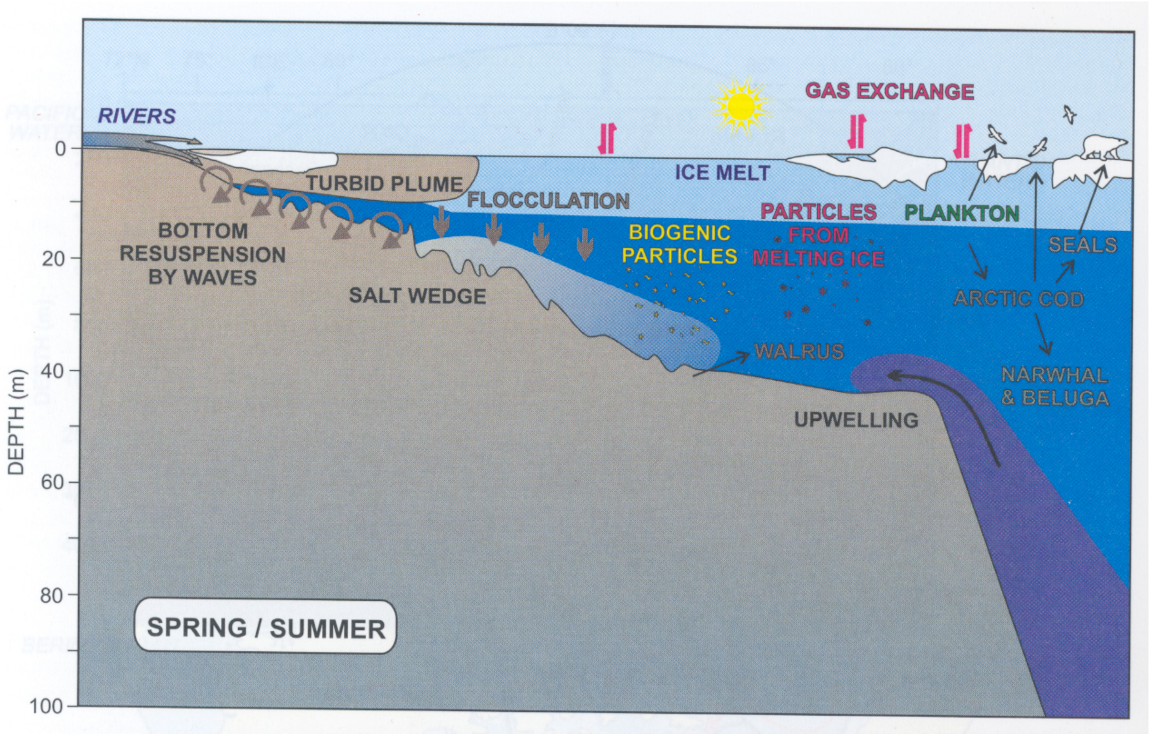

Fig.1.12 Major processes that determine particulate organic matter flux associated with the seasonality of sea ice in the Arctic (taken from Jakobsson et al., 2004, modified after MacDonald and Bewers, 1996)

Chapter 2

Diagenetic controls on pigment- and protein-based organic carbon degradation indices

A. Ahke [1]

Potential co-authors for a manuscript based on this chapter for submission to *Geochimica et Cosmochimica Acta:*

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Abstract

The composition of molecular organic carbon pools, pigments and proteins, was studied during different time frames of organic matter degradation and compared for coastal sediments of the Arctic shelf and Benguela upwelling area. Results demonstrated that the reactivity of both organic carbon pools was closely related to their ability to associate with sediment structures as well as to the inherent chemical reactivity of molecular compounds. This was confirmed by anoxic bag incubations of sediments that were enriched with fresh algae. The experiments revealed a delay of sulfate reduction activity with respect to the enzymatic breakdown of macromolecular matter at the early stage of the experiments. This rate-limiting step of anoxic carbon mineralisation was reflected by total chlorin concentrations and the degradation state of chlorin organic matter, which was characterized by the Chlorin Index (CI). However, neither the amount of total hydrolysable amino acids (THAA) nor its molecular composition, indicated by the protein-based Degradation Index (DI), did respond to the initial degradation of organic carbon. Down core changes of THAA and the DI in sediment profiles revealed changes over longer time scales of organic matter degradation. Hence, the CI was sensitive to the very early stages of organic matter degradation; the DI corresponded to later organic matter decay, but provided a higher resolution of organic matter degradation.

The observed diagenetic controls of molecular degradation indices were manifold. In particular primary production, organic matter transport ways and physical protection techniques affected organic matter composition. Refractive organic matter, reflected by total chlorin amounts, usually regarded as “unreactive” carbon compounds, acted as the major driver of anoxic carbon degradation in the studied sediments.

Acknowledgements

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Introduction

Cycling of organic carbon and nutrient elements through marine reservoirs plays a key role controlling atmospheric CO_2 concentrations and thus, global climate (Jahnke, 1996). For a better understanding of the future development of atmospheric CO_2 and interpretation of past changes from the sedimentary record, more efficient estimates of carbon fluxes and assessment of factors that control organic carbon transfer are required. Continental margin sediments are particularly suited to study controls of organic carbon cycling as they represent major sites of carbon burial and mineralization (Muller-Karger et al., 2005; Hedges and Keil, 1995; Berner, 1989; Jørgensen, 1983).

Settling particulate organic matter is rapidly decomposed through bacterial mineralisation that consequently changes its molecular composition down the water column. Physical and microbial processes within the benthic boundary layer and at the seafloor as well as oxygen conditions further alter its composition and reduce the degradability of organic matter (Inthorn et al., 2005; Hartnett et al., 1998; Hartnett and Devol, 2003) – that is referred to "organic carbon reactivity".

Natural organic matter represents a heterogeneous mixture of recently introduced fresh and older refractory material (Cowie and Hedges, 1994). Principally the amount and degradability of supplied organic matter determine the overall rate of carbon degradation (Berner, 1980; Westrich and Berner, 1984). During decomposition biologically labile compounds will be preferably depleted, whereas sediments become enriched in refractory compounds, thus its degradability is decreased. This decrease results from a number of different carbon pools that are successively depleted, each at its own degradation characteristics and at exponential rates (Westrich and Berner, 1984; Jørgensen, 2006). Therefore molecular proxies and their related degradation indices can be used to study the diagenetic controls of organic matter degradation.

To investigate diagenetic controls of organic matter in upwelling and Arctic shelf and slope sediments, we studied two major organic carbon pools, chlorins and proteins, in marine sediments. Chlorins are a measure of immediate chlorophyll degradation products and as well include chlorophyll *a* and phytoplankton pigments. The protein pool was assessed by the total of hydrolysable amino acids (THAA). Molecular organic matter composition was characterized with respect to the degradation pattern of these pools and determined by specific degradation indices, the

Chlorin Index (CI) and the protein-based Degradation Index (DI) (Schubert et al., 2002 and 2005; Dauwe et al., 1999). They have been applied to characterize organic matter composition of marine sediments in the Peru, Chile and northern Benguela upwelling systems, the North Sea and Skagerrak (Schubert et al., 2002 and 2005; Niggemann, 2005; Dauwe et al., 1999). However, information of their applicability on short time scales of organic matter degradation and with respect to environmental controls, such as seasonal high carbon supply and conditions of organic matter deposition, remain scarce.

The time scales and diagenetic controls of the CI and DI are the focus of this study. Therefore, molecular organic carbon pools, chlorins and THAA, and their degradation indices will be studied and compared to rates of carbon mineralisation in sediment incubations. With this approach we aim to assess molecular composition changes on short-term periods that are representative to the time of initial organic matter deposition. We apply these degradation indices to various sediment types from the temperate Benguela upwelling system and the Arctic shelf (Spitzbergen) to examine longer time frames.

Methods

Samples

Multicorer cores for site comparison of sediment profiles and for bag incubations from the Benguela shelf and slope were collected during cruises with RV Meteor in 1996 and 2003 (M34/2; M57/2). Recovered cores ranged from 70 to 1500m water depth and contained organic-rich sediments from the anoxic shelf (“mudbelt”) and oxic slope.

Arctic sediment from the oxic Spitzbergen shelf was collected onboard of RV Jan Mayen in summer 2003 (CABANERA project cruise). Selected stations represented the Marginal Ice Zone, MIZ (ARC-1), and the northern ice pack (ARC-2) and covered 200 - 350 m water depth.

Sampling and Processing

A multiple corer was used to retrieve undisturbed sediment cores (25-40cm). Sediment cores were kept at *in situ* temperature (4°C) and immediately sub-sampled for organic geochemical analysis. Sediment samples were stored in the dark at -20°C until further analysis.

Sediment for bag incubations was collected from a total of eight cores. These were back-to-back sub-sampled and sediments transferred into prepared gas-tight bags, the residual air removed and the bags immediately sealed with an electric welder. Samples were stored at 4°C in the dark.

Experimental setup

Anoxic incubations were performed on sediments from three sites. Sediment was taken from the main sulfate reduction zone (5-10cm) and transferred into gas-proof plastic bags (Würgler-Hansen et al., 2000). During the experiments all incubated sediments were kept at 4°C in the dark.

Under nitrogen atmosphere, we prepared slurries from original sediment and freeze-dried algae (diatom species) that were soaked in ~ 2ml of filtered sea water. The appropriate amount of sediment volume and added algae was calculated prior to the setup and depended on the experiment site (see below). Sediment volume was admeasured, the algae added and the mixture stirred with a metal spatula until combined. The slurry was then transferred into a separate Würgler bag, sealed and incubated at 4°C in the dark.

Bags were sub-sampled under nitrogen atmosphere at weekly or biweekly intervals. Aliquots of sediment were taken for the analysis of solid sediment geochemical parameters. Aliquots of pore water have been obtained from sediment samples by use of a pore water squeezer.

Experimental sites:

Spitzbergen shelf

ARC-1

Sediment from site ARC-1 represented an open-water station within the Marginal Ice Zone (MIZ) southeast of Spitzbergen (75°N). From the stratified water column, a relatively deep chlorophyll *a* maximum (~ 40m) and the dominance of colony-forming diatoms (*Phaeocystis*), we supposed that a post-bloom situation determined local organic matter supply (Reigstad M., pers.communication; see also chapter 4; Kristiansen et al., 1994).

We added 0.3g of dried algae to the slurry. Based on a concentration of 12.5 % of TOC in the deployed species (diatom *S. costatum*) this was equal to 37.5mg algal carbon. Incubations started onboard and were terminated after 72 days in the Bremen laboratory.

ARC-2

Sediment represented an ice-covered site northeast of Spitzbergen (79°N). Less stratified water and a shallow chlorophyll *a* maximum (25m) suggested a pre-bloom situation. Prior to the experiment we prepared a dilution series of dry sediment and freeze-dried algae (0.01-1%) series whose samples were analyzed for their chlorin content and CI value. To obtain a measurable effect in artificially freshened sediment by the CI, we had to add 0.5% dried algae (per g dry sediment) to the slurry. That was equal to 104mg algal carbon based on a TOC content of 23% in the deployed species (*A. kufferatii*).

Benguela slope

T2-600m

Sediment for incubations was taken from the upper Benguela slope at 25°S and 600m water depth. Based on a similar dilution series as described for ARC-2, we added 1% of the same algae species to provide a measurable effect by the CI and total chlorin amounts in slope sediments. This was equal to 92.3 mg algal carbon.

DIC measurement using flow-injection analysis

Dissolved inorganic carbon (DIC) in pore water samples was measured by flow injection analysis following Hall and Aller (1992). Principally, CO_2 evolving in the acidic carrier stream crosses a gas-permeable membrane and is trapped in an alkaline receiver stream. We used 30 mM HCl as carrier, the receiving agent was 10 mM NaOH. Prior to measurement, the instrument was calibrated using standard concentrations of 0–20 mM $NaHCO_3$ freshly prepared standard solution. Triplicate measurements of filtered sample aliquots of ~ 300µl were performed.

Sulfate reduction rate measurements (SRR)

Experiments

Sediment was sub-sampled from the control and slurry bag incubation and collected in triplicate sample aliquots of 2.5ml in glass cylinders, sealed with a soft butyl rubber stopper at the bottom. Immediately after sampling, sediments in the glass cylinders were incubated at 8-10 hours at 4°C in the dark after injection of 5 µl of 200 kBq radioactive sulfate tracer (Amersham) through the rubber stopper. Microbial activity in sediment samples was stopped with 20% ZnAc-solution and storage at

-20°C. The distillation of radioactive end products and calculations of sulfate reduction rates were performed following Kallmeyer et al. (2004).

Multicores

Sulfate reduction rate measurements on multicores were conducted using the whole-core $^{35}SO_4^{2-}$ method by Jørgensen (1978). Incubation of the sub cores has been performed at one cm intervals with 5 µl of 100 kBq ml^{-1} $^{35}SO_4^{2-}$ tracer (Amersham) at 4°C in the dark for 8-12 hrs. Microbial activity was terminated as described for experiments.

Bulk geochemical analysis

Freeze-dried homogenized samples were analyzed for total carbon (TC) and nitrogen (TN) with a Fisons NA 1500 (Series 2) Elemental Analyzer. Total inorganic carbon (TIC) was measured by coulometry at a TIC autoanalyser CM 5240 Orbis BV. Total organic carbon concentration (TOC) was calculated by subtracting TIC from TC.

Organic parameters: Total chlorins, Chlorin Index, Pigments

Total Chlorin concentrations and a related degradation state indicator, the Chlorin Index (CI), were determined according to the method by Schubert et al. (2002). Total chlorins were extracted from 5-20mg freeze-dried samples by threefold solvent extraction in HPLC-grade acetone. During extraction samples were cooled with ice and kept dark to prevent chlorin decomposition. Extracts were measured immediately after extraction at a Hitachi F-2000 Fluorimeter at excitation wavelength 428 nm and emission wavelength 671 nm. Chlorophyll *a* (SIGMA) was transformed to the chlorin phaeophytin *a* through acidification using ~ 100 µl of hydrochloric acid and used as a standard for total chlorin concentrations.

Sediment extracts were acidified just as the standard and remeasured. The derived Chlorin Index, CI, following Schubert et al. (2002) is defined as the ratio of the fluorescence units of the acidified sample over the original extract (Equ.1). CI values are on a scale from 0.2 (fresh organic matter) to 1 (refractory organic matter).

$$CI = \text{fluorescent intensities}_{\text{acidified sample}} / \text{fluorescent intensities}_{\text{original sample}} \qquad (1)$$

Pigments

Pigments were solvent-extracted from freeze-dried sediments by ultra sonication (Bandelin Sonoplus HD 200 ultra sonication probe, MS73/D, 30 sec) following Buffan-Dubau & Carman (2000). For extraction, 100% HPLC-grade acetone was used, providing dark and cool conditions.

Chlorophyll *a*, pheophorbide *a*, pheophytin *a* and algal pigments were analysed with a reversed-phased HPLC system and a protocol described in Wright et al. (1991). Original sample aliquots of 100 µl were injected into a Waters HPLC advice (Waters 2690 Separation Module) equipped with a photo diode array detector (PDA 996). Pigment detection was performed at 430.3 nm with an additional PDA spectrum from 350-800 nm recorded every second.

Organic parameters: THAA, Degradation Index

Total hydrolysable amino acids (THAA) were analysed following a method by Dauwe and Middelburg (1998), and is further described in chapter 3. 100µl sample aliquots were reacted with fluorescent agent, *o*-phtaldialdehyde (OPA) and analysed at excitation/emission wavelengths 340/455 nm with a Hitachi F-2000 Fluorometer.

To calculate the degradation index (DI), the concentrations of 17 individual amino acids were determined via pre-column *o*-phtaldialdehyde derivatisation (Hill et al., 1979; Lindroth & Mopper, 1979), including an internal standard (SIGMA AA-S-18) from 100 ml aliquots of neutralized sample. Individual amino acids were separated by reverse-phased HPLC with a heated C_{18} – column (30°C) and binary solvent system with subsequent fluorescence detection.

A principal component analysis (PCA) (Meglen, 1992) was performed to determine organic matter degradation state based on the sediment amino acid composition and the selective degradation pattern of THAA. Mole percentages of individual amino acids were standardized with this method and resulted in individual site scores, termed Degradation Index (DI) as introduced by Dauwe and Middelburg (1998). Their DI varied between values >1 to ≥ 2 (highly reactive matter, fresh phytodetritus) to values < -1 or lower (strongly degraded organic matter) (Dauwe et al., 1999).

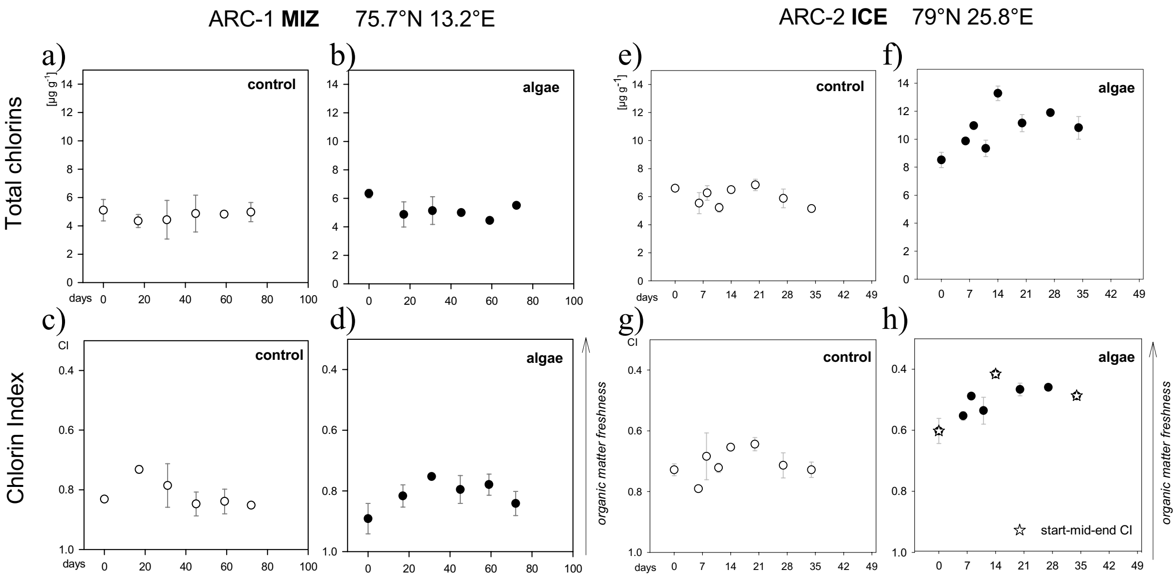

Fig. 1 Anoxic incubations of Arctic shelf sediment from the Marginal Ice Zone, ARC-1 MIZ (a-d), and beneath the ice cover, ARC-2 ICE (e-h) for variations of total chlorin concentrations and the CI in control (open circle) and slurry sediments (filled circles).

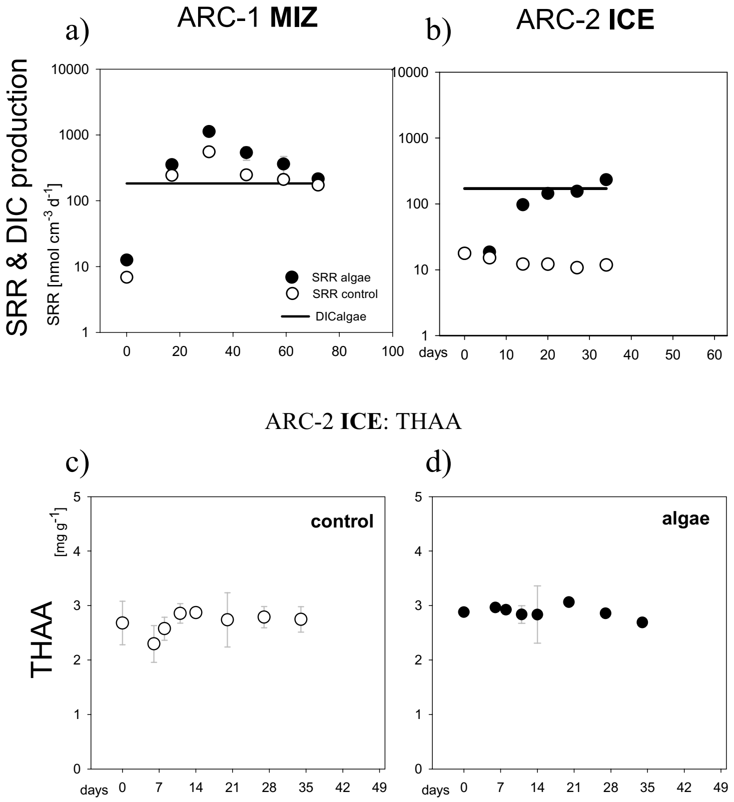

Fig. 2 Areal SRR and total DIC production (black line) in both incubations, ARC-1 MIZ (a) and ARC-2 ICE (b). THAA concentration (c) and the DI (d) in the ARC-2 experiment.

Results

Experiments (Fig. 1-3)

ARC-1

Chlorin concentrations in control and slurry varied between 4 and 5 µg g^{-1} and were only enhanced in the slurry at the beginning of the incubation (6µg g^{-1}) (Fig.1.a and b). CI values increased in both incubations (Fig. 1.c and d). In the control, the CI changed from ~0.8 to 0.7 after 20 days and then inclined back to a value of ~0.85. In the slurry, an initial CI of 0.9 decreased to 0.75 after 31 days and to ~0.84 at the end of the experiment (72 days).

Sulfate reduction rates (SRR) were overall higher in the slurry (6-563 nmol cm^{-3} d^{-1}) than in the control (3-276 nmol cm^{-3} d^{-1}) (Fig.2.a). In control and slurry, SRR increased to peak rates after 31 days that were already larger than the total DIC production of 184 nmol cm^{-3} d^{-1} calculated for the entire experiment (72 days).

ARC-2

Chlorin concentrations varied between 5.1 – 6.8 µg g^{-1} in the control and 8.5 – 13.3 µg g^{-1} in the slurry (Fig. 1.e and f). Total chlorin content in the control remained at ~ 6 µg g^{-1}. Slurry chlorin concentrations increased within 14 days (8.5 to 13.2 µg g^{-1}) and then declined again (~ 11 µg g^{-1}).

CI values in the control were between 0.7 and 0.8, and 0.4-0.6 in the slurry (Fig. 1.g and h). In the slurry, an initial CI of ~0.6 decreased from an initial value of ~ 0.6 after 7 days to 0.4 (took 14 days) and finally back to 0.5 (34 days).

Similar concentrations of ~ 3 mg g^{-1} of total hydrolysable amino acid (THAA) were constant in control and slurry (Fig.2.c and d).

Sulfate reduction rates of 6-8.8 nmol cm^{-3} d^{-1} and 8.8 – 116 nmol cm^{-3} d^{-1} were measured in control and slurry (Fig.2.b). Initial SRR were low in both incubations (0-6 days). Microbial acticivity in the slurry increased to 48 (after 14 days) and finally to 116 nmol cm^{-3} d^{-1} (34 days). SRR exceeded the total DIC production rate of 171 nmol cm^{-3} d^{-1} at the end of the experiment.

BUS / T2-600m

Total chlorin concentrations differed between the control (165-227 µg g^{-1}) and the slurry (217-442 µg g^{-1}) (Fig. 3.a). In the control, chlorins slightly decreased throughout the experiment (221 to 165 µg g^{-1}). In contrast, slurry chlorin concentrations increased after an initial lag phase of 14 days from 223 to 442 µg g^{-1} (42days) and finally dropped close to initial amounts.

CI values were ~ 0.8 in the control (Fig. 3.b). In the slurry, an initial CI value of 0.7 decreased to 0.6 after ~10 days of incubation time.

Chlorophyll *a* concentrations ranged from 0.2-0.3 µg g^{-1} in control and 0.3-1µg g^{-1} in the slurry (Fig. 3.c). In the slurry, chlorophyll *a* increased within ~ 6 to 28 days from ~ 0.4 to maximum concentrations of 1.2 µg $g^{-1}$and finally declined to 0.6 µg g^{-1}.

Compared to chlorophyll *a*, pheophytin *a* concentrations inclined continuously between 8 and 42 days from ~0.4 to 1 µg g^{-1} (Fig.3.d). Final pheophytin *a* concentrations resembled those in the control (~0.5µg g^{-1}).

THAA concentrations varied from 14 - 25 mg g^{-1} in the control and from 14 – 30 mg g^{-1} in the sediment slurry (Fig.3.e). During the first 10 days THAA concentrations declined in both incubations, and were slightly lower in the slurry than in the control. Between 12 to ~28 days of incubation THAA concentrations particularly increased in the slurry with maximum concentrations of 34 mg g^{-1} after 28 days.

DI values were in a similar range in the control (-1.7 to -0.4) and exhibited a slight variability in the slurry sediments (-2 to -0.4) (Fig. 3.f). DI values in the slurry followed THAA concentrations: values first decreased and inclined to a maximum DI value of -0.3 after 14 days.

Sulfate reduction rates of 22.3 – 37.9 and 1.6 – 187.0 nm cm^{-3} d^{-1} were measured in the control and slurry incubation, respectively (Fig. 3.g). In the control, as expected, SR determined the overall total organic carbon mineralisation (DIC). Microbial activity by SR in the slurry started to increase (beyond SRR in the control) after 22days of incubation and determined total organic matter mineralisation after 42 days-that was a 2.5fold increase in SRR if compared to the control.

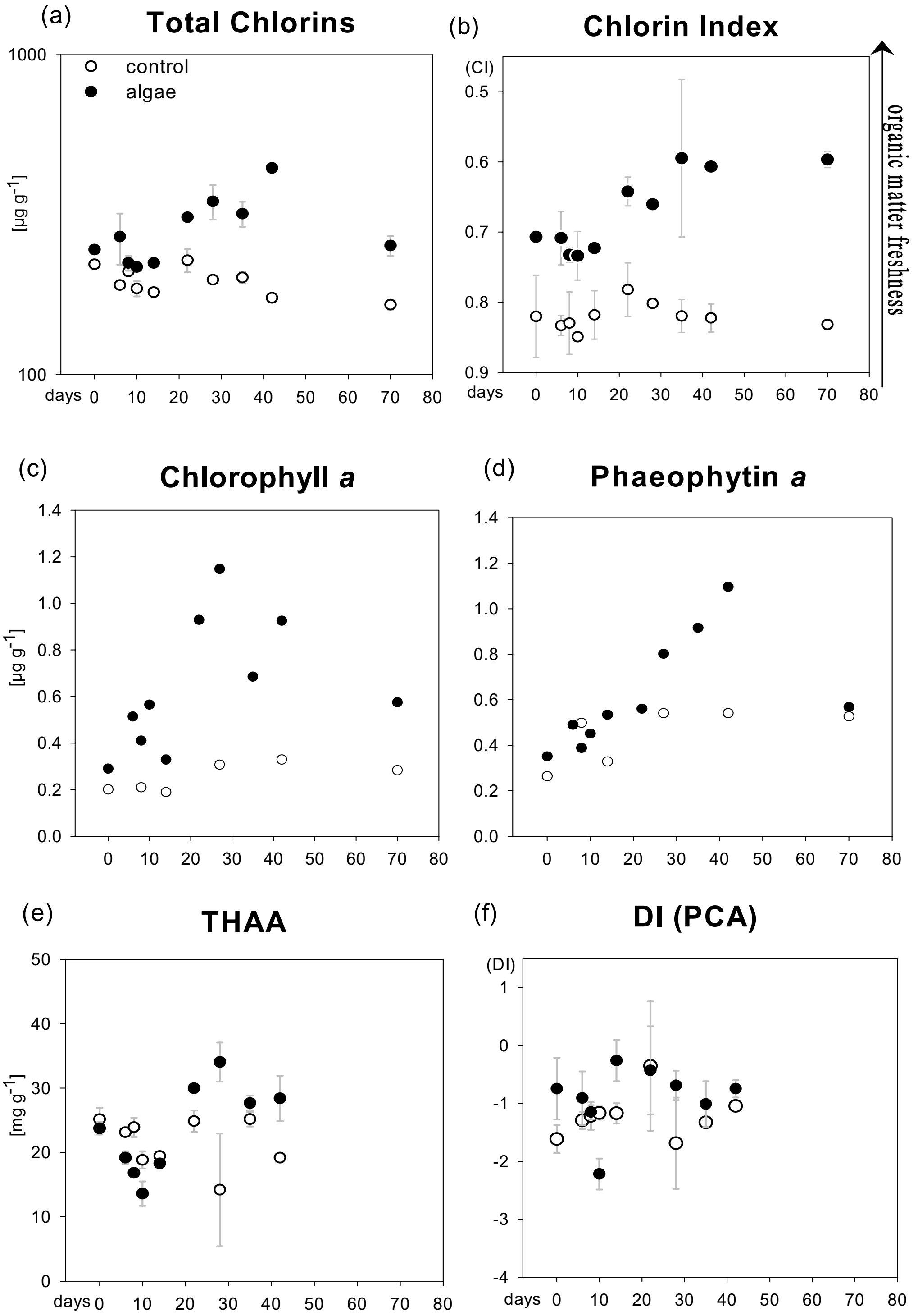

Fig.3 T2-600m: Chlorin content (a) and CI (b), chlorophyll *a* (c) and phaeophytin *a* (d), THAA concentration (e) and DI (f) in the slope incubation.

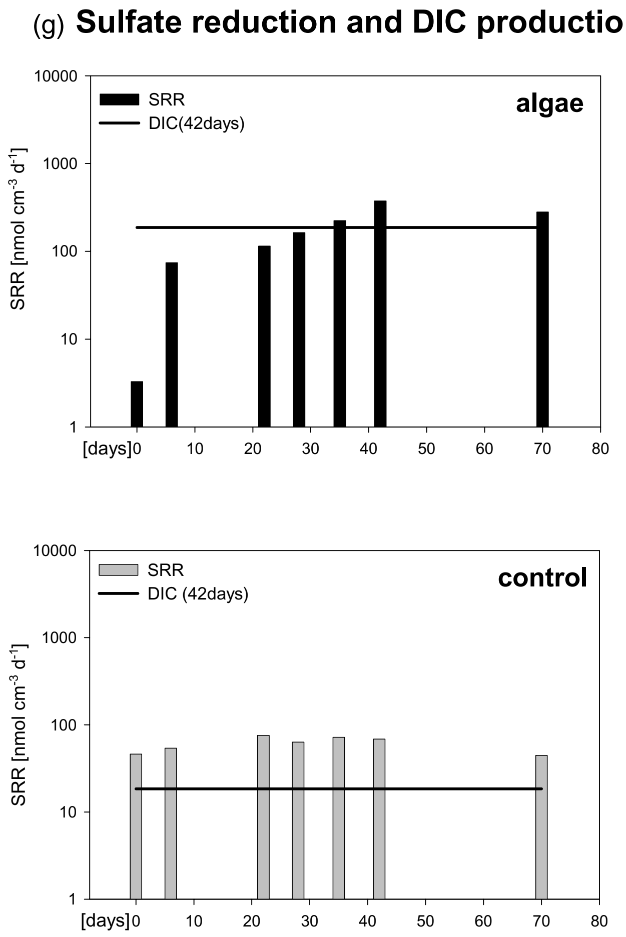

Fig.3.g) T2-600m: Organic matter mineralisation, areal SRR and DIC production (equal to Total organic carbon mineralisation) in the slope incubation.

Multicores

Molecular organic matter composition, bulk organic carbon characteristics and sulfate reduction rates in sediment profiles of the studied areas will be described. The sites have been arranged side by side for one parameter in Fig. 4 for a) sulfate reduction rate, SRR, b) phytoplankton pigment concentration, c) total chlorins and d) the CI. Fig.5 illustrates for the same sites a) THAA concentrations, b) the DI, c) the percentage of amino acid carbon and nitrogen to TOC and TN, THAA-%C and THAA-%N, d) total organic carbon content, TOC, and e) the molar C/N ratio.

Arctic (oxic shelf)

Total organic carbon, total chlorins, pigments, THAA and THAA-%C and -%N were characterized by general downcore decreasing and subsurface peak concentrations. Variations were 1.5 – 2.5 % TOC, 4-31 µg g^{-1} for total chlorins, 3 – 11 mg g^{-1} THAA, 9-21% THAA-%C and 33-58 % THAA-%N. A converse trend was observed for C/N values of 10-13 and CI values of 0.5 – 1. DI values were generally larger at the surface (>0.0) and decreased with depth (< -2).

Sulfate reduction rates varied between 0.05 and 4.3 nmol cm^{-3} d^{-1} with lowest rates close to the sediment surface. SRR increased to maximum rates at 3.5-8cm with peak SRR at 6cm.

TOC, chlorin and THAA concentrations and CI and C/N values were low within the upper 2 cm sediment layer. Concentrations and degradation indices showed largest variations within the major sulfate reduction zone: chlorins, THAA and TOC decreased (31-5µg g^{-1}, 11-5 mg g^{-1}, 2.4-1.8%) and CI and C/N values increased (0.5-0.9, 10-11.4).

Benguela anoxic shelf and mudbelt

21°S (70m water depth)

TOC, total chlorin, pigments, THAA and THAA-%C / %N exhibited greatest variability within the upper 10cm anoxic sediment layer (MB-21°). In contrast to sub-surface peak concentrations of pigments, THAA and TOC, total chlorin amounts were largest at the surface and decreased with depth. Concentrations varied from 3 – 8 % TOC, 155 – 937 µg g^{-1} total chlorins, 20 – 72 mg g^{-1} THAA, 17 – 49 % THAA-%C and 48 – 95 % THAA-%N (Tab.3 A, for pigments refer to Tab.3 B).

CI values mainly increased within the upper 10 cm of the core (CI of 0.5 to 0.7) and did not exceed values of ~ 0.7. C/N values varied between 7 and 11 and, except for a sub-surface decrease at 3.5 cm, continuously increased with depth.

The DI was only estimated for half of the samples and varied between -7 and 3. Largest DI values of 2.6-3 were measured within surface sediments (0-2.5cm) that decreased to a value of ~ 0.7 at 10cm and an of all of the sites lowest DI of -8 at 30cm depth.

Sulfate reduction rates varied from 0.3-43 nmol cm^{-3} d^{-1} and below 1.5 cm sediment depth continuously decreased. At the core base (30-40cm) SRR slightly increased again to 4 nmol cm^{-3} d^{-1}.

At the bottom of the core, total chlorin, THAA and TOC concentrations increased (to 391 µg g^{-1}, 42 mg g^{-1}, 8 %), and were consistent with SRR. CI values in turn decreased from 0.65 to 0.6 and DI values increased from -7 to 2.6. The C/N ratio increased to ~ 11. Base values of the CI, DI and C/N were similar to the core top (1.5cm).

23°S (110m water depth)

Greatest variability of organic matter content was measured within the upper core (15cm). Concentrations varied from 290 – 1088 µg g^{-1} of total chlorins, 15 – 47 mg g^{-1} THAA, 8-33% THAA-%C and 24 – 75% THAA-%N and 6 – 9 % TOC down the core. Total chlorin amounts continuously decreased by ~ 50% in the upper core. THAA and TOC exhibited sub-surface peak concentrations and after that TOC values inclined, whereas THAA slightly decreased down core. In the upper core, rising CI values (0.6 to 0.7) mirrored chlorin concentrations. In the upper core, DI values scattered between ~ 2 and -2 and then decreased; the C/N increased consistently with depth throughout the core.

Sulfate reduction rates were higher at 23°S than at 21°S (1.5 – 127 nmol cm^{-3} d^{-1}). In the upper core (0-14cm), rates varied less and declined from 127 to ~ 80 nmol cm^{-3} d^{-1}. In the lower core (16-28cm) SRR further decreased to 1.5 nmol cm^{-3} d^{-1}.

In the lower core, THAA, THAA-%C and %N and DI values decreased consistent with SRR. In contrast to rising total chlorin and TOC concentrations as well as C/N values, the CI declined back to an initial value of ~ 0.6.

Benguela (oxic slope)

600m water depth

Total chlorin, chlorophyll a, phaeophytin a and TOC varied a lot within the upper surface sediments (0-2.5cm). Changes of THAA, THAA-%C and -%N and peridinin (dinoflagellate pigment) concentrations, however, were rather apparent at lower depth (~5-10cm).

Total chlorin concentrations varied from 48 – 75 µg g^{-1} , and decreased from peak surface values to relatively constant concentrations (~ 50 µg g^{-1}) within 5cm. Chlorophyll a and pheophytin a concentration declined from maximum surface concentrations to relatively constant amounts within the upper 2.5cm (Tab.4B). In contrast to pigments, TOC concentrations increased within surface sediments (6-7%) and below remained at ~ 6%.

THAA concentrations of 16-23 mg g^{-1} hardly varied within the upper core (~ 22 mg g^{-1}), but decreased in the lower core (> 6cm) to minimum amounts. THAA%C and %N and peridinin concentrations changed in a similar manner with sub-surface peak concentrations at 5cm followed by a decrease.

CI values varied throughout the core between 0.75 – 0.77. The DI was only measured for core top and bottom sediments and gave values of 0.4 and -2.6 (14cm), respectively. C/N values also increased within surface sediments (0.5-2.5cm) and remained at 10 to 12 throughout the core.

Sulfate reduction rates (6-15 nmol cm^{-3} d^{-1}) were high close to the surface (0.5cm, 10 nmol cm^{-3} d^{-1}), then increased to peak rates at 5cm, and after that declined to values of 5.8 nmol cm^{-3} d^{-1}.

1500m water depth

Concentrations of total chlorins (21-28 µg g^{-1}), TOC (7-9 %), THAA (19-25 mg g^{-1}) were lower than on the upper slope and hardly varied with core depth. THAA%C and-%N showed sub-surface peak concentrations of 21 and 15 % at 4cm.

Consistent with total chlorin concentrations, CI values oscillated around ~ 0.8. DI values at the core top and bottom (14cm) were around ~ 0.0 with 0.3 and 0.2, respectively. C/N values increased from ~ 10 (surface) to ~ 11 (core bottom) except for one major increase to a C/N ratio of ~13 below the surface (1.5cm).

Sulfate reduction rates (3-17 nmol cm^{-3} d^{-1}) increased to peak rates at 5cm depth and declined to rates similar to surface values at the bottom of the core (at 20cm).

Discussion

The term reactivity reflects the joint signal of organic matter composition and source, (microbial) degradation pathways and particle association in sediments (Schubert et al., 2005; Keil et al., 1994). Degradation indices, the CI and DI, provide a measure of the degradation state of reactive carbon pools. Molecular composition is changed when these carbon pools are exposed to microbial degradation, leading to reduced organic carbon reactivity (Wakeham et al., 1997). CI and DI have been applied to characterize sediments off the high-productivity Chilean and Peruvian coastal systems and at the northern Benguela upwelling area (Niggemann et al, subm.

2005; Schubert et al., 2000, 2002, 2005). Organic matter freshness in these regions was primarily determined by the extent of degradation during transit in the water column. However, the applicability of indices in sediments that are exposed to seasonal (high) carbon supply and their time scales have not been discussed.

Short time scales

Short-term changes of organic matter composition and the extent of carbon mineralisation were comparable in Arctic shelf and Benguela slope sediments despite different site characteristics. At all sites organic carbon mineralisation by sulfate reduction was initially retarded, between 8-14 days on the shelf (ARC-2) and 14-22 days on the slope (Fig.2.a and b, Fig.3.i). The delay was indicated by one unit decreasing CI values, from an initial CI of 0.6 to 0.5 in the shelf and a CI of 0.7 to 0.6 in the slope sediments, followed by an increase of SRR. In contrast to the continuously inclining chlorin and DIC concentrations at ARC-2, an overall delay of parameters was observed in slope sediments. Interestingly, subsequent to the lag periods (after 34 days) total DIC production and instantaneous SRR were comparable for organic-poor Arctic and organic-rich slope sediments.

The increasing apparent freshness in the slurries reflected the release of “fresher” organic material from the added algal substrate. Subsequent to release no further compositional changes were observed due to a constant CI. We consider that SRR took off as small, reactive molecular compounds had now become available for microbial degradation.

Protein organic matter concentration and composition on the slope and shelf (ARC-2) showed only minor differences between control and enriched sediments. THAA amounts were slightly enhanced, but protein degradation indicators did not significantly distinguish between incubations. In contrast to total chlorins, THAA therefore exhibited a low availability to short-term microbial degradation.

On early time scales, organic matter composition, thus its availability to microorganisms, appeared to be the primary driver of carbon mineralisation in Arctic shelf sediments, whereas organic matter amount was an additional factor of carbon degradation on the slope (SRR).

We observed high organic carbon mineralisation rates that corresponded to lower organic matter freshness (CI of 0.8 to 0.75) and concentration in MIZ sediments (ARC-1) and fresher material (CI of 0.6 to 0.5) but lower SRR at the ice station

(ARC-2). At ARC-2 DIC production in contrast to SRR was not delayed, probably due to instantaneous uptake of small reactive organic matter compounds followed by depolymerisation of the fresher (more complex) substrate. Initially refractive matter at ARC-1 required less extensive hydrolysis, thus possessed a faster availability of OM to microbial mineralisation. Depolymerisation by extra cellular enzymes into smaller sized compounds (~600Da, Weiß et al., 1991) usually precedes microbial degradation, and the "fresher" the organic material the more time-consuming is its depolymerisation.

The activity of aerobic microorganismns has been suggested to affect the breakdown of macromolecular organic matter and thus the release of bound chlorophyll *a* (Sun et al., 1993; Jørgenson, 1983; Kristensen et al., 1991). On the oxygenated slope (BUS), where the sedimentary OM composition was comparable to the MIZ (CI of 0.7 to 0.6, CI of 0.5), the by contrast much larger chlorin concentrations seemed to balance the relation between carbon reactivity/availability and supply as microbial decomposition of organic matter through SRR increased rafter an initial delay. Large amounts of more refractive organic matter thus promoted microbial mineralisation on the Namibian slope.

Our results were consistent with these of Aspetsberger et al. (subm. 2006) who demonstrated faster uptake and more efficient growth of microbial biomass for altered phytoplankton due to already largely depolymerised carbon compounds in Benguela slope sediments. Fresher phytodetritus was rapidly mineralized due to take up of low molecular weight compounds of the fresh substrate, however further mineralisation due to depolymerisation was temporally delayed.

Alternative degradation processes such as Fe reduction might compete with microbial sulfate reduction and retard SRR. On the Benguela slope iron reduction was considered as a minor process (Aspetsberger et al., 2005); however, in Arctic sediments characterized by a lower carbon content (e.g. at extensive ice cover), metal reduction could be more important to total carbon mineralisation than SRR (Vandieken et al., 2006). As we used sediment from the major sulfate reduction zone (usually below that of metal reduction), such processes should be minor and not result in the observed differences in degradation indices and carbon mineralisation rates.

Long-term degradation and diagenetic controls

Water column depth, sedimentation rate and the prevailing carbon oxidation pathways were major controls on the molecular composition and total quantity of the chlorin and protein organic carbon pools. Whereas chlorin (matter) freshness and degradation were closely related to processes in the water column and at the sediment-water interface, protein (matter) diagenesis focused notably on sedimentary processes within the mixed layer.

A strong response of aerobic as well as anaerobic mineralisation rates to total organic carbon content in terms of increased Total Oxygen Uptake (TOU) rates and SRR was reported for Arctic shelf as well as slope sediments at intermediate water depth of the BUS (Hulth et al., 1994; Vandieken et al., 2006; Ferdelman et al., 1999; Glud et al., 1998). Comparison of SRR and chlorin amounts in oxic/anoxic shelf and slope sediments (Fig.4.a,c+d, 7.a) clearly demonstrated the influence of sedimentation rate on anoxic carbon mineralisation, consistent with the global compilation of carbon oxidation rates by Canfield et al.(2005 and 1993). Sulfate reduction accounts for a larger fraction of total carbon mineralisation at sites of high chlorin supply (sedimentation rates) such as the organic-rich anoxic Benguela shelf or oxic slope but is minor in less productive areas such as the ice-covered oxic shelf. Increasing sedimentation and intermediate chlorin freshness (CI of 0.6–0.7) apparently promoted sulfate reduction rates (Fig.7b).

Water depth was a major control of chlorin freshness in Peruvian coastal sediments (Niggemann et al., 2005). Applied to the Arctic shelf and Benguela slope, the rate of sedimentation (and thus oxygen exposure time) is even more significant to chlorin freshness. Examples from short-term experiments revealed that the organic matter degradation state is particularly crucial at the early stage of carbon diagenesis (Fig.1-3).

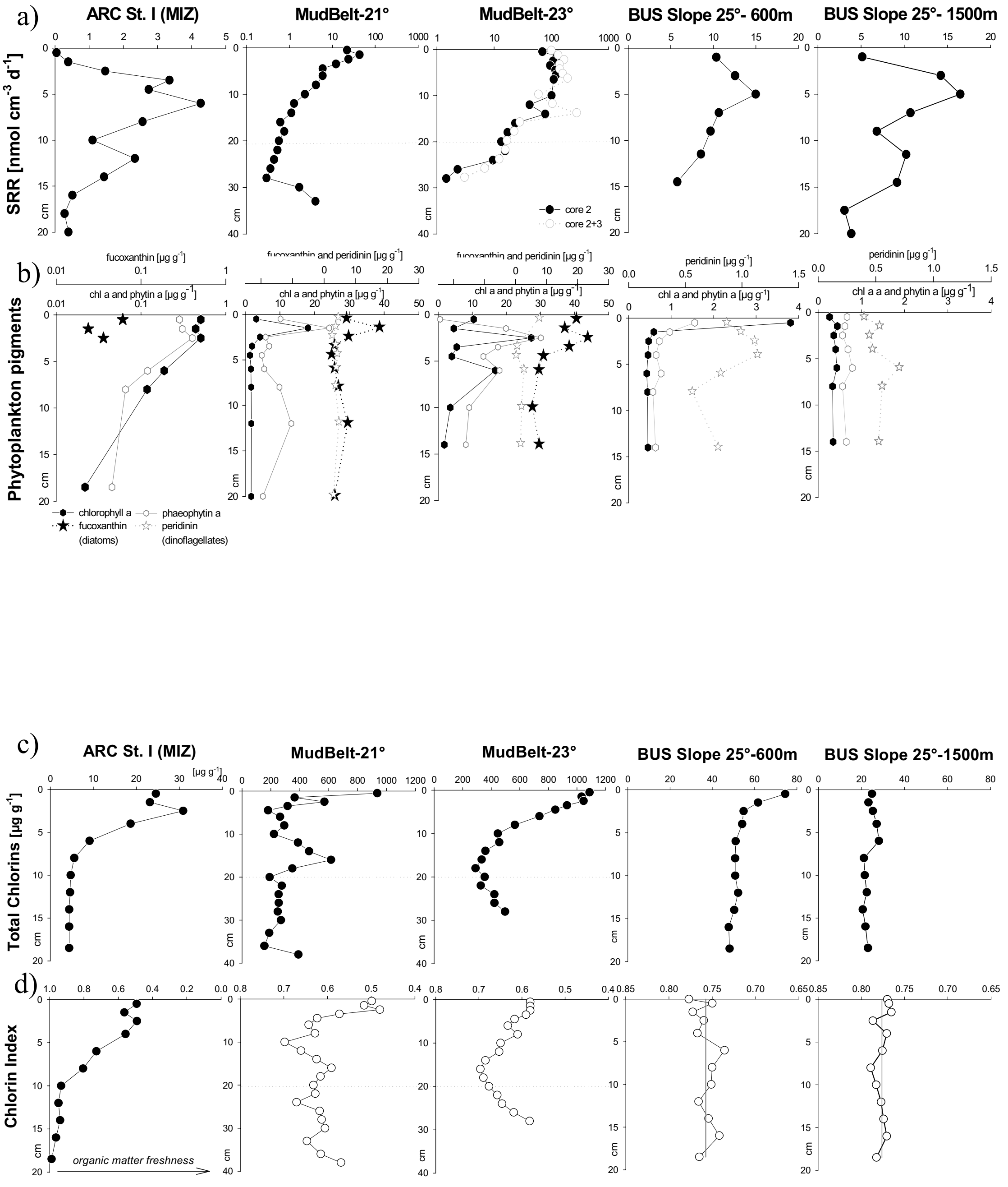

Fig.4 Sediment profiles representing oxic shelf sediments (Arc-1 MIZ), anoxic shelf sediments of the Benguela upwelling system (mudbelt) at 21°S (MB-21°, 226750) and 23°S (MB-23°, 226680) and oxic slope sediments of the Benguela upwelling system at 25°S at 600 and 1500m water depth. Demonstrated are a) sulfate reduction rate, SRR, b) phytoplankton pigment concentration: Chlorophyll *a*, pheophytin *a*, fucoxanthin (diatoms), peridinin (dinoflagellates), c) total chlorin concentration, and d) the CI.

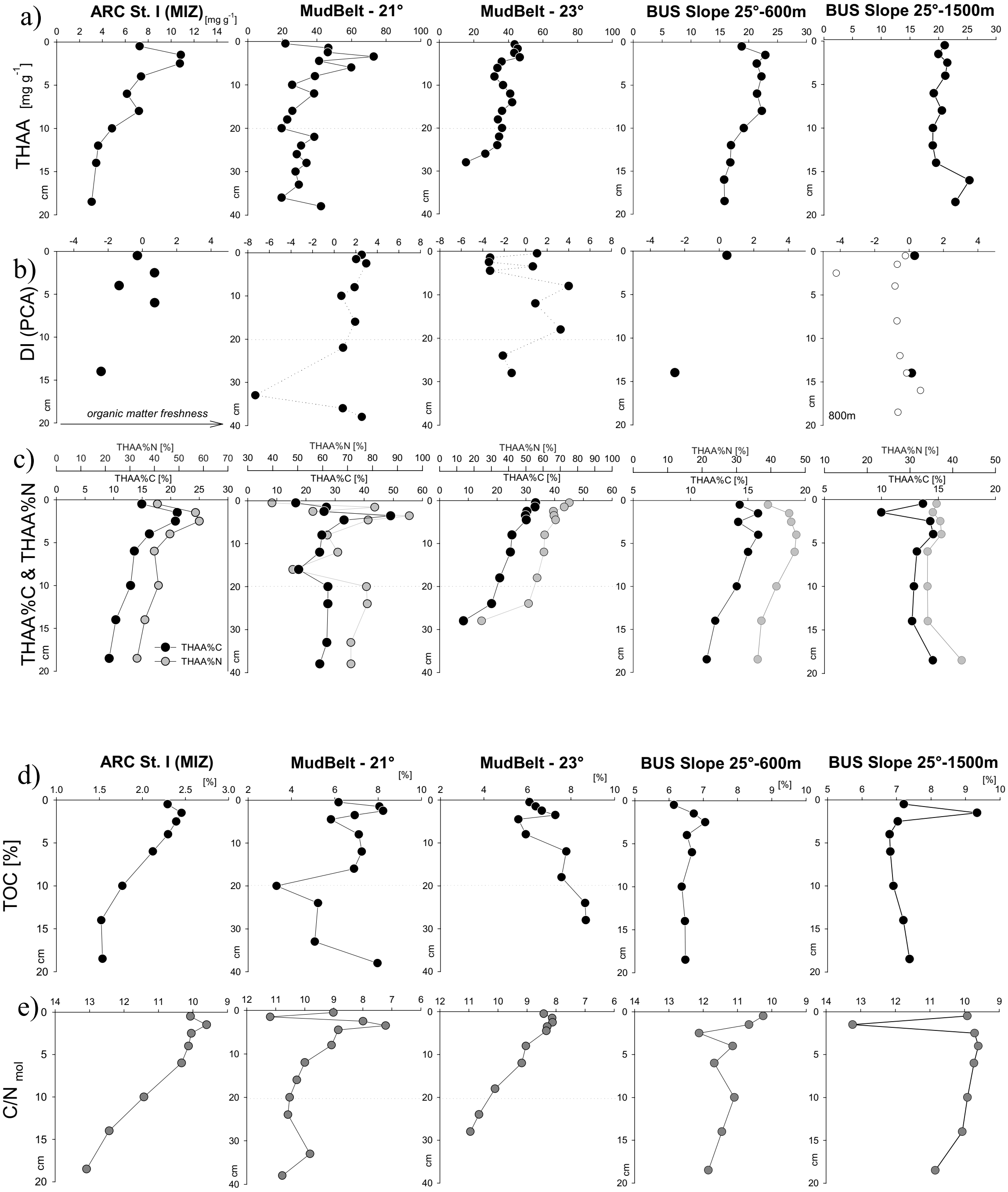

Fig.5 Sediment profiles representing oxic shelf sediments (Arc-1 MIZ), anoxic shelf sediments of the Benguela upwelling system (mudbelt) at 21°S (MB-21°, 226750) and 23°S (MB-23°, 226680)(long cores; the dotted line indicates 20cm depth as shown for all other site profiles). Oxic slope sediments represent the Benguela upwelling system at 25°S at 600 and 1500m water depth.

Demonstrated are a) THAA concentration, b) the DI, c) percentage of amino acid carbon and nitrogen to TOC and TN, THAA-%C and THAA-%N,d) total organic carbon content, TOC and e) the molar C/N ratio.

Site comparison

Overall organic carbon mineralisation as measured by sulfate reduction rates was closely associated with the supply and composition of total chlorins. Anoxic shelf sediments (BUS) were characterized by largest concentrations of relatively fresh, unaltered chlorin organic matter (~200-1000 µg g^{-1}) as shown by CI values of 0.5 – 0.6 (Fig. 4.c+d). Chlorin concentrations were consistent with measured areal SRR of 12 mmol m^{-2} d^{-1} (integrated over 15 cm), which could be as high as 63 mmol m^{-2} d^{-1} on the northern Benguela shelf (Brüchert et al., 2003). On the oxic slope of the southern Benguela upwelling system total chlorin concentrations of 20-75 µg g^{-1} and a CI of ~ 0.75 suggested intermediate accummulation of refractive matter that corresponded to likewise lower sulfate reduction rates (~ 1.6 mmol m^{-2} d^{-1})(Fig.4.a). Coastal sediments of the Peru upwelling region were characterized by a comparable chlorin composition with CI values of ~ 0.6 and ~ 0.8 on the shelf and slope. However, Peruvian sediments contained less chlorin amounts (shelf: ~ 300 µg g^{-1}; slope (1300m): 13-22 µg g^{-1}) and correspondingly lower sulfate reduction activity of 6 to 0.3 mmol m^{-2} d^{-1} (Niggemann, 2005). In contrast to the Peru upwelling area, organic carbon content in the Benguela shelf sediments was largely composed of chlorin-derived carbon (Fig.6; Tab.4.C). This was demonstrated by TOC-normalized chlorin amounts that were by 2-5 fold higher (~ 16000 µg $gTOC^{-1}$) in Benguela than in Peruvian shelf sediments (~3000-7000µg g TOC $^{-1}$), however, the contribution of chlorins to total organic carbon was similar in the slope sediments of both upwelling regions (~ 400µg g TOC $^{-1}$). Organic carbon content that was made up from chlorins in sediments at the Marginal Ice Zone on the Arctic shelf was similar than on the upper Benguela slope depocenter (600m, Fig.6). Chlorin organic matter was as fresh as those on the anoxic Benguela shelf (CI of 0.5-0.6) (Fig.2) and corresponded to very low rates of microbial SRR (0.3 mmol m^{-2} d^{-1}).

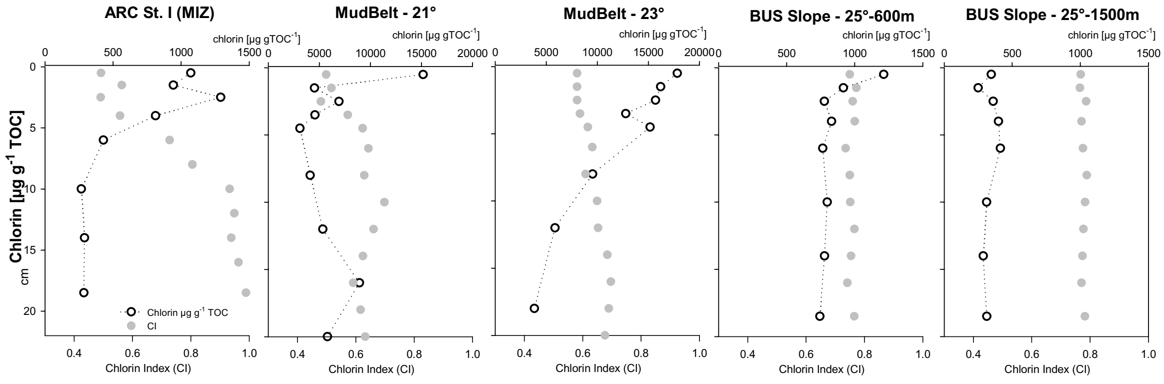

Fig.6 Comparison of oxic/anoxic shelf (ARC-1, MIZ; BUS shelf) and oxic slope sediments (BUS-600, 1500m) for their organic carbon content consisting of total chlorins as shown by TOC-normalized chlorin concentrations (open circle) (see Tab.4C). For comparison of chlorin degradation with organic carbon reactivity as measured by the Chlorin Index, the CI is as well plotted for each station (filled circles).

Similar chlorin freshness at the Arctic MIZ and at the anoxic Namibian shelf (CI ~ 0.5-0.6)as well as the much larger chlorin amounts on the Arctic can be explained by both the larger upwelling-induced carbon flux to the Benguela shelf (Campillo-Campbell and Gordoa, 2004; Mitchell-Innes et al., 2002) and the anoxic conditions on the shelf (Bailey, 1991).

On the oxic Benguela slope, the enhanced amount of less altered chlorins (~20-80µg g^{-1}, CI ~ 0.75) if compared to the overall lower content of refractive matter (~ 10-30 µg g^{-1}, CI ~ 0.8, see chapter 3), indicate a shortened oxygen exposure of chlorins. High organic matter sedimentation rates were reported for this area and must have reduced aerobic decay which would usually increase at greater water depths (Inthorn et al, 2005; Hartnett et al., 1998).

Large amounts of comparatively less refractive chlorins at the Arctic MIZ reflected the seasonal enhanced primary production and release of lithogenic matter at the ice-edge – a result of increased nutrient supply and stratification due to the emerging melt water of the retreating pack ice (Reigstad et al., 2002; Hebbeln & Wefer, 1991). Like on the BUS slope, the deposition of fresher chlorin-carbon (lower CI values) can only result from a minimized oxygen exposure of such easily oxidized pigments (Sun et al., 1993). Pigments may also escape from aerobic degradation through physical protection. Chlorin organic matter particularly sorbs to inorganic surfaces, e.g. clays, and thus enhances OM transport down the water column

(Satterberg et al. 2003; Keil et al., 1994). Pigments might also escape oxidation by enclosure in fecal pellets, which arefound in sediments beneath the ice, and which are characterized by low amounts of very fresh chlorin material (CI ~0.3, see chapter 4). Hence, low CI values must not necessarily imply high productivity or mineralisation, but may be induced by multiple factors: the mode of carbon deposition, sedimentation rate and carbon source.

Protein organic matter freshness was largely determined by the extent of water depth, sedimentation rate and their susceptibility to oxygen. Largest DI values of ~2-4 indicated freshest, source-like, proteins in anoxic shelf sediments that contrasted low DI values of ~ 0 – 0.3, thus fairly altered protein matter, on the oxic shelf and slope sites (Fig.5.b). THAA amounts were consistent with SRR. Similar to chlorin content and CI, protein concentrations and freshness were slightly enhanced when compared to the remaining Benguela slope, particularly on the upper slope (25°S, 400m) with DI values ~1-2 (refer to chapter 3).

Carbon oxidation pathways

Carbon oxidation pathways are reflected by the chlorin-and protein-based degradation indices. In contrast to anoxic shelf sediments where one process prevailed (SRR) several anaerobic degradation pathways altered the CI and DI profiles on the oxic shelf and slope. Organic carbon pools degraded at different time scales, with chlorins first and followed by proteins. Different redox conditions controlled the expansion of the major chlorin and protein decomposition zones. In anoxic shelf sediments major chlorin degradation within the upper 10-15cm was characterized by decreasing concentrations and increasing CI values by 1-2 units (CI 0.5/0.6 to 0.7, Fig.4.d) and were consistent with nearly entirely declining SRR. As chlorin freshness and amount again increased, THAA degradation continued. That was indicated by decreasing DI values (~ 4 to -2) and THAA%C and %N that matched decreasing rates of sulfate reduction. By contrast in upper sediments, protein organic matter composition reflected source material (DI ~ 2-4, THAA%N of 75-95%, Tab.3A; Dauwe et al., 1999; Lee, 1988). Under similar redox conditions, the CI and DI could thus be applied to study their different time scales during early digenetic changes.

In oxygenated sediments the interpretation of the CI and DI was strongly biased by site characteristics (sedimentation rates, water depth) that determined variety and extent of oxidation processes. On the shallow, oxygenated Arctic shelf most chlorin matter was degraded within the upper sediment layer (10cm); this was indicated by an s-shaped decline of CI values (Fig.4.d). The CI profile reflected a total of several processes: instantaneous oxic decay in surface sediments (CI 0.5 to 0.6, 0-2cm), degradation of chlorins by SRR (CI 0.6 to 0.9 within the SR zone, ~3-10cm), and probably also metal reduction that can be a significant fraction of the total carbon mineralisation in Arctic sediments (Vandieken et al., 2006; Arnosti & Holmer, 2003). Overall protein degradation was similar to chlorins. In the deep sediment layer of the MIZ, CI values of 0.9 to 1, maximum DI values (-2.4) and a slight decrease of THAA%C and-%N were consistent with another deep SRR maximum, which demonstrated ongoing degradation. Total carbon mineralisation of both carbon pools was efficient. All in all this suggests that the high seasonal supply of reactive chlorin matter (> 1000 µg g TOC^{-1}) and fast response of sediment bacteria ignites and maintains chlorin decomposition (CI of 0.5 to 1).

Selective preservation

Even though not visible from the DI, subsurface organic matter degradation of the refractory THAA pool (THAA%C/%N) proceeded (e.g. at the mudbelt or MIZ). As phytoplankton pigments (e.g. peridinin) were consistent with the preferential degradation of proteins, they represented potential sources of both pools. THAA degradation is selective and physical protection of amino acids in association with the sediment matrix (or within cell aggregates) possible (Satterberg et al., 2003; Sanei et al., 2005; Keil et al., 1994; Pichevin, 2004). As degradation proceeds most (>90%) organic material, including amino acids, is desorbed and becomes available to microbial degradation (Satterberg et al., 2003; Thimsen and Keil, 1998). Release of reactive compounds from both pools could thus drive SRR, however they may not always be detected with degradation indices that are based on the bulk of the predominantly refractive molecular pools. Arnosti and Holmer (2003) suggested that microbial degradation would thrive on a small and rapidly cycled fraction within the organic carbon pool not detectable by bulk organic matter proxies (C/N, TOC). This could be confirmed for the Arctic shelf: in contrast to little TOC and C/N changes, the CI tracked overall mineralisation. In organic-rich sediments (slope), the CI did not characterize the zone where SRR took place; neither did the C/N ratio and DI. The DI merely decreased close to the sediment surface, probably indicating *in situ* production of refractory bacterial cell wall resulted from decomposition of the reactive protein pool from deposited organic matter (Grutters et al., 2002). This way embedded refractory organic matter may account for one third of THAA within the mixed layer and might enhance amino acid (hence organic matter) preservation.

Particularly in oxic sediments, where several factors control organic matter deposition, the CI and DI could only be interpreted by application of multiple proxies. The Chlorin Index might be selective enough to indicate small fractions of reactive carbon that play a major role to organic matter degradation on short time scales (6-14 days) as demonstrated in experiments.

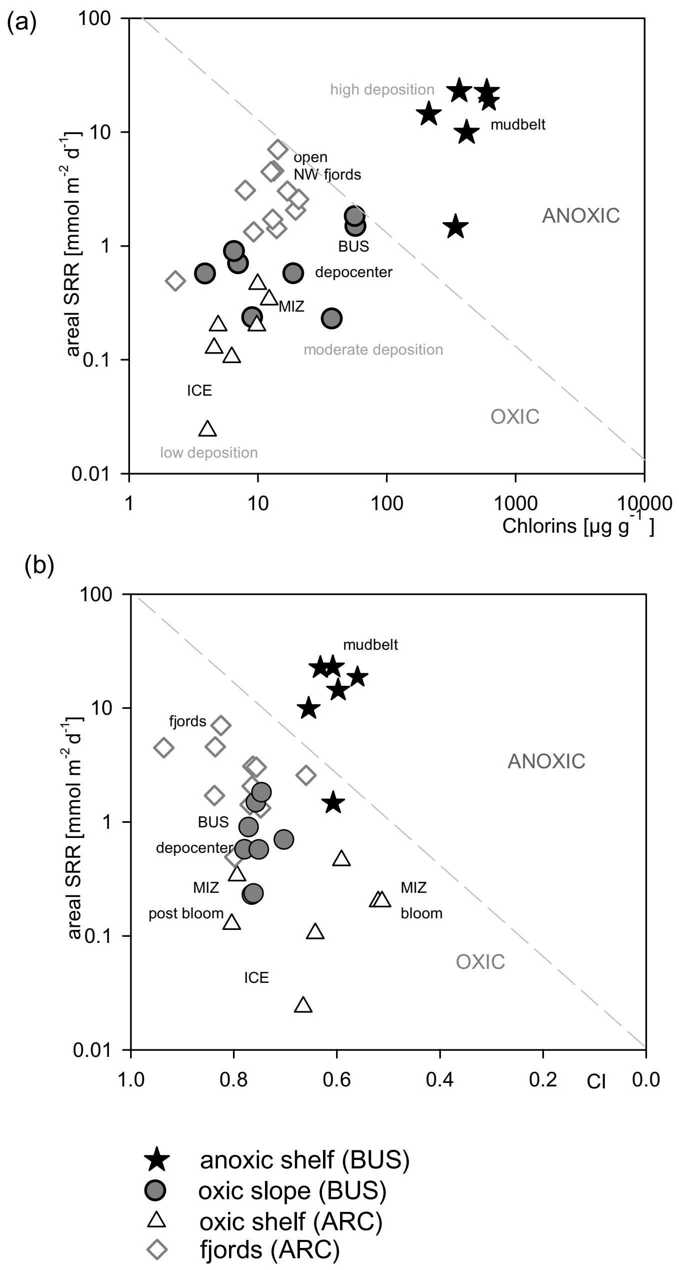

Fig.7 Average areal SRR in anoxic shelf (mudbelt) (★), oxic shelf (Arctic) (Δ) and slope (BUS depocenter)(O) and Arctic fjord sediments (◇) compared to total chlorin concentrations (a) and average CI values (b).

SRR were proportionally related to total chlorin amounts at all studied sites with large organic matter content and high SRR in anoxic but low mineralisation rates consistent with low chlorin concentrations in oxic shelf sediments (Arctic).

Increasingly decomposed chlorins were related to higher SRR within oxic shelf and slope sediments of moderate carbon deposition. Highest SRR were related to chlorins of intermediate freshness of anoxic shelf sediments.

Conclusions

The joint application of the CI and DI provides insight into present and later stage of early diagenesis due to a higher reactivity of chlorin compared to protein carbon. Reactivity in this sense must be understood as the grade of availability of organic material to microbial degradation. Per definition, the overall decomposition of organic carbon to CO_2 via the sum of all terminal electron processes is a direct measure of the reactivity of the organic carbon pool. The reactivity of these major organic carbon pools is closely related to their ability to associate with sediment structures as well as to the chemical reactivity of molecules.

Chlorins and the CI can be linked to SRR, hence the CI represents a reliable measure of present organic carbon reactivity and associated chlorin fluxes. High anoxic carbon mineralisation rates were driven by large concentrations of more refractive chlorins. This means that the refractory carbon, supposed to be less reactive, possesses a high availability to microbial degradation. In short-term sediment incubations could be demonstrated that hydrolytic breakdown of macromolecular organic matter delayed carbon mineralisation. Therefore, the decomposition of already altered carbon is of less effort to bacteria. This emphasizes that the CI is particularly suited to track organic matter changes on short time scales. The DI and THAA concentration characterize mainly later organic matter degradation. As the DI provides a higher resolution of organic matter extent of degradation, it might as well serve as geological proxy.

Careful application of degradation indices can be used to distinguish the impact of carbon supply and composition to the extent of organic matter mineralisation, and thus distinguish between productivity and preservation. Diagenetic controls such as water depth, oxygen exposure, sedimentation rate and possible physical protection of organic matter associated with the sediment matrix must be considered if the CI and DI are interpreted.

Appendix Chapter 2

Tab.1 Results from anoxic bag incubation (ARC-1, ARC-2, T2-600m)

ARC-1	time point	days	Total Chlorins [µg g^{-1}]	Chlorin Index	Std Dev Total chlorins	Std Dev CI	SRR [nmol cm^{-3} d^{-1})	Std Dev SRR	DIC [mMol]	Std Dev DIC
control	t 0	0	**5.1**	**0.83**	0.76	0.002	**3.4**	0.2		
	t 1	17	**4.3**	**0.73**	0.46	0.01	**121.2**	14.7		
	t 2	31	**4.4**	**0.79**	1.36	0.07	**276.3**	231.5		
	t 3	45	**4.9**	**0.85**	1.30	0.04	**123.8**	1.3		
	t 4	59	**4.8**	**0.84**	0.18	0.04	**104.6**	8.2	**10.6**	0.15
	t 5	72	**5.0**	**0.85**	0.68	0.01	**86.2**	4.3		
algae	t 0	0	**6.3**	**0.89**	0.30	0.05	**6.3**	1.6	**2.5**	0.02
	t 1	17	**4.9**	**0.82**	0.88	0.04	**175.7**	44.1		
	t 2	31	**5.1**	**0.75**	0.97	0.00	**563.1**	120.1	**23.8**	0.04
	t 3	45	**5.0**	**0.80**	0.17	0.05	**268.8**	125.4		
	t 4	59	**4.4**	**0.78**	0.03	0.03	**180.8**	107.1	**22.3**	0.14
	t 5	72	**5.5**	**0.84**	0.22	0.04	**107.1**	1.7	**19.0**	0.21

ARC-2	time point	days	Total Chlorins [µg g^{-1}]	Chlorin Index	Std Dev Total chlorins	Std Dev CI	SRR [nmol cm^{-3} d^{-1})	Std Dev SRR	DIC [mMol]	Std Dev DIC
control	t 0	0	**6.6**	**0.73**	0.10	0.02	8.8	0.5	4.7	0.10
	t 1	6	**5.5**	**0.79**	0.75	0.01	7.5	2.5	4.4	0.10
	t 2	8	**6.2**	**0.68**	0.52	0.08			4.4	0.08
	t 3	11	**5.2**	**0.72**	0.32	0.02			4.9	0.19
	t 4	14	**6.4**	**0.65**	0.07	0.01	6.0	0.1	5.0	0.25
	t 5	20	**6.8**	**0.64**	0.40	0.02	6.0	0.6	4.3	0.07
	t 6	27	**5.8**	**0.71**	0.67	0.04	5.3	0.2	4.5	0.06
	t 7	34	**5.1**	**0.73**	0.11	0.03	5.8	0.9	4.8	0.07
	t 8	55							5.3	0.07
algae	t 0	0	**8.5**	**0.60**	0.54	0.04	8.8	0.5	3.6	2.97
	t 1	6	**9.8**	**0.55**	0.03	0.01	9.2	1.3	6.7	0.67
	t 2	8	**10.9**	**0.49**	0.03	0.00			7.8	0.07
	t 3	11	**9.3**	**0.54**	0.58	0.04			8.9	0.42
	t 4	14	**13.2**	**0.42**	0.52	0.01	48.4	0.7	10.0	0.87
	t 5	20	**11.1**	**0.47**	0.62	0.02	71.5	3.1	10.2	0.15
	t 6	27	**11.8**	**0.46**	0.13	0.00	77.3	12.1	12.7	0.19
	t 7	34	**10.8**	**0.49**	0.81	0.01	115.6	19.0	14.5	0.63
	t 8	55							17.0	0.80

T2 600m	time point	days	Total Chlorins [µg g^{-1}]	Chlorin Index	Std Dev Total chlorins	Std Dev CI	Chlorophyll a [µg g^{-1}]	Pheophytin a [µg g^{-1}]	Pheo-phorbide a [µg g^{-1}]
control	t 0	0	**220.8**	**0.82**	4.7	0.06	**0.20**	**0.26**	**0.001**
	t 1	6	**190.3**	**0.83**	1.3	0.01			
	t 2	8	**209.7**	**0.83**	0.6	0.04	**0.21**	**0.50**	**0.003**
	t 3	10	**185.6**	**0.85**	10.1	0.00			
	t 4	14	**180.7**	**0.82**	5.0	0.03	**0.19**	**0.33**	**0.002**
	t 5	22	**227.5**	**0.78**	18.9	0.04			
	t 6	28	**197.8**	**0.80**	3.1	0.00	**0.31**	**0.54**	**0.003**
	t 7	35	**200.9**	**0.82**	8.2	0.02			
	t 8	42	**173.5**	**0.82**	4.8	0.02	**0.33**	**0.54**	**0.004**
	t 9	70	**165.2**	**0.83**	5.7	0.01	**0.28**	**0.53**	**0.003**
algae	t 0	0	**245.8**	**0.71**	6.3	0.00	**0.29**	**0.35**	**0.002**
	t 1	6	**269.7**	**0.71**	49.0	0.04	**0.51**	**0.49**	**0.003**
	t 2	8	**223.1**	**0.73**	12.0	0.01	**0.41**	**0.39**	**0.003**
	t 3	10	**216.9**	**0.73**	6.4	0.03	**0.57**	**0.45**	**0.004**
	t 4	14	**223.1**	**0.72**	2.4	0.01	**0.33**	**0.53**	**0.003**
	t 5	22	**309.9**	**0.64**	7.1	0.02	**0.93**	**0.56**	**0.005**
	t 6	28	**347.8**	**0.66**	43.0	0.00	**1.15**	**0.80**	**0.007**
	t 7	35	**318.1**	**0.59**	28.6	0.11	**0.68**	**0.92**	**0.007**
	t 8	42	**441.8**	**0.61**			**0.93**	**1.10**	**0.006**
	t 9	70	**252.8**	**0.60**	18.0	0.01	**0.58**	**0.57**	**0.003**

T2 600 m	**time point**	**days**	**THAA [mg g^{-1}]**	**DI (PCA)**	**Std Dev THAA**	**Std Dev DI**	**SRR [nmol cm^{-3} d^{-1})**	**Std Dev SRR**	**DIC [mMol]**
control	t 0	0	**25.13**	**-1.62**	6.5	0.24	**23.1**	2.3	**5.8**
	t 1	6	**23.14**	**-1.29**	2.2	0.15	**26.9**	0.9	**5.5**
	t 2	8	**23.90**	**-1.22**	1.5	0.24			**5.9**
	t 3	10	**18.83**	**-1.17**	1.9	0.11			**5.1**
	t 4	14	**19.43**	**-1.17**	0.2	0.17			**5.0**
	t 5	22	**24.87**	**-0.36**	0.7	1.11	**37.9**	2.9	**6.5**
	t 6	28	**14.19**	**-1.69**	11.7	0.79	**31.7**	20.2	**5.6**
	t 7	35	**25.16**	**-1.33**	4.1	0.06	**35.9**	3.2	**6.5**
	t 8	42	**19.17**	**-1.05**	6.2	0.06	**34.3**	4.0	**6.9**
	t 9	70					**22.3**	6.3	
algae	t 0	0	**23.74**	**-0.75**	0.97	0.53	**1.6**	0.1	**6.1**
	t 1	6	**19.19**	**-0.91**	0.99	0.46	**37.2**	4.2	**8.1**
	t 2	8	**16.81**	**-1.15**	0.70	0.12			**8.4**
	t 3	10	**13.59**	**-2.22**	1.89	0.27			**8.2**
	t 4	14	**18.29**	**-0.26**	0.11	0.36			**8.5**
	t 5	22	**29.97**	**-0.43**	0.12	0.76	**57.4**	16.4	**13.5**
	t 6	28	**34.05**	**-0.69**	3.04	0.25	**81.6**	15.5	**11.5**
	t 7	35	**27.67**	**-1.01**	1.18	0.40	**111.8**	23.6	**14.2**
	t 8	42	**28.40**	**-0.75**	3.54	0.15	**187.0**	20.8	**17.5**
	t 9	70					**140.2**	21.6	

Tab.2 Molecular and geochemical proxies on the oxic shelf (ARC-1)

ARC-1	Depth [cm]	Total Chlorins [µg g^{-1}]	Chlorin Index	TOC %	TN %	C/N	THAA [mg g^{-1}]	THAA %C	THAA %N	DI (PCA)	BALA & GABA	ASP / β-ALA	Depth [cm]	SRR [nmol cm^{-3} d^{-1}]
Marginal Ice Zone	0.5	24.6	0.49	2.3	0.3	10.1	7.3	15.0	41.2	-0.30	4.2	4.3	0.5	0.04
	1.5	23.2	0.56	2.5	0.3	9.6	10.9	21.2	56.8				1.5	0.39
	2.5	30.9	0.49	2.4	0.3	10.0	10.8	20.8	58.3	0.71	5.4	5.3	2.5	1.47
	4	18.7	0.56	2.3	0.2	10.1	7.4	16.3	46.3	-1.35	6.8	1.0	3.5	3.35
	6	9.1	0.73	2.1	0.2	10.3	6.2	13.6	40.0	0.71	6.4	4.4	4.5	2.74
	8	5.6	0.81		0.2		7.2						6	4.27
	10	4.7	0.93	1.8	0.2	11.4	4.8	13.0	41.7				8	2.56
	12	4.6	0.95		0.2		3.6						10	1.10
	14	4.4	0.94	1.5	0.1	12.4	3.5	10.4	36.1	-2.41	8.3	0.2	12	2.34
	16	4.4	0.96		0.1								14	1.44
	18.5	4.4	0.99	1.5	0.1	13.1	3.1	9.2	32.9				16	0.51
													18	0.28
													20	0.39

Tab.3 A Molecular and geochemical proxies on the anoxic shelf (Benguela Mudbelt)

21° S	Depth [cm]	Total Chlorins [µg g^{-1}]	Chlorin Index	TOC %	TN %	C/N	THAA [mg g^{-1}]	THAA %C	THAA %N	DI (PCA)	Depth [cm]	SRR [nmol cm^{-3} d^{-1}]
MUDBELT 226750 (77m)	0.5	936.6	0.50	6.2	0.8	9.0	21.8	16.5	39.7	2.56	0.5	22.1
	1.5	364.8	0.52	8.1	0.8	11.2	46.6	27.0	80.9	2.04	1.5	43.1
	2.5	570.4	0.48	8.2	1.2	8.0	46.3	26.2	56.1	2.97	2.5	23.8
	3.5	316.0	0.57	6.9	1.1	7.2	72.8	49.1	94.8		3.5	12.2
	4.5	180.2	0.62	5.8	0.8	8.8	41.3	33.1	78.3		4.5	6.0
	6	263.3	0.64				59.8				6	5.9
	8	292.1	0.63	7.1	0.9	9.1	38.8	25.5	61.9	1.89	8	4.2
	10	221.5	0.70				25.7			0.67	10	2.3
	12	387.5	0.66	7.3	0.8	10.0	38.4	24.7	66.1		12	1.3
	14	464.4	0.62								14	1.1
	16	615.9	0.59	6.9	0.8	10.3	25.8	17.5	48.1	1.95	16	0.6
	18	348.5	0.62				22.8				18	0.8
	20	191.8	0.63	3.3	0.4	10.5	19.6	27.6	77.6		20	0.6
	22	275.3	0.63				38.5			0.82	22	0.5
	24	253.2	0.67	5.2	0.6	10.6	30.8	27.5	77.9		24	0.4
	26	254.2	0.62				28.3				26	0.4
	28	247.1	0.61				33.9				28	0.3
	30	269.3	0.61				27.6				30	1.7
	33	189.0	0.65	5.1	0.6	9.8	29.5	27.2	71.3	-7.31	33	4.0
	36	154.9	0.62				19.6			0.80		
	38	390.6	0.57	8.0	0.9	10.8	42.3	24.8	71.4	2.57		

23° S	Depth [cm]	Total Chlorins [µg g^{-1}]	Chlorin Index	TOC %	TN %	C/N	THAA [mg g^{-1}]	THAA %C	THAA %N	DI (PCA)	Depth [cm]	SRR [nmol cm^{-3} d^{-1}]
MUDBELT 226680 (110m)	0.5	1087.7	0.58	6.1	0.8	8.4	43.6	33.4	75.2	1.05	0.5	70.2
	1.5	1032.3	0.58	6.4	0.9	8.1	45.3	33.2	72.3	-3.32	1.5	126.8
	2.5	1046.8	0.58	6.7	1.0	8.1	43.3	30.4	66.0	-3.42	2.5	108.6
	3.5	930.8	0.59	7.3	1.0	8.3	46.6	29.9	66.4	0.66	3.5	95.6
	4.5	848.1	0.62	5.6	0.8	8.3	36.1	30.2	67.3	-3.32	4.5	118.2
	6	737.0	0.63				33.7				5.5	121.2
	8	565.2	0.61	5.9	0.8	9.0	32.0	25.2	60.9	4.01	6.5	110.4
	10	446.3	0.65				36.9				10	101.3
	12	456.0	0.65	7.8	1.0	9.2	41.1	24.6	60.5	0.90	12	42.0
	14	359.0	0.68				42.2				14	78.7
	16	332.9	0.70				36.4				16	23.4
	18	290.2	0.69	7.6	0.9	10.1	33.9	20.9	56.6	3.26	18	17.2
	20	353.5	0.68				36.4				20	13.3
	22	326.7	0.66				34.6				22	15.6
	24	421.3	0.65	8.6	0.9	10.6	33.5	18.1	51.6	-2.12	24	9.6
	26	422.6	0.62				26.7				26	2.3
	28	496.5	0.58	8.7	0.9	11.0	15.4	8.3	24.3	-1.31	28	1.5

Tab.3 B Pigment concentrations on the anoxic shelf (Benguela Mudbelt)

	Pigments [µg g^{-1}]							
Station	**Depth [cm]**	**Chlorophyll *a***	**Pheophorbide *a***	**Pheophytin *a***	diatoms	dinoflagellates	Coccolithophorides	
					fucoxanthin	**peridinin**	**diadinoxanthin**	**β - carotene**
MUDBELT 21°	0.5	3.2	0.014	10.2	7.1	1.4	0.101	5.0
	1.5	18.1	0.065	24.2	17.5	0.8	0.066	20.3
	2.5	4.3	0.037	5.9	7.7	0.0	0.029	7.0
	3.5	2.0	0.010	6.9	3.3	0.8	0.001	2.9
	4.5	1.4	0.026	4.7	2.4	1.2	0.001	31.4
	6	1.6	0.032	5.5	3.3	0.9	0.002	6.4
	8	1.7	0.041	9.9	4.5	0.8	0.004	4.0
	12	1.8	0.035	13.3	7.5	1.6	0.005	11.9
	20	1.7	0.017	5.1	3.4	0.3	0.007	10.0
	30	1.8	0.013	5.0	4.3	0.7	0.001	10.7
MUDBELT 23°	0.5	10.4	0.006	0.6	19.6	7.6	0.013	0.35
	1.5	4.6	0.088	19.9	15.8		0.207	2.39
	2.5	27.3	0.233	30.1	23.3		0.377	1.10
	3.5	5.4	0.126	17.5	17.3	0.5	0.182	2.40
	4.5	4.0	0.098	13.3	9.0	0.1	0.088	2.15
	6	16.8	0.152	18.0	7.5	2.7	0.104	1.36
	10	3.6	0.062	9.1	5.4	1.9	0.040	1.15
	14	1.8	0.052	8.1	7.6	1.6	0.020	6.71

Tab.4 A Molecular and geochemical proxies on the oxic slope (Benguela)

BUS SLOPE	Depth [cm]	Total Chlorins [µg g^{-1}]	Chlorin Index	TOC %	TN %	C/N	THAA [mg g^{-1}]	THAA %C	THAA %N	DI (PCA)	Depth [cm]	SRR [nmol cm^{-3} d^{-1}]
25°S-600 m 8449	0.5	74.5	0.75	6.1	0.7	10.3	18.8	14.3	39.2	0.44	1	10.4
	1.5	61.6	0.77	6.7	0.7	10.7	22.9	15.9	45.3		3	12.6
	2.5	54.8	0.76	7.1	0.7	12.1	21.4	14.2	45.9		5	15.0
	4	54.1	0.77	6.5	0.7	11.1	22.2	15.9	47.4		7	10.7
	6	51.1	0.74	6.7	0.7	11.7	21.4	15.0	46.9		9	9.7
	8	50.8	0.75				22.3				11.5	8.5
	10	50.9	0.75	6.4	0.7	11.1	19.1	14.0	41.6		14.5	5.8
	12	52.2	0.77				16.9					
	14	50.4	0.75	6.5	0.7	11.5	16.8	12.2	37.3	-2.57		
	16	47.8	0.74				15.7					
	18.5	48.2	0.76	6.5	0.6	11.8	15.8	11.4	36.2			
25°S-1500m 8455	0.5	24.9	0.77	7.2	0.8	9.9	21.1	13.6	36.2	0.33	1	5.1
	1.5	23.3	0.77	9.3	0.8	13.2	20.0	10.0	35.3		3	14.2
	2.5	25.3	0.79	7.0	0.8	9.7	21.5	14.3	37.1		5	16.5
	4	27.1	0.77	6.8	0.8	9.6	21.2	14.5	37.4		7	10.7
	6	28.2	0.78	6.8	0.8	9.7	19.1	13.1	34.1		9	6.8
	8	21.2	0.79				20.6				11.5	10.2
	10	21.6	0.78	6.9	0.8	9.9	19.0	12.9	34.1		14.5	9.2
	12	22.5	0.78				19.0				17.5	3.1
	14	20.7	0.77	7.2	0.8	10.1	19.6	12.7	34.2	0.15	20	3.9
	16	21.9	0.77				25.4					
	18.5	23.1	0.78	7.4	0.8	10.8	22.9	14.5	42.1			

Tab.4 B Pigments on the oxic slope (Benguela)

	Pigments [µg g^{-1}]						
BUS SLOPE	**Depth [cm]**	**Chlorophyll *a***	**Pheophorbide *a***	**Pheophytin *a***	dinoflagellates	coccolithophorides	
					peridinin	**diadinoxanthin**	**β-carotene**
25°S-600m 8449	0.5	3.81	0.013	1.55	0.86	0.022	0.598
	1.5	0.59	0.005	0.97	0.99	0.001	0.874
	2.5	0.47	0.006	0.72	1.11	0.003	0.837
	4	0.46	0.005	0.65	1.14	0.005	0.910
	6	0.43	0.005	0.76	0.81	0.001	0.824
	8	0.45	0.005	0.57	0.56	0.004	0.247
	14	0.46	0.005	0.63	0.79	0.001	1.000
25°S-1500m 8455	0.5	0.27	0.014	0.67	0.40	0.005	0.140
	1.5	0.45	0.004	0.62	0.53	0.002	0.234
	2.5	0.36	0.003	0.57	0.44	0.001	0.199
	4	0.41	0.004	0.69	0.47	0.002	0.199
	6	0.43	0.005	0.79	0.70	0.001	0.198
	8	0.33	0.002	0.57	0.55	0.001	0.245
	14	0.35	0.004	0.65	0.53	0.002	0.329

Tab.4 C Total chlorin concentrations normalized to total organic content in sediments of the Arctic shelf and the Benguela shelf and slope.

Station									
ARC-I St. I		**MudBelt-21°**		**MudBelt-23°**		**BUS Slope-25° 600m**		**BUS Slope-25° 1500m**	
Depth [cm]	µg g^{-1} TOC	Depth [cm]	µg g^{-1} TOC	Depth [cm]	µg g^{-1} TOC	Depth [cm]	µg g^{-1} TOC	Depth [cm]	µg g^{-1} TOC
0.5	1072	0.5	15165	0.5	17842	0.5	1214	0.5	346
1.5	944	1.5	4525	1.5	16196	1.5	917	1.5	250
2.5	1292	2.5	6927	2.5	15705	2.5	777	2.5	360
4	813	3.5	4563	3.5	12781	4	830	4	399
6	430	4.5	3093	4.5	15180	6	766	6	413
8		6		6		8		8	
10	267	8	4106	8	9536	10	799	10	312
12		10		10		12		12	
14	290	12	5344	12	5861	14	779	14	287
16		14		14		16		16	
18.5	286	16	8937	16		18.5	744	18.5	313
		18		18	3836				
		20	5786	20					
		24	4842	24	4873				
		26		26					
		28		28	5715				
		33	3723						
		38	4898						

Tab.5 Amino acids (mol%) in multicore profiles and experiment T2-600m for PCA

	Depth [cm]	ASP	GLU	SER	HIS	GLY	THR	ARG	βALA	ALA	TYR	GABA	MET	VAL	PHE	ILEU	LEU	LYS	βALA & GABA	ASP/ βALA
Mudbelt 21°	0.5	11.8	9.0	5.9	1.8	15.6	5.4	2.8	1.2	14.0	0.8	2.6	0.9	7.5	4.1	4.8	6.4	5.4	3.8	9.8
	1.5	12.7	10.8	6.0	1.8	15.7	5.3	2.8	1.3	13.2	0.8	2.2	0.7	7.9	3.6	4.6	5.8	4.9	3.5	10.0
	2.5	10.7	9.6	5.9	2.0	16.0	6.0	2.9	1.4	14.3	0.7	2.3	0.8	8.0	4.1	5.1	6.4	3.7	3.7	7.6
	8	11.4	9.5	6.2	2.1	17.6	6.0	2.9	1.5	13.7	0.8	2.4	0.7	7.4	3.9	4.3	5.9	3.8	3.9	7.6
	10	10.7	8.9	6.3	3.2	19.8	5.1	3.5	1.8	13.8	0.9	2.2	0.7	6.7	3.5	4.0	5.5	3.3	4.0	6.0
	16	11.7	7.9	6.4	3.2	16.6	5.5	2.7	1.6	12.1	1.2	2.2	0.6	7.4	4.4	4.4	6.3	5.7	3.8	7.1
	22	13.4	10.4	6.7	2.7	16.5	5.8	3.4	1.6	16.4	0.9	2.1	0.2	6.5	3.8	3.9	5.4	0.4	3.7	8.4
	33	11.1	9.1	7.3	0.0	39.0	5.0	1.9	0.4	19.6	1.1	0.2	0.0	2.9	0.2	0.8	0.8	0.6	0.6	27.9
	36	13.4	9.5	7.3	3.2	16.8	5.5	3.1	1.8	16.8	0.6	2.0	0.8	6.4	3.6	3.4	5.0	0.8	3.7	7.6
	38	15.1	9.2	7.4	4.1	11.4	5.9	2.8	2.0	13.7	1.0	2.8	0.3	7.1	4.5	4.6	6.5	1.8	4.8	7.6
Mudbelt 23°	0.5	14.1	9.9	7.6	2.6	9.3	5.8	2.4	2.1	15.5	0.6	3.0	1.3	8.2	4.1	4.8	6.5	2.0	5.1	6.6
	2.5	11.1	8.8	7.1	2.4	20.5	5.8	2.8	0.8	12.3	0.9	2.6	1.0	6.1	3.7	3.8	5.5	4.8	3.4	14.2
	8	15.2	9.1	7.5	2.6	9.4	5.5	3.1	0.1	14.3	0.7	3.0	0.5	7.8	4.5	5.0	6.5	5.1	3.1	149.0
	18	11.2	7.9	6.5	5.2	22.4	5.4	3.6	1.1	13.9	1.2	1.4	0.1	6.2	2.1	2.9	4.0	5.0	2.5	10.1
	28	11.4	9.3	6.9	0.2	21.1	5.5	3.9	1.0	14.3	1.8	1.9	0.0	5.9	3.0	3.5	5.0	5.4	2.9	11.8
Slope 25°- 600m	0	10.9	8.9	5.8	2.1	23.2	5.0	3.7	1.7	12.5	1.1	0.0	0.6	6.7	3.5	3.7	4.7	5.8	1.7	6.3
	14	8.5	7.6	4.8	4.0	28.2	3.7	3.8	2.2	11.7	1.7	2.1	0.5	5.1	2.9	3.0	4.3	5.9	4.3	3.9
Slope 25°- 800m	0.5	15.1	10.1	7.6	4.0	17.1	6.3	3.7	2.9	14.0	1.0	2.1	0.7	7.0	3.5	3.8	0.1	0.9	5.0	5.3
	1.5	11.1	8.3	6.7	3.7	25.1	5.7	3.8	2.6	11.7	1.1	1.7	0.7	6.0	3.5	3.1	4.5	0.7	4.3	4.3
	2.5	6.7	5.8	4.8	2.4	36.2	3.6	4.1	2.5	9.5	1.2	1.5	0.3	4.0	3.1	2.3	3.7	8.4	4.0	2.7
	4	11.0	8.4	5.9	3.1	23.9	4.7	4.0	2.4	12.7	1.0	1.8	0.7	6.3	3.2	3.4	4.3	3.2	4.2	4.5
	8	11.1	8.0	6.3	3.5	22.8	5.5	4.3	2.8	11.5	1.1	1.9	0.7	6.5	3.1	3.3	4.3	3.3	4.7	4.0
	12	13.4	9.1	5.8	3.4	20.6	4.9	4.2	2.5	11.3	1.0	1.6	0.6	6.2	3.1	3.7	4.7	3.9	4.1	5.3
	14	11.5	8.2	5.8	3.4	22.1	5.2	4.2	2.6	12.1	1.0	1.9	0.7	6.7	3.7	3.5	4.3	3.2	4.5	4.4
	16	14.6	9.3	7.0	4.5	15.8	5.8	4.2	2.3	12.5	0.9	2.2	0.7	6.6	3.3	3.7	5.2	1.6	4.4	6.4
	18	11.9	8.3	6.2	3.2	24.1	5.2	4.0	2.4	11.8	1.1	2.0	0.8	6.2	3.2	3.4	4.4	1.9	4.5	4.9
Slope 25°- 1500m	0	12.7	9.0	6.1	2.5	22.8	0.6	4.3	2.0	12.6	1.2	1.8	0.6	6.3	3.5	3.4	4.8	5.9	3.8	6.2
	0.5	16.0	10.2	6.1	5.6	9.9	5.4	4.1	1.5	14.3	1.2	2.1	0.6	6.6	3.0	3.6	4.4	5.3	3.6	10.6
	14	16.3	10.2	6.5	6.1	13.6	5.9	3.8	1.9	13.5	1.3	2.0	0.5	6.3	3.3	3.3	4.5	1.0	3.9	8.7

Tab.5 Amino acids (mol%) in multicore profiles and experiment T2-600m

for PCA	Depth [cm]	ASP	GLU	SER	HIS	GLY	THR	ARG	βALA	ALA	TYR	GABA	MET	VAL	PHE	ILEU	LEU	LYS	βALA & GABA	ASP/ βALA
Mudbelt 21°	0.5	11.8	9.0	5.9	1.8	15.6	5.4	2.8	1.2	14.0	0.8	2.6	0.9	7.5	4.1	4.8	6.4	5.4	3.8	9.8
	1.5	12.7	10.8	6.0	1.8	15.7	5.3	2.8	1.3	13.2	0.8	2.2	0.7	7.9	3.6	4.6	5.8	4.9	3.5	10.0
	2.5	10.7	9.6	5.9	2.0	16.0	6.0	2.9	1.4	14.3	0.7	2.3	0.8	8.0	4.1	5.1	6.4	3.7	3.7	7.6
	8	11.4	9.5	6.2	2.1	17.6	6.0	2.9	1.5	13.7	0.8	2.4	0.7	7.4	3.9	4.3	5.9	3.8	3.9	7.6
	10	10.7	8.9	6.3	3.2	19.8	5.1	3.5	1.8	13.8	0.9	2.2	0.7	6.7	3.5	4.0	5.5	3.3	4.0	6.0
	16	11.7	7.9	6.4	3.2	16.6	5.5	2.7	1.6	12.1	1.2	2.2	0.6	7.4	4.4	4.4	6.3	5.7	3.8	7.1
	22	13.4	10.4	6.7	2.7	16.5	5.8	3.4	1.6	16.4	0.9	2.1	0.2	6.5	3.8	3.9	5.4	0.4	3.7	8.4
	33	11.1	9.1	7.3	0.0	39.0	5.0	1.9	0.4	19.6	1.1	0.2	0.0	2.9	0.2	0.8	0.8	0.6	0.6	27.9
	36	13.4	9.5	7.3	3.2	16.8	5.5	3.1	1.8	16.8	0.6	2.0	0.8	6.4	3.6	3.4	5.0	0.8	3.7	7.6
	38	15.1	9.2	7.4	4.1	11.4	5.9	2.8	2.0	13.7	1.0	2.8	0.3	7.1	4.5	4.6	6.5	1.8	4.8	7.6
Mudbelt 23°	0.5	14.1	9.9	7.6	2.6	9.3	5.8	2.4	2.1	15.5	0.6	3.0	1.3	8.2	4.1	4.8	6.5	2.0	5.1	6.6
	2.5	11.1	8.8	7.1	2.4	20.5	5.8	2.8	0.8	12.3	0.9	2.6	1.0	6.1	3.7	3.8	5.5	4.8	3.4	14.2
	8	15.2	9.1	7.5	2.6	9.4	5.5	3.1	0.1	14.3	0.7	3.0	0.5	7.8	4.5	5.0	6.5	5.1	3.1	149.0
	18	11.2	7.9	6.5	5.2	22.4	5.4	3.6	1.1	13.9	1.2	1.4	0.1	6.2	2.1	2.9	4.0	5.0	2.5	10.1
	28	11.4	9.3	6.9	0.2	21.1	5.5	3.9	1.0	14.3	1.8	1.9	0.0	5.9	3.0	3.5	5.0	5.4	2.9	11.8
Slope 25°- 600m	0	10.9	8.9	5.8	2.1	23.2	5.0	3.7	1.7	12.5	1.1	0.0	0.6	6.7	3.5	3.7	4.7	5.8	1.7	6.3
	14	8.5	7.6	4.8	4.0	28.2	3.7	3.8	2.2	11.7	1.7	2.1	0.5	5.1	2.9	3.0	4.3	5.9	4.3	3.9
Slope 25°- 800m	0.5	15.1	10.1	7.6	4.0	17.1	6.3	3.7	2.9	14.0	1.0	2.1	0.7	7.0	3.5	3.8	0.1	0.9	5.0	5.3
	1.5	11.1	8.3	6.7	3.7	25.1	5.7	3.8	2.6	11.7	1.1	1.7	0.7	6.0	3.5	3.1	4.5	0.7	4.3	4.3
	2.5	6.7	5.8	4.8	2.4	36.2	3.6	4.1	2.5	9.5	1.2	1.5	0.3	4.0	3.1	2.3	3.7	8.4	4.0	2.7
	4	11.0	8.4	5.9	3.1	23.9	4.7	4.0	2.4	12.7	1.0	1.8	0.7	6.3	3.2	3.4	4.3	3.2	4.2	4.5
	8	11.1	8.0	6.3	3.5	22.8	5.5	4.3	2.8	11.5	1.1	1.9	0.7	6.5	3.1	3.3	4.3	3.3	4.7	4.0
	12	13.4	9.1	5.8	3.4	20.6	4.9	4.2	2.5	11.3	1.0	1.6	0.6	6.2	3.1	3.7	4.7	3.9	4.1	5.3
	14	11.5	8.2	5.8	3.4	22.1	5.2	4.2	2.6	12.1	1.0	1.9	0.7	6.7	3.7	3.5	4.3	3.2	4.5	4.4
	16	14.6	9.3	7.0	4.5	15.8	5.8	4.2	2.3	12.5	0.9	2.2	0.7	6.6	3.3	3.7	5.2	1.6	4.4	6.4
	18	11.9	8.3	6.2	3.2	24.1	5.2	4.0	2.4	11.8	1.1	2.0	0.8	6.2	3.2	3.4	4.4	1.9	4.5	4.9
Slope 25°- 1500m	0	12.7	9.0	6.1	2.5	22.8	0.6	4.3	2.0	12.6	1.2	1.8	0.6	6.3	3.5	3.4	4.8	5.9	3.8	6.2
	0.5	16.0	10.2	6.1	5.6	9.9	5.4	4.1	1.5	14.3	1.2	2.1	0.6	6.6	3.0	3.6	4.4	5.3	3.6	10.6
	14	16.3	10.2	6.5	6.1	13.6	5.9	3.8	1.9	13.5	1.3	2.0	0.5	6.3	3.3	3.3	4.5	1.0	3.9	8.7

Tab.6 Areal SRR, average total chlorin concentrations and CI values of selected samples (0-30cm multicore) in anoxic and oxic shelf, slope (depocenter) and Arctic fjord sediments

Region	Station	Areal SRR [mmol $m^{-2}d^{-1}$]	Total Chlorin [µg g^{-1}]	Chlorin Index (CI)
BUS - anoxic shelf *(mudbelt)*				
20°S	226820	0.23	37.36	0.77
21°S	226750	1.47	342.22	0.61
22°S	mpi-3	14.40	211.61	0.60
23°S	mpi-5	9.92	416.44	0.65
23°S	226680	11.95	597.22	0.63
23°S	226700	23.00	365.06	0.61
25°S	mpi 8	0.70	7.00	0.70
BUS - oxic slope *(depocenter)*				
24°S	T1-1000 (8418)	0.57	18.75	0.78
24°S	T1-1500 (8424)	0.90	6.52	0.77
24°S	T1-2000 (8422/25)	0.57	3.87	0.75
25°S	T2-600 (8449/94)	1.59	57.05	0.76
25°S	T2-1300 (1500)	1.65	56.42	0.75
25°S	T2-2300 (8462)	0.24	9.02	0.76
Arctic - oxic shelf (*SE Spitzbergen*)				
	C-03-I	0.34	12.23	0.79
	C-03-IV	0.13	4.58	0.80
	C-03-II	0.02	4.06	0.67
	C-03-III	0.11	6.27	0.64
	C-04-(X)	0.20	9.82	0.52
	C-04-(XII)	0.46	9.96	0.59
	C-04-(VIII)	0.20	4.91	0.51
* fjord	C-03-V*	2.06	19.61	0.76
Arctic - fjords *(NW Spitbergen)*				
	J 200	2.57	20.71	0.66
	DB 204		18.35	0.58
	DD	1.42	13.99	0.77
	DF	4.57	13.28	0.84
	DJ	7.03	14.24	0.83
	DI	3.08	7.97	0.76
	DG	3.03	16.92	0.76
	DK	1.71	13.00	0.84
	DL	0.49	2.29	0.80
	F 303	1.33	9.26	0.75
	A	4.48	12.65	0.94

Tab.7 Chlorin concentration normalized to total organic carbon content (TOC) in anoxic and oxic shelf, and slope sediments on the Arctic shelf and Namibian continental slope

Station

ARC-I St. I		**MudBelt-21°**		**MudBelt-23°**		**BUS Slope-25° 600m**		**BUS Slope-25° 1500m**	
Depth [cm]	µg Chlorins g^{-1} TOC	Depth [cm]	µg Chlorins g^{-1} TOC	Depth [cm]	µg Chlorins g^{-1} TOC	Depth [cm]	µg Chlorins g^{-1} TOC	Depth [cm]	µg Chlorins g^{-1} TOC
0.5	1072	0.5	15165	0.5	17842	0.5	1214	0.5	346
1.5	944	1.5	4525	1.5	16196	1.5	917	1.5	250
2.5	1292	2.5	6927	2.5	15705	2.5	777	2.5	360
4	813	3.5	4563	3.5	12781	4	830	4	399
6	430	4.5	3093	4.5	15180	6	766	6	413
8		6		6		8		8	
10	267	8	4106	8	9536	10	799	10	312
12		10		10		12		12	
14	290	12	5344	12	5861	14	779	14	287
16		14		14		16		16	
18.5	286	16	8937	16		18.5	744	18.5	313
		18		18	3836				
		20	5786	20					
		24	4842	24	4873				
		26		26					
		28		28	5715				
		33	3723						
		38	4898						

Chapter 3

Organic matter composition of the Benguela shelf and slope depocenters: characterization by productivity proxies and molecular degradation indices

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Abstract

Organic matter of the shelf and slope depocenters of the Benguela upwelling system (BUS) was characterized for two major carbon pools, pigments and proteins, and compared to organic carbon mineralisation as estimated by sulfate reduction rates (SRR). Overall pigments and protein concentrations were estimated by measurements of total chlorin and total hydrolysable amino acid (THAA) concentrations. The reactivity of the total organic carbon pool was estimated by application of molecular degradation indices, CI and DI (Schubert et al., 2002; Dauwe et al., 1999).

Organic matter concentration and reactivity were different in shelf and slope sediments. On the anoxic inner shelf, large amounts of highly-reactive source-like organic matter decreased with distance from shore in both, total concentration and reactivity. In contrast to the shelf and to overall lower concentrations of highly degraded material on the slope, sediment of the slope depocenter was characterized by larger amounts of slightly more reactive organic matter. High total chlorin, THAA and moderate phytoplankton pigment concentrations and peak organic carbon reactivity (by CI and DI) suggest a high flux of fresher material to the depocenter, provided by upwelling over the upper slope.

CI and DI likewise revealed a different composition of carbon-rich shelf and slope organic matter, and could be related to SRR. High concentrations of very reactive organic matter primarily drive SRR on the shelf; large amounts of strongly degraded material determine carbon mineralisation on the slope.

The variable pattern of CI and DI values was related to water depth and a different reactivity of chlorin- and protein-based organic carbon pools. These induce the CI to respond to short and the DI to longer degradation stages. Both organic carbon pools are highly susceptible to oxygen exposure, and external controls such as sedimentation rates, hydrographic settings and potential sources have to be considered when the CI and DI is interpreted.

Introduction

Continental margin systems play a major role for the budget of the global carbon cycle, where major burial and global benthic carbon mineralisation takes place (Suess, 1980; Middelburg et al., 1996; Lohse et al., 1998; Berner, 1989; Hedges and Keil, 1995). As most buried organic carbon is stored in the continental shelf (82 %) and slope sediments (16 %), the bulk of aerobic and anaerobic mineralisation of organic material is focused on ocean margins (Wollast, 1998; Jørgensen and Kasten, 2006). In upper margins (down to 1000m water depth) 70 % of the oxygen uptake and 96 % of sulfate reduction of the global ocean area are included, with sulfate reduction predominating in sediments underlying highly-productive and/or oxygen-depleted waters such as e.g upwelling areas (Jørgensen and Kasten, 2006).

The Benguela upwelling system (BUS) represents an important part of the global carbon cycle as it is one of the most productive upwelling areas and characterized by high organic carbon accumulation (Carr, 2001; Summerhayes et al., 1995; Mollenhauer et al., 2002). Particularly high carbon accumulation at the BUS has been reported for glacial periods with outstanding high accumulation of organic material during the last glacial maximum cold period, exceeding the Holocene by 84 %, and was also enhanced at interglacials (Mollenhauer et al., 2002; Summerhayes et al., 1995). Interglacial carbon accumulation has been attributed to an increased *in situ* production. However glacial increased carbon fluxes have been suggested to have two causes, lateral supply of eroded material from exposed organic-rich shelf deposits and an offshore displacement of the upwelling center due to a lower glacial sea level (Summerhayes et al., 1995, Mollenhauer et al., 2002). Understanding organic carbon dynamics in continental margin sediments of major upwelling centers is therefore critical to understanding global ocean carbon dynamics both presently and throughout the geological record.

In the Benguela Upwelling, perennially high rates of primary production (15-255 mg C m^{-2} h^{-1}, Mitchell-Innes et al., 2002) center along the Namibian coast at 26°S near Lüderitz Bay (Shannon, 1985). Organic matter is subsequently deposited on the shelf "mudbelt" (100-150m water depth) and on the southern Benguela slope (600-1300m) at 25°S (Bremner and Willis, 1993). These shelf and slope depocenters are rich in total organic carbon (TOC) with up to 20 % and 8 % TOC, respectively.

The shelf depocenter stretches parallel to the Namibian coastline between the Walvis Bay and Lüderitz upwelling cells. It is characterized by largely anoxic sediments due to a widespread oxygen minimum zone (150-450m water depth) that contains a diatomaceous facies rich in biogenic opal (88 %) (Bremner and Willis, 1993; Bailey, 1991). Deposits of organic carbon on the continental slope between 24 and 26°S are also characterized by a depocenter and show organic carbon enrichment as high as ~9 % TOC (Inthorn et al., 2006).

A relatively high petroleum quality has been accredited to organic-rich sediments on the upper slope by Inthorn et al. (2006) who reported enhanced concentrations of labile organic matter (high HI values) that have been consistent with high sedimentary ^{14}C ages and enhanced organic matter accumulation. A similar situation has been reported for organic-rich sediments by the observation of high HI values during glacial stages, indicating enhanced organic matter supply and preservation, and likewise increased sediment ages, suggesting a major lateral contribution of shelf-derived, reworked OM to slope deposits (Inthorn et al., 2006; Pichevin et al. 2004; Summerhayes et al., 1995; Mollenhauer et al., 2002).

Consistent with the high concentrations of organic carbon within the sediments, high rates of organic carbon mineralization rates have been reported for both the inner shelf (Brüchert et al., 2003) and within the slope depocenter (Glud et al., 1994; Ferdelman et al., 1999; Aspetsberger, 2006).

Sulfate reduction (SR) is a major mineralisation process in continental shelf and upper slope sediments, where it accounts for 25-50% of the total mineralisation (Jørgensen, 1982). It may account for half or more of total carbon mineralisation in environments with high sedimentation rates but as sedimentation drops, the significance of sulfate reduction to overall carbon mineralisation as well decreases (Canfield, 2005). In upwelling-affected sediments at mid-water depths (~ 1300m) on the southern Benguela slope, average depth-integrated sulfate reduction rates of 1.25 ± 0.31 mmol m^{-2} d^{-1} have been reported and SR comprises 20-96% of total organic carbon mineralisation (Ferdelman et al., 1999); however, SR still account for 9-16% of mineralisation on the lower continental slope (average SRR of 0.31 ± 0.02 mmol m^{-2} d^{-1} at 3700m water depth). Total oxygen uptake rates in the BUS are consistent with estimates of sulfate reduction as well as organic carbon amounts (Glud et al. 1994). Although there is a general trend of increasing organic carbon mineralisation with increasing carbon content, as measured both with total oxygen utilization and with sulfate reduction rate measurements, it is not absolutely clear as to which fraction of the total organic matter pool may be driving SR rates.

So far the availability or "reactivity" of organic matter to microbial mineralisation has not been characterized. A major question remains: does the reactivity or type of organic matter deposited at the surface vary throughout the Benguela upwelling system?

Overall organic carbon mineralisation depends on the degradability or reactivity of organic matter composition and its total amount. Organic matter reactivity (its degradability) is continuously decreased during early diagenesis (e.g. with sediment depth). This can be ascribed to various carbon pools organic material is composed of, i.e. proteins. Each carbon pool possesses its specific degradation pattern and is exponentially degraded with depth and time (Westrich and Berner, 1984). Hence, total carbon mineralisation (overall OM reactivity) results from the sum of exponential decays from all these carbon pools. This basic principle was addressed i.e. in the "classic" multi-G or the *pseudo*-G model (Westrich and Berner, 1984; Canfield, 1994). We will assess total carbon pool concentrations and describe organic carbon reactivity by its grade of degradation.

In this study, we focus on surface sediments from the slope depocenter, which we characterize for two major organic carbon pool, pigments and amino acids. Both compound classes are abundant in organisms i.e. primary producers; they are estimated in terms of total chlorin and total hydrolysable amino acid (THAA) concentrations. Chlorophylls are major photosynthetic pigments of all primary producers (Rowan, 1989). Their immediate degradation products, total chlorins, assess present and past primary production (Harris et al., 1996; Schubert et al., 1998; Shankle et al., 2002). Chlorophyll *a* and phytoplankton pigment concentrations add to the composition of the chlorin pool. Nitrogen-rich compounds such as amino acids are known to play a regulatory role in benthic ecology and are preferably degraded during diagenesis (Grutters et al., 2001; Dauwe et al., 1999; Cowie and Hedges, 1993; Cowie and Hedges, 1994).

We assess organic compound reactivity by the application of molecular degradation indices such as the Chlorin Index (CI) (Schubert et al., 2002) and a protein-based degradation indicator (DI) (Dauwe et al., 1999). They link compositional characteristics of these two organic carbon pools to its extent of degradation.

Methods

Study site

The main working area during RV Meteor cruise M57/2 2003 was located in the vicinity of the perennial upwelling zone at Lüderitz and the adjacent North Cape basin (Fig.1; station map). Major transects in 2003 were located at 24°, 25° and 26°S. This study was amended with results of analysed samples recovered on cruises in 1999 and 2004 (Tab.1-4), mainly from the Northern Cape Basin (≤23°S).

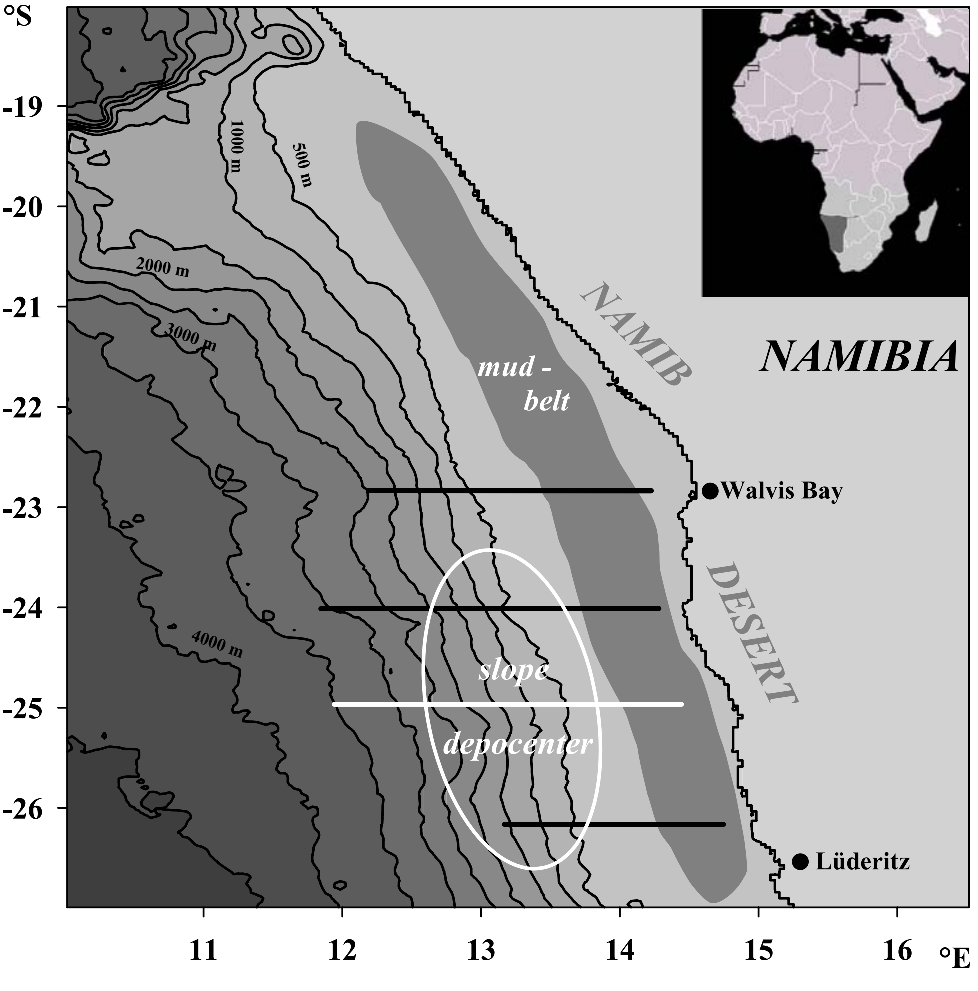

Fig.1 Map of the research area. The slope depocenter is schematically drawn as a white ellipse.

Sub-sampling and sediment processing from the multiple corer

Undisturbed surface samples were recovered using a multiple corer (25-40cm length). Sediment cores were kept at *in situ* temperature (4°C) and processed within six hours after recovery. Sediment cores were extruded and sliced into one cm intervals within the upper three cm and in two cm intervals from 3-30 cm down-core. We siphoned the bottom water to 1 cm excess water with plastic tubing and gently shook the cores to separate the topmost aqueous fluffy layer from the surface sediment. The fluff was carefully siphoned into brown glass bottles and stored at -20°C. Solid sediment and fluff samples were stored in brown glass jars.

Sulfate reduction rate measurements

Sulfate reduction rate measurements were conducted using the whole-core $^{35}SO_4^{2-}$ method (Jørgensen, 1978). Three core liners (ID 2.6 cm) containing silicone sealed injection ports were used for sub-sampling the multiple corer sediment cores. Incubation of the sub cores has been performed at one cm intervals with 5 µl of 100 kBq ml^{-1} $^{35}SO_4^{2-}$ tracer (Amersham) at 4°C in the dark for 8-12 hrs. Following incubation the microbial activity of the sulfate reducing bacteria was stopped by slicing the cores in 1 cm intervals, transferring the sediment into equal volumes of 20% ZnAc-solution and storage at -20°C. The distillation of radioactive end products in the samples, resulting from microbial sulfate reduction, and calculations of sulfate reduction rates were performed following Kallmeyer et al. (2004).

Bulk geochemical analysis

Total carbon (TC) and nitrogen (TN) were determined from freeze-dried homogenized samples with a Fisons NA 1500 (Series 2) Elemental Analyzer. Total inorganic carbon (TIC) was analysed by coulometric titration using a TIC autoanalyser CM5240 Orbis BV. The total organic carbon content (TOC) was calculated by subtracting TIC from TC concentrations.

Pigment analysis

Total chlorins and the Chlorin Index

Total Chlorin concentrations and a related degradation state indicator, the Chlorin Index (CI), were determined following the method by Schubert et al. (2005). Total chlorins were extracted from freeze–dried, homogenized sediment by ultra sonication (ultra sonication bath; type *Omnilab 1300*). Sample aliquots of 5 to 20 mg (depending on TOC) suspended in HPLC-grade acetone were extracted four times at 15 min intervals. Following each extraction, sample and solvent were centrifuged and the extract collected in a separate vial. During this procedure, samples were kept cool, light-protected and sealed with parafilm to prevent chlorin decomposition and solvent volatility. Extracts were measured immediately after extraction at a Hitachi F-2000 Fluorimeter at excitation wavelength 428 nm and emission wavelength 671 nm. Chlorophyll *a* (SIGMA) that has been transformed to the chlorin pheophytin *a* through acidification using ~ 100 µl purified hydrochloric acid (shaken with *n*-hexane) was used as a standard for total chlorin concentrations. Careful attention was paid to the relation between sample weight and total extraction volume (8ml) in order to achieve fluorescence intensities in the lower standard range so that any interference due to concentration quenching could be excluded.

Chlorin Index (CI) values are on a scale from 0.2, indicating fresh and highly reactive organic carbon, to 1, characterizing progressively altered organic matter. Acidification transforms pigments from labile organic material into refractory chlorin compounds that feature lower fluorescent intensities than extracts from fresh organic material. The derived Chlorin Index (CI) is defined as the ratio of the fluorescence units of the acidified sample over the original extract:

$$\text{CI} = \text{fluorescent intensities}_{\text{acidified sample}} / \text{fluorescent intensities}_{\text{original sample}} \qquad (1)$$

HPLC analysis of Pigments

Sediment extraction for analysis followed Buffan-Dubau and Carman (2000). Pigments were extracted from freeze-dried samples in 5 ml 100% HPLC-grade acetone, obtaining light-protection and ice-cooling, by ultra sonication (*Bandelin Sonoplus HD 200* ultra sonication probe, MS73/D, 30 sec) and incubated 24 hours at -20°C in the dark.

Chlorophyll *a* and accessory algal pigments were analysed with a reversed-phased HPLC system and a protocol described in Wright et al. (1991). Original sample aliquots of 100 µl were injected into a Waters HPLC advice (Waters 2690 Separation Module) equipped with a photo diode array detector (PDA 996). Pigment detection was performed at 430.3 nm with an additional PDA spectrum from 350-800 nm recorded every second and operating at a flow rate of 1 ml/min. The solvent system consisted of three reagents: solvent A, 80:20 methanol : 0.5 M ammonium acetate, solvent B, 90:10 acetonitrile: water, solvent C, ethyl acetate. Chlorophyll *a*, major chlorins (pheophytin *a*, pheophorbide *a*) and selected accessory pigments (fucoxanthin, peridinin, diadinoxanthin,), were quantified with commercial pigment standards (*DHI*, Denmark).

Total hydrolysable amino acids (THAA) and Degradation Index

Total hydrolysable amino acids (THAA) were analysed following a method by Dauwe and Middelburg (1998). Amino acids were released from 100mg freeze-dried, homogenized sediment by addition of 6 N hydrochloric acid under nitrogen atmosphere and subsequent hydrolysis at 110°C for 24 hours. Post hydrolysis, samples were cooled to room temperature, separated from the sediment via centrifugation (0°C, 5000 rpm, 10 min) and the extract stored at -20 °C until analysis. Prior to fluorescent measurement, 100µl sample aliquots were mixed with 1.8 ml sodium borate buffer (pH10) and neutralized with 100 µl of 6 N NaOH. 100µl sample aliquots were reacted with fluorescent agent, *o*-phtaldialdehyde (OPA), and, after five minutes reaction time, analysed at excitation/emission wavelengths 340/455 nm with a Hitachi F-2000 Fluorometer.

The concentrations of 17 individual amino acids were determined via pre-column *o*-phtaldialdehyde derivatisation (Hill et al., 1979; Lindroth and Mopper, 1979) including an internal standard (SIGMA AA-S-18) from 100 ml aliquots of neutralized hydrolysate. Individual amino acid derivatives have been separated by reverse-phased HPLC with a heated C_{18} – column (30°C) and binary solvent system with subsequent fluorescence detection. We detected the individual amino acids D-alanine, arginine, asparagine, aspartic acid, amino-n-butyic acid, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, methionine, phenylalanine, serine, threonine, tyrosine, β-alanine. The amino acids proline, tryptophan, and cysteine could not be quantified with this method.

Amino acid composition was related to its degradation dynamics by application of a principal component analysis (PCA). PCA is a variance-orientated method that uses standardized variables to represent each site in a multidimensional space. Basic variables - in our case the mole percentages of individual amino acids - were standardized by subtracting the mean and dividing by their standard deviation (Dauwe & Middelburg, 1998; Meglen, 1992). Principal components for this transformed dataset are linear vectors of our original values that describe their maximum variance in a multidimensional space. By application of factor coefficients as defined in Dauwe et al. (1999) the DI can be calculated as:

$$DI=\sum I[(var_i-AVGvar_i)/STDvar_i]\times fac\cdot coef_i \tag{2}$$

where var_i is the original, non-standardized mole percentage of amino acid *i*, $AVGvar_i$ and $STDvar_i$ represent the average and standard deviation of the original mole percentage of all amino acids included; $fac\cdot coef_i$ is the respective factor coefficient for amino acid *i*.

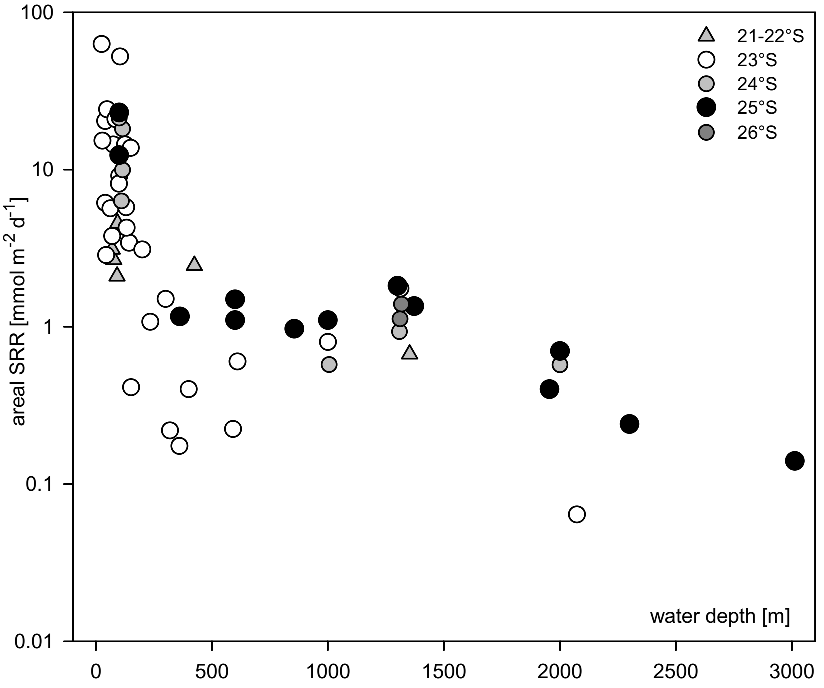

Fig.2 Integrated (0-20cm) areal sulfate reduction rates (SRR) in the Benguela upwelling system (20 – 26°S) as a function of water depth.

Results

Sulfate reduction rates (SRR)

Areal sulfate reduction rates (SRR integrated over 0-20 cm sediment depth) measured in this study were consistent with earlier studies (Brüchert et al., 2003, 2005; Ferdelman et al, 1999) and ranged from 0.2 to 62.2 mmol m^{-2} d^{-1} (Tab.1, Fig. 2). Highest sulfate reduction rates (23-63 mmol m^{-2} d^{-1}) occurred below 150m water depth on the entire coast and decreased 100 fold with increasing water depth. Low areal rates of ~ 0.1-1 mmol m^{-2} d^{-1} were typical of the slope sediments, except for those sediments at intermediate water depths (1300m), and in particular at the southern slope (25°S), where a peak SRR of 1.8 mmol m^{-2} d^{-1} occurred.

Bulk organic carbon and elemental composition

Total organic carbon (TOC) concentrations ranged from 1–14 % and C/N ratios varied between 6.3 – 19.9 in surface sediments and fluff (Tab.2 and Fig.3.a+b). Bulk organic matter of the inner shelf mudbelt (~ 100-114 m) was characterized by TOC contents of up to 14 % and low C/N ratios of 7-9. Lowest C/N ratios of 6 occurred close to the coast (25m). At all transects on the slope, total organic carbon concentrations were ~4 % with C/N ratios of 10-11. TOC concentrations nearly doubled (TOC of 8%) at 25°S compared to the northern study area (23-24°S) and exhibited slightly lower C/N ratios of ~10.

Total chlorins, chlorophyll a and pigments

Total chlorin concentrations varied from 5 to 1100 µg g^{-1} dry weight in shelf and slope sediments (Tab. 3). The highest chlorin concentrations of 242-1087 µg g^{-1} were observed within shelf sediments, and decreased by two orders of magnitude with greater water depth (Fig.3.c). Chlorin concentrations in northern slope surface sediments (23+24°S) ranged from 23-27 µg g^{-1} and were doubled on the southern Benguela slope with 64-88µg g^{-1} of total chlorins. At all latitudes chlorin concentrations of the topmost fluff organic layer were much higher than total chlorins content in the corresponding surface sediments at ~ 100m water depth and the shelf break (250m). Higher chlorin concentrations on the slope were most pronounced in sediments at 25°S, between 600 and 1300m water depth. Here, peak chlorin concentrations of 143 and 84µg g^{-1} were measured at 800 and 1300 m water depths, respectively.

Surface sediment distributions of chlorophyll *a* concentrations showed a similar trend as total chlorins (Tab.3, Fig.4.a) and ranged from 0.1 to 10.4 µg g $^{-1}$. Highest chlorophyll *a* values occurred on the shelf across all transects. At intermediate water depths (600 to 1000m), chlorophyll *a* concentrations decreased to values of ~ 0.3 µg g^{-1}. Peaks in chlorophyll *a* concentration were found at 300-400m water depths on the northern transect (2.4–2.7 µg g^{-1}) and at 600 m water depth on the southern (25°S) Benguela slope (~4 µg g^{-1} of chlorophyll *a*).

Major chlorophyll degradation products, pheophorbide *a* and pheophytin *a*, generally decreased with increasing water depth (Fig.4.b+c). Pheophorbide *a* concentrations (0.001-1µg g $^{-1}$) were by 3 orders of magnitude lower than pheophytin *a* concentrations (0.2-34 µg g $^{-1}$).

Indicative pigments for major phytoplankton groups, including fucoxanthin (diatoms), peridinin (dinoflagellates), and diadinoxanthin (coccolithophorides), exhibited surface distributions similar to those for total chlorins (Tab. 3, Fig.4.d-f). Fucoxanthin concentrations dominated all other pigments on the shelf (Tab.3, Fig.4.d). Fucoxanthin concentrations (0.3-17.3 µg g $^{-1}$) at the shelf "mudbelt" (<250m) were twice as high as peridinin (0.1-8.2 µg g^{-1}), but decreased to very low and often undetectable concentrations within the slope sediments (<0.4 µg g^{-1}). On the slope, peridinin concentrations dominated the group of species indicative phytoplankton pigments (0.1-1.1 µg g^{-1}). Diadinoxanthin concentrations were in a range of 0.001 to 0.23 µg g^{-1} (Tab.3).

Consistent with all other pigments, the largest diadinoxanthin concentrations (0.12–0.23 µg g^{-1}) occurred on the inner shelf, and decreased with increasing water depth by two orders of magnitude (Fig.4.f). Diadinoxanthin concentrations of 0.02 µg g^{-1} between 400 to 800m water depths in the southern Benguela slope (25°S) sediments exceeded those in the northern region (23°S) by one order of magnitude.

THAA

Protein concentrations in the 0-1cm sediments ranged from 5 mg THAA g $^{-1}$ at 2000 m water depth to 44 mg THAA g $^{-1}$ dry sediment on the inner shelf (Tab.4). Compared to total chlorins, overall THAA concentrations showed less variability on the shelf (14 and 44 mg g $^{-1}$) and on the upper slope (10-35 mg g $^{-1}$) (Fig. 3.e). Likewise, THAA concentrations in surface and fluff material were similar and on the shelf decreased at greater water depths. However, THAA concentrations, in both the southern slope (25°S) fluff and surface sediments, were about twice the amount than in the North (23°S). Fluff and surface THAA concentrations were slightly enhanced at 600 and 1300m water depths on the southern slope. In contrast to linearly decreasing THAA amounts in fluff organic material down the southern Benguela slope, surface sediment THAA concentrations increased to peaks at 1300 and 2000m water depth.

The relative contribution of amino acids to total sedimentary organic carbon and nitrogen (THAA-%C and %N) was largest in shelf sediments compared to the slope (Fig.5.a+b). Surface percentages of organic carbon identifiable as amino acid carbon were measured between ~21-27 % and ~ 14-20% on the shelf and slope, respectively, and within the typical range of continental margins (12 ± 10 % THAA-%C, Keil et al., 2000). Total sedimentary nitrogen content measurable as amino acid nitrogen was comparatively larger and characterized fresh organic matter (>75 %, Lee 1988) on the shelf (~ 40-96 %). On the slope, THAA-%N between 40-60% identified sinking aggregate material and by far exceeded typical continental margin values (10-30 %).

Chlorin Index

Chlorin Index (CI) values ranged 0.26 to 0.96 (Tab.3, Fig.3.d). Source organic material, as measured for the diatom species *Skeletonema costatum*, exhibited a CI value of ~0.3. On the shelf, low CI values of ~0.26 were measured close to the coast and increased with greater water depth to a value of 0.9 at the shelf break (200m). CI values on the continental slope averaged ~0.8 for the northern region. CI values of ~ 0.7 occurred on the southern slope (25°S). Below 1500m the CI values averaged ~0.8 at all latitudes. CI values in fluff and surface sediments were comparable except for spot-wise CI decreases of ~ 0.66 in surface and fluff material at 600m and 1300m on the southern slope (25°S).

Degradation Index (DI)

The amino acid based Degradation Index (DI) values, calculated with factor coefficients given in Dauwe et al. (1999) and equation (2), provided merely spatial trends. As the standardized factor coefficients calculated by Dauwe et al. (1998, 1999) are based on a wide range of organic matter sources, application of these coefficients apparently lowered the amplitude of calculated degradation indices. Therefore we quantitatively assessed the variation of amino acid composition in our samples by use of a principal component analysis (PCA). In accordance with Dauwe and Middelburg (1998) we only used the first axis of the PCA to estimate the Degradation Index. These DI values resulted in clear latitude and depth-related changes (latter not shown) and were moreover consistent with likewise estimated degradation indices in the Chilean upwelling region by Lomstein et al. (2006) and Niggemann (2005).

Degradation Index (DI) values estimated from PCA were in a range of – 5.8 to 4.7 (Tab.4, Fig. 3.f) and comparable to the amino acid composition in coastal Chilean sediments (DI ~ -1.5 to 2.8, Lomstein et al., 2006). Source organic material, as measured for the diatom species *Skeletonema costatum*, exhibited a DI value of 4.55. Shelf organic matter was described by DI values of 1.2 – 4.4 with largest values for inner shelf (mudbelt) sediments. Overall on the Benguela slope DI values linearly decreased towards greater water depths to values of 0.2 to -1.0. DI values of 0.2 to -0.4 along the southern transect (25°S) were slightly higher than in sediments of the northern slope (DI values of – 0.01 to -1.0). An exceptionally low DI value of -6 occurred at 400m water depth at 25°S.

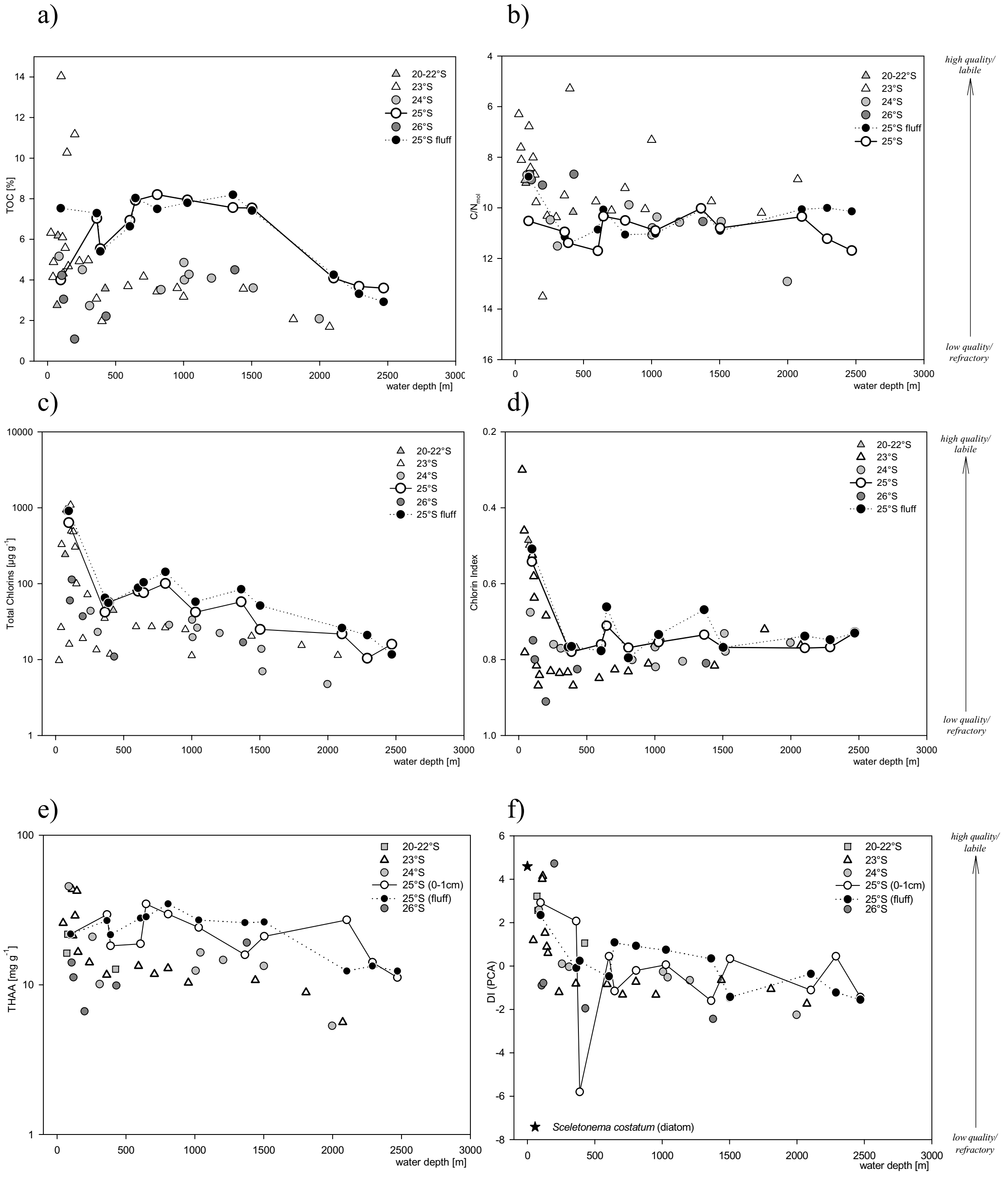

Fig.3 Organic matter concentration and composition in the Benguela upwelling system as shown by total organic carbon content (TOC) (a) and C/N ratio (b), total chlorin concentrations (d) and the Chlorin Index, CI, (e) and total hydrolysable amino acid content (THAA) (e) and the Degradation Index (DI) (f).

Discussion

Shelf versus slope depocenter

Based on pigments, THAA and related degradation indices surface sediments of the Benguela upwelling system can be clearly delimited into two major zones: (1) the shelf sediments, which include an anoxic inner shelf zone and an outer "weathered" zone; (2) the slope, which shows a distinct enhancement of all parameters at 25°S between 500–1500m water depths.

Surface sediments on the inner shelf zone are characterized by large amounts of highly reactive (less degraded) organic matter. This could be shown by highest measured concentrations of total chlorins, phytoplankton pigments and THAA as well as surface percentages of sedimentary amino acid carbon and nitrogen (Fig. 3-5). DI values of ~ 4 (close to the DI of 4.55 for the diatom *Skeletonema costatum*, Fig. 3.f, filled star) and CI values of 0.5 to 0.6 (Fig. 3.d) suggest that shelf organic matter was composed of reactive, source-like material. This was supported by high diatom and dinoflagellate pigment as well as chlorophyll *a* concentrations (Fig. 4). In contrast, smaller amounts of strongly degraded (less reactive) organic matter occur on the outer shelf as shown by ten and four times lower total chlorin and THAA amounts, respectively, and CI and DI values of ~ 0.8 and ~ -1 (Fig.3, Tab.3+4).

Organic carbon turnover on the entire shelf was consistent with organic matter amounts and grade of reactivity and affected by two factors: (1) a large fraction of total organic carbon that is fresh and reactive on the inner shelf, and (2) anoxic sediments. Even accounting for a ten times increase in sulfate reduction due to a lack of oxygen, sulfate reduction rates on the inner shelf exceeded mineralisation rates on the outer shelf zone by more than ten times (inner shelf SRR of 22 to 52 mmol m^{-2} d^{-1} contrary to SRR of ~ 1 mmol m^{-2} d^{-1} at the outer shelf break). Thus, organic matter amount and carbon reactivity and not merely anoxic conditions are important to carbon turnover on the inner and outer shelf.

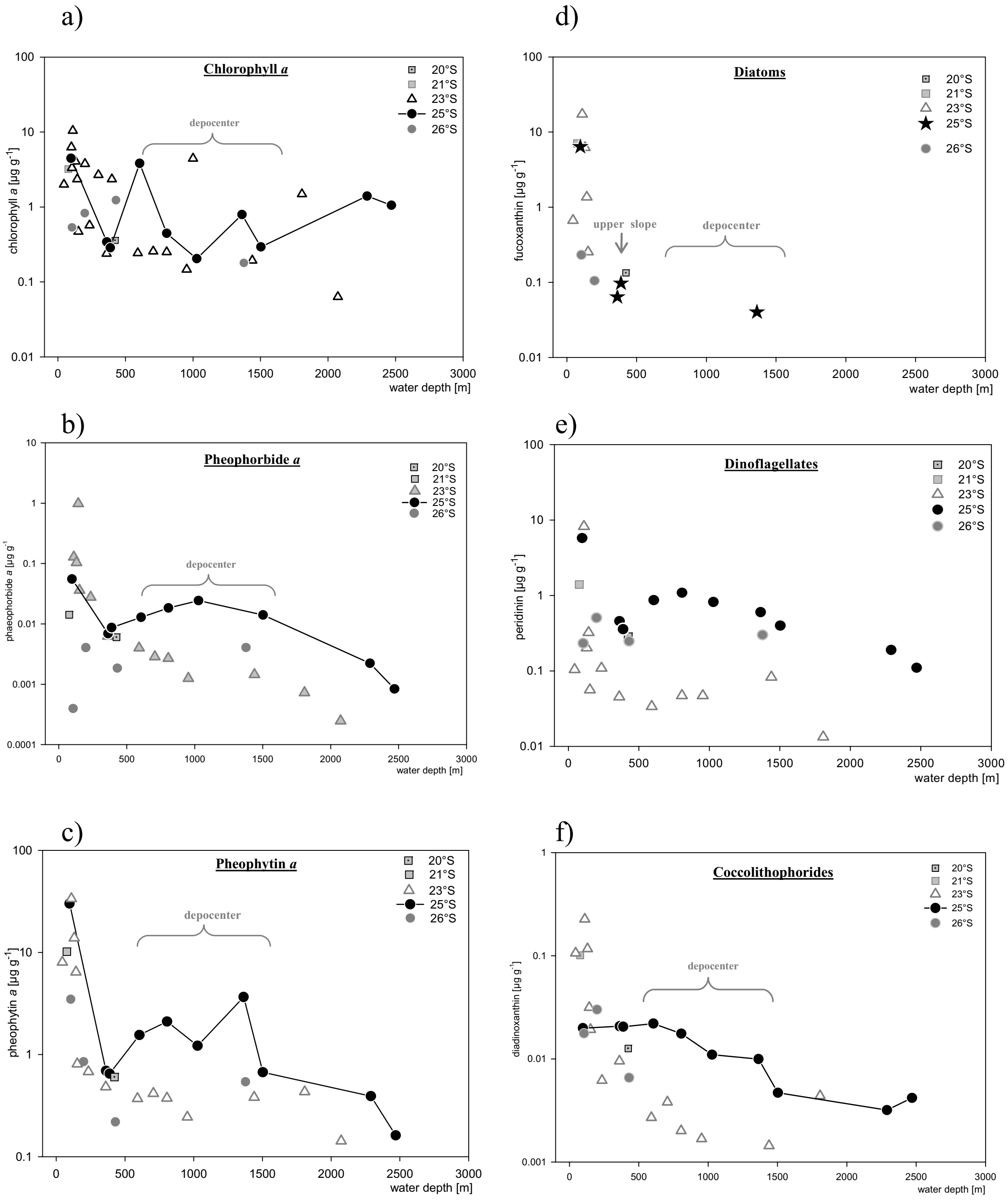

Fig.4 Pigments in Shelf and slope surface sediments shown for Chlorophyll *a* (a) and its major degradation products phaeophorbide *a* (b) and phaeophytin *a* (c) and phytoplankton-specific pigments fucoxanthin (diatoms) (d), peridinin (dinoflagellates) (e), diadinoxanthin (coccolithophorides) (f).

Benguela slope and slope depocenter

Overall low concentrations of strongly degraded organic matter and tenfold lower sulfate reduction rates characterize Benguela slope sediments. This was shown by up to 90 and 70% lower total chlorin and THAA amounts if compared to the inner shelf zone. Refractory organic matter on the slope was characterized by DI values of 0.2 to -0.4 and CI values of ~ 0.8.

Contrary to the northern (23-24°S) and southern continental slope (26°S), a distinct depocenter of organic material exists at 25°S between 500 and 600m water depths. Depocenter sediments are distinguished from the southern and northern transects by elevated organic matter amounts and slightly higher carbon reactivity compared to overall refractory slope sediments. Organic matter concentration, as measured by total chlorin and THAA concentrations was nearly doubled at the depocenter.

Noteworthy were as well the observed high surface percentages of amino acids presented as organic carbon (~10-20% THAA-%C) and nitrogen (~26-56% THAA-%N) in upper slope sediments (Fig.5). Such contributions were characteristic of sinking aggregate organic matter (Lee, 1988) and largely exceeded amino acid carbon as well as nitrogen percentages that have been measured in the Chilean upwelling region (~ 7% THAA-%C and 22-25% THAA-%N, Lomstein et al., 2006) and the northeastern Atlantic continental slope (~10-13 % THAA-%C and ~ 30 % THAA-%N, Grutters et al., 2001).

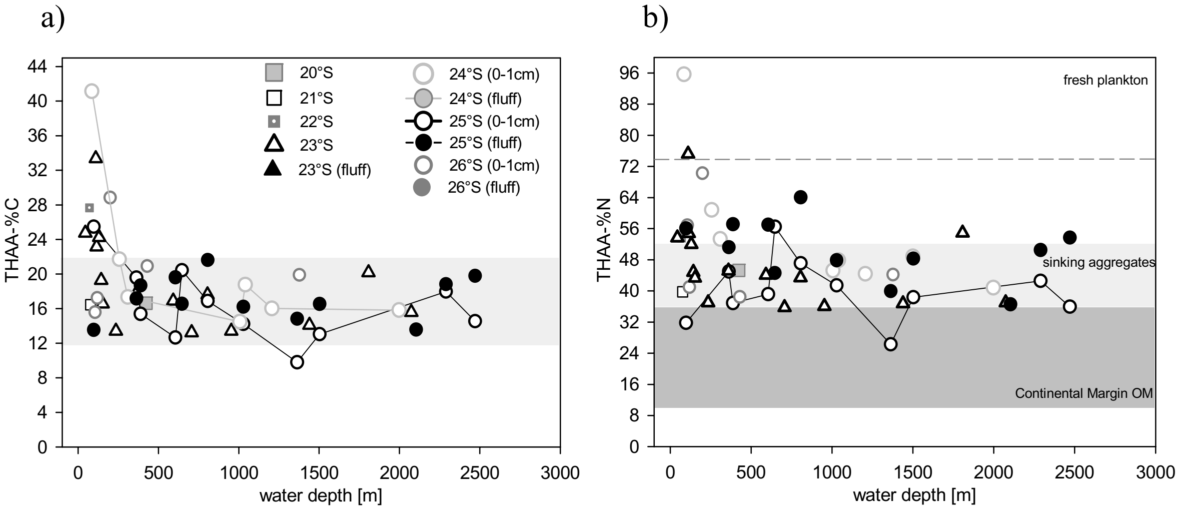

Fig.5 Percentage contribution of amino acids to sedimentary total organic carbon and nitrogen, THAA-%C (a) and THAA-%N (b).

CI values of ~ 0.74 and peak DI values of 1.0 for the depocenter compared to overall CI and DI values of 0.8 and ~ -1, respectively (Fig. 3a-d) suggested a higher reactivity, but nevertheless refractory composition of organic matter. This was further supported by the characterization of only a small fraction of less degraded organic material, which was composed of chlorophyll *a* and phytoplankton pigments (Fig.4).

Carbon turnover at the slope depocenter is consistent with elevated organic matter amounts of slightly higher reactivity. Even though sulfate reduction rates on the entire upper Benguela slope averaged ~1 mmol m^{-2} d^{-1} (Fig.2, Tab.1), almost doubled rates of 1.5 and 1.8 mmol m^{-2} d^{-1} occurred at the depocenter. In contrast to the inner shelf zone, mineralisation is not determined by sulfate reduction alone but also by aerobic carbon degradation (measured as total oxygen uptake rates, TOU, see Tab. 1). Aerobic degradation dominated anoxic processes only at 600m water depths; at 1300 – 1500m, sulfate reduction is more important to total mineralisation (50 percent of TOU). Aerobic as well as anaerobic turnover rates coincided with elevated total chlorin and THAA amounts. This was consistent with Aspetsberger (2006) who also related high rates of benthic activity such as TOU and biological processing rates to high organic contents at the southern slope depocenter. This and major preservation of less reactive chlorophyll degradation products such as pheophytin *a* and other chlorins (Stephens et al., 1997), emphasize the importance of organic matter amount to carbon turnover. Organic matter reactivity appears to be less significant to mineralisation on the slope at 1300m water depth.

Implications of organic matter composition

Organic matter concentration and composition on the shelf and slope depocenter appear to be mainly affected by sedimentation rates, water depth and exposure to oxygen. In particular on the shelf oxygen exposure time seems to exert major control of carbon burial and preservation as suggested by Hartnett et al. (1998). For the inner shelf (below 120m water depth) Mollenhauer et al. (2002) reported high sedimentation rates of 150 cm ky^{-1} that decreased to ~ 50 cm ky^{-1} towards the outer shelf. They are related to likewise largest chlorin and THAA amounts on the inner shelf that declined towards the outer shelf just as sedimentation rates. High amounts of very reactive (less degraded) organic matter are (most probably) preserved due to anoxic bottom-water and inner shelf sediments, as reported by Bailey (1991). This is a contrast to the conditions on the oxygenated outer shelf, where organic matter amounts and reactivity decrease due to low sedimentation and increasing oxygen exposure time as a function of water depth. In addition, strong poleward flowing undercurrents weather organic material on the outer shelf (Brüchert et al., 2003; Summerhayes et al., 1995; Mollenhauer et al., 2002), and thus alter organic particle reactivity.

At the slope depocenter, high sedimentation rates and sorption to inorganic particles lower organic carbon oxygen exposure time and result in a high flux of more reactive organic matter. As Hedges and Keil (1995) pointed out, carbon burial and preservation appears to be a competition between protective sorption processes and aerobic degradation. This could explain high chlorin and protein amounts that correspond to high sedimentation rates of 112 and 40 cm k^{-1} at the southern Benguela slope. Particularly high chlorin and phytoplankton pigment amounts, high organic carbon reactivity (CI of 0.6) and likewise increased mineralisation rates at 600m and 1300m water depth imply a higher flux of fresher material to the slope depocenter. High carbon burial at these sites was supported by Inthorn et al. (2006), who related high TOC concentrations (of ~9 %) to enhanced sedimentation of organic particles at the depocenter. We consider slightly fresher organic material to be derived from a second upwelling front over the southern Benguela slope, which has been described by Summerhayes et al. (1995).

Implications for degradation indices of the chlorin and protein carbon pool

Degradation index profiles showed different patterns for the CI and DI and are considered to vary with water depth, oxygen exposure and grade of reactivity of the carbon pool. On the shelf, organic carbon reactivity likewise indicated by CI and DI values, linearly decreased from the inner to the outer shelf. Parallel increasing oxygen exposure time due to rising water depth (and lower sedimentation) appear to be the major controls on organic matter degradation and reactivity on the shelf. Here, the different reactivity of the chlorin and protein carbon pools seems to be less significant to mineralisation.

However, on the permanently oxygenated slope, different CI and DI down slope profiles primarily result from the different aerobic degradability of chlorins and THAA, sedimentation rate and different sorptive capacities of organic matter to inorganic particles. Chlorins exhibit highest sensitivity to oxygen exposure and are more quickly degraded than proteins, as demonstrated by an almost straight profile with similar CI values of ~ 0.75 and ~ 0.8 down the southern and northern slope (Fig. 3.d). Peak CI values of 0.6 on the upper southern slope thus result from shortened oxygen exposure time due to high sedimentation rates and sorptive capacities of chlorin organic matter (Sanei et al., 2005). In contrast, particular DI values in fluff organic matter showed a linear decrease of protein carbon reactivity that was consistent with increasing water depth, rising oxygen exposure time and lower sedimentation (Fig.3.f). However, a higher variability of the DI in surface sediments allover the Benguela slope might result from selective preservation of amino acids in sediments. External preservation controls such as sorption to sediment particles or protection in mineral matrices (Hedges and Keil, 1995; Ingalls et al.,2003; Satterberg et al., 2003; Sanei et al., 2005) appears to affect burial of chlorin and protein organic matter differently on the Benguela slope.

Conclusions

Different organic matter reactivity and the type of organic carbon separate the Benguela upwelling system into major zones, shelf and slope sediments, including a depocenter on the southern upper slope. Carbon mineralisation on the shelf is likewise affected by high total organic matter reactivity and concentration, whereas mainly high amounts of less reactive organic matter account for reduced carbon turnover on the slope.

Organic matter amount and reactivity, demonstrated by the CI and DI, are strongly affected by sedimentation rate, water depth and oxygen exposure times. On the inner shelf organic matter amounts and reactivity are controlled by sedimentation rate but primarily by low oxygen exposure due to anoxic sediments. On the slope (depocenter), high sedimentation rates that shortened oxygen exposure time result in a high flux of slightly more reactive organic material. In addition, sorption and selective preservation due to association with sediment particles are considered to aid carbon burial in the Benguela upwelling system. The different degradation and preservation characteristics of the chlorin and protein pools could also be used to reveal further insight in organic matter preservation controls in future studies. These should also include other organic carbon pools of sedimentary organic matter.

Appendix Chapter 3

Tab.1 Mineralisation rates in Benguela surface sediments. Total oxygen uptake (TOU) and areal sulfate reduction rates (SRR) in mmol $m^{-2}d^{-1}$, bottom water oxygen concentration (µmol) and sedimentation rates (k y^{-1}).

	Station	Lat °S	Long °E	[m]	[km]	Areal SRR [mmol $m^{-2}d^{-1}$]	Oxygen [µmol]	TOU [mmol m^{-2} d^{-1}]	Areal SRR % of TOU	Sedimentation rate [cm kyr^{-1}]
20°S	226820	20.06	11.52	424	170.3	2.45 [3]				
	2131	20.65	11.40	1400		0.61 [6]	185.0 [7]	2.1 [7]	58.9	
21°S	226750	21.55	13.52	77	36.7	1.47 [3]				
	3707	21.63	12.19	1352		0.67 [6]	193.0 [7]	11.6 [7]	11.6	12.3 [8]
22°S	mpi-3	22.64	14.30	70	24.0	14.40 [2]				
	3706	22.72	12.60	1313		1.75 [6]	195.0 [7]	16.0 [7]	21.9	16.0 [8]
23°S	1	22.87	14.48	25	4	62.7 [1]	3.0 [2]			
	2	22.82	14.45	40	8	20.3 [1]				
	184-3	23.00	14.37	44	9.2	2.86 [1]	4.9 [5]			
	20	23.43	14.23	104	24.2	52.20 [2]	0.0 [2]			
	mpi-5	23.76	14.27	114	27.9	9.92 [1]	9.2 [2]			
	226680	23.47	14.17	110	31.2	11.95 [3]	2.0 [5]			
	187-3	23.00	14.05	130	44.6	5.76 [1]	2.4 [5]			
	4	22.42	14.05	100	52	9.1 [1]				
	188-3	23.00	13.87	143	64.6	3.42 [1]				
	212-3	23.00	13.68	152	85.3	0.41 [1]	24.2 [5]			
	7	23.17	13.53	200	106	3.1 [1]				
	213-3	23.00	13.50	234	105.9	1.08 [1]	19.5 [5]			
	191-5	23.00	13.50	360	106.0	0.17 [1]	22.6 [5]			
	8	23.18	13.40	300	121	1.5 [1]				
	215	23.00	13.15	319	144.8	0.22 [1]	108.4 [2]			
	9	23.22	13.18	400	145	0.4 [1]				
	173-2	23.00	12.95	591	167.0	0.22 [1]	97.8 [5]			
	8484-3	23.00	12.78	953	185.5		156.4 [5]			
	1712	23.25	12.80	992		0.80 [2]	160.0 [7]	5.6 [7]	28.6	8.0 [8]
	11	23.25	12.81	1000	187	0.8 [1]				
	8498-2	23.00	12.58	1439	207.9	1.75 [2]	189.4 [5]			
	226700	23.01	12.26	1807	218.9					
	1711	23.34	12.38	1947		0.06 [2]	215.0 [7]	3.0 [7]	4.0	10.0 [8]
	176-3	23.00	12.33	2073	235.6	0.06 [1]	218.1 [5]			
24°S	T1-1000 (8418)	24.24	13.14	1006	161.1	0.57 [3]	164.8 [4]	8.4 [4]	13.7	14.6 [9]
	3718/3705	24.30	12.99	1308		0.93 [6]	194.0 [7]	13.0 [7]	14.3	
	T1-1500 (8424)	24.42	12.93	1519	184.6	0.90 [3]				
	T1-2000 (8422/25)	24.46	12.71	1997	208.4	0.57 [3]	216.7 [4]	4.7 [4]	24.2	8.0 [9]
25°S	T2-600 (8449/94)	25.48	13.55	605	144.4	1.59 [3]	144.8 [4]	16.4 [4]	18.2	111.5 [9]
	3718	24.89	13.15	1317		1.39 [6]	195.0 [7]	9.7 [7]	28.7	7.7 [8]
	T2-1300	25.62	13.27	1363	176.3	1.65 [3]	194.9 [4]	7.4 [4]	48.9	39.2 [9]
	3719	24.99	12.87	1955		0.40 [6]	236.0 [7]	19.8 [7]	4.0	
	T2-2300 (8462)	25.53	12.94	2289	213.1	0.24 [3]	108.2 [4]	1.1 [4]	41.3	21.8 [9]
	3721	25.15	12.39	3013		0.14 [6]	248.0 [7]	22.8 [7]	1.2	5.2 [8]

1 Brüchert et al., subm.2005, 2 Brüchert et al. 2003, 3 this study, 4 Aspetsberger et al., subm.2006, 5 Mohrholz V., cruise report M57/2
6 Ferdelman et al., 1999, 7 Wenzhöfer et al., 2002 8 Mollenhauer et al., 2002, 9 Inthorn et al., 2006

Tab.2 Bulk organic matter composition of surface sediments for the total organic carbon content (TOC) in percent and the molecular carbon to nitrogen ratio, the C/N.

			surface			*fluff*		
	Station	**[m]**	**TOC [%]**	**TON [%]**	**C/N_{mol}**	**TOC [%]**	**TON [%]**	**C/N_{mol}**
20°S	226820	424	3.6	0.4	10.2			
21°S	226750	77	6.2	0.8	9.0			
22°S	mpi-3	70	2.8	0.4	8.9			
23°S	1	25	6.3		6.3			
	2	40	4.1		7.6			
	184-3	44	4.9	0.7	8.1			
	20	104						
	mpi-5	114	4.3	0.6	8.9			
	226680	110	6.1	0.8	8.4			
	187-3	130	5.6	0.8	8.0			
	4	100	14.0		6.8			
	188-3	143	10.3	1.4	8.7			
	212-3	152	4.7	0.6	9.8			
	7	200	11.2		13.5			
	213-3	234	4.9	0.6	10.3			
	191-5	360	3.1	0.4	9.5			
	8	300	5.0		10.4			
	215	319						
	9	400	2.0		5.3			
	173-2	591	3.7	0.4	9.7			
	8482-2	706	4.2	0.5	10.1			
	8483-1	805	3.4	0.4	9.2			
	8484-3	953	3.6	0.4	10.1			
	11	1000	3.2		7.3			
	8498-2	1439	3.6	0.4	9.7			
	226700	1807	2.1	0.2	10.2			
	176-3	2073	1.7	0.2	8.9			
24°S	ww24005	85	5.2	0.7	8.7	6.8	0.9	8.5
	ww24040	256	4.5	0.5	10.5	3.6	0.4	10.9
	ww24060	309	2.7	0.3	11.5	3.9	0.4	10.7
	T1-800 (8419)	834	3.5	0.4	9.9	4.7	0.5	11.0
	T1-1000 (8418)	1006	4.0	0.4	10.8			
	T1-1000	1003	4.8	0.5	11.1	5.3	0.6	10.4
	T1-1200 (8421)	1205	4.1	0.5	10.6	4.5	0.5	11.5
	ww24080	1040	4.3	0.5	10.4	4.2	0.5	9.4
	T1-1500 (8424)	1519		0.4		5.6	0.4	16.9
	T1-1500	1512	3.6	0.4	10.5	4.0	0.4	10.4
	T1-2000 (8422/25)	1997	1.6	0.2	9.4		0.2	

Tab.2 continued

			surface			*fluff*		
	Station	**[m]**	**TOC [%]**	**TON [%]**	**C/N $_{\text{mol}}$**	**TOC [%]**	**TON [%]**	**C/N $_{\text{mol}}$**
25°S	MPI-8	97	4.0	1.0	10.5	7.5	0.6	8.8
	T2-360 (8429/28)	362	7.0	1.0	11.0	7.3	0.8	11.2
	T2-400 (8452)	388	5.5	0.7	11.4	5.4	0.6	11.4
	T2-600 (8449/94)	605	6.9	0.7	11.7	6.6	0.7	10.9
	T2-600	646	7.9	0.9	10.3	8.0	0.9	10.1
	T2-800 (8448)	806	8.2	0.9	10.5	7.5	0.8	11.1
	T2-1000 (8451)	1028	7.9	0.8	10.9	7.8	0.8	11.0
	T2-1300	1363	7.6	0.9	10.0	8.2	0.9	10.1
	T2-1500 (8455)	1503	7.5	0.8	10.8	7.4	0.8	10.9
	T2-2000	2103	4.1	0.5	10.4	4.3	0.5	10.1
	T2-2300 (8462)	2289	3.7	0.5	11.2	3.3	0.4	10.0
	T2-2500 (8470)	2470	3.6	0.5	11.7	2.9	0.3	10.1
26°S	MPI-6	105	4.2	0.4	8.7			
	ww26010	118	3.0	0.4	8.9	5.2	0.6	9.5
	ww26030	199	1.1	0.1	9.1			
	T3-400 (8464)	430	2.2	0.4	8.7	6.0	0.6	12.4
	T3-1400 (8465)	1377	4.5	0.6	10.5	5.4	0.6	10.7

Tab.3 Overview of pigment data. Measurements included total chlorin concentrations, their derived degradation index, the Chlorin Index (CI), and chlorophyll *a* and phytoplankton pigments.

			surface			*fluff*				*Chlorophyll degradation products*		*diatoms*	*dinofla-gellates*	*Cocco-litho-phorides*
	Station	**[m]**	**Total Chlorin [µg g^{-1}]**	**Total Chlorin [µg gTOC^{-1}]**	**Chlorin Index (CI)**	**Total Chlorin [µg g^{-1}]**	**Total Chlorin [µg gTOC^{-1}]**	**Chlorin Index (CI)**	**Chlorophyll *a* [µg g^{-1}]**	**Pheophorbide *a* [µg g^{-1}]**	**Pheophytin *a* [µg g^{-1}]**	**Fuco-xanthin [µg g^{-1}]**	**Peridinin [µg g^{-1}]**	**Diadino-xanthin [µg g^{-1}]**
20°S	226820	424	44.6	1250.1	0.77				0.36	0.006	0.60	0.13	0.28	0.013
21°S	226750	77	936.6	15155.5	0.50				3.21	0.014	10.16	7.06	1.40	0.101
22°S	mpi-3	70	242.0	8798.9	0.49									
23°S	1	25	9.8	154.5	0.30									
	2	40	26.5	641.6	0.46									
	184-3	44	329.8	6758.8	0.78				1.99	0.000	8.02	0.67	0.10	0.106
	20	104	8.5		0.26				3.33					
	mpi-5	114	494.9	11483.4	0.64									
	226680	110	1087.7	17831.5	0.58				10.43	0.128	33.68	17.29	8.21	0.226
	187-3	130	484.5	8691.2	0.82				4.06	0.104	13.82	6.23	0.20	0.117
	4	100	16.0	114.0	0.52				6.29					
	188-3	143	304.4	2965.0	0.87				2.35	0.985	6.43	1.36	0.32	0.032
	212-3	152	99.9	2139.3	0.84				0.47	0.036	0.81	0.25	0.06	0.019
	7	200	19.0	170.2	0.68				3.78					
	213-3	234	71.8	1460.5	0.83				0.57	0.028	0.68	0.00	0.11	0.006
	191-5	360	35.1	1142.1	0.83				0.24	0.006	0.48	0.00	0.05	0.010
	8	300	13.5	272.1	0.84				2.68					
	215	319												
	9	400	11.8	600.8	0.87				2.35					
	173-2	591	27.2	736.7	0.85				0.24	0.004	0.37	0.00	0.03	0.003
	8482-2	706	27.2	653.4	0.83				0.26	0.003	0.42	0.00	0.00	0.004
	8483-1	805	26.3	767.3	0.83				0.25	0.003	0.37	0.00	0.05	0.002
	8484-3	953	24.9	691.0	0.81	38.7		0.77	0.15	0.001	0.24	0.00	0.05	0.002
	11	1000	11.3	356.4	0.76				4.44					
	8498-2	1439	20.4	571.6	0.82				0.19	0.001	0.38	0.00	0.08	0.001
	226700	1807	15.4	748.6	0.72				1.49	0.001	0.43	0.00	0.01	0.004
	176-3	2073	11.4	674.6	0.76				0.06	0.0002	0.14	0.00	0.00	0.000

Tab.3 continued

			surface			*fluff*			*Chlorophyll degradation products*			*diatoms*	*dinoflagellates*	*Coccolithophorides*
	Station	**[m]**	**Total Chlorin [µg g^{-1}]**	**Total Chlorin [µg gTOC^{-1}]**	**Chlorin Index (CI)**	**Total Chlorin [µg g^{-1}]**	**Total Chlorin [µg gTOC^{-1}]**	**Chlorin Index (CI)**	**Chlorophyll *a* [µg g^{-1}]**	**Phaeo-phorbide *a* [µg g^{-1}]**	**Phaeophy- tin *a* [µg g^{-1}]**	**Fuco- xanthin [µg g^{-1}]**	**Peridinin [µg g^{-1}]**	**Diadino- xanthin [µg g^{-1}]**
24°S	ww24005	85	896.3	17373.3	0.68	891.6	13080.6	0.62						
	ww24040	256	43.9	975.3	0.76	89.4	2496.5	0.79						
	ww24060	309	23.1	847.3	0.77	35.4	908.2	0.67						
	T1-800 (8419)	834	28.7	814.8	0.80	27.6	587.6	0.78						
	T1-1000 (8418)	1006	19.7	492.8	0.82									
	T1-1000	1003	33.5	690.9	0.77	31.3	590.7	0.76						
	T1-1200 (8421)	1205	22.3	546.0	0.80	34.0	754.6	0.79						
	ww24080	1040	26.2	614.0	0.75	30.2	717.9	0.73						
	T1-1500 (8424)	1519	7.0		0.78	16.2	292.5	0.77						
	T1-1500	1512	13.8	383.4	0.73	22.3	556.7	0.78						
	T1-2000 (8422/25)	1997	4.7	302.4	0.76	4.8		0.76						
25°S	MPI-8	97	636.7	15917.4	0.54	905.9	12030.7	0.51	4.45	0.055	30.08	6.40	5.76	0.020
	T2-360 (8429/28)	362	42.1	598.9	0.77	64.9	890.4	0.77	0.34	0.007	0.69	0.06	0.46	0.021
	T2-400 (8452)	388	56.6	1022.6	0.78	55.7	1031.4	0.77	0.29	0.009	0.65	0.10	0.36	0.020
	T2-600 (8449/94)	605	79.6	1148.4	0.76	88.2	1328.5	0.78	3.81	0.013	1.55	0.00	0.86	0.022
	T2-600	646	75.9	959.0	0.71	103.9	1294.6	0.66						
	T2-800 (8448)	806	100.7	1228.1	0.77	142.9	1907.1	0.80	0.44	0.018	2.10	0.00	1.08	0.018
	T2-1000 (8451)	1028	42.1	530.9	0.75	57.7	740.2	0.73	0.20	0.024	1.22	n.v.	0.82	0.011
	T2-1300	1363	57.6	762.0	0.73	84.3	1029.4	0.67	0.79	0.000	3.66	0.04	0.60	0.010
	T2-1500 (8455)	1503	24.9	330.7	0.77	51.4	693.3	0.77	0.29	0.014	0.67	0.00	0.40	0.005
	T2-2000	2103	21.7	532.0	0.77	26.0	612.1	0.74						
	T2-2300 (8462)	2289	10.4	283.1	0.77	21.0	635.6	0.75	1.40	0.002	0.39	0.00	0.19	0.003
	T2-2500 (8470)	2470	15.9	442.8	0.73	11.7	400.8	0.73	1.05	0.001	0.16	0.00	0.11	0.004
26°S	MPI-6	105	59.9	1419.9	0.75				0.53	0.000	3.47	0.23	0.23	0.018
	ww26010	118	113.3	3724.6	0.80	827.0	15847.4	0.71						
	ww26030	199	37.2	3452.8	0.91	127.7		0.96	0.83	0.004	0.85	0.11	0.51	0.030
	T3-400 (8464)	430	10.9	495.5	0.83	49.3	817.9	0.77	1.23	0.002	0.22	0.00	0.25	0.007
	T3-1400 (8465)	1377	16.8	375.1	0.81	48.5	906.9	0.83	0.18	0.004	0.54	0.00	0.30	0.000

Tab.4 Proteins have been measured to assess THAA content, surface percentages of sedimentary amino aid carbon and nitrogen, THAA-%C and THAA-%N. Protein organic matter composition was determined with PCA and resulting Degradation Index (DI) values are indicated as DI (PCA).

			surface				***fluff***			
	Station	**[m]**	**THAA [mg g^{-1}]**	**DI (PCA)**	**THAA%C**	**THAA %N**	**THAA [mg g^{-1}]**	**DI (PCA)**	**THAA %C**	**THAA %N**
20°S	226820	424	12.7	1.05	16.6	45.3				
21°S	226750	77	21.8	2.56	16.5	39.7				
22°S	mpi-3	70	16.3	3.22	27.7	53.6				
23°S	1	25								
	2	40								
	184-3	44	25.85	1.18	24.7	53.7				
	20	104								
	mpi-5	114	21.4	4.14	23.1	54.8				
	226680	110	43.6	4.01	33.4	75.2				
	187-3	130	28.95	1.53	24.2	52.0				
	4	100								
	188-3	143	42.40	0.89	19.3	44.8				
	212-3	152	16.55	0.60	16.6	43.3				
	7	200								
	213-3	234	14.10	-1.21	13.4	37.0				
	191-5	360	11.67	-0.81	17.7	45.1				
	8	300								
	215	319								
	9	400								
	173-2	591	13.4	-0.84	16.9	44.1				
	8482-2	706	11.79	-1.3	13.2	35.8				
	8483-1	805	12.91	-0.7	17.6	43.4				
	8484-3 = 8414	953	10.33	-1.32	13.4	36.0	14.5	0.35		-0.14
	11	1000								
	8498-2	1439	10.74	-0.65	14.1	36.7				
	226700	1807	8.9	-1.06	20.2	54.9				
	176-3	2073	5.63	-1.74	15.6	37.0				

Tab.4 continued

			surface				***fluff***			
	Station	**[m]**	**THAA [mg g^{-1}]**	**DI (PCA)**	**THAA %C**	**THAA %N**	**THAA [mg g^{-1}]**	**DI (PCA)**	**THAA %C**	**THAA %N**
24°S	ww24005	85	45.4	2.59	41.1	95.7	32.9	1.72	22.5	51.0
	ww24040	256	20.9	0.10	21.7	60.8	22.4	0.84	29.1	84.7
	ww24060	309	10.1	-0.04	17.3	53.4	9.9	0.09	11.9	34.1
	T1-800 (8419)	834					17.0	0.34		
	T1-1000 (8418)	1006	12.4	-0.27	14.5	45.2				
	T1-1000	1003					14.1	0.27		
	ww24080	1040	16.42	-0.52	18.8	47.9	15.1	-0.04	15.7	48.5
	T1-1200 (8421)	1205	14.6	-0.66	16.0	44.4	18.0	0.05	20.0	50.0
	T1-1500 (8424)	1500	13.4	-1.47		48.8	13.8	-0.16		52.3
	T1-1500	1512					10.2	-0.90		
	T1-2000 (8422/25)	1997	5.3	-2.25	15.8	40.8	7.7	-1.92		46.5
25°S	MPI-8	97	21.8	2.92	25.5	31.8	21.8	2.31	13.5	56.1
	T2-360 (8429/28)	362	29.5	2.07	19.6	45.0	26.8	-0.13	17.2	51.2
	T2-400 (8452)	388	18.2	-5.80	15.4	36.8	21.6	0.20	18.7	57.1
	T2-600 (8449/94)	605	18.8	0.44	12.7	39.2	27.8	-0.51	19.6	57.0
	T2-600	646	34.63	-1.16	20.4	56.5	28.5	1.05	16.6	44.6
	T2-800 (8448)	806	29.6	-0.21	16.9	47.1	34.7	0.90	21.6	64.0
	T2-1000 (8451)	1028	24.2	0.05	14.2	41.4	27.1	0.71	16.2	47.8
	T2-1300	1363	15.85	-1.60	9.8	26.2	26.0	0.31	14.8	39.9
	T2-1500 (8455)	1503	21.1	0.33	13.0	38.4	26.2	-1.46	16.5	48.3
	T2-2000	2103	27.14	-1.11	31.0	85.8	12.4	-0.40	13.6	36.5
	T2-2300 (8462)	2289	14.1	0.45	18.0	42.6	13.3	-1.26	18.8	50.5
	T2-2500 (8470)	2470	11.2	-1.44	14.5	35.9	12.3	-1.59	19.8	53.7
26°S	MPI-6	105	14.1	-0.90	15.6	56.9				
	ww26010	118	11.21	-0.79	17.2	40.9	13.5	1.17	12.1	30.7
	ww26030	199	6.65	4.71	28.8	70.2	13.2	1.79		
	T3-400 (8464)	430	9.9	-1.95	20.9	38.4	19.6	0.73	15.1	50.3
	T3-1400 (8465)	1377	19.1	-2.44	19.9	44.2	20.8	-0.63	18.1	51.8

Chapter 4

Organic carbon reactivity of Arctic sediments (Spitzbergen Shelf) characterized by molecular degradation indices of two major carbon pools, pigments and proteins

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Abstract

Molecular productivity proxies, total chlorins and proteins, and their molecular degradation state have been applied to Arctic shelf and fjord sediments and compared to the extent of benthic microbial mineralisation. Both proxies implied a close coupling of seasonal changing primary productivity due to hydrographic conditions and benthic mineralisation. Largest contents of slightly refractive chlorin organic matter and high benthic mineralisation rates were related to earlier ice retreat influenced by warm Atlantic water inflow and thus annually larger carbon supply at the South and Northwest coast. Northeast of Spitzbergen, which is affected by cold Arctic water, later ice retreat retarded primary productivity as reflected by lower chlorin and protein concentrations.

Organic matter content and degradation state of both pools revealed a slightly different pattern of benthic mineralisation. Whereas high concentrations of refractive chlorins were strongly correlated with microbial sulfate reduction at locations of high organic matter supply, e.g. along the marginal ice zone (MIZ) and the Northwest coast, low amounts of very fresh chlorin organic matter was related to low rates of sulfate reduction at sites of generally low carbon supply, such as the ice-covered regions.

Regional distributions of THAA did not reflect seasonality but apparently pictured later stages of organic matter degradation. As major THAA amounts occurred in sediments affected by annually high carbon supply (MIZ, Northwest) but decreased towards the northern, permanently ice-covered regions, suggested that protein contents track the long-term carbon supply at the MIZ. Down core changes of THAA in sediment profiles at ice-covered sites as well implied later degradation stages.

Introduction

Permanently cold temperatures and seasonal variability of organic matter flux to the sea floor affect benthic microbial mineralisation in sediments of the Arctic Ocean. Primary production depends on the short ice-free periods in the summer when sufficient light is available for photosynthesis (Wassmann and Slagstad, 1993). Productivity around Spitzbergen is linked to hydrographic conditions determined by two major current systems, warm Atlantic water from the northward flowing West Spitzbergen Current at the southwest coast and cold polar water from the Arctic Ocean that affect Northeast Spitzbergen. Warm and nutrient-rich water results in earlier ice-melt, therefore earlier primary production and sedimentation of biogenic material at the South coast (Vandieken, 2005). In the northeast ice retreat still continues during the summer leading to a later onset of primary productivity and annually lower sedimentation of organic material (Wassmann et al., 2002; Hulth et al., 1996).

Ice retreat and subsequent stratification of ice-free waters result in increased vertical mixing of the water column, enhanced primary productivity, and pelagic retention of fresh and export of degraded organic matter to the sediments (Reigstad et al., 2002). Arctic primary productivity by phytoplankton blooms associated with the ice edge can account for a large annual production of 50 to 150 g C m^{-2} (Falk-Petersen et al, 1990; Olli et al., 2002). Due to microbial degradation of sinking organic particles in the water column (biological pump) and in benthic mineralisation processes, the molecular composition of organic material (its reactivity) is changed. Earlier work in the study area focused on primary productivity estimates and pelagic processes related with seasonal variability of sea-ice extent and oceanographic conditions (Sakshaug, 1997; Kristiansen et al., 1994; Engelsen et al., 2002; Falk-Petersen et al., 2000). Benthic mineralisation was studied rather in terms its diversity and relative contribution of oxic and anoxic carbon oxidation pathways in various fjord sediments of Spitzbergen (Glud et al., 1998; Kostka et al., 1999; Hulth et al., 1993, Jørgensen et al., 2003). Major anoxic carbon degradation processes were microbial sulfate reduction, Fe and Mn reduction and relative benthic activity suggested that microbial communities were not limited by permanently cold temperatures but rather responded to organic carbon supply and availability (Glud et al., 1998; Kostka et al., 1999; Vandieken et al., 2006). Hulth et al. (1996, 1994) proposed that organic matter reactivity in Spitzbergen sediments would be primarily related to water depth and carbon concentration. They defined organic matter reactivity as the total sediment oxygen consumption rate normalized to the organic carbon content of surface sediments. According to Hulth et al. (1996) differences of organic matter reactivity reflected hydrographic conditions such as ice cover and organic matter production and import. However, occasional terrestrial organic matter input observed in Spitzbergen sediments could not be separated from overall biological activity with this approach.

Hulth' approach was based on the aerobic degradability of TOC but did not consider the degradation state and thus availability of organic material. Moreover, Kostka et al. (1999) could show that sulfate reduction may dominate aerobic decomposition of organic carbon in southeastern fjord sediments.

In this study we present for the first time a regional assessment of Arctic primary productivity, benthic carbon mineralisation and molecular organic matter fluxes. Molecular organic carbon pools, total chlorins and proteins, will be quantified and the degradability (reactivity) of each pool determined by the Chlorin Index (Schubert et al., 2002) and a protein-based Degradation Index (Dauwe et al., 1999). These indices were previously applied to characterize organic-rich sediments of the Benguela Upwelling System (chapters 2 and 3; Schubert et al., 2002), the Peru and Chile upwelling regions (Niggemann et al., 2005) as well as the Arabian Sea (Schubert et al., 2005).

This study was part of the Norwegian CABANERA project (Carbon flux and ecosystem feed back in the northern Barents Sea in an era of climate change) with its principal aim to assess how global warming might change Arctic Ocean primary productivity and organic carbon flux. Polar regions, including the European Artic, are sensitive indicators of global climate changes. Global warming will broaden the extent of the Marginal Ice Zone (MIZ) and may reduce future ice thickness by 20 to 80% during winter and summer, respectively (Johannessen et al, 2002). This will significantly alter the Arctic organic carbon cycle and thus the extent and composition of benthic mineralisation processes.

With the objective to assess the role of organic carbon availability to seasonally variable benthic activity in Spitzbergen shelf sediments, two major organic carbon pool, pigments and proteins, and their related degradation indices, the CI and DI, will be estimated and compared to aerobic and anaerobic benthic mineralisation rates, TOU and SRR, in sediments of the Marginal Ice Zone (MIZ), beneath the ice pack and in ice-free fjord sediments along the west coast of Spitzbergen.

Methods

Study area and site characteristics

Samples from the eastern Spitzbergen shelf were taken during the first cruise with RV Jan Mayen within the scope of the CABANERA project (see also www.nfh.uit.no/cabanera) in July 2003 July/August 2004. Stations I, IV, II and III were located on a northern transect southeast of Spitzbergen. The transect crossed the seasonal highly-productive Marginal Ice Zone (MIZ) (phytoplankton bloom) and open waters close to the retreating ice-edge (I), the closed ice pack (IV,II,III), the northern MIZ with open water (XIII,VII) and melting ice floes (X) (Fig.1). The southern transect was influenced by both, warm Atlantic and colder Arctic waters; the northern stations were mainly exposed to cold water from the Arctic Ocean (see Tab.1). Station V represented a Fjord site. Fjord sediments from the Northwest coast of Spitzbergen were sampled during an expedition in July/August 2003 with MS Farm and crew. Coastal sites were affected by northward flowing warm Atlantic water and several fjords were located close to glaciers.

Sample recovery

Undisturbed sediment samples were recovered with a multiple corer and processed immediately. The sediment texture and colour was characteristic of sites. At station I, sediment was of black-brown colour, clayey texture and contained worm tubes and clams. Stations IV, II and III were characterized by an upper brown-red layer (0-5/10cm) followed by olive-grey sediment, partly containing empty worm tubes. At Station III, a thick layer of fecal pellets was observed at 5-7 cm depth. There was no fluffy material on top of cores. Extruded sediments were transferred into glass vials and stored in the dark at -20 °C until further processing.

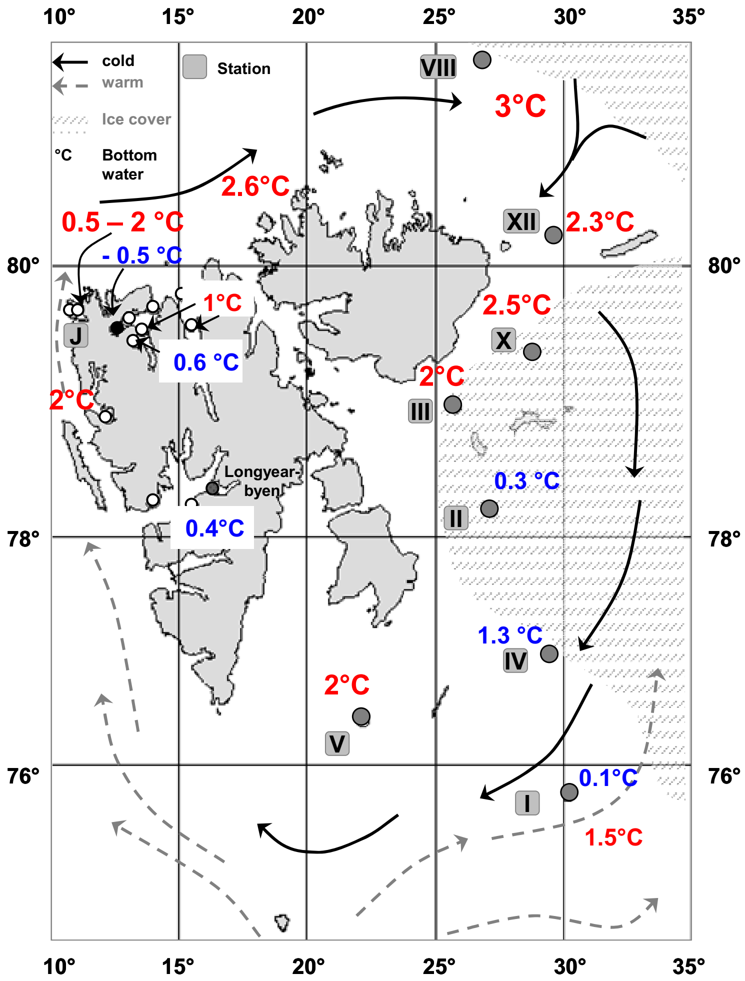


Fig.1 Map of the study area: stations, oceanographic features (including bottom water temperatures during cruises in 2003/04; hatched: approximate ice cover). Arrows represent a simplified illustration of Arctic polar and North Atlantic currents. Stations I-V were sampled during the CABANERA cruise with RV Jan Mayen in summer 2003, stations X, XII and VIII in 2004. All West Spitzbergen stations (fjords) were sampled with RV Farm in summer 2003.

Elemental composition (TOC, TIC)

We determined total carbon (TC) and nitrogen (TN) contents from freeze-dried homogenized samples with a Fisons NA 1500 (Series 2) Elemental Analyzer. Total inorganic carbon (TIC) was analysed by coulometric titration using a TIC autoanalyser CM5240 Orbis BV. The total organic carbon content (TOC) was calculated by subtracting TIC from TC concentrations. Part of the samples were pretreated with HCL and then analyzed for their TOC content likewise using a Fisons NA 1500 Elemental Analyzer.

Pigments (Chlorins and CI; Chlorophyll a and phytoplankton pigments)

Total Chlorin concentrations and its related degradation state indicator, the Chlorin Index (CI), were determined following Schubert et al. (2005) and as described in chapter 2. Total chlorins were extracted from ~20mg freeze-dried samples by threefold ultra sonication and centrifugation in HPLC-grade acetone. Samples were cooled with ice and kept light-protected to prevent chlorin decomposition. Extracts were measured immediately after extraction at a Hitachi F-2000 Fluorimeter at excitation wavelength 428 nm and emission wavelength 671 nm. Chlorophyll *a* (SIGMA) was transformed to the chlorin phaeophytin *a* through acidification using ~ 100 µl hydrochloric acid and used as a standard for total chlorin concentrations.

Sediment extracts were acidified just as the standard and remeasured. The derived Chlorin Index according to Schubert et al. (2002) is defined as the ratio of the fluorescence units of the acidified sample over the original extract (Equ.1). Chlorin index values are on a scale from 0.2 (fresh material) to 1 (refractory organic matter).

$$\mathrm{CI} = \text{fluorescent intensities}_{\text{acidified sample}} / \text{fluorescent intensities}_{\text{original sample}} \qquad (1)$$

Chlorophyll and phytoplankton pigments were extracted from ~ 2g freeze-dried sediments following Buffan-Dubau and Carman (2000). Chlorophyll *a*, pheophorbide *a*, pheophytin *a* and algal pigments were analysed with a reversed-phased HPLC system and a protocol as described in Wright et al. (1991). Original sample aliquots of 100 µl were injected into a Waters HPLC (Waters 2690 Separation Module) equipped with a photo diode array detector (PDA 996). Pigment detection was performed at 430.3 nm with an additional PDA spectrum from 350-800 nm recorded every second.

Proteins (THAA and DI)

Total hydrolysable amino acids (THAA) were analysed following a method by Dauwe and Middelburg (1998), and as described in chapter 1. Sample aliquots of 100µl were reacted with fluorescent agent, *o*-phtaldialdehyde (OPA) and analysed at excitation/emission wavelengths 340/455 nm with a Hitachi F-2000 Fluorometer.

To calculate the Degradation Index (DI), the concentrations of 17 individual amino acids were determined via pre-column *o*-phtaldialdehyde derivatisation (Hill et al., 1979; Lindroth and Mopper, 1979) including an internal standard (SIGMA AA-S-18) from 100 ml aliquots of neutralized hydrolysate. Individual amino acids were separated by reverse-phased HPLC with a heated C_{18} – column (30°C) and binary solvent system with subsequent fluorescence detection.

A principal component analysis (PCA) was performed to determine the organic matter degradation state, which is based on the sediment amino acid composition and the selective degradation pattern of THAA. This method standardizes mole percentages of individual amino acids, which results in individual site scores, termed degradation index (DI) (Dauwe and Middelburg, 1998; Meglen, 1992). The DI as defined by Dauwe et al. (1999) varies between values >1 to ≥ 2 (labile matter, fresh phytodetritus) to values < -1 or lower (strongly degraded, refractory organic matter).

Sulfate reduction rates

Sulfate reduction rate measurements were measured in three parallel cores of 3 cm diameter each using the $^{35}SO_4^{2-}$ whole-core injection technique by Jørgensen (1978). Subcores were injected at one cm intervals with 5 µl of 100 kBq ml^{-1} $^{35}SO_4^{2-}$ tracer (Amersham) at 4°C in the dark for 8-10 hours. Following incubation microbial activity of sediment samples was stopped with 20% ZnAc-solution and storage at -20°C. Total reduced inorganic sulfur was analyzed by cold chromium distillation and calculations of sulfate reduction rates according to Kallmeyer et al. (2004).

Results

Sulfate reduction rates (SRR)

Areal sulfate reduction rates, SRR, (integrated over 15 cm) varied between 0.02–7 mmol m^{-2} d^{-1} (Tab.2+4). Rates did not exceed 0.5 mmol m^{-2} d^{-1} in sediments along the southeastern transect. Higher SRR of 0.4-0.5 mmol m^{-2} d^{-1} occurred at the southern MIZ (I) and in the North (XII). Relatively high rates of 2 mmol m^{-2} d^{-1} were measured at fjord station V.

In Northwest Spitzbergen fjord sediments (Tab.2+7, Fig.10) we measured by one order of magnitude higher areal sulfate reduction rates from 0.5 to 7 mmol m^{-2} d^{-1} (Wood-, Bock- and Liefdjefjord) (Fig.8). At the coast, a maximum rate of ~2.6 mmol m^{-2} d^{-1} was measured (station J).

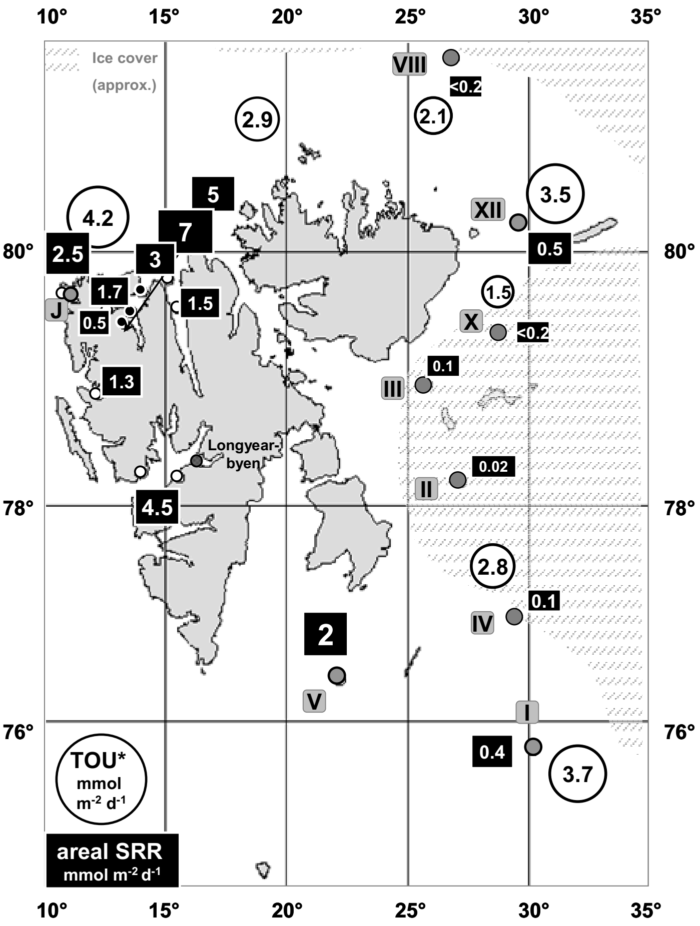
Northwest Spitzbergen sediments were characterized by two major sulfate reduction zones, at 4-5 cm and at approximately 10 cm sediment depth (Fig.8+10). Peak rates in the upper zone were mostly higher than in the lower sulfate reduction zone and overall varied between 0.2 – 145 nmol cm^{-3} d^{-1} (Tab.7).

Areal sulfate reduction rates in the southeast varied between 0.2 and 2 mmol m^{-2} d^{-1}. Largest SRR occurred at station V (Southeast) that were similar to the northwest coast. SRR at the MIZ and ice covered stations were lower with ~0.5 and <0.2 mmol m^{-2} d^{-1}, respectively (Fig.2). Maximum sulfate reduction depth shifted from ~ 5 cm at MIZ to ~10 cm at ice-covered stations (Fig.5).

TOC and C/N

Total organic carbon (TOC) content was between 1.2 and 3.3 % in all sediments and C/N values ranged from 8 – 19 (Tab.3+6). Largest surface TOC content and C/N ratio were measured at station V (3 % TOC, C/N of 11), I and IV (both 2.3 %, C/N of 10-11) that decreased (1.3-1.6 %, C/N of 9) at the northern stations (Fig.6a+b).

Sediment profiles of TOC concentrations and C/N values showed three major trends. TOC and C/N remained relatively constant as at station J (Smeerenburgfjord) at a TOC content of ~1.5 % and with low C/N values of ~ 8.5 (Fig.8). A graduate decrease of TOC content but increase of C/N values was observed at fjord station V and the southern MIZ (Station I) (TOC from 3.5 to ~ 2.5 %, ~2.5 to 1.5 % and C/N ~11 to 14, ~10 to 13 at V and I). A steep decline of TOC content and incline of C/N ratios that were constant at depth below ~5cm occurred at ice-covered stations and the northern MIZ. MIZ surface TOC content and C/N varied between 1.2-1.6 % and 12 and in cores from ~1- 1.6% and ~12-14. One exception were further increased C/N values of 19 at 15cm depth at station IV. Northern MIZ surface TOC was ~ 1.5 % (C/N ~9.5) and in cores ~ 1.3-1.5 % (C/N ~ 9.5-10).



* vanDieken V., Nickel M. (2003-2005)

Fig.2 Regional distribution of organic carbon mineralisation rates: Areal sulfate reduction rates (SRR) and total oxygen uptake (TOU) rates in mmol m^{-2} d^{-1}.

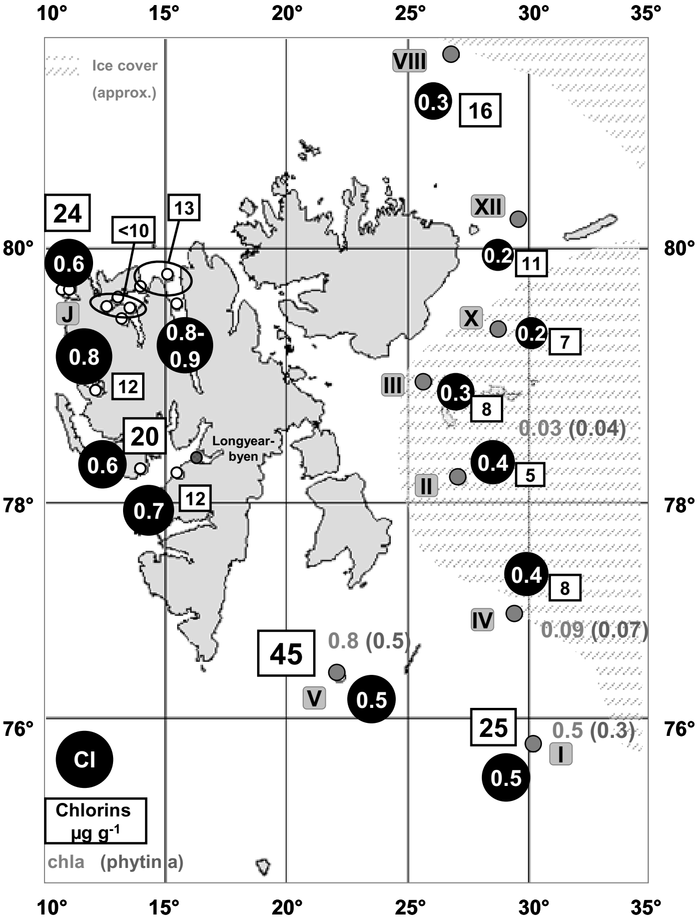


Fig.3 Regional distribution of total chlorin and pigment concentrations and the Chlorin Index. CI values are on a scale of 0 to 1.0 with fresh CI values of ~0.2-0.3 and highly refractive matter at values of ~ 0.8-1.0.

Pigments (chlorins, chlorophyll a) and CI

Surface sediments:

Total chlorin concentrations ranged 1.3–58 µg g^{-1} in cores (0-20cm) of northwest and southeastern Spitzbergen sediments (Tab.3+6). CI values varied between 0.13 - 1.00.

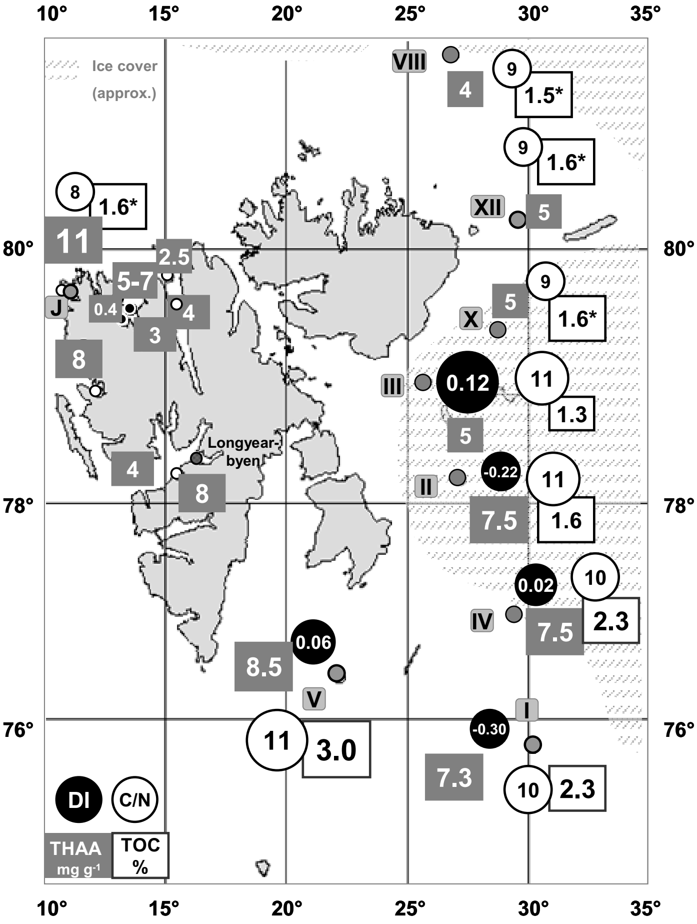
Largest surface chlorin concentrations of 45 and 25 µg g^{-1} occurred at station V and I (Fig.6d). Across the northern transect chlorin concentrations decreased below 10 µg g^{-1} (Stations II, III, IV, X) but were enhanced to 11-16 µg g^{-1} further north at stations XII and VIII. High chlorin amounts at the northwest coast were measured at station J (24 µg g^{-1}), DA (18 µg g^{-1}) and F (14 µg g^{-1}) (Fig.8, 9.a+b).

CI values in surface sediments were larger at the northwest coast (CI > 0.6) than in the southeast (CI of 0.2–0.5) (Fig.3). Across the northern transect, CI values declined from ~0.5 to 0.2-0.3. Stations DA, DB and J at the Northwest coast were characterized by CI values of 0.5-0.6. Fjord sites showed higher CI values between 0.7 and 1.

Sediment profiles: Southeast

Total chlorin concentrations were usually high at the sediment surface and decreased continuously with sediment depth at open-water stations (I, V, XII, VIII) (Fig.6.d). Chlorin amounts and sub surface decreases were lower and steeper (within ~5cm) at northernmost stations compared to the graduate decline at stations I and V. Low chlorin concentrations of 5-7 µg g^{-1} were observed at ice-covered stations IV, II and III. Station X (ice-floes) and I were characterized by subsurface peak amounts at 3.5cm (16 and ~ 30 µg g^{-1}).

CI profiles were similar to chlorin concentrations (Fig.6.e). In the south, surface CI values of ~ 0.5 gradually inclined with depth to 0.9-1.0 (I, V). Ice-covered and northernmost stations showed low surface CI values (~0.25-0.4 and ~ 0.2) that increased to CI values of ~ 0.8-1.0 at stations II, III and IV and constant CI values of ~ 0.7 at stations X and XII. CI values of ~ 0.5 in northernmost station VIII were the lowest constant values in subsurface sediments (>5cm) that only increased to ~ 0.8 at ~ 15cm.



* vanDieken V., Nickel M. (2003-2005)

Fig.4.a Regional distribution of protein (THAA) and total organic carbon concentration (TOC), the Degradation Index (DI) (calculated by PCA, according to Dauwe et al., 1999), and C/N ratio.

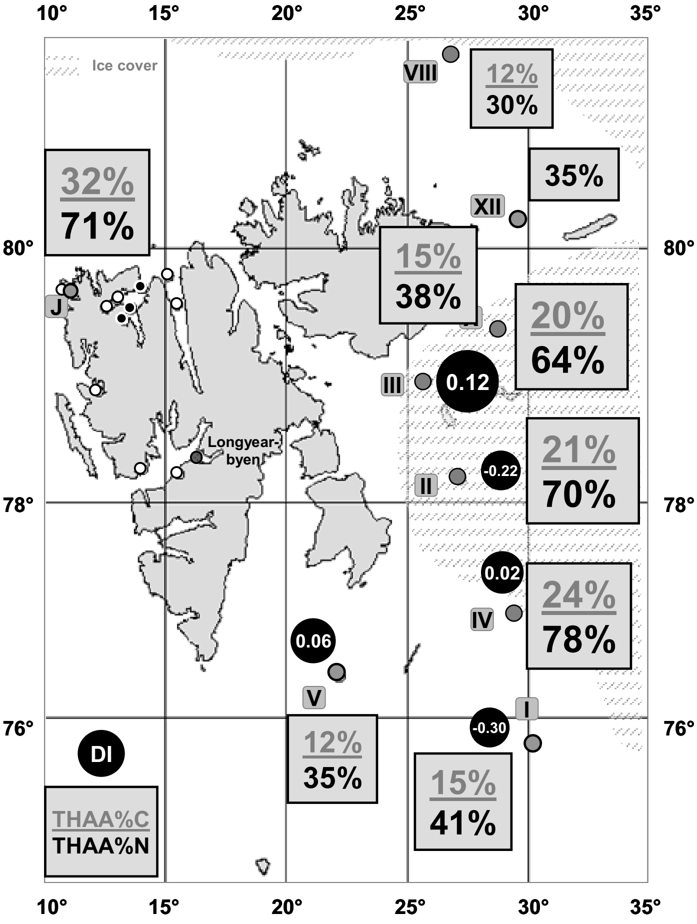


Fig.4.b Regional distribution of THAA content and its relative contribution to the TOC and TN pools, THAA%C and THAA%N, respectively.

Pigments

Pigment concentrations were consistent with total chlorin amounts and generally decreased from southeastern stations towards the north (Tab.5, Fig.3). Largest chlorophyll *a*, pheophytin *a* and pheophorbide *a* concentrations of 0.8, 0.5 and 0.007 µg g^{-1} were measured at station V. Pigment contents at station I were approximately half as much as concentrations of station V. Fucoxanthin concentrations (diatom pigment) were threefold enhanced at station I (0.061 µg g^{-1}) compared to station V (0.022µg g^{-1}) but could not be detected at stations II-IV.

THAA and DI

THAA concentrations varied between 0.4–14 mg g^{-1} (Tab.3+6). Surface sediment concentrations of THAA were lower at the Southeast (4-8 mg g^{-1}) than at the Northwest coast and northern fjords (0.4-11 mg g^{-1}) (Fig.4.a).THAA concentrations of 7-8 mg g^{-1} at stations V and I were comparable to the West Coast.

Across the southeastern transect (I, IV and II) THAA concentrations of 7-7.5 mg g^{-1} decreased to 4 mg g^{-1} in the north (VIII). Northwest coastal sites (J, DB) contained largest THAA amounts of 8-11 mg g^{-1} that were lower in fjord sediments (0.4–5 mg g^{-1}).

Degradation Index (DI) values between -2.4–1.6 were only calculated on the southeastern transect (Tab.3). Overall largest values of 0.12 occurred in the north. Stations IV and V showed positive DI values (0.02 and 0.06), Stations I and II showed slightly lower DI values of -0.3 and -0.22.

THAA concentrations at stations II and IV hardly varied down core (Fig.7.a). At stations III, V and I subsurface peak concentrations occurred that continuously decreased to constant amounts.

DI values in profiles were similar at the surface and below 10 cm sediment depth, except for station I, where the lowest DI value of -2.41 occurred (Fig.7.b). Largest variability of DI values occurred at station IV between 0.5 to 4 cm (DI of 0.02, -2.38, 0.74) and also at stations II, V and I.

The DI was not determined in Northwest Spitzbergen sediments. THAA concentrations were largest at station J of all fjord stations and will be described for major sites in the following section.

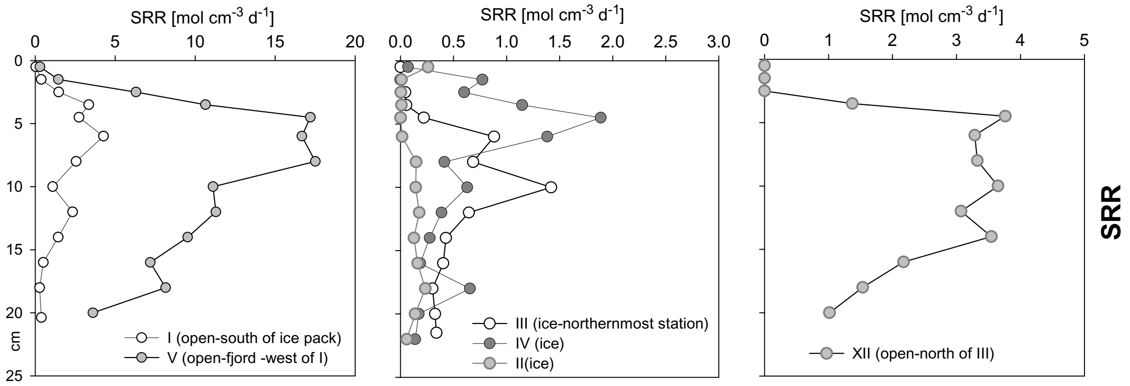


Fig.5 Southeast sediment profile (southern MIZ – ice cover – northern MIZ): Sulfate reduction rates (nmol cm^{-3} d^{-1}) were largest in fjord and southern MIZ sediments (stations V and I). At ice-covered stations SRR were by one order of magnitude lower and peak SR depth shifted deeper into the sediment. In the northern MIZ SRR were only measured at station XII and similar to ice-covered stations.

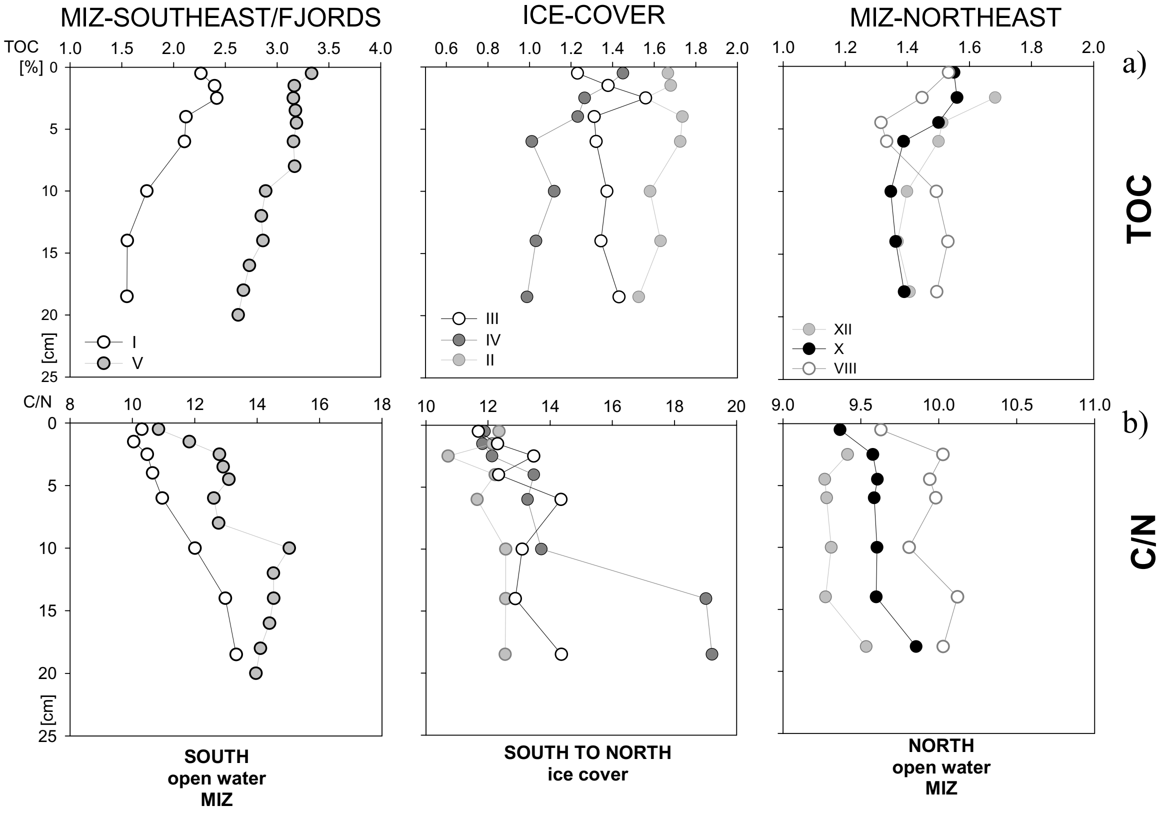


Fig.6 Southeast sediment profiles (southern MIZ – ice cover – northern MIZ) shown for total organic carbon content (TOC) (a) and C/N ratio (b). TOC content was largest in the southern MIZ and gradually decreased with depth compared to a steep decline of overall lower TOC concentration in the upper 5cm sediment layer in northern stations.

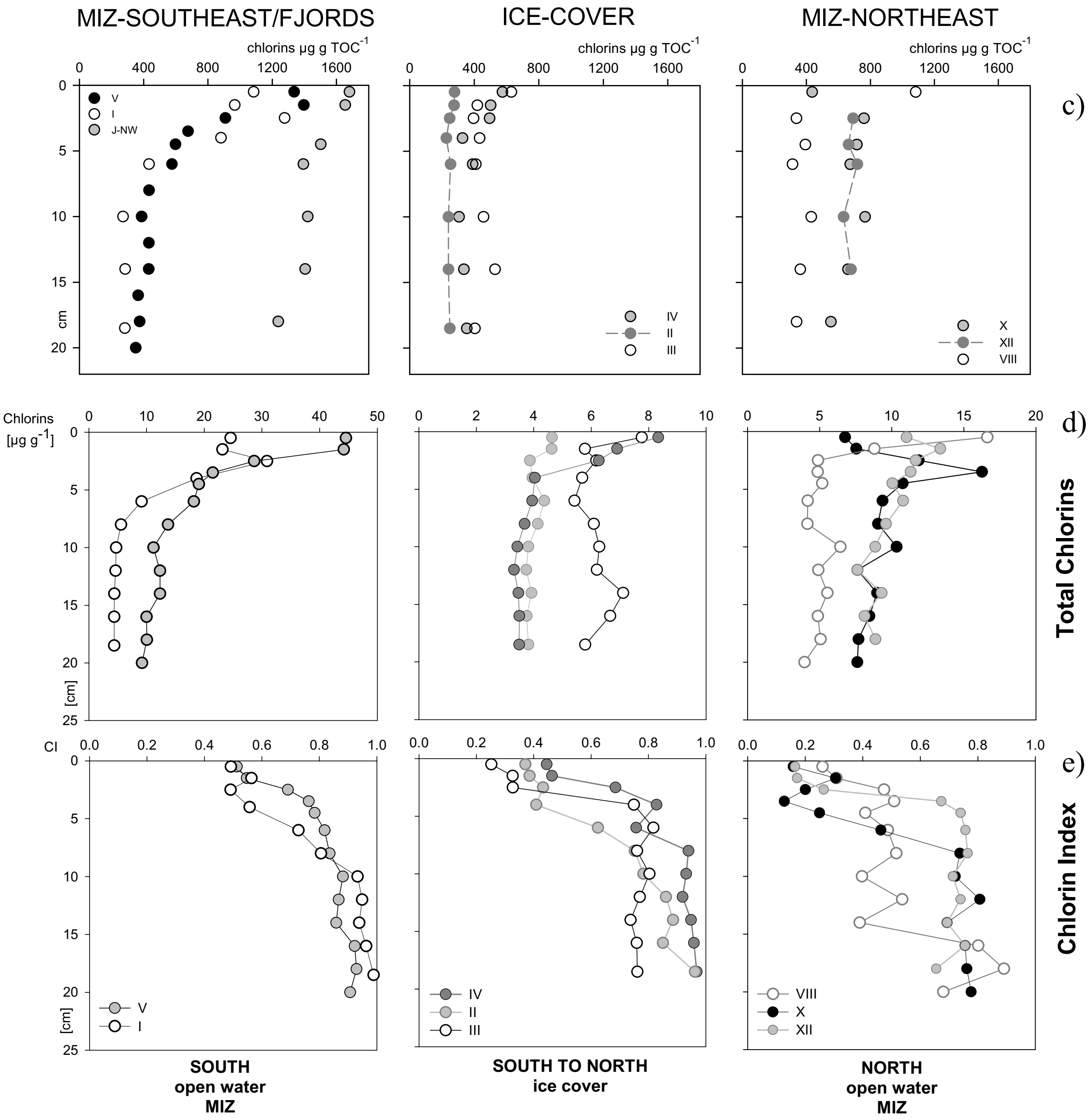


Fig.6 (continued) Southeast sediment profile (southern MIZ – ice cover – northern MIZ): Total chlorins normalized to TOC (chlorins µg g TOC^{-1}) (c), Total chlorins (d) and CI (e).

Largest contribution of chlorin carbon to TOC content occurred at northwest station J, the southern MIZ and station VIII at the northern MIZ, however TOC consisted of less chlorin carbon at ice covered stations. Total chlorin concentrations were largest at the southern MIZ stations and gradually decreased with depth getting steeper and close to the sediment surface in northern stations. Larger surface CI values were consistent with chlorins.

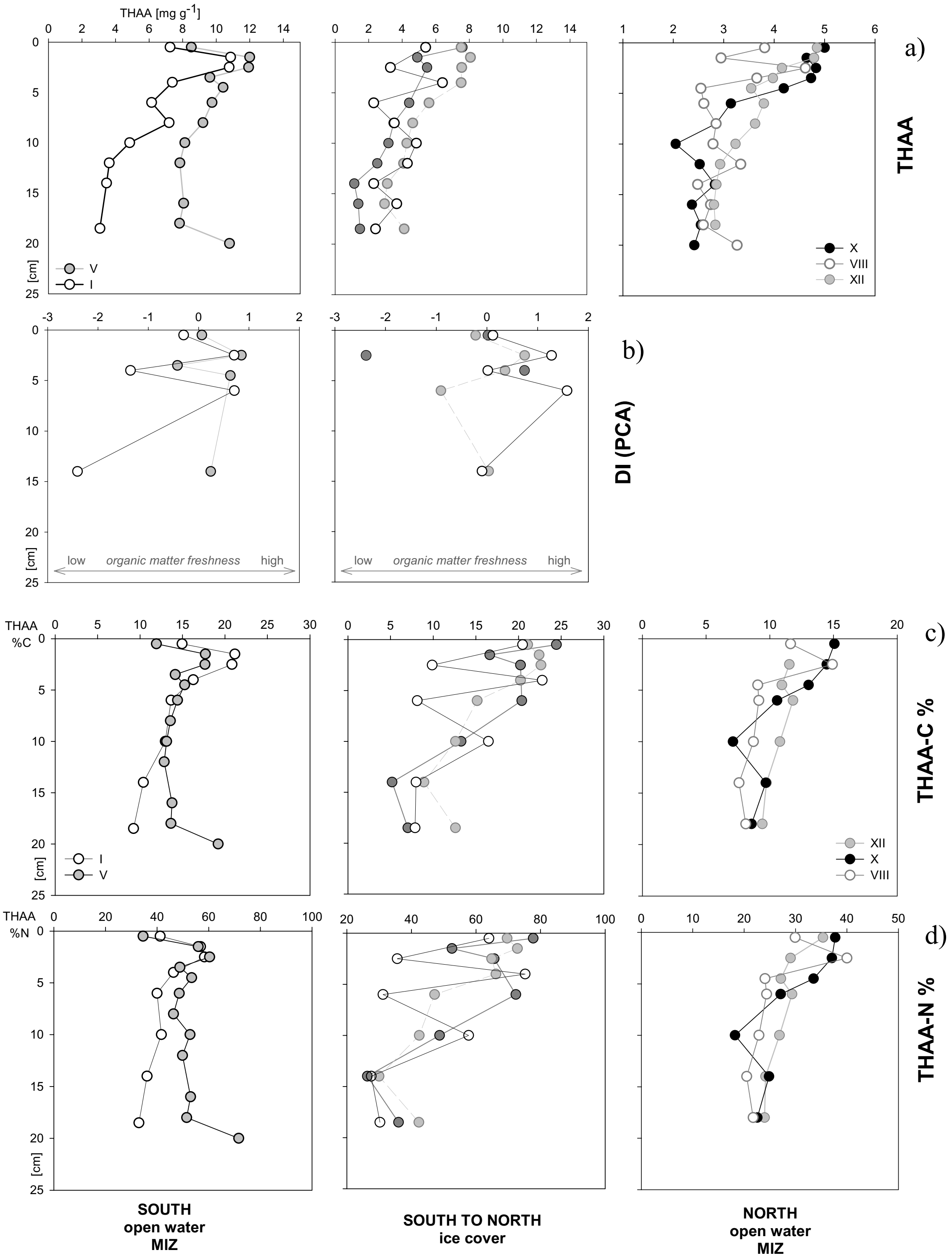


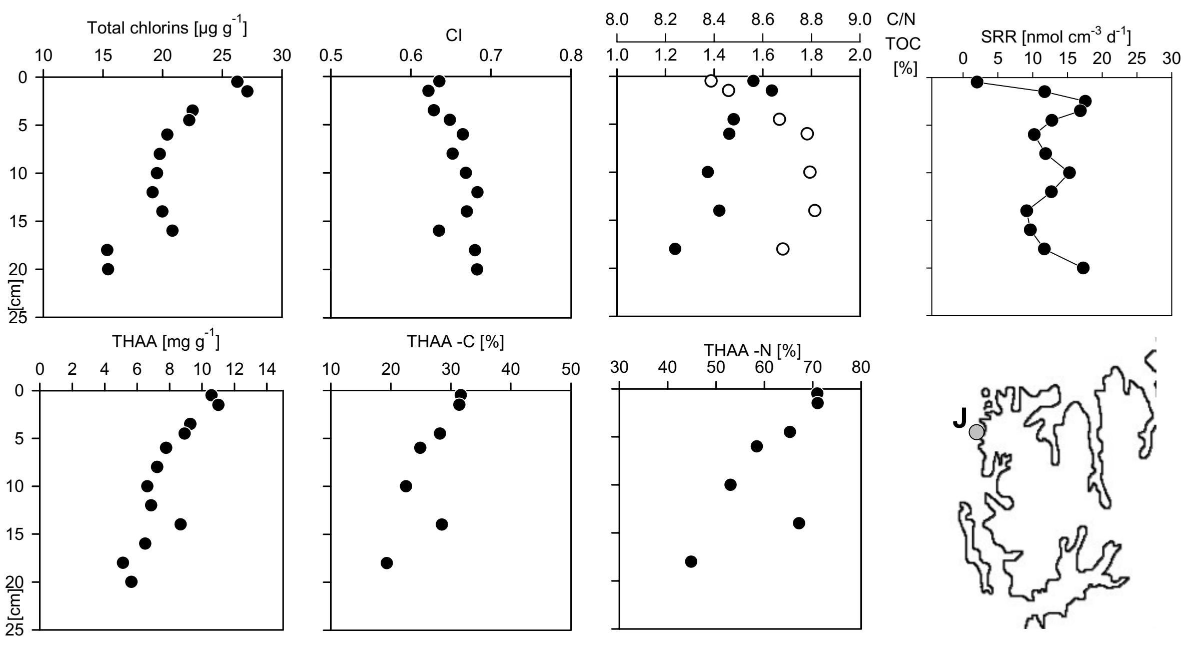
Fig.7 Southeast sediment profiles (southern MIZ – ice cover – northern MIZ) of THAA concentration (a) and DI (b), THAA%C and THAA%N (c,d). THAA concentrations followed that of chlorins in the southern MIZ but in contrast also decreased with depth at ice covered stations, indicating continuous degradation of THAA.

Northwest Coast

Smeerenburgfjord (Station J, DB) and Ymerbukta (Station DA) (Fig.7+9.b)

Station J and DB (215m and 28m water depth) exhibited highest total chlorin concentrations (12-27 µg g^{-1}) and lowest CI values of all fjord stations (CI of ~ 0.53-0.68) at the Northwest coast. Chlorin concentrations, THAA, THAA-%C and %N declined from surface to sediments at ~ 10cm depth (~ 27 – 20 µg g^{-1} chlorins, ~ 11 – 7 mg g^{-1} THAA, ~ 30 – 20 THAA-%C, ~ 70 – 50 THAA-%N), whereas CI values (~ 0.65), C/N ratios (~ 8.4-8.8) and the TOC content (1.6-1.4 %) hardly varied (Fig.7).

Station DA (Ymerbukta) at the Southwest coast close to Adventfjorden (Fig.1, Fig.9.b) contained slightly lower surface chlorin concentrations of ~18 µg g^{-1} and similar CI values of ~ 0.6. Chlorins decreased and the CI inclined within the upper surface layer (2cm) to ~ 5 µg g^{-1} and a CI of ~ 0.8. Likewise THAA amounts decreased (4 to 2 mg g^{-1}).



Station J - Northwest Coast Spitzbergen

Fig.8 Northwest Spitzbergen profiles: organic matter content and composition and microbial sulfate reduction rates (SRR) at Station J, Smeerenburgfjorden. This site was affected by warm Atlantic water .

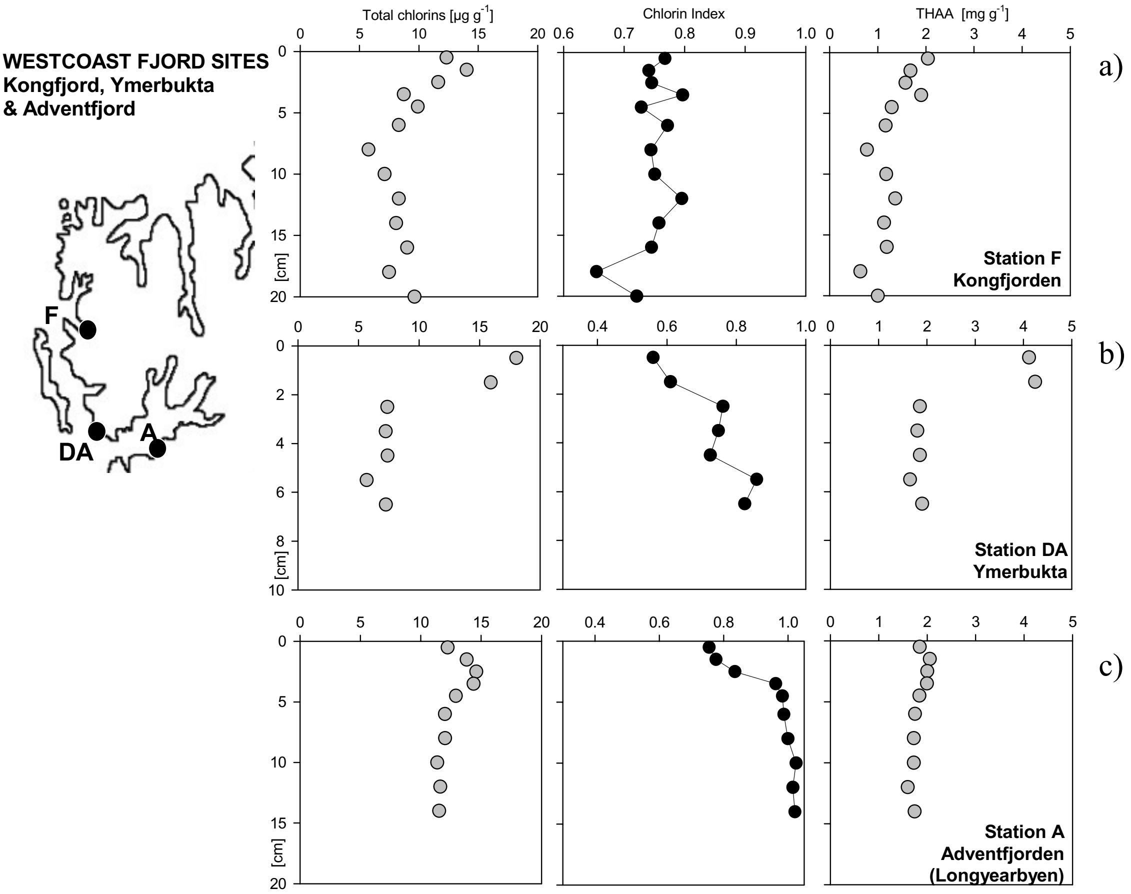


Fig.9 Westcoast Spitzbergen profiles of organic matter content and composition at fjord stations: Kongfjorden (F) (a), Ymerbukta (DA) (b) and Adventfjorden (A) (c).
High chlorin concentrations and organic matter of intermediate freshness are observed in upper sediments of the open coastal station DA that was affected by warm Atlantic water.

Liefdjefjord (Stations DK , 180m, DL, 100m)(Fig.10.a)

Total chlorin concentrations at station DK (~13 µg g^{-1}) were higher than at DL (~ 2µg g^{-1}). Whereas chlorin amounts at DL slightly increased, DK exhibited shallow subsurface peak amounts of ~ 15µg g^{-1} (~5 cm).

CI values of ~0.8 were similar at DL and DK. Opposite to DL, CI values of 1 in surface sediments declined to ~ 0.8 (0-3.5cm) at station DK. THAA content at DL (~ 0.5 mg g^{-1}) remained and at DK slightly decreased with depth (~ 3.5 – 2 mg g^{-1}). SRR was higher at station DK (2-16 nmol cm^{-3} d^{-1}) than at DL (0.2 – 7 nmol cm^{-3} d^{-1}).

Woodfjorden and Bockfjorden (Station DF, DI and DG, mudflat) (Fig.10.b)

Total chlorin amounts in Woodfjorden (DF) (11-15 µg g^{-1}) were larger than at Bockjforden (6-9 µg g^{-1}) and only slightly decreased within sediments. Surface CI values of ~ 0.8 and ~0.7 were larger at DF than DI and both increased to values of ~ 0.85 and ~ 0.8, respectively, within surface sediments (5cm). THAA amounts were nearly fourfold increased at station DF (~7 mg g^{-1}) compared to DI (~2mg g^{-1}) contents that were similar to station DK (Liefdjefjord). SRR was larger at the open station DF than at DI (areal SRR of 5 compared to 3 mmol cm^{-2} d^{-1}).

Particular high surface chlorin and THAA concentrations (58 µg g^{-1}, ~9 mg g^{-1}) were measured in a mudflat if compared to the deeper Bockfjorden sites. Surface CI values of ~0.6 increased to ~0.8 within 5 cm. Consistent with chlorins and CI and THAA contents subsurface SRR of ~ 100 nmol cm^{-3} d^{-1} declined to lowest rates of ~ 2 within that zone.

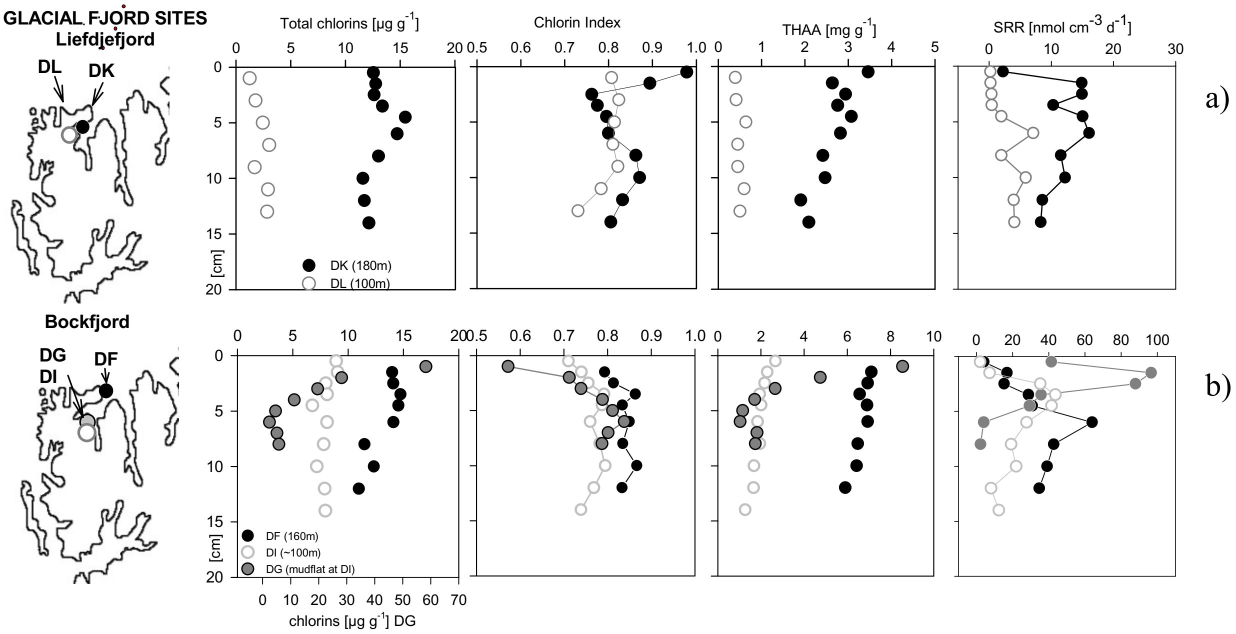


Fig.10 Northwest Spitzbergen profiles of organic matter content and composition and microbial sulfate reduction rates (SRR) in fjord stations: Liefdjefjorden (DK,DL) (a), Bockfjorden (DI/DG) and Woodfjorden (DF) (b). These sites were exposed to terrestrial organic matter input due to driftwood and glaciers. Chlorin content was in the medium range observed at all sites and organic matter freshness (CI values) at the lower end and mainly refractory. SRR varied but low rates were observed along with low chlorin concentrations.

Discussion

Regional variability of organic matter concentration, composition and benthic mineralization

Molecular organic matter concentration, its composition, and rates of benthic carbon mineralisation, all exhibited regional features that clearly reflected oceanographic conditions.

High chlorin concentrations in west coast sediments (20-24 µg g^{-1}) were comparable to the southeastern Marginal Ice Zone (MIZ) with intermediate amounts at the northeastern MIZ. Lowest chlorin contents <1-10 µg g^{-1} characterized stations still covered by the withdrawing ice shield.

The degradation state of chlorins revealed three major organic carbon types: very fresh chlorin material in the Northeast and at ice coverage (CI ~0.2-0.4), intermediate chlorin freshness at the southern MIZ and warm-water influenced south/northwest coast (CI ~0.5-0.6) and largely refractive chlorin carbon in fjord sediments (CI 0.8-1).

Benthic mineralisation corresponded to the supply of chlorin organic matter. Rates of total oxygen consumption as well as anoxic sulfate reduction rates were higher in Northwest Spitzbergen coastal sediments influenced by warm and nutrient-rich Atlantic water (up to 3°C) (1.3-4.5 mmol m^{-2} d^{-1} areal SRR) compared to the southeast coast (0.02-0.5mmol m^{-2} d^{-1} areal SRR), which was affected by cold polar water with Arctic summer temperatures below 0°C (Jørgensen et al., 2005; Tab.1, Fig.1+2).

Northwest Coast

Overall higher benthic activity at the west coast was reported in earlier studies according to enhanced sediment oxygen consumption rates and larger aerobic degradability of surface organic carbon content (Hulth et al., 1996; Glud et al., 1998). Vandieken et al. (2006) reported that half of total organic matter mineralisation in Northwest sediments (Station J) was performed by oxic degradation, followed by 34% of sulfate reduction and 13% by Fe (III) reduction. High chlorin amounts (20-25 µg g^{-1}) and consistent CI values of ~ 0.6 (Fig.8) suggested that enhanced sediment oxygen consumption and microbial sulfate reduction rates were driven by a constant large supply of slightly refractive organic matter. This was consistent with Hebbeln and Wefer (1991) who reported annually high particle fluxes of ~150 mg m^{-2} d^{-1} for the west coast due to increased organic carbon and opal fluxes. Warm Atlantic water

(>2°C) maintains a predominantly biogenic particle flux in winter, however the early ice retreat and melting (January to April) results in a sudden high sedimentation of ice-rafted lithogenic material that contributes 50% of the total annual particle flux. We suggest that enhanced chlorin accumulation was associated with enhanced sedimentation rates and sorption of chlorins to sedimentary matter. Physical protection of labile phytoplankton organic matter occurs as this easily sorbs onto fine-grained (clay) particles and thus reduces its oxygen exposure time during vertical transport (Keil et al., 1994, Satterberg et al., 2003; Ransom et al., 1998; Hartnett et al., 1998).

Molecular organic matter content and carbon freshness were both slightly lower in sediments from Liefdjefjord and Bockfjord (Fig.10). Chlorin amounts varied greatly among selected stations (~ 3-15 $\mu g\ g^{-1}$) in contrast to an overall similar low chlorin freshness (CI ~0.7-0.8), with higher sulfate reduction rates corresponding to larger chlorin concentrations. Low organic matter freshness might be related to the greater distance from site locations to the estuary mouth by dilution with terrestrial or lithogenic material. Woodfjorden is known for frequent appearance of driftwood and stations in both fjords were close to glaciers (V. Brüchert, pers. comm.). Extremely degraded chlorin material (indicated by a CI of 0.9-1) was observed in Liefdjefjord surface sediments followed by a layer of slightly less refractive matter (CI ~0.8). This might have been the result of a sudden supply of release lithogenic material due to a major deglaciation or input of terrestrial material.

Southeast Coast

MIZ-South

Ice melting and inflow of nutrient-rich Atlantic water gave rise to a stratified water column with characteristic phytoplankton blooms within the MIZ, which followed the receding ice edge during retreat (Sakshaug, 1997). Enhanced primary productivity was suggested from large amounts of slightly refractive chlorin matter (CI~0.5) and an observed low chlorophyll maximum (by onboard CTD measurements) characteristic of post-bloom conditions that are usually accompanied by high organic carbon fluxes and particle sedimentation along the ice margins in Barents Sea (Eilertsen et al. 2002; Andreassen et al., 1996; Hebbeln and Wefer, 1991). Ice-edge productivity was further indicated by high chlorophyll and diatom pigment concentrations of 0.5 $\mu g\ g^{-1}$ chlorophyll *a* and 0.06$\mu g\ g^{-1}$ fucoxanthin, whereas fucoxanthin occurred solely in the meltwater region. Si-demanding phytoplankton such as diatoms and related high opal fluxes have been associated with new production in the MIZ and at the ice edge in the southern Barents Sea (Reigstad et al., 2002, Hebbeln and Wefer, 1991.

Although oxygen consumption rates (~3.8 mmol m^{-2} d^{-1}) were comparable in the MIZ (I) and northwest sediments (J) SRR constituted less of total carbon mineralisation in the southeast (20%). As chlorin carbon contributed more to the total organic carbon pool at the warmer northwest coast (~1600 compared to ~ 1300 µg g TOC $^{-1}$) and chlorin freshness hardly varied in northwest profiles, this could be attributed to the annual higher carbon supply, which was related to an earlier ice retreat supported by warm Atlantic water inflow.

Earlier ice retreat and associated higher phytoplankton productivity might explain the overall largest flux of refractive organic matter (45 µg g^{-1} chlorins, CI ~0.5, 3% of TOC, C/N of 11) and increased sulfate reduction rates observed in Storfjorden (V) (50% of total mineralisation).

In fjord sediments, the highest chlorin and chlorophyll but low diatom pigment concentrations and C/N ratios of ~12-15 pointed at an annually higher primary production if compared to the MIZ but also a significant contribution of terrestrial OM.

In contrast to the MIZ, lower fluxes of very fresh chlorin organic matter were consistent with reduced benthic carbon mineralisation rates in sediments at ice-covered sites. SRR contributed less than 6% of total carbon mineralisation beneath the ice. A northward decrease of primary productivity but increased organic carbon freshness, typical of phytoplankton, was demonstrated by reduced chlorin, chlorophyll and protein amounts and declining CI values (~ 0.4 to 0.2), was consistent with earlier studies of this area (Reigstad et al., 2002). From a shallow chlorophyll maximum (recorded by CTD) and fresh chlorin matter we assumed the fresh organic material in surface sediments to be derived from ice algae and zooplankton production as we observed fecal pellets at the northernmost ice station (III). These most probably enhanced the sedimentation of fresh chlorin organic matter due to low oxygen exposure of OM being protected by biogenic aggregates. The mode of carbon deposition therefore played an important role to chlorin burial in ice-covered regions and the related MIZ.

MIZ-North

Benthic mineralisation, organic matter concentration and composition reflected hydrographic features at the northernmost stations (X, XII, VIII, all taken in 2004), located northeast of Nordaustlandet. Whereas X was located north of Kong Karlsland and affected by melting ice floes, stations XII (200m) and VIII (500m) were situated along a trench close to Kvitoya and ice-free during sampling (Fig.1, Tab.1). Largest aerobic and anaerobic mineralisation rates, TOU and SRR of 3.5 and 0.5 mmol m^{-2} d^{-1} respectively, occurred at the shallower trench station XII. Vandieken et al (2006) attributed this higher benthic activity to a larger annual carbon supply related to seasonally earlier ice retreat. This theory was supported by a consistent high amount of refractive chlorins in subsurface sediments (~ 10 µg g^{-1}total chlorins and ~ 700 µg g TOC^{-1}, CI~0.7, Fig.6.c.-e.) that suggested an intermediate flux of mostly decomposed chlorin organic matter. Moreover, increased chlorin concentrations were observed along with enhanced benthic mineralisation through microbial sulfate reduction (13% of total carbon oxidation).

Slightly higher oxygen consumption rates were reported for the most northern station VIII and compared to the southern site X by Vandieken et al. (2006) who suggested, that a northward transport of sediment derived from the Northeastern slope along the trench increases sedimentation rates, and thus, benthic mineralisation at VIII. However, overall similar TOC content (1.5-1.6%) and composition (C/N values of ~9) could not identify regional changes of organic matter reactivity in contrast to slightly larger chlorin amounts and slightly lower freshness (CI 0.3). We agree that enhanced organic matter supply enhanced local benthic activity, however suggest that increased particle fluxes were primarily associated with meltwater release of lithogenic matter as noted for the southern MIZ and west coast and productivity at the ice margin.

Organic matter supply at VIII was slightly lower for total chlorin amounts (~ 15 compared to 25 µg g^{-1}, Fig.6.c-e) and a similar contribution of chlorins to total organic carbon was observed (~1200 µg $gTOC^{-1}$, Fig.6.c). Chlorin freshness was slightly higher (CI~0.5) in subsurface sediments at the northern ice margin than at the southern MIZ (CI~0.6 to 0.9), which might be related to the seasonally later ice retreat and thus lower carbon supply in the north. CI profiles at the southern MIZ and fjord estuary (V) did show gradually increased degradation of fresher to highly-refractive chlorin matter (CI 0.5 to 0.9 and 1.0) within a broader sediment zone (~ 10cm), whereas at the northern MIZ degradation proceeds quickly (~5cm) leaving not as much refractive chlorin matter behind (CI 0.3 to 0.5). As total oxygen consumption and the relative contribution of microbial SR to total benthic activity were likewise higher in the south (20-45 % SR compared to ~ 10% in north), this suggested that the microbial sediment community can utilize large amounts of slightly refractive OM (MIZ-south) easier than low amounts of fresher OM at the northern MIZ. Aspetsberger (2006) has recently shown that the depolymerisation and uptake of organic matter lagged the mineralisation on the Benguela continental margin. Ahke et al. (chapter2) demonstrated from anoxic sediment incubations that a larger supply of fresh algal carbon resulted in a later stimulation of benthic sulfate reduction rates due to preliminary enzymatic breakdown of organic substrate. As benthic mineralisation rates were larger in MIZ compared to ice covered sediment incubations, the microbial community in the MIZ (sulfate reducers) must be better adapted (equipped with hydrolytic enzymes) to the enhanced carbon supply.

Vandieken et al. (2006) showed that microbial Fe and Mn reduction were the most important carbon oxidation pathways (69 to >90% of anaerobic oxidation) at northern MIZ stations. Higher supply of refractive carbon apparently supported microbial sulfate reduction and lower/intermediate supply promoted subsurface processes such as Fe reduction. As some sulfate reduction still took place at low deposition regions, the ice pack and northern MIZ (Fig.5 IV, II, III, and XII), but total refractory chlorin organic matter remained unchanged at SR depth (Fig.6), benthic activity was probably maintained by another carbon source.

Implications from protein organic matter content and composition

THAA content was slightly differently distributed than chlorin concentrations. Largest THAA amounts (11mg g^{-1}) occurred at the northwest coast and slightly lower amounts (8-7.5 mg g^{-1}) in southeast fjord (Storfjorden) and sediments until 78°N (southern MIZ and ice-covered area, I,IV,II) that further decreased in the northeast (5-4 mg g^{-1})(Fig.7-10).

Protein carbon freshness was slightly higher at some ice covered stations than at the southern MIZ, however there were too few samples analyzed in order to sufficiently resolve regional protein organic matter composition with the DI. Contributions of protein carbon and nitrogen, THAA%C and -%N, to total organic carbon in contrast revealed a similar regionalization as chlorin organic matter freshness (by the CI)(Fig.4b). THAA%C amounts were largest at the northwest coast (~30%) and ice cover (20-25%), thus proteins were less degraded. Lower THAA%C (12-15%) in the southern MIZ indicated further processed matter. Largest THAA%N of ~60-80%, typical of source-like organic matter, characterized ice sediments and lower values of 30-40% (typical for coastal surface sediments) occurred in MIZ and northwest (J) sediments (Cowie and Hedges, 1994).

Decreasing THAA amounts towards the north were most likely associated with the seasonally withdrawing ice cover and thus, on the long term, displayed the average higher protein carbon accumulation in the southern region compared to the later ice-free northern Spitzbergen shelf. High MIZ particle sedimentation could be associated with high opal and opaline silica accumulation rates due to increased primary productivity on the northwest and east coast (Hebbeln and Wefer, 1991, 4-6 µmol SiO_2 $m^{-2}d^{-1}$ at the northwest shelf, by Hulth et al., 1996). Silicate biominerals were found to be important vehicles that enhanced amino acid preservation throughout the water column and supported THAA burial in the Southern Antarctic Ocean (Ingalls et al., 2003). Although "classic" THAA measurements cannot sufficiently assess the fraction of silica-bound THAA, only amino acids sorbed onto calcium carbonate and sediment particles are measured. We speculate that biominerals as well contributed to THAA deposition in Spitzbergen sediments.

In northern MIZ and ice-covered sediments proteins appeared to be the major carbon source to benthic mineralisation as soon as the reactive chlorin pool was depleted. Proteins are easily hydrolyzed and degraded by bacteria to the ultimate end-product ammonium, which can be further oxidized to nitrate in the oxic zone of sediments. Large organic matter accumulation would reduce and lower supply extends this zone where nitrification can occur. We found that the strong increase of protein degradation at sites of low carbon supply in the northern MIZ (stations X, VIII, indicated by a decrease of THAA%C and %N) was consistent with enhanced nitrification and subsequent Fe and Mn reduction, the latter representing the major anaerobic carbon oxidation pathway at these sites (Vandieken et al., 2006). A similar trend of preferential protein carbon and nitrogen degradation was observed at ice covered stations (II, IV) where the fraction of THAA to TOC was even higher. Thus at sites of lower seasonal and pulsed carbon supply the small reactive carbon pool was quickly oxidized at the sediment surface and proteins probably represented an important carbon source to microbial degradation processes on the long term.

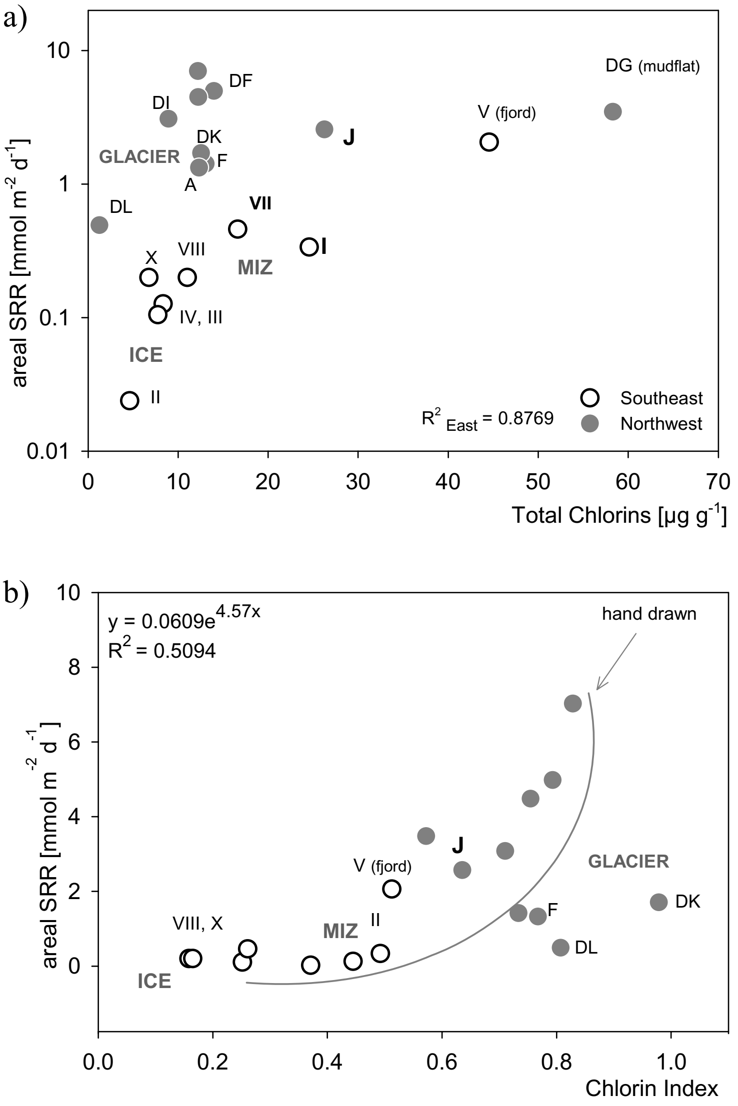


Fig.11 Areal sulfate reduction rates compared to surface chlorin content (a) and organic matter reactivity (availability) as indicated by the Chlorin Index (b) of West and Southeast stations.

Conclusions

Molecular productivity proxies, chlorins and proteins, revealed that high primary productivity and benthic mineralisation were obviously coupled at sites affected by warm Atlantic water or early ice retreat. Benthic mineralisation in Arctic sediments was apparently mainly driven by the supply and availability (reactivity) of organic carbon.

Benthic sulfate reduction activity was strongly correlated to the chlorin content in sediments (Fig. 9), whereas chlorin freshness (CI) was apparently inversely related to carbon mineralisation. High fluxes of slightly refractive carbon were coupled to highly productive sites such as the northwest coast and the southern MIZ and reflected by enhanced total carbon mineralisation (aerobic and anaerobic). In contrast lower fluxes of very fresh organic carbon corresponded to overall lower benthic mineralisation rates. Increased chlorin accumulation at ice margins was promoted by sorption of refractive chlorins to particles, whereas lower fluxes of fresh chlorin matter associated with ice cover were probably related to sedimentation of biogenic matter (fecal pellets) derived from ice algae and zooplankton productivity. Associated with different modes of carbon supply at the MIZ and ice covered regions, the relative contribution of carbon oxidation pathways and major degradation pattern of molecular carbon sources probably also varied.

We could assess chlorins as convenient proxy of present high productivity associated with the seasonal changing carbon supply along the ice margin. Proteins addressed long-term organic carbon degradation, in particular at sites that were not exposed to a consistent high carbon supply (ice cover).

Appendix Chapter 4

Tab.1 List of sampling locations in Northwest and Southeast Spitzbergen.

	Station	Region	Environment	Latidude °N	Longitude °E	Water Depth [m]	Bottom Water/ Sediment Temp.°C
Southeast Spitzbergen		**marine**					
	C-03-I	Hopen Trench	open, MIZ	75.7	30.2	338	0.09
	C-03-V	Southeast Storfjord	outer fjord	76.4	22.2	185	1.84
	C-03-IV	Hopen Bank	ice	77.0	29.5	219	1.31
	C-03-II	South Kong Karlslandet	ice	78.2	27.2	315	0.31
	C-03-III	East Erik Eriksenstretet	ice	79.0	25.8	191	1.97
	C-04-(X)	North Kongkarlsland	ice floes	79.4	28.8	303	2.50
	C-04-(XII)	Central Kvitoya Trench	open	80.2	29.6	286	2.30
	C-04-(VIII)	North Kvitoya Trench	open, MIZ	81.3	26.9	503	2.90
		fjords					
Northwest Spitzbergen	J 200	Smeerenburgfjord	coastal fjord	79.7	11.1	215	1.6
	DB 204	Virgohamna	close to J	79.7	10.9	28	
Northcoast (fjord system)	DE	Wijdefjord Entrance	outer fjord	79.8	15.1	52	
	DD	Wiedjefjord central		79.6	15.5	127	0.8
	DF	Woodjforden NW of Mushamna	often old woods	79.7	14.0	164	0
	DJ	Woodfjorden		79.6	13.6	123	1.3
	DI	Bockfjorden	Glacier (?)	79.5	13.3	104	0.6
	DG	Mudflat in Bockfjorden		79.4	13.4	164	5.7 - 6.8
	DK	Liefdjefjord central		79.6	13.0	180	
	DL	Liefdjefjord	Glacier	79.6	12.6	107	-0.50
Southwest Spitzbergen	F 303	Kongfjorden	glacial input	78.9	12.2	114	1.8
	DA2	Ymerbukta		78.3	14.0		6.5-8
	A	Adventfjorden/Longy.	glacial input	78.2	15.6	63	0.4

Tab. 2 Molecular proxies and organic carbon mineralisation rates in Spitzbergen shelf surface sediments. Listed are total chlorin concentrations (per g dry sediment and normalized to TOC), the Chlorin Index (CI), THAA, THAA as percent of TOC and TN (THAA%C, THAA%N), the PCA-based DI, total organic carbon content (TOC) and the C/N ratio, pigment concentrations of chlorophyll *a*, its degradation products (chlorins) pheophorbide and pheophytin *a*, fucoxanthin (diatom pigment) and depth integrated (0-15cm) (areal) sulfate reduction rates. If no value is listed, this sample was not measured for the respective parameter.

Station	Total Chlorins [µg g^{-1} dry sed]	chlorins [µg g TOC^{-1}]	Chlorin Index	THAA [mg g^{-1} dry sed]	THAA%C	THAA%N	DI (PCA)	TOC [%]	C/N	Depth integrated * (areal) SRR [mmol cm^{-2}d^{-1}]		Chloro phyll *a* [µg g^{-1}]	fucoxanthin [µg g^{-1}]	pheophorbide *a* [µg g^{-1}]	pheophytin *a* [µg g^{-1}]
C-03-I	24.6	1071.5	0.49	7.3	15.0	41.2	-0.30	2.3	10.1	0.34		0.51	0.061	0.0045	0.28
C-03-V	44.5	1336.5	0.51	8.5	11.9	34.6	0.06	3.3	12.0	2.06		0.84	0.022	0.0071	0.47
C-03-IV	8.3	358.8	0.44	7.6	24.4	77.7	0.02	2.3	10.2	0.13		0.09		0.0014	0.07
C-03-II	4.6	277.9	0.37	7.5	21.1	69.6	-0.22	1.7	11.6	0.02		0.03		0.0004	0.04
C-03-III	7.8	577.3	0.25	5.1	20.5	64.0	0.12	1.3	11.1	0.11		0.03		0.0010	0.04
C-04-(X)	6.8	435.9	0.16	5.0	15.1	37.7		1.6	9.4	<0.2	1				
C-04-(XII)	11.0	719.1	0.16	4.9		35.3		1.5	9.6	0.46 +/- 0.13	1				
C-04-(VIII)	16.6	987.7	0.26	3.8	11.6	29.9		1.7	9.4	<0.2	1				
J 200	26.3	1681.0	0.64	10.6	31.6	71.0		1.6	8.4	2.57	2				
DB 204	23.1		0.57	8.1											
DE	7.2		0.90	2.6											
DD	13.1		0.73	4.3						1.42					
DF	14.0		0.79	7.1						4.57					
DJ	12.2		0.83	4.7						7.03					
DI	8.9		0.71	2.7						3.08					
DG	58.3		0.57	8.6						3.03					
DK	12.6		0.98	3.5						1.71					
DL	1.3		0.81	0.4						0.49					
F 303	12.3		0.77	2.0						1.33					
DA2	18.0		0.56	4.1											
A	12.2		0.75	1.8						4.48					

TOC, C/N and SRR taken from Vandieken et al. 2006 (1) and Vandieken 2005 (2)

Tab. 3 Sediment profiles from multicores on the Southeast Spitzbergen shelf. Listed are total chlorin concentrations (per g dry sediment and normalized to TOC), the Chlorin Index (CI), THAA, THAA as percent of TOC and TN (THAA%C, THAA%N), the PCA-based DI, total organic carbon content (TOC in %) and C/N. If no value is listed, this sample was not measured for the respective parameter.

Station	Sediment depth [cm]	TOC [%]	TN [%]	C/N	Total Chlorins [µg g^{-1}]	chlorins [µg g TOC^{-1}]	Chlorin Index	THAA [mg g^{-1}]	THAA%C	THAA%N	DI (PCA)
St. V	0.5	3.3	0.36	10.8	44.5	1336.5	0.51	8.5	11.9	34.6	0.06
	1.5	3.2	0.31	11.8	44.2	1396.5	0.55	12.0	17.7	55.9	
	2.5	3.2	0.29	12.8	28.7	908.3	0.69	11.9	17.6	60.3	0.85
	3.5	3.2	0.29	12.9	21.5	675.6	0.76	9.6	14.1	48.8	-0.42
	4.5	3.2	0.28	13.1	19.1	598.1	0.78	10.4	15.2	53.4	0.63
	6	3.2	0.29	12.6	18.2	575.8	0.82	9.7	14.4	48.6	
	8	3.2	0.29	12.8	13.7	433.4	0.84	9.2	13.6	46.3	
	10	2.9	0.22	15.0	11.2	387.6	0.88	8.1	13.1	52.8	
	12	2.8	0.23	14.5	12.3	432.9	0.87	7.8	12.8	49.9	
	14	2.9	0.23	14.5	12.3	430.7	0.86				0.24
	16	2.7	0.22	14.4	10.0	365.5	0.92	8.1	13.8	53.0	
	18	2.7	0.22	14.1	10.0	375.6	0.93	7.8	13.6	51.4	
	20	2.6	0.22	14.0	9.2	350.6	0.91	10.8	19.2	71.7	
St. I	0.5	2.3	0.26	10.3	24.6	1084.8	0.49	7.3	15.0	41.2	-0.30
	1.5	2.4	0.28	10.0	23.2	966.6	0.56	10.9	21.2	56.8	
	2.5	2.4	0.27	10.5	30.9	1277.9	0.49	10.8	20.8	58.3	0.71
	4	2.1	0.23	10.6	18.7	881.1	0.56	7.4	16.3	46.3	-1.35
	6	2.1	0.22	11.0	9.1	433.1	0.73	6.2	13.6	40.0	0.71
	8		0.20		5.6		0.81	7.2			
	10	1.7	0.17	12.0	4.7	271.3	0.93	4.8	13.0	41.7	
	12		0.15		4.6		0.95	3.6			
	14	1.6	0.14	13.0	4.4	284.4	0.94	3.5	10.4	36.1	-2.41
	16		0.14		4.4		0.96				
	18.5	1.5	0.14	13.3	4.4	283.3	0.99	3.1	9.2	32.9	

Tab. 3 continued

Station	Sediment depth [cm]	TOC [%]	TN [%]	C/N	Total Chlorins [µg g^{-1}]	chlorins [µg g TOC^{-1}]	Chlorin Index	THAA [mg g^{-1}]	THAA%C	THAA%N	DI (PCA)
St. IV	0.5	1.4	0.14	11.9	8.3	574.9	0.44	7.6	24.4	77.7	0.02
	1.5	1.4	0.14	11.8	6.9	501.6	0.46	4.9	16.6	52.6	
	2.5	1.3	0.12	12.1	6.3	495.1	0.68	5.5	20.2	65.6	-2.38
	4	1.2	0.11	13.5	4.0	327.8	0.83				0.74
	6	1.0	0.09	13.3	3.9	390.5	0.76	4.4	20.4	72.4	
	8		0.10		3.7		0.94	3.5			
	10	1.1	0.10	13.7	3.4	306.5	0.93	3.2	13.3	48.7	
	12		0.08		3.3		0.92	2.5			
	14	1.0	0.06	19.0	3.5	335.8	0.95	1.1	5.2	26.4	
	16		0.06		3.5		0.96	1.4			
	18.5	1.0	0.06	19.2	3.5	353.4	0.97	1.5	7.0	36.1	
St. II	0.5	1.7	0.16	12.4	4.6	278.2	0.37	7.5	21.1	69.6	-0.22
	1.5	1.7	0.16	12.1	4.6	275.4	0.39	8.1	22.4	72.8	
	2.5	1.6	0.17	10.7	3.9	248.1	0.43	7.6	22.6	64.9	0.74
	4	1.7	0.17	12.2	4.0	228.0	0.41	7.5	20.2	66.2	0.36
	6	1.7	0.17	11.6	4.4	253.0	0.62	5.6	15.1	47.2	-0.91
	8		0.16		4.1		0.75	4.6			
	10	1.6	0.15	12.6	3.8	241.2	0.78	4.3	12.6	42.4	
	12		0.15		3.7		0.86	4.1			
	14	1.6	0.15	12.6	3.9	240.4	0.89	3.1	8.9	30.0	0.03
	16		0.15		3.8		0.85	2.9			
	18.5	1.5	0.14	12.6	3.8	249.8	0.96	4.1	12.6	42.3	

Tab. 3 continued

Station	Sediment depth [cm]	TOC [%]	TN [%]	C/N	Total Chlorins [µg g^{-1}]	chlorins [µg g TOC^{-1}]	Chlorin Index	THAA [mg g^{-1}]	THAA%C	THAA%N	DI (PCA)
St. III	0.5	1.2	0.12	11.7	7.8	630.1	0.25	5.4	20.5	64.0	0.12
	1.5	1.4	0.13	12.3	5.8	419.4	0.33				
	2.5	1.6	0.13	13.5	6.2	396.2	0.33	3.3	9.9	35.6	1.27
	4	1.3	0.12	12.3	5.7	433.6	0.75	6.4	22.8	75.2	0.02
	6	1.3	0.11	14.3	5.4	410.2	0.82	2.3	8.1	31.2	1.58
	8		0.11		6.1		0.76	3.5			
	10	1.4	0.12	13.1	6.3	457.8	0.80	4.8	16.5	57.7	
	12		0.12		6.2		0.77	4.3			
	14	1.3	0.12	12.9	7.1	529.2	0.74	2.3	8.0	27.5	-0.10
	16		0.12		6.7		0.76	3.7			
	18.5	1.4	0.12	14.4	5.8	404.6	0.76	2.4	7.9	30.3	
St. X	0.5	1.6	0.19	9.4	6.8	435.9	0.16	5.0	15.1	37.7	
	1.5				7.5		0.31	4.6			
	2.5	1.6	0.19	9.6	11.9	760.8	0.20	4.8	14.5	37.1	
	3.5				16.3		0.13	4.7			
	4.5	1.5	0.18	9.6	10.7	716.3	0.25	4.2	13.0	33.5	
	6	1.4	0.17	9.6	9.4	674.4	0.46	3.1	10.6	27.1	
	8				9.1		0.74	2.8			
	10	1.3	0.16	9.6	10.3	767.9	0.72	2.0	7.1	18.2	
	12				7.6		0.81	2.5			
	14	1.4	0.17	9.6	9.0	660.1	0.69	2.8	9.7	24.9	
	16				8.5		0.76	2.4			
	18	1.4	0.16	9.9	7.7	553.7	0.76	2.5	8.6	22.6	
	20				7.6		0.78	2.4			

Tab. 3 continued

Station	Sediment depth [cm]	TOC [%]	TN [%]	C/N	Total Chlorins [µg g^{-1}]	chlorins [µg g TOC^{-1}]	Chlorin Index	THAA [mg g^{-1}]	THAA%C	THAA%N	DI (PCA)
St. XII	0.5				11.0		0.16	4.9		35.3	
	1.5				13.4		0.17	4.8			
	2.5	1.7	0.21	9.4	11.7	692.5	0.26	4.2	11.5	29.0	
	3.5				11.3		0.67	4.0			
	4.5	1.5	0.19	9.3	10.1	664.5	0.74	3.5	11.0	27.2	
	6	1.5	0.19	9.3	10.8	718.8	0.76	3.8	11.8	29.3	
	8				9.6		0.76	3.6			
	10	1.4	0.18	9.3	8.9	633.2	0.71	3.2	10.8	26.9	
	12				7.6		0.74	2.9			
	14	1.4	0.17	9.3	9.3	679.8	0.69	2.9	9.7	24.2	
	16				8.1		0.76	2.8			
	18	1.4	0.17	9.5	8.9		0.66	2.8	9.4	24.0	
St.VIII	0.5	1.5	0.19	9.6	16.6	1084.5	0.26	3.8	11.6	29.9	
	1.5				8.8		0.31	2.9			
	2.5	1.4	0.17	10.0	4.9	338.0	0.47	4.6	14.9	40.0	
	3.5				4.9		0.51	3.7			
	4.5	1.3	0.15	9.9	5.2	394.1	0.41	2.6	9.1	24.1	
	6	1.3	0.16	10.0	4.2	313.0	0.49	2.6	9.1	24.4	
	8				4.2		0.52	2.9			
	10	1.5	0.18	9.8	6.4	430.7	0.40	2.8	8.7	22.9	
	12				4.9		0.54	3.3			
	14	1.5	0.18	10.1	5.5	362.0	0.39	2.5	7.6	20.5	
	16				4.9		0.80	2.7			
	18	1.5	0.17	10.0	5.1	339.0	0.89	2.6	8.1	21.8	
	20				4.0		0.68	3.3			

Tab. 4 Sulfate reduction rate measurements from multicores in Southeast Spitzbergen sediments. Listed are average rates from three parallel cores (unit: nmol cm^{-3} d^{-1}).

Station	Sediment depth [cm]	SRR [nmol/cm^{-3} d^{-1}]	SRR dev [nmol/cm^{-3} d^{-1}]
St. I	0.5	**0.04**	0.02
	1.5	**0.39**	0.36
	2.5	**1.47**	0.94
	3.5	**3.35**	0.77
	4.5	**2.74**	2.10
	6	**4.27**	1.24
	8	**2.56**	0.31
	10	**1.10**	0.41
	12	**2.34**	0.20
	14	**1.44**	0.75
	16	**0.51**	0.03
	18	**0.28**	0.14
	20	**0.39**	0.16
St. II	0.5	**0.26**	0.05
	1.5	**0.01**	
	2.5	**0.00**	0.00
	3.5	**0.01**	0.01
	4.5	**0.00**	0.00
	6	**0.02**	0.03
	8	**0.15**	0.10
	10	**0.14**	0.11
	12	**0.18**	0.26
	14	**0.13**	0.07
	16	**0.16**	0.13
	18	**0.23**	0.05
	20	**0.14**	0.05
	22	**0.06**	0.02
ST. IV	0.5	**0.07**	0.01
	1.5	**0.77**	0.87
	2.5	**0.60**	0.27
	3.5	**1.15**	0.22
	4.5	**1.89**	0.76
	6	**1.38**	0.47
	8	**0.41**	0.35
	10	**0.63**	0.50
	12	**0.39**	0.14
	14	**0.28**	0.11
	16	**0.19**	0.04
	18	**0.65**	0.81
	20	**0.17**	0.16
	22	**0.14**	0.02
St. V	0.5	**0.30**	0.33
	1.5	**1.45**	1.40
	2.5	**6.30**	5.64
	3.5	**10.65**	8.62
	4.5	**17.21**	6.50
	6	**16.67**	1.66
	8	**17.52**	3.30
	10	**11.12**	4.77
	12	**11.30**	1.77
	14	**9.54**	2.32
	16	**7.19**	1.58
	18	**8.16**	3.74
	20	**3.61**	2.67

Tab. 4 continued

Station	Sediment depth [cm]	SRR [nmol/cm^{-3} d^{-1}]	SRR dev [nmol/cm^{-3} d^{-1}]
St. III	0.5	**0.00**	0.00
	1.5	**0.00**	0.00
	2.5	**0.05**	0.06
	3.5	**0.06**	0.02
	4.5	**0.22**	0.10
	6	**0.88**	0.26
	8	**0.68**	0.19
	10	**1.42**	0.53
	12	**0.64**	0.14
	14	**0.43**	0.09
	16	**0.40**	0.13
	18	**0.30**	0.24
	20	**0.33**	0.20
	22	**0.34**	0.23

Station	Sediment depth [cm]	SRR [nmol/cm^{-3} d^{-1}]	SRR dev [nmol/cm^{-3} d^{-1}]
St. XII	0.5	**b.d**	b.d
	1.5	**b.d**	b.d
	2.5	**b.d**	b.d
	3.5	**1.37**	1.46
	4.5	**3.76**	3.05
	6	**3.29**	2.72
	8	**3.33**	1.96
	10	**3.65**	0.74
	12	**3.07**	0.83
	14	**3.55**	0.66
	16	**2.17**	1.36
	18	**1.54**	0.43
	20	**1.02**	0.15

b.d.: below detection t taken from Vandieken et al. (2006)

Tab. 5 Pigment concentrations in Southeast Spitzbergen sediment profiles. Chlorophyll *a*, its degradation products pheophorbide and pheophytin *a*, and fucoxanthin, a pigment in diatom phytoplankton. Fucoxanthin could only be measured at station I and V. Stations are listed from south to north

Station	Sediment depth [cm]	Chlorophyll *a* [µg g^{-1}]	Pheophorbide *a* [µg g^{-1}]	Pheophytin *a* [µg g^{-1}]	Fucoxanthin [µg g^{-1}]
St. V	0.5	0.84	0.0071	0.47	0.02
	1.5	0.70	0.0096	0.35	0.14
	2.5	0.52	0.0093	0.32	0.08
	6	0.41	0.0078	0.26	0.05
	8	0.37	0.0068	0.22	
	19.5	0.15	0.0019	0.10	
St. I	0.5	0.51	0.0045	0.28	0.06
	1.5	0.44	0.0045	0.31	0.02
	2.5	0.51	0.0048	0.40	0.04
	6	0.19	0.0010	0.12	
	8	0.12	0.0004	0.07	
	18.5	0.02	0.0000	0.05	
St. IV	0.5	0.09	0.0014	0.07	
	1.5	0.09	0.0010	0.06	
	2.5	0.08	0.0007	0.06	
	6	0.03	0.0003	0.03	
	8	0.02	0.0008	0.02	
	18.5	0.01	0.0000	0.00	
St. II	0.5	0.03	0.0004	0.04	
	1.5	0.03	0.0003	0.04	
	2.5	0.02	0.0003	0.05	
	6	0.02	0.0002	0.05	
	8	0.02	0.0001	0.04	
	18.5	0.02	0.0001	0.02	
St. III	0.5	0.03	0.0010	0.04	
	1.5	0.01	0.0044	0.32	
	2.5	0.04	0.0008	0.06	
	6	0.02	0.0004	0.03	
	8	0.02	0.0003	0.03	
	18.5	0.01	0.0001	0.03	

Tab. 6 Sediment profiles from multicores in coastal and fjord sediments (Northwest Spitzbergen). Listed are total chlorin concentrations, the Chlorin Index (CI) and THAA concentrations at all stations. TOC and TN, C/N, chlorins normalized to TOC and THAA%C and THAA%N were only measured at station J. TOC and C/N data were kindly provided by V. Vandieken (dissertation in 2005). THAA as percent of TOC and TN (THAA%C, THAA%N), the PCA-based DI, total organic carbon content and C/N. If no value is listed, this sample was not measured for the respective parameter.

Station	Sediment depth [cm]	Total Chlorins [µg g^{-1}]	Chlorin Index	THAA [mg g^{-1}]	THAA%C	THAA%N	TOC [%]	TN [%]	C/N	chlorins [µg g TOC^{-1}]
J 200	0.5	26.3	0.64	10.6	31.6	71.0	1.6	0.22	8.4	1681.0
Smeerenburg-fjord	1.5	27.1	0.62	11.0	31.4	71.0	1.6	0.23	8.5	1654.7
215m wd	3.5	22.5	0.63	9.3						
	4.5	22.2	0.65	8.9	28.2	65.3	1.5	0.20	8.7	1502.1
	6	20.4	0.66	7.8	24.9	58.5	1.5	0.19	8.8	1394.0
	8	19.8	0.65	7.2						
	10	19.5	0.67	6.6	22.5	53.0	1.4	0.18	8.8	1421.3
	12	19.2	0.68	6.9						
	14	20.0	0.67	8.7	28.5	67.2	1.4	0.19	8.8	1405.1
	16	20.8	0.64	6.5						
	18	15.4	0.68	5.1	19.3	44.9	1.2	0.17	8.7	1238.4
	20	15.4	0.68	5.7						
DB 204	0.5	23.1	0.57	8.1						
Virgohamna	1.5	23.1	0.54	7.8						
28m wd	2.5	21.9	0.54	7.7						
	3.5	23.5	0.53	8.0						
	4.5	18.7	0.55	8.8						
	6	23.7	0.53	8.1						
	8	13.9	0.59	5.1						
	10	13.9	0.65	4.2						
	12	12.0	0.64	4.3						
	14	12.1	0.64	5.6						
	16	15.9	0.59	6.4						

Tab. 6 continued

Station	Sediment depth [cm]	Total Chlorins [µg g^{-1}]	Chlorin Index	THAA [mg g^{-1}]
DF	1.5	14.0	0.79	7.1
Woodfjorden	2.5	14.1	0.81	6.9
NW of Mushamna	3.5	14.7	0.86	6.6
164 m wd	4.5	14.5	0.83	6.9
	6	14.1	0.85	6.9
	8	11.5	0.83	6.5
	10	12.3	0.87	6.4
	12	11.0	0.83	5.9
DJ	0.5	12.2	0.83	4.7
Woodfjorden	1.5	13.8	0.86	4.0
123 m wd	2.5	16.0	0.85	4.0
	3.5	15.1	0.78	3.5
	4.5	14.8	0.79	2.7
	6	15.4	0.80	3.2
	8	14.3	0.80	3.0
	10	13.6	0.85	2.9
	12	13.9	0.86	2.6
	14	13.4	0.83	2.7
DI	0.5	8.92	0.71	2.7
Bockfjorden	1.5	9.06	0.74	2.3
104m wd	2.5	7.98	0.76	2.2
	3.5	8.10	0.79	1.9
	4.5	6.77	0.79	2.0
	6	8.10	0.76	1.8
	8	7.79	0.78	1.9
	10	7.18	0.79	1.7
	12	7.90	0.77	1.7
	14	7.95	0.74	1.3
DG	0.5	58.3	0.57	8.6
Mudflat /	1.5	28.2	0.71	4.7
Bockfjorden	2.5	19.6	0.74	2.7
	3.5	11.3	0.79	1.7
	4.5	4.6	0.81	1.2
	6	2.4	0.84	1.0
	8	5.1	0.80	1.8
	10	5.8	0.79	1.7

Tab. 6 continued

Station	Sediment depth [cm]	Total Chlorins [µg g^{-1}]	Chlorin Index	THAA [mg g^{-1}]
DK	0.5	12.6	0.98	3.5
Liefdjefjord central	1.5	12.8	0.89	2.6
180 m wd	2.5	12.6	0.76	2.9
	3.5	13.4	0.77	2.8
	4.5	15.5	0.80	3.1
	6	14.7	0.80	2.8
	8	13.0	0.86	2.4
	10	11.6	0.87	2.5
	12	11.7	0.83	1.9
	14	12.1	0.81	2.1
DL	1	1.26	0.81	0.4
Liefdjefjord	3	1.78	0.82	0.4
107m wd	5	2.45	0.81	0.6
	7	3.04	0.81	0.4
	9	1.70	0.82	0.4
	11	2.93	0.78	0.6
	13	2.84	0.73	0.5
DE	0.5	7.15	0.90	2.6
Wiedjefjord end	1.5	9.12	0.87	2.9
5.2m wd	2.5	9.36	0.93	3.2
	3.5	10.08	0.85	3.1
	4.5	8.83	0.87	2.9
DD	0.5	13.07	0.73	4.3
Wiedjefjord central	1.5	17.11	0.69	3.9
127m wd	2.5	16.32	0.77	3.7
	3.5	14.82	0.78	3.5
	4.5	13.58	0.77	3.8
	6	12.85	0.80	3.4
	8	10.20	0.84	3.3

Tab. 6 continued

Station	Sediment depth [cm]	Total Chlorins [µg g^{-1}]	Chlorin Index	THAA [mg g^{-1}]
F 303	0.5	12.33	0.77	2.0
Kongsfjorden	1.5	14.02	0.74	1.7
114m wd	2.5	11.63	0.75	1.6
	3.5	8.74	0.80	1.9
	4.5	9.90	0.73	1.3
	6	8.30	0.77	1.2
	8	5.76	0.74	0.8
	10	7.11	0.75	1.2
	12	8.31	0.80	1.4
	14	8.08	0.76	1.1
	16	9.01	0.75	1.2
	18	7.48	0.65	0.6
	20	9.62	0.72	1.0
DA	0.5	18.04	0.56	4.1
Ymerbukta	1.5	15.92	0.61	4.2
	2.5	7.37	0.76	1.9
	3.5	7.25	0.75	1.8
	4.5	7.40	0.73	1.9
	5.5	5.67	0.86	1.7
	6.5	7.25	0.82	1.9

Station	Sediment depth [cm]	Total Chlorins [µg g^{-1}]	Chlorin Index	THAA [mg g^{-1}]
A	0.5	12.23	0.75	1.8
Adventfjorden	1.5	13.81	0.78	2.1
Longyearbyen	2.5	14.60	0.83	2.0
69m wd	3.5	14.38	0.96	2.0
	4.5	12.91	0.98	1.8
	6	12.01	0.99	1.7
	8	12.02	1.00	1.7
	10	11.38	1.03	1.7
	12	11.63	1.01	1.6
	14	11.53	1.02	1.7

Tab. 7 Sulfate reduction rate measurements from multicores in Northwest Spitzbergen coastal and fjord sediments. Listed are average rates from three parallel cores (unit: nmol cm^{-3} d^{-1}).

Station	[cm]	SRR [nmol cm^{-3} d^{-1}]
J 200	0.5	2.01
Smeerenburgfjord	1.5	11.75
	2.5	17.59
	3.5	16.88
	4.5	12.78
	6	10.24
	8	11.89
	10	15.30
	12	12.70
	14	9.15
	16	9.67
	18	11.69
	20	17.29
DF	0.5	4.07
Woodfjorden	1.5	16.88
NW of Mushamna	2.5	15.27
	3.5	28.69
	4.5	30.82
	6	63.96
	8	42.69
	10	39.08
	12	34.69
DJ	0.5	0.81
Woodfjorden	1.5	10.22
	2.5	28.93
	3.5	64.24
	4.5	33.95
DJ	6	17.16
Woodfjorden	8	32.11
	10	145.08
	12	65.83
	14	22.03
DG	0.5	41.41
Mudflat	1.5	96.57
/Bockfjorden	2.5	87.89
	3.5	35.70
	4.5	29.34
	6	3.97
	8	2.22
DK	0.5	2.24
Liefdjefjord	1.5	14.90
central	2.5	14.93
	3.5	10.29
	4.5	15.04
	6	16.07
	8	11.52
	10	12.22
	12	8.57
	14	8.32
DI	0.5	2.05
Bockfjorden	1.5	7.25
	2.5	35.26
	3.5	43.60
	4.5	41.53
DI	6	27.74
Bockfjorden	8	19.18
	10	21.94
	12	8.04
	14	12.35
DL	0.5	0.22
Liefdjefjord	1.5	0.23
	2.5	0.38
	3.5	0.42
	4.5	1.98
	6	7.11
	8	1.97
	10	5.87
	12	3.96
	14	4.07
DD	0.5	1.07
Wiedjefjord	1.5	7.01
central	2.5	11.85
	3.5	12.01
	4.5	13.43
	6	8.87
	8	16.03
	10	9.84
	12	7.80
	14	5.70

Chapter 5

Paleoenvironmental implications from molecular productivity proxies and degradation indices on the Benguela continental slope (GeoB 8425)

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Abstract

Molecular productivity proxies, total chlorins and THAA, and their related degradation indicators, CI and DI (Schubert at al., 2002,2005; Dauwe et al., 1998, 1999) have been applied to reconstruct past organic carbon fluxes with respect to climate variations of the past ~130 000 y^{-1} on the northern Benguela slope (24°S-2000m water depth).We introduced a basic model of the BUS slope carbon cycle that describes how paleo sulfate reduction rates and organic carbon fluxes may be reconstructed from chlorin deposits. Results show that, as could be expected from a deep sea site, most of the supplied organic carbon was recycled (89-99.5%). Less organic carbon burial (<1%) took place at warm stages, however increased at glacial periods (maximum 2.5% at LGM). Organic carbon mineralisation during the Last Glacial Maximum (LGM) was apparently driven by mostly decomposed organic carbon. This was demonstrated by an increased burial of mostly refractive chlorin organic matter, which was consistent with peaks of microbial sulfate reduction rates. We attribute this to sorptive properties of pigments leading to preferred chlorin burial during that cold period. Most likely enhanced resuspension of sedimentary matter (lateral transport, stronger wind forcing, lower glacial sea-level) diluted supplied organic matter and promoted fast burial of chlorin carbon. Organic matter at interglacial upwelling events was determined by "undiluted" material, as indicated by its fresher composition, in particular of protein organic matter (DI ~ 4 to 2), in contrast to only slightly less degraded chlorins (CI ~ 0.75). We suggest that enhanced sedimentation of intact or cell aggregate matter favoured protein burial. Sedimentary protein can form complexes that are composed of largely refractive compounds (bacterial biomass, organic carbon complexes), likely enclosing very reactive carbon compounds e.g. in intact cells. Unlike chlorins, THAA degradation, as indicated by decreasing peak DI values, proceeded with increased sediment depth (age). Chlorin composition (degradation state) remained similar during glacial/interglacial periods (CI of ~ 0.8-0.75) and thus represents a major carbon source that is available to microbial sulfate reduction since that time (of deposition).

Introduction

Understanding past climatic changes is an important issue with respect to global climatic change. The present and past extent of atmospheric carbon dioxide removal is a key factor within the global carbon cycle. Particularly high rates of carbon sequestration occurred during glacial periods due to increased oceanic productivity and associated larger organic carbon burial rates (Sarntheim et al., 1988; Mollenhauer et al., 2002). This so-called "biological pumping" tends to be increased in high productivity and upwelling areas of mid and low latitudes. These regions account for 80-90% of the global modern new production (Summerhayes et al., 1995a).

The Benguela upwelling system (BUS) links two warm water systems, the salty waters of the South Atlantic and the Agulhas Current and the equatorial Angola Current, supplying the Gulf Stream. Most intense upwelling is focused to the southern Benguela system and located near Lüderitz and Walvis Bay close to our sampling site on the lower continental slope (2000m) (Fig.1). Productivity for these regions varied with the upwelling pattern and ranged from 0.36 to 6.12 g C $m^{-2}d^{-1}$ (Mitchell-Innes et al., 2002), with most primary production at the edge of upwelling cells (Mollenhauer et al., 2002).

Maximum rates of organic matter accumulation associated with low paleo sea surface temperatures (alkenone-based SST) have been reported for the Benguela slope during the previous cold period (21-17 ky^{-1}), when global cooling and glaciation reached its largest extension during the Last Glacial Maximum (LGM, ~19-17 ka^{-1}) (Kirst et al., 1999; Summerhayes et al, 1995b). Increased carbon accumulation probably reflected enhanced glacial primary productivity, but could have been as well caused by an offshore displacement of the upwelling centre due to a by 120m lowered glacial sea-level (Lavik, 2001; Mollenhauer et al., 2002; Bertrand, 2003).

However, the total rate of organic carbon mineralisation can not sufficiently be resolved by bulk organic carbon based productivity estimates and paleo SST alone. Buried total organic carbon represents the amount that remains after organic matter mineralisation. Buried TOC does not necessarily correspond to total microbial degradation activity as has been demonstrated by Fossing et al. (2000) for the Benguela continental slope. They found sporadic high rates of sulfate reduction that were not identified by TOC content or C/N ratios and attributed this phenomenon to particularly reactive layers of sub seafloor sediments. Sole application of total organic carbon is furthermore problematic in low-productive oceanic regions or if terrestrial carbon sources have to be considered such as on continental margins or at sites of high river discharge (Rühlemann et al., 1999). Schubert et al. (2005) recently demonstrated that chlorins and a derived degradation index, the CI, were by contrast robust indicators of marine organic matter composition and productivity and not biased by terrestrial contributions in coastal sediments off Chile. Moreover, these proxies have been applied to characterize Arctic sediments known to be affected by terrestrial carbon supply by glacier debris or release from sea ice (Ahke et al., see chapter 4). Harris et al. (1996) and Schubert et al. (2005) showed that chlorins were suitable indicators of paleo productivity over the past 200 000 – 300 000 years in slope sediments of the Arabian Sea and off Northwest Africa. Studies in deep cores of the South Pacific and Antarctic Ocean revealed that buried protein organic matter likewise corresponds to glacial/interglacial productivity changes in late Quaternary and even late Palaeocene sediments (Gupta et al., 2002; Kawahata and Ishizuka, 1993, 2000).

Organic carbon-based proxies are easily modified e.g. through dissolution processes or aerobic decay (Gingele et al., 1999). However, incorporation of settling molecular organic material into the sediment depends on microbial dissolution and also on its interaction (protection) with the sediment matrix or sequestration of organic matter with non organic bioclasts such as diatom frustules (Ransom et al., 1998; Keil et al., 1994b). The degradation state of molecular organic compound pools rather than bulk organic carbon could be used to implicate past organic matter burial and productivity changes. As molecular organic matter content and composition vary on a geological time scale, such reactive sub-classes within the total carbon pool have been suggested as more promising indicators of the biogeochemical processes, which are modulated by past environmental changes.

In this study chlorin and protein-based molecular degradation indices, the CI and DI, and their related organic carbon pools, total chlorins and proteins, (Schubert et al., 2002; Dauwe et al., 1999 and1998), will be applied. Molecular indicators will be compared to conventional paleoceanographic proxies, i.e. TOC, C/N, paleo sea surface temperature, oxygen isotopes, and to microbial sulfate reduction rates to characterize organic carbon degradation state and reactivity of deep sediments located on the northern Benguela slope (24°S-2000m water depth), close to the Benguela upwelling centre.

As there is no age model of core GeoB 8425 we will refer to sediment ages of the nearby station GeoB 1711 as given in Kirst et al. (1999). Ages were determined from oxygen isotope analyses of benthic foraminifera (*Cibicidoides wuellerstorfi*) (Kirst et al., 1999; Little et al., 1997b) and related to the record of oxygen isotopic stages (OIS) according to Imbrie et al. (1984) and Martinson et al. (1987) (Fig.2). Oxygen isotopic values are applied in paleo oceanography to identify past climate variability. Significant climate changes are indicated by particular high (cold stages) or low (warm stages) isotopic values that are classified in different oxygen isotopic stages (OIS). Core sediments of GeoB 8425 cover ~ 135 000 y^{-1} of the past climate record (OIS1-5) that included two major glacial periods, at 12-24 ky-1 (OIS 2) and 59-74 ky-1 (OIS 4).

Three major objectives direct this study. First, we will test if molecular degradation indices reflect past oceanic and productivity changes and second, to what extent organic matter composition and present day carbon mineralisation are related to these changes. Finally, we will introduce a basic model that demonstrates how past geochemical fluxes might be reconstructed from molecular productivity proxies.

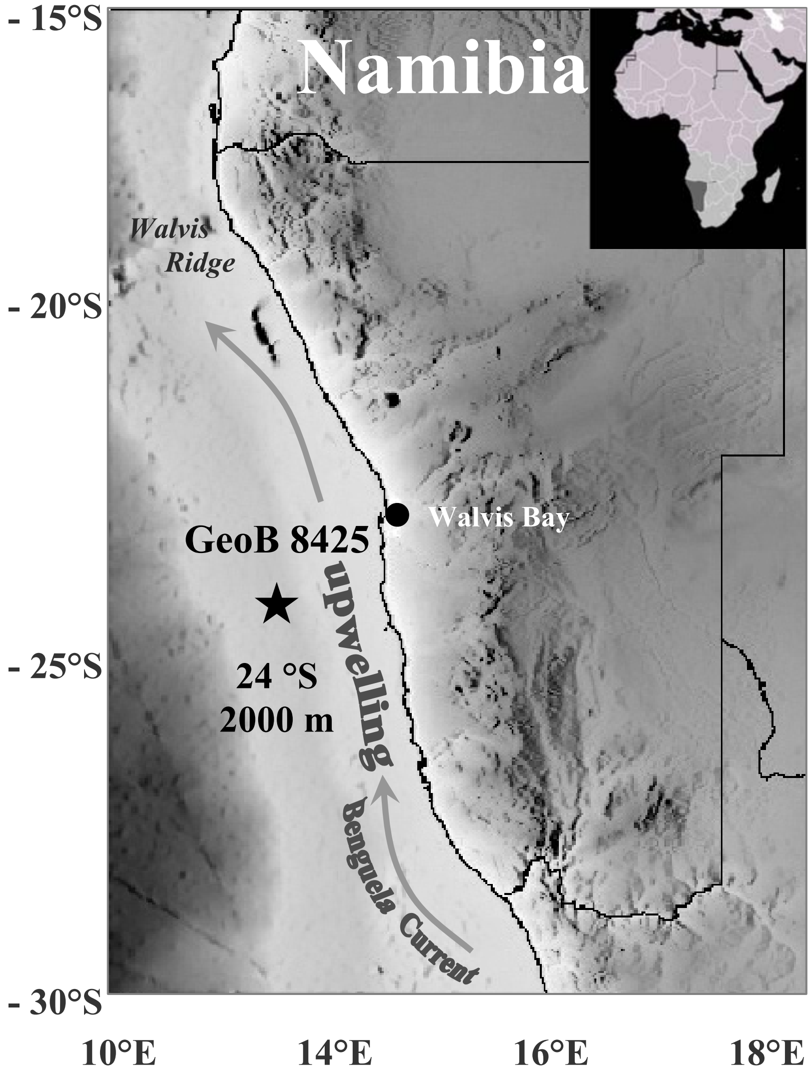


Fig. 1 Map of the Benguela Upwelling System and location of core GeoB 8425 on the northern slope.

Material and methods

Gravity core GeoB 8425 was recovered at 24.46 °S 12.71 °E on the Benguela continental slope at 2000m water depth during Meteor cruise M57/3 (Cruise report M57/3) in spring 2003. Sediment was recovered from 10.6m depth and its position located slightly more offshore and north of the main slope depocenter at 25°C (Ahke et al., chapter 3; Inthorn et al., 2006). The sediment consisted primarily of olive to olive-grey diatom or foram bearing nannofossil oozes. Holocene sediment was of slightly more yellowish colour. A detailed core stratigraphy of the sister core GeoB 8422 can be retrieved from http://www.pangaea.de.

Bulk organic matter analysis

Sampling

Subsequent to recovery 22 core sections were sub sampled at in situ temperature (4°C) for geochemical analysis and adjacent sulfate reduction rate incubations (see 2.4). Samples for geochemical analysis were transferred into sterile brown glasses and stored light-protected at -20°C.

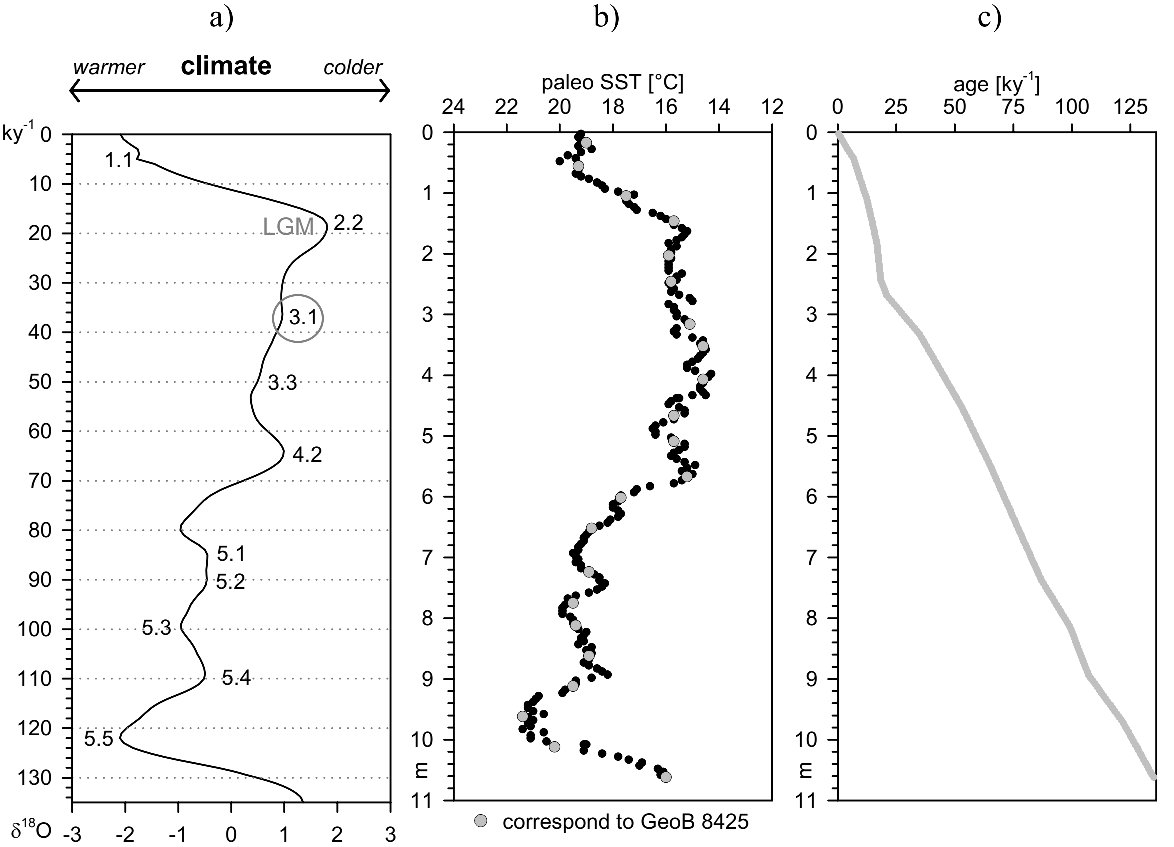
Elemental analysis

Total carbon (TC) and nitrogen (TN) were analyzed from freeze-dried homogenized samples using a Fisons NA 1500 (Series 2) Elemental Analyzer. Total inorganic carbon (TIC) was measured by coulometry at a TIC autoanalyser CM 5240 Orbis BV. Total organic carbon concentration (TOC) was then calculated by subtracting TIC from TC.

Pigment analysis and CI

Total Chlorin concentrations and the Chlorin Index (CI) were estimated with the method given in Schubert et al. (2002, 2005). A detailed description of the analysis can be found in chapter 3. In short, sedimentary chlorin content was released by threefold solvent extraction in acetone. Ice-cooling and protection from light during extraction (ultra sonication) was applied to prevent chlorin decomposition. Extracts were measured immediately after extraction at a Hitachi F-2000 Fluorimeter at excitation wavelength 428 nm and emission wavelength 671 nm. Chlorophyll *a* (SIGMA) which has been transformed to pheophytin *a* through acidification was used as a standard for total chlorin concentrations. First, original sediment extracts were analysed, then acidified and remeasured against the standard. The Chlorin Index by Schubert et al. (2002) is defined as the ratio of the fluorescence units of the acidified sample over the original extract (Equ.1). Chlorin Index values are on a scale from 0.2 (fresh organic matter) to 1 (heavily altered, refractory organic matter).

$$\text{CI} = \text{fluorescent intensities}_{\text{acidified sample}} / \text{fluorescent intensities}_{\text{original sample}} \qquad (1)$$



Oxygen isotopic stages (OIS) based on Imbrie et al., 1984, Martinson et al, 1987)

Alkenone-based paleo sea surface temperatures (SST) and sediment ages taken from Kirst et al.,1999, 2001 (GeoB 1711)

Fig. 2 Oxygen isotopic stages (OIS) (2.a) according to Imbrie et al. (1984) and Martinson et al. (1985) and paleo sea surface temperatures (SST) versus sediment depth [m] (2.b). On the left: the related sediment ages measured by Kirst et al. (1999) for a comparable station (2.c).

Protein analysis and DI

Protein content in the sediment was analyzed as the concentration of total hydrolysable amino acids (THAA). Analysis was based on the method given in Dauwe and Middelburg (1998), and further details can be referred to chapter 3. In brief, THAA were retrieved from hot extraction with 6N HCl. Sample aliquots were reacted with fluorescent agent, *o*-phtaldialdehyde (OPA) and measured at the fluorometer at excitation/emission wavelengths 340/455 nm.

The concentrations of 17 individual amino acids were determined via pre-column *o*-phtaldialdehyde derivatisation (Hill et al., 1979; Lindroth and Mopper, 1979) from neutralized sample aliquots charged with an internal standard (SIGMA

AA-S-18). Individual amino acids have been separated by reversed-phased HPLC with a binary solvent system and subsequent fluorescence detection.

A principal component analysis (PCA) (Meglen, 1992) was performed to determine the degradation index, DI. The DI represents a measure of the molecular composition of the THAA pool, which results from the selective degradation pattern of protein organic matter in sediments. By application of a PCA, mole percentages of individual amino acids were standardized and yielded individual site scores, the designated “degradation index “ (Dauwe and Middelburg, 1998; Dauwe et al., 1999). The DI varied between values >1 to ≥ 2 for very reactive matter, fresh phytodetritus, to values < -1 or lower representing heavily degraded organic material.

Using the factor coefficients given in Dauwe et al. (1999) the DI can as well be calculated as:

$$DI=\sum I[(var_i-AVGvar_i)/STDvar_i]\times fac\cdot coef_i \qquad (2)$$

where var_i is the original, non-standardized mole percentage of amino acid *i*, $AVGvar_i$ and $STDvar_i$ represent the average and standard deviation of the original mole percentage of all amino acids included; $fac\cdot coef_i$ is the respective factor coefficient for amino acid *i*.

Sulfate reduction rates

Sulfate reduction rate measurements on gravity core sub samples were performed using the $^{35}SO_4^{2-}$ method as described in Fossing et al. (2000). Adjacent sampling glass syringes (~5cm^3 sediment) were injected with 5-10 ml of 200-400 kBq $^{35}SO_4^{2-}$ tracer (Amersham) and incubated onboard at 4°C for 16 days. Microbial reactivity of sediment samples was stopped with 20 % ZnAc-solution and storage at -20°C. The distillation of radioactive end products and calculations of sulfate reduction rates followed Kallmeyer et al. (2004).

Results

Visual core description and sediment properties

Based on the colour scan and core lithology, major dark coloured bands were observed particularly within the upper six meters of the core, except for Holocene sediments from the top core meter (Appendix.: colour scan of GeoB 8425 sister core GeoB 8422-3). Particularly dark layers occurred as well at 5-6, ~7.5-8 meter depth and as a sharp boundary layer at 9.5m. Between 1-3 m olive sediments were sporadically spotted with darker patches compared to rather continuous streaks in the lower core section. The upper as well as the lowermost meter of the core was of a lighter green colour than its centre. The sediment was mainly composed of diatom and foram bearing nannofossil oozes. Pure foram bearing nannofossil oozes were observed in core top sediments as well as adjacent to the sharp boundary below 9 m. Clay layers were scarce and occurred twice in the core, at 2-3m and ~7m depth.

A detailed visual description of the core can be found at the Pangäa database *(http://www.pangäa.de)* or in the cruise report at *http://elib.suub.uni-bremen.de/publications/ELibD1189_220.pdf* (by Eberwein A., Franke. C, Heslop D., Mulitza S., Rathmann S., Romero O., v. Dobeneck T.).

Total chlorins and the CI

Total chlorin concentrations of 1.7–18 µg g^{-1} have been measured in surface and gravity core sediments (Tab.1+2, Fig.3.a). Chlorin amounts of 3.5-5 µg g^{-1} in surface sediments hardly changed until 1 m but then increased to largest concentrations of 17-18µg g^{-1} at 1.5-2m. Below chlorins generally decreased, except for peak concentrations of 15, 11 and 5 µg g^{-1} at 3.5, 5.7 and 7.7 m, to similar amounts as in topmost sediments (~3µg g^{-1}).

CI values varied between 0.73 and 0.85 with a similar pattern in the cores as chlorin concentrations although not following their generally declining trend (Tab.1+2, Fig.3.a). Lower CI values of ~ 0.75 hardly changed within upper sediments (16cm), however increased to 0.85 at 0.6m. Throughout the gravity core The CI moves between values of 0.82 and 0.74 with smallest values corresponding to peak chlorin concentrations. Consistent peak CI values were ~0.8 at 1.5-2m and ~ 0.75, 0.8, ~0.75 at 3.5, 5.7 and 7.7 m. Slightly larger CI values corresponded to major glacial periods (see OIS scale, Fig.1).

THAA and amino-acid based DI

THAA concentrations in core sediments varied between 3 and 18.5 mg g^{-1} (Tab.1+2, Fig.3.a). THAA amounts of ~ 6 mg g^{-1} barely changed until 1m and subsequently increased to ~11 mg g^{-1} at 2m and further to largest concentrations of 18.3 mg g^{-1} at 3.5m in the sediment. Below THAA concentrations generally declined down the core except for sub peaks of 9.3, 8.7 and 5.5 mg g^{-1} at 6, 7.7 and 9m. THAA concentrations at the bottom of the core were slightly smaller than in surface sediments (~3mg g^{-1}).

DI values were estimated between –6.4 and 3.4 that ranged from fairly altered to fresh organic material. In surface sediments DI values were below 0 and ~ -2. Below 20cm the DI increased to a first peak value of ~2 at 1.5m (LGM) and in subjacent sediments (2-9 m) varied between ~ 3 and 0. Positive peak DI values corresponded to peak THAA amounts except for the LGM (1.5-2.5m) and generally declined with depth (opposite to the CI). Peak DI values of 3.4, 3 and 2 were furthermore determined at 3.5, 5.7 and 7.7 m down core. Consistent with a sharp visible boundary layer, we measured a steep decline of DI values from ~0.3 to -6.4 at 9 to 10 m. The DI at the core bottom was similar to the lowermost surface sediment (0.2m) with values of ~ -3.2.

Contribution of protein carbon and nitrogen to TOC and TN was largest in the upper core layers and THAA-%C and -%N varied between 5 – 19 % and 12.3 – 55 % down the core (Fig.3.b, Tab.1+2). Largest amounts of THAA-%C and -%N of ~ 16 and ~45 % were measured in surface sediments (0.16m) that both exhibited sub surface peaks of 19 % (0.1m) and 55 % (0.04m). THAA-%C and -%N changed dramatically from 17 to 8 % and from 46 to 13 %, respectively, between 0.16 and 1m. At1-3m THAA-%C hardly varied in contrast to increasing THAA-%N to 23 %. Both parameters slightly increased again at 3.5m to 10 and 29 % THAA-C and-N. Whereas THAA-%C remained fairly consistent with depth (~ 6-8 %), THAA-%N started to decrease subjacent to 8.6m depth (6.7 to 5.3 %).

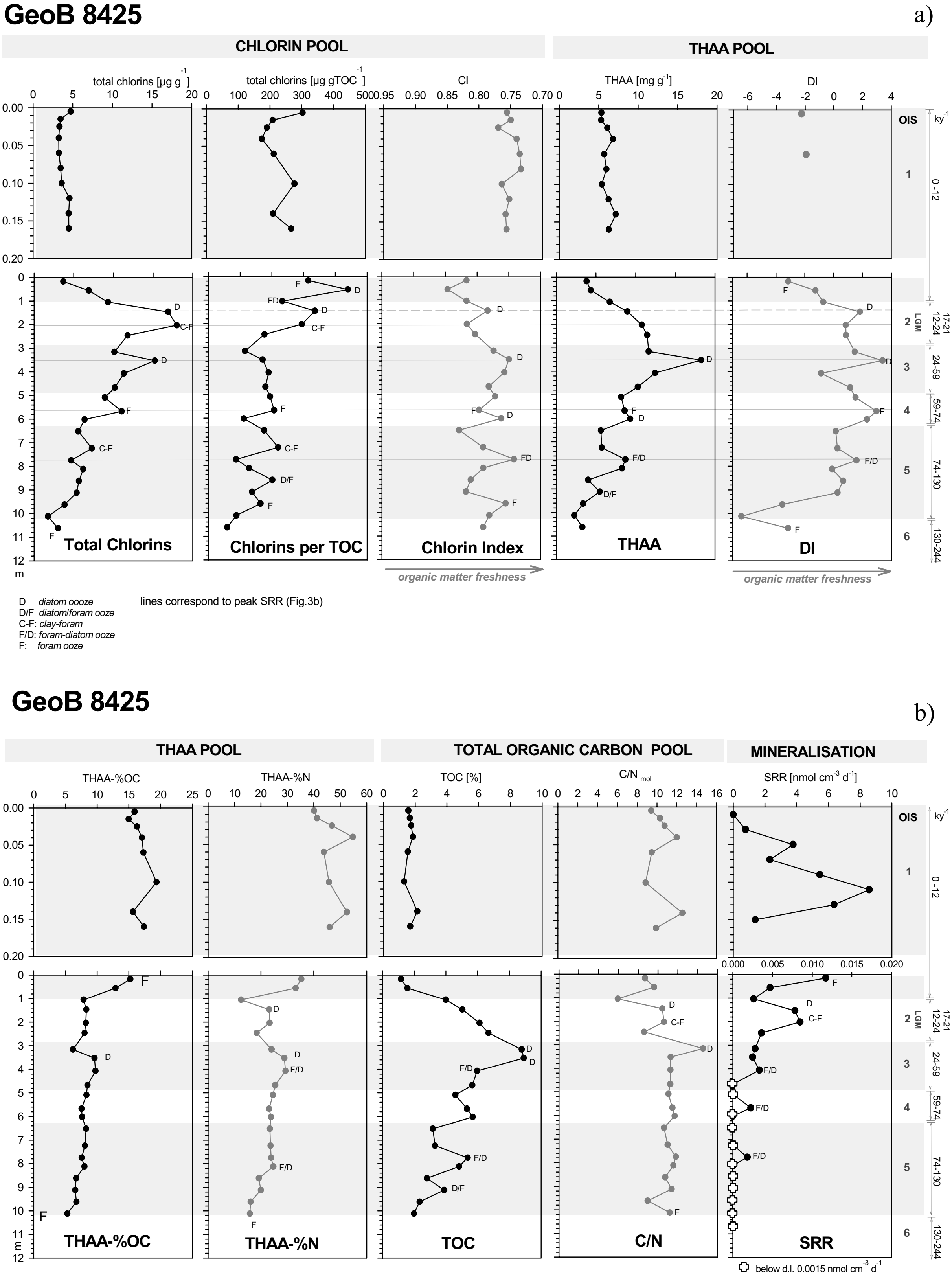


Fig.3 a) and b): Molecular productivity proxies, total chlorins and THAA, in sediments and percentage of the total organic carbon pool, degradation indices, the CI and DI, total organic carbon content and C/N ratios, and sulfate reduction rates for gravity core 8425 (24°S, 2000m)

TOC and C/N

Total organic carbon content (TOC) in core sediments varied between 1 and 9 % and C/N ratios ranged from 6 to 14.5 (Tab.1+2, Fig.3.b). TOC values of ~ 2 % in the upper sediment layer (1m) increased to maximum values of 9 % at 3.5m depth. Below TOC content continuously declined except for peak values at ~6, 8 and 9 m depth (6, 5 and 4 %) back to similar low contents as at the core top.

Overall C/N ratios varied around ~ 11 with exceptions in the upper 5 cm and between 2.5 to 3m (LGM to OIS 3), where values increased from ~9 to 12 and ~ 8 to 14. Below 3.5m C/N ratios were unchanged (~11).

Sulfate reduction rates

Sulfate reduction rates in surface sediments ranged from 0.8-8.6 nmol cm^{-3} d^{-1} (Tab1.) SRR decreased by two orders of magnitude below the surface mixed layer from 1.4 to 0.012 nmol cm^{-3} d^{-1} (15-18cm). Subsequent SRR varied between 0.0018-0.008 nmol cm^{-3} d^{-1} in gravity core sediments (Tab.2, Fig.3.b). Overall SRR declined with increasing sediment depth. In the gravity core we have measured major sulfate reduction with peak rates of 0.012, 0.008 and 0.003 nmol cm^{-3} d^{-1} at 0.2, 1.8m and at 4m, respectively. At greater depths SRR were scarce and barely above the detection limit (0.0015 nmol cm^{-3} d^{-1}). No sulfate reduction could be detected beyond 8m sediment depth.

Discussion

Interactions between carbon cycling and climatic changes can be understood if one can assess past changes in the biological productivity. Present phytoplankton productivity can be estimated from chlorophyll *a* concentration in surface waters and is used by satellite mapping of sea surface productivity (Behrenfeld and Falkowski, 1997). Due to the inherent lability of chlorophyll *a*, its degradation products chlorins serve as reliable proxy of total paleoproductivity as they are the transformation products of chlorophyll *a*, which is produced by all phytoplankton species (Harris, 1996; Rowan, 1989). Proteins are abundant in all living organisms and similar to chlorins as well common in marine primary producers, where they occur either inside of cells or as building compound of phytoplankton and also bacterial cell walls. As degradation proceeds, the composition of these molecular carbon pools changes so that refractive compounds get selectively enriched to the expense of labile carbon compounds that are depleted in both pools (Wakeham et al., 1997). Consistent with the increasingly altered fraction, the reactivity of the chlorin and protein pools decreases, and so reflects the progressing degradation of the characterizable proportion of bulk organic matter. Thus molecular proxies should be better suited to estimate past carbon fluxes better than the total organic carbon content as the latter includes both, the characterizable and the by far larger fraction of uncharacterizable organic matter.

The BUS constitutes one of the most productive global upwelling systems. As it is characterized by high organic matter accumulation (Carr, 2001) that result in two major carbon deposits, the shelf and slope depocenters (chapter 3), formed by lateral and vertical organic matter transport, it might represent a prominent sink of atmospheric CO_2 within the global carbon cycle (Mollenhauer et al., 2002; Inthorn et al., 2006).

Chlorins and proteins possess both a different availability to microbial degradation processes with respect to different modes of carbon deposition, which we will show in this study. The extent of organic carbon mineralisation was correlated with chlorins from short to long-term organic matter degradation as we demonstrated earlier (chapter2-4). Carbon fluxes based on chlorins should therefore result in more specific estimates. Her we will introduce a basic model that shows how chlorins can be used to calculate past carbon fluxes and demonstrate how these are related to the paleoceanographic setting on the Benguela slope.

Reconstruction of past carbon fluxes

The degradation of organic carbon takes place mainly within the active surface sediment layer (~30cm). This was demonstrated by measurements of sulfate reduction activity for this core (Fig.4), and is consistent with other sites on the Benguela slope (Fossing et al., 1999) or the Peru continental margin (Fossing, 1990; Parkes et al., 1994). We have measured particularly high SRR between 1.5 to 2.5m that correspond to the last glacial maximum (LGM), but below that zone sulfate reduction activity occurred only occasionally at rates barely above the detection limit (4, 5.6, 7.7m).

A similar pattern of sporadic sulfate reduction activity was observed by Fossing et al. (1999) who found that particular reactive layers in slope sediments were not indicated by total organic carbon content or the C/N ratio. By contrast at our site sulfate reduction activity was overall reflected by outstanding high chlorin concentrations and peak CI values (~0.75-0.8) (Fig.4). Thus we propose that chlorins represent a major fraction of rapidly buried reactive OM which is still slowly consumed by microbial sulfate reduction. We have previously demonstrated that organic matter sedimentation rate significantly enhanced total chlorin burial and overall carbon mineralisation rates on the Benguela upwelling slope (chapter 2) and here that chlorin amount and carbon mineralisation via SRR are directly related (Fig.4.a).

Given the methodical uncertainties of SRR measurements at larger sediment depths and the very low rates measured by us (albeit the extreme sensitivity of this technique), we developed the idea to determine past rates of sulfate reduction that should as well be proportional to total carbon mineralisation.

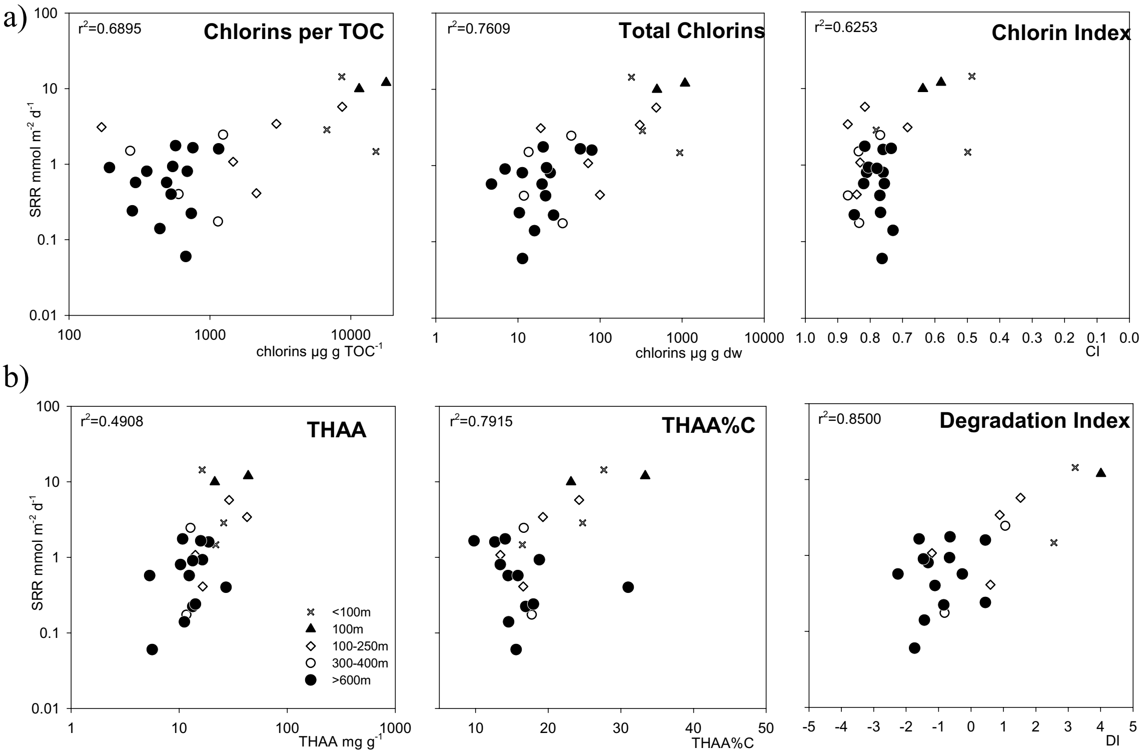


Fig.4.a and b

Correlations of SRR and total chlorins (a) and THAA (b) (and their relative proportion of TOC, chlorins: µg g TOC^{-1}, THAA: mg gTOC^{-1}) and their related degradation indices, the CI and DI. Symbols represent different water depths of sediments: ✕ < 100m, ▲ 100m, ◇ 100-250m, ○ 300-400m, ● > 600m.

In the first step, we will predict paleo sulfate reduction rates of our core based on chlorin amounts. As organic matter degradation occurred mainly in the upper sediment layer of our slope site, we assume that organic carbon influx and the total extent of mineralisation are related. We compared overall areal SRR (anoxic process of benthic mineralisation) to surface chlorin concentrations of the Benguela upwelling system (all data in appendix of chapter 3) and found a good linear fit (r2=0.8) for total chlorins (Fig.4.a). Thus we can use the correlation between chlorin carbon concentrations and SRR to calculate paleo SRR from the derived slope of that curve. Rates of paleo sulfate reduction were by two orders of magnitude higher than SRR measurements at present (Tab.4).

Taking into account the stochiometry of the sulfate reduction process (Equation 3) with two moles of carbon oxidized per one mol sulfate, we can further estimate the paleo organic carbon flux through sulfate reduction simply by multiplying SRR by two (Tab.5).

Sulfate reduction: $SO_4{}^{2-} + 2\ CH_2O \rightarrow 2\ HCO^{3-} + H_2S$ (3)

Likewise we can calculate an estimate of other microbial degradation pathways e.g. suboxic carbon oxidation processes by denitrification, Mn (IV) and Fe (III) reduction that are more energetic than sulfate reduction (Table1 in chapter1). Respective paleo rates are estimated with respect to carbon equivalents utilized in each process (Equation 4-6).

Denitrification: $5\ CH_2O + 4\ NO^{3-} \rightarrow 2N_2 + 4\ HCO^{3-} + CO_2 + 3\ H_2O$ (4)

Mn-Reduction: $CH_2O + 3CO_2 + H_2O + 2MnO_2 \rightarrow 2Mn^{2+} + 4\ HCO^{3-}$ (5)

Fe-Reduction: $CH_2O + 7CO_2 + 4Fe(OH)_3 \rightarrow 4\ Fe^{2+} + 8\ HCO^{3-} + 3\ H_2O$ (6)

We know that chlorin concentrations proportionally increased SRR. SR is the major anoxic carbon degradation process; its relative proportion to total oxygen consumption rates (TOU is equal to total carbon mineralisation) can be used to calculate the total organic carbon flux into the sediment. Total oxygen uptake was 4.7 mmol m^{-2} d^{-1} at our location (2000m) (see chapter3 and Aspetsberger, 2005); therefore areal SRR contributed 25 % to total mineralisation. Thus by multiplying the estimated paleo SRR Flux by 4 the total carbon influx can be determined. For now, we have to assume that the relative contribution of SRR to total mineralisation remains unchanged at this site. Based on the relation of total carbon flux and SRR carbon flux we can deduct the sum of the remaining carbon mineralisation pathways, aerobic respiration, denitrification, Fe and Mn reduction (Tab.5).

Finally we can determine organic carbon burial from the total carbon concentration and the sedimentation rate (this was calculated with sediment ages taken from Kirst et al., 1999, see Tab.2), and basically describe organic matter recycling and preservation for GeoB 8425.

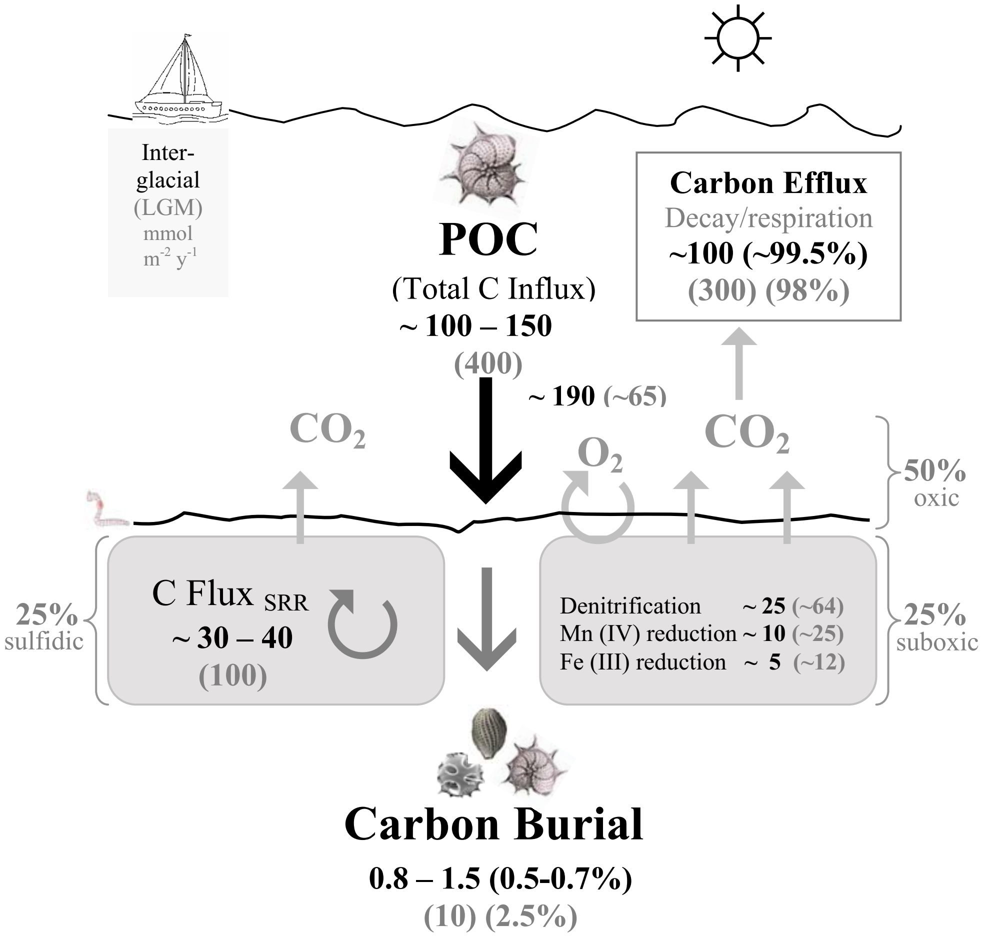


Fig.5 Organic carbon influx, mineralisation (efflux) and burial estimated from total chlorins and paleo sulfate reduction rates. In the left box the sulfidic and in the right the suboxic respiration processes are shown. Based on an assumed contribution of 25% of sulfate reduction, suboxic processes constitute 25% and oxic respiration ~ 50% of total carbon mineralisation. The bulk of supplied organic carbon is remineralized and between 0.5-0.7% finally buried (interglacials). Note exceptional high carbon burial of 2.5% during the LGM. Units of fluxes are mmol C m^{-2} y^{-1}. Glacial carbon fluxes are presented in brackets (LGM).

Organic carbon fluxes of our model revealed that most of the deposited carbon gets recycled and mineralized by oxic respiration, sulfate reduction and other anoxic processes (Fig.5, Tab.5). Total carbon fluxes were lower during warm periods (~100-150 mmol C m^{-2} y^{-1}) and largest during the LGM (400 mmol C m^{-2} d^{-1}). Assuming a constant contribution of 25 % SRR to total organic carbon mineralisation in surface sediments, oxic respiration accounted for half of total carbon mineralisation. Denitrification and microbial Mn (IV) and Fe (III) reduction contributed ~ 25%. Whereas only 0.5-0.7 % were buried at warm stages, during the last glacial maximum (LGM) 2.5 % of supplied organic carbon (from chlorins) and during the latter glacial period in OIS 4 ~ 1% was buried. Therefore the bulk of supplied organic carbon is decomposed by microbial activity (97.5-99%). Our results were comparable to Berger et al. (1989) who reported major degradation and respiration of organic material by 87.5-97 % for the coastal and open ocean. However, carbon burial was ~20 times increased at warm periods (also present conditions) and even ~80 times increased during the LGM if compared to typical organic carbon burial of ~ 0.03% of exported particles in the open ocean (Berger et al., 1989). According to Zabel and Hensen (2006) carbon burial in coastal regions may exceed that of the deep sea by 30times (~0.9%). Hence, during warm stages our estimated carbon burial was in a normal range and extraordinary high carbon burial took place during the LGM. Both cases support the significance of the Benguela slope as important carbon sink.

Implications from Paleooceanography

Given the extensive remineralisation and low fraction of buried organic carbon during warm periods of 0.5-0.9%, the much higher carbon burial of 2.5% during the LGM is noteworthy. Outstanding high chlorin concentrations and peak sulfate reduction rates were consistent with LGM enhanced carbon preservation, however largest protein and total organic carbon contents occurred during the last interglacial period at OIS 3 (Fig.3.a+b).

Proxies, chlorins and THAA were consistent with low paleo sea surface temperatures (alkenone-based SST), and therefore with intensified upwelling. LGM organic matter consisted of more refractive material, more dominated by chlorins that was diluted by lithogenic matter, whereas increased accumulation of fresher material of both pools prevailed at the interglacial upwelling period (OIS 3, ~38ky^{-1}).

We propose that the differences of buried molecular organic carbon could be attributed to different chemical and physical preservation properties of the chlorin and protein pools.

Glacial increases of chlorin concentrations were consistent with (trade-wind induced) intensified upwelling, a cooler and drier climate and the deposition of primarily fine–grained muds (Stuut et al., 2002). Potential sources of lithogenic matter might have been aeolian input or resuspended material that results from lateral particle transport and dilutes supplied organic carbon (Hebbeln and Wefer, 1991; Stuut et al., 2002; Inthorn et al., 2006). Alternatively, an offshore displacement of the major upwelling center due to the by 120m lowered glacial sea-level could have increased the supply of organic material to the lower slope (Summerhayes et al., 1995). The latter hypothesis is supported by increased TOC mass accumulation rates during the LGM (1.4-3.3 g C m^{-2} yr^{-1}) on the Walvis Bay slope and from stable nitrogen isotope records (Mollenhauer et al., 2002; Lavik, 2001). Increased sedimentation of biogenic and lithogenic matter would thus favour enhanced carbon burial by reducing its oxygen exposure time (Hartnett et al., 1998).

Burial of chlorin organic matter was most possibly enhanced by sorption of reactive chlorin matter to fine lithogenic particles e.g. clays or nonorganic bioclasts such as diatom frustules (Ransom et al., 1998; Satterberg et al., 2003) and corrobated by maximum diatom accumulation rates that occurred at the Benguela LGM (Abrantes, 2000). Opal content, in contrast to diatom abundances, was lower in LGM sediments (~4 %) but slightly larger (5 %) at OIS 3 (~38 ky^{-1}). Opal matched the largest amounts of freshest protein organic matter (~ 18 mg g^{-1} THAA, DI ~ 3.4) at OIS 3, and THAA content corresponded to a coarser sediment structure and maximum trade wind strength, hence maximum upwelling intensities (Stuut et al., 2002; Summerhayes et al., 1995). Therefore, we suggest that protein accumulation was primarily controlled by enhanced sedimentation of organic aggregates such as bioclasts. Physical protection of amino acids can be related to the sediment matrix or spaces within cell aggregates that are inaccessible to hydrolytic enzymes (Satterberg et al., 2003; Keil et al., 1994; Pichevin, 2004). Peak THAA content at depths of sulfate reactivity probably reflected the incorporation of protein matter into bacterial biomass, accounting for one third of sedimentary proteins (according to Grutters, 2002). The general decline of peak DI values (~4 to 0.8) with sediment depth revealed a continuous but very slow enzymatic degradation of buried protein aggregates with time (Gupta et al., 2002).

The mode of carbon burial and associated molecular degradation state primarily determines its availability (≈reactivity) to microbial degradation. Peaks of sulfate reduction activity were mostly consistent with the variability of refractive chlorin throughout the core, and thus suggested a continuous supply of highly altered carbon to SRR. This was comparable to conditions of carbon supply and adherent composition of chlorins at the present BUS slope depocenter (chapter 3). In addition, a similar chlorin record with nearly identical peak chlorin concentrations at the LGM and interglacial upwelling (OIS3) was reported by Harris et al. (1996) for the Northwest African slope, where strong Aeolian dust input occurs. Dilution by lithogenic particles apparently exerts major influence on high chlorin and thus high total carbon burial on the Benguela continental slope.

Conditions and rates of organic carbon deposition are a major issue if past carbon fluxes would be reconstructed from chlorin deposits as in our model. High carbon burial at the LGM revealed that refractory chlorins were more available to microbial degradation than proteins. On a regional scale, chlorins probably represent the major carbon reservoir on the Benguela (and Northwest African) slope, whose sediments own a large capacity to sequester organic carbon dioxide, in particular during the LGM. High chlorin carbon fluxes were apparently related to enhanced sedimentation rates that both were largest during the LGM, and closely linked to its sorptive capacities and storage in clayey sediments (Fig.2, Fig.6, Stuut et al., 2002). Water-column depth, sedimentation rate and oxygen exposure time are closely connected (Hartnett et al., 1999) and must be considered for regional estimates with this approach. Consistent with our model both molecular carbon pools decayed even at great depths but at extremely slow pace with respect to measured microbial sulfate reduction merely above the detection limit, and thus support chlorins as a reliable paleoceanographic proxy to reconstruct carbon fluxes.

Conclusions

We have introduced a basic model how paleo sulfate reduction rates and organic carbon fluxes may be reconstructed from chlorin deposits. Results showed that the major proportion of supplied carbon is recycled (89-99.5 %) and less burial (<1 %) occurred at warm compared to glacial periods (maximum 2.5 % at LGM). Major diagenetic controls of chlorins were sedimentation rate, mineral composition and water depth (lower during glacials) (oxygen exposure time). The mode of carbon supply and burial was a principal factor that determined organic carbon availability (reactivity) to microbial sulfate reduction.

At this deep continental margin site carbon burial was as expected slightly higher than in the deep ocean (0.03% burial) and most of the supplied carbon was degraded by aerobic respiration. Both, carbon burial and microbial sulfate reduction activity were increased during the LGM, which we attribute to different physical properties that favoured chlorin burial during that cold period of lower sea-level. Probably enhanced resuspension of sedimentary matter (lateral transport, stronger wind forcing) diluted and promoted a fast and effective burial of chlorin carbon. Both carbon pools implied following differences:

a) glacial upwelling productivity was associated with increased sedimentation of organic and lithogenic matter resulted in enhanced burial of refractive chlorin material (diluted with inorganic particles) as supported by sorptive protection of reactive chlorins on particles (reduced oxygen exposure)

b) interglacial (“pure”) upwelling productivity was undiluted and determined by enhanced sedimentation of intact or cell aggregate matter that is favourable of protein burial as such complexes are composed of largely refractive compounds (bacterial biomass, organic carbon complexes) that may enclose very reactive carbon compounds e.g. in intact cells.

Conditions of outstanding high carbon burial (LGM) were comparable to the slope depocenter. At both cases a high supply of refractive chlorin organic matter was related to the enhanced microbial mineralisation and high carbon deposition rates, emphasizing the global importance of the BUS to atmospheric CO_2 sequestration. So far we can give a realistic total estimate of carbon flux but lack a very detailed overview of the individual oxidation pathways. This could be resolved if sufficient data of oxygen uptake rates were available in order to deduce a similar correlations as performed on total chlorins. Future work on this promising approach should also include proteins as their degradation kinetics are slower than for chlorins but close to total organic carbon (TOC) in order to review their preservation potential and contribution to the Benguela continental margin carbon sink.

Appendix Chapter 5

Tab.1 Molecular productivity proxies, total chlorins and THAA, in sediments and percentage of the Total organic carbon pool, degradation indices, the CI and DI, and sulfate reduction rates for surface sediments (0-20cm) at GeoB 8425 (24°S, 2000m).

Depth [m]	Age [kyr^{-1}]	Total Chlorins [µg g^{-1}]	Chlorin Index	THAA [m g^{-1}]	DI (AA)	THAA-%C	THAA-%N	TOC %	TN %	C/N	SRR depth [m]	SRR [nmol cm^{-3} d^{-1}]
0.005	0.10	4.75	0.76	5.34	-2.25	15.9	40.1	1.57	0.19	9.4	0.01	0.00
0.015	0.20	3.46	0.75	5.32		15.0	41.3	1.66	0.19	10.3	0.03	0.78
0.025	0.35	3.33	0.77	6.10		16.3	46.8	1.75	0.19	10.8	0.05	3.77
0.04	0.55	3.25	0.74	6.81		17.1	54.7	1.86	0.18	12.0	0.07	2.31
0.06	0.90	3.27	0.74	5.71	-1.93	17.3	43.8	1.54	0.19	9.5		
0.08	1.20	3.48	0.73	5.99								
0.1	1.50	3.61	0.76	5.40		19.3	45.8	1.30	0.17	8.8	0.09	5.45
0.12	1.80	4.58	0.75	6.26							0.11	8.57
0.14	2.05	4.49	0.76	7.16		15.6	52.6	2.14	0.20	12.6	0.13	6.35
0.16	2.40	4.51	0.76	6.29		17.4	46.0	1.69	0.20	9.9	0.15	1.39

Tab.2 Molecular productivity proxies, total chlorins and THAA, in sediments and percentage of the Total organic carbon pool, degradation indices, the CI and DI, and sulfate reduction rates for gravity core 8425 (24°S, 2000m).

Iso-tope stage **		ID	section (cm)	[m]	*age [ky^{-1}]	*SST [°C]	TotalChlorins		Chlorin Index		THAA [mg g^{-1}]	THAA %C	THAA %N	DI (PCA)	TOC %	TIC %	TN %	C/N_{mol}
							µg g^{-1}	Std Dev	CI	Std Dev								
1	Holocene	**SL 1**	17-18	0.18	**2.7**	**19.0**	**3.68**	**0.12**	**0.82**	**0.004**	**4.04**	**16.10**	**37.37**	**-3.15**	**1.17**	**9.68**	**0.16**	**8.7**
		SL 2	55-57	0.56	7.9	19.3	6.89	0.44	0.85	0.009	4.03	11.99	30.80	-1.26	1.57	9.29	0.19	9.6
		SL 3	104-106	1.05	12.6	17.5	9.30	0.20	0.82	0.015	7.63	8.93	14.17	-0.72	3.99	7.32	0.79	5.9
2	LGM	**SL 4**	145-148	1.47	**15.0**	**15.7**	**16.90**	0.60	**0.78**	0.002	**10.22**	**9.47**	**26.40**	**1.82**	**5.04**	5.59	**0.56**	**10.4**
		SL 5	202-204	2.03	17.3	15.9	17.99	0.88	0.82	0.013	12.78	9.76	27.66	0.84	6.12	5.06	0.67	10.6
		SL 6	245-247	2.46	19.3	15.8	11.79	1.32	0.80	0.004	14.76	10.32	23.74	0.86	6.68	5.15	0.91	8.6
3	Interglacial	**SL 7**	315-317	3.16	**31.7**	**15.1**	**10.13**	**1.35**	**0.77**	**0.024**	**14.81**	**7.88**	**30.63**	**1.46**	**8.78**	**3.46**	**0.70**	**14.5**
		SL 8	352-353	3.53	**38.0**	**14.6**	**15.21**	**1.40**	**0.75**	**0.005**	**18.46**	**9.68**	**29.17**	**3.39**	**8.91**	**4.77**	**0.92**	**11.3**
		SL 9	406-408	4.07	**46.2**	**14.6**	**11.32**	**0.21**	**0.76**	**0.007**	**13.49**	**10.55**	**31.78**	**-0.87**	**5.97**	**6.07**	**0.62**	**11.3**
		SL 10	466-468	4.67	54.9	15.7	10.18	0.82	0.78	0.033	13.14	10.82	32.54	1.14	5.67	6.50	0.59	11.2
		SL 11	508-510	5.09	59.9	15.7	8.93	0.08	0.77	0.011	11.13	11.32	33.46	1.51	4.59	6.15	0.48	11.1
4	Gla-cial	**SL 12**	566-568	5.67	**67.3**	**15.2**	**11.04**	**0.52**	**0.80**	**0.013**	**10.65**	**9.33**	**28.58**	**2.97**	**5.33**	**4.75**	**0.54**	**11.5**
		SL13	601-603	6.02	**71.3**	**17.7**	**6.37**	**1.54**	**0.76**	**0.009**	**11.47**	**9.41**	**29.36**	**2.31**	**5.69**	**5.90**	**0.57**	**11.7**
5	Interglacial	**SL 14**	651-653	6.52	77.1	18.8	5.58	0.08	0.83	0.004	6.56	9.65	27.35	0.14	3.18	7.52	0.35	10.6
		SL 15	723-725	7.24	85.3	18.9	7.28	0.55	0.79	0.012	6.70	9.45	27.72	0.26	3.31	6.84	0.35	11.0
		SL 16	774-776	7.75	**92.6**	**19.5**	**4.69**	**0.04**	**0.74**	**0.003**	**10.62**	**9.24**	**29.14**	**1.58**	**5.37**	**6.56**	**0.53**	**11.8**
		SL 17	811-813	8.12	99.0	19.4	6.21	0.62	0.79	0.001	9.31	9.00	27.77	-0.10	4.84	5.72	0.49	11.5
		SL 18	861-863	8.62	104.0	18.9	5.65	0.04	0.81	0.014	5.71	9.52	27.30	0.66	2.80	7.71	0.30	10.7
		SL 19	911-913	9.12	110.8	19.5	5.37	0.10	0.82	0.012	8.18	9.81	29.84	0.27	3.89	7.07	0.40	11.4
		SL 20	961-963	9.62	**120.1**	**21.4**	**3.84**	**0.13**	**0.76**	**0.002**	**4.85**	**9.66**	**23.14**	**-3.56**	**2.34**	**7.94**	**0.31**	**9.0**
		SL 21	1011-1013	10.12	127.8	20.2	1.76	0.21	0.78	0.017	3.41	*8.01	23.94	-6.40		9.21	0.21	
6		**SL 22**	1061-1063	10.62	135.0	16.0	3.04	1.80	0.79	0.068	3.03	*2.75	22.39	-3.16		8.03	0.20	

* (GC 1711) in Kirst et al., 2001,calculated THAA-%C with TOC by Kirst et al.

** after Kirst et al., 2001, Little et al., 1997; Imbrie et al., 1984

Tab.2 continued

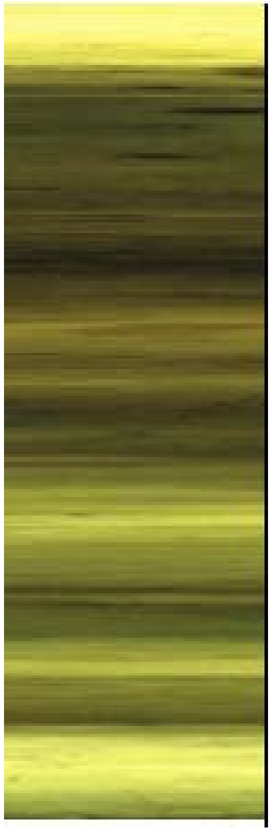
section (cm)	depth [m]	Sulfate depth [m]	Sulfate [µmolml^{-1}]	SRR [nmol cm^{-3} d^{-1}]
16-17	0.15	0.35	23.9	**0.0078**
55-57	0.56	0.60	25.3	0.0023
103-104	1.04	1.10	22.7	0.0009
148-157	1.53	1.60	24.8	**0.0078**
201-202	2.02	2.10	20.9	0.0056
247-248	2.48	2.35	22.4	0.0024
314-315	3.15	3.10	17.5	**0.0028**
350-351	3.51	3.35	16.2	**0.0012**
405-406	4.06	4.15	15.4	**0.0022**
465-466	4.66	4.65	13.9	b.d.
507-508	5.08	5.15	10.7	b.d.
565-566	5.66	5.65	10.7	**0.0015**
600-601	6.01	5.90	8.7	b.d.
650-651	6.51	6.65	7.5	b.d.
722-723	7.23	7.20	5.8	b.d.
774-776	7.75	7.70	4.1	**0.0009**
810-811	8.11	8.20	2.9	b.d.
860-861	8.61	8.70	3.0	b.d.
910-911	9.11	9.20	2.9	b.d.
960-961	9.61	9.70	1.6	b.d.
1010-1011	10.11	9.95	1.3	b.d.
1060-1061	10.61	10.70	0.0	b.d.

** after Kirst et al., 2001, Little et al., 1997; Imbrie et al., 1984

Tab.3 Amino acids as mole percentages of THAA for gravity core 8425 (24°S, 2000m)

Isotope stage **		Sample	[m]	*age [ky^{-1}]	*paleo SST [°C]	ASP	GLU	SER	HIS	GLY	THR	ARG	ALA	βALA	TYR	GABA	MET	VAL	PHE	ILEU	LEU	LYS
1	Holocene	SL-1	0.18	2.7	19.0	33.7	10.0	5.1	1.1	10.5	5.2	6.4	9.1	1.0	1.3	1.0	0.5	5.3	2.9	3.0	4.0	0.0
		SL-2	0.56	7.9	19.3	21.1	9.6	4.8	0.9	20.0	5.7	7.3	9.4	1.5	1.4	1.9	0.4	5.8	2.9	2.8	4.4	0.0
		SL-3	1.05	12.6	17.5	30.0	10.3	4.4	0.7	12.0	5.0	5.7	9.0	1.0	1.6	0.9	0.3	6.7	3.6	3.7	5.1	0.1
2	LGM	SL-4	1.47	15.0	15.7	23.6	11.4	5.0	-0.1	13.6	5.8	5.9	9.7	1.1	2.1	1.0	0.2	6.9	3.9	3.7	5.6	0.6
		SL-5	2.03	17.3	15.9	24.9	10.9	4.6	0.6	11.5	5.6	6.0	10.2	1.1	1.9	1.3	0.5	7.3	3.7	3.8	5.6	0.5
		SL-6	2.46	19.3	15.8	21.7	11.4	4.9	0.6	14.9	5.8	6.2	10.0	1.2	1.8	1.4	0.5	6.6	3.8	3.7	5.4	0.0
3	Interglacial	SL-7	3.16	31.7	15.1	24.9	10.9	4.5	0.4	12.0	5.4	5.7	9.9	1.0	2.1	1.0	0.5	7.4	4.2	4.2	5.9	0.0
		SL-8	3.53	38.0	14.6	17.8	9.0	4.9	0.5	15.0	6.1	5.6	11.7	1.0	2.5	1.7	0.5	7.7	4.6	4.9	6.4	0.0
		SL-9	4.07	46.2	14.6	22.9	9.3	3.8	0.4	12.3	4.5	5.8	8.6	0.9	1.9	1.0	0.4	6.4	3.9	3.8	5.9	8.4
		SL-10	4.67	54.9	15.7	16.4	9.3	4.2	0.5	18.9	5.5	7.7	10.3	1.8	2.0	1.7	0.5	6.6	3.5	3.8	6.2	0.9
		SL-11	5.09	59.9	15.7	16.3	9.7	4.3	0.5	15.8	5.1	7.9	9.9	1.6	1.8	1.8	0.5	7.1	4.2	4.0	7.1	2.5
4	Glacial	SL-12	5.67	67.3	15.2	16.8	9.6	4.0	0.3	14.4	5.1	7.1	10.4	1.5	2.0	1.8	0.5	8.0	4.9	4.9	7.3	1.4
		SL-13	6.02	71.3	17.7	19.2	9.7	4.0	0.4	14.4	4.9	7.6	10.9	1.5	2.5	1.7	0.5	6.8	4.6	4.3	6.5	0.4
5	Interglacial	SL-14	6.52	77.1	18.8	19.2	9.7	4.9	1.2	17.5	6.0	6.9	9.5	1.5	1.7	1.5	0.3	6.0	4.1	3.1	5.6	1.3
		SL-15	7.24	85.3	18.9	19.4	9.0	4.2	1.1	15.8	5.0	8.1	9.6	1.6	1.7	1.7	0.3	6.8	4.0	4.0	6.0	1.7
		SL-16	7.75	92.6	19.5	17.9	8.9	4.0	0.5	15.4	4.9	9.0	10.0	1.6	1.8	1.7	0.2	6.8	4.6	4.3	6.6	1.7
		SL-17	8.12	99.0	19.4	26.7	9.1	3.7	0.4	8.8	4.3	7.2	9.6	0.9	1.8	1.0	0.2	7.3	3.7	4.3	6.0	4.9
		SL-18	8.62	104.0	18.9	24.3	9.8	4.0	1.2	9.6	5.0	8.7	10.0	1.5	1.6	1.1	0.4	7.8	4.1	4.3	6.6	0.0
		SL-19	9.12	110.8	19.5	23.9	9.9	3.9	1.4	14.9	5.1	7.4	9.7	1.6	1.8	1.5	0.3	7.2	4.8	0.2	6.3	0.0
		SL-20	9.62	120.1	21.4	19.3	8.4	5.1	1.9	16.9	5.4	7.8	10.3	1.5	0.3	3.3	0.5	4.9	2.7	2.7	4.5	4.4
		SL-21	10.1	127.8	20.2	22.5	7.3	4.0	1.4	7.0	4.6	7.3	8.2	1.3	1.0	0.6	0.8	5.1	2.8	3.0	3.8	19.4
6		SL-22	10.6	135.0	16.0	24.2	8.4	3.8	1.4	11.0	4.7	6.6	8.5	1.7	1.2	1.1	0.6	6.3	3.7	3.7	4.8	8.5

Visual core description and colour scan of GeoB 8422, sister core of GeoB 8425 (cruise report M57/2, 2003)



Depth [m]	Stratigraphic horizones	Index
0.2	**foram bearing nannofossil ooze**	**F**
0.6	diatom ooze	D
1.1	foram/diatom ooze	F/D
1.5	diatom bearing foram/nannofossil ooze	D
2.0	**foram**	**C-F**
2.5	**clay /foram**	**C-F**
3.2	**diatom/foram bearing nannofossil ooze**	**D/F**
3.5	**diatom bearing foram/nannofossil ooze**	**D**
4.1	foram bearing diatom/nannofossil ooze	F/D
4.7	diatom/foram bearing nannofossil ooze	D
5.1	foram bearing diatom/nannofossil ooze	F/D
5.7	**foram bearing diatom/nannofossil ooze**	**F/D**
6.0	**diatom/foram bearing nannofossil ooze**	**D**
6.5	diatom/foram bearing nannofossil ooze	D
7.2	clay/foram	C-F
7.8	**foram/diatom bearing nannofossil ooze**	**F/D**
8.1	diatom/foram bearing nannofossil ooze	D/F
8.6	diatom/foram bearing nannofossil ooze	D/F
9.1	diatom/foram bearing nannofossil ooze	D/F
9.6	**foram bearing nannofossil ooze**	**F**
10.1	foram bearing nannofossil ooze	F
10.6	foram bearing nannofossil ooze	F

Tab.4 Reconstructed paleo sulfate reduction rates, total carbon fluxes and burial based on total chlorin content

			25% $_{\text{const}}$								includes CO_2 release from suboxic and oxic degradation					25%	50%
OIS	depth [m]	Age* [ky^{-1}]	Paleo SRR $_{\text{totchlorin}}$	C Flux SRR	C Flux SRR	Total C Flux	Total C Flux	Sedimen-tation rate*	Carbon Burial		C efflux (excludes SRR)		Nitrifi-cation	Fe (III) - reduction	Mn(IV)-red.	Sum (Fe,Mn, NO$_3^-$)	aerobic respira-tion
			mmol m^{-2} d^{-1}	mmol C m^{-2} d^{-1}	mmol C m^{-2} y^{-1}	mmol C m^{-2} d^{-1}	mmol C m^{-2} y^{-1}	cm y^{-1}	mmol C m^{-2} y^{-1}	%	mmol C m^{-2} y^{-1}	%	mmol C m^{-2} y^{-1}	mmol C m^{-2} y^{-1}	mmol C m^{-2} y^{-1}	mmol C m^{-2} y^{-1}	mmol C m^{-2} y^{-1}
1	0.2	2.7	0.03	0.06	21.5	0.2	86.0	0.007	0.64	0.7	63.9	74.3	13.4	2.7	5.4	21.5	42.4
	0.6	7.9	0.06	0.11	40.3	0.4	161.1	0.010	1.68	1.0	119.1	74.0	25.2	5.0	10.1	40.3	78.9
	1.1	12.6	0.07	0.15	54.3	0.6	217.3	0.017	3.76	1.7	159.2	73.3	33.9	6.8	13.6	54.3	104.9
2	**1.5**	**15.0**	**0.14**	**0.27**	**98.7**	**1.1**	**394.9**	**0.025**	**9.70**	**2.5**	**286.5**	**72.5**	**61.7**	**12.3**	**24.7**	**98.7**	**187.7**
	2.0	**17.3**	**0.14**	**0.29**	**105.0**	**1.2**	**420.2**	**0.022**	**9.03**	**2.2**	**306.1**	**72.9**	**65.7**	**13.1**	**26.3**	**105.0**	**201.1**
	2.5	19.3	0.09	0.19	68.8	0.8	275.3	0.006	1.55	0.6	204.9	74.4	43.0	8.6	17.2	68.8	136.1
3	3.2	31.7	0.08	0.16	59.2	0.6	236.7	0.006	1.38	0.6	175.9	74.3	37.0	7.4	14.8	59.2	117.0
	3.5	38.0	0.12	0.24	88.8	1.0	355.4	0.007	1.57	0.4	264.1	74.3	55.5	11.1	22.2	88.8	176.1
	4.1	**46.2**	**0.09**	**0.18**	**66.1**	**0.7**	**264.5**	**0.007**	**2.45**	**0.9**	**195.9**	**74.1**	**41.3**	**8.3**	**16.5**	**66.1**	**129.8**
	4.7	54.9	0.08	0.16	59.4	0.7	237.7	0.008	2.22	0.9	176.1	74.1	37.1	7.4	14.9	59.4	116.6
	5.1	59.9	0.07	0.14	52.1	0.6	208.5	0.008	1.86	0.9	154.5	74.1	32.6	6.5	13.0	52.1	102.4
4	**5.7**	**67.3**	**0.09**	**0.18**	**64.5**	**0.7**	**257.9**	**0.009**	**2.26**	**0.9**	**191.1**	**74.1**	**40.3**	**8.1**	**16.1**	**64.5**	**126.7**
	6.0	71.3	0.05	0.10	37.2	0.4	148.7	0.009	1.28	0.9	110.3	74.1	23.2	4.6	9.3	37.2	73.1
5	6.5	77.1	0.04	0.09	32.6	0.4	130.4	0.009	1.14	0.9	96.7	74.1	20.4	4.1	8.1	32.6	64.1
	7.2	85.3	0.06	0.12	42.5	0.5	170.0	0.007	1.19	0.7	126.3	74.3	26.6	5.3	10.6	42.5	83.8
	7.8	92.6	0.04	0.07	27.4	0.3	109.5	0.006	0.63	0.6	81.5	74.4	17.1	3.4	6.8	27.4	54.1
	8.1	99.0	0.05	0.10	36.2	0.4	145.0	0.010	1.45	1.0	107.3	74.0	22.7	4.5	9.1	36.2	71.0
	8.6	104.0	0.05	0.09	33.0	0.4	132.0	0.007	0.97	0.7	98.0	74.3	20.6	4.1	8.3	33.0	65.0
	9.1	110.8	0.04	0.09	31.3	0.3	125.3	0.005	0.67	0.5	93.3	74.5	19.6	3.9	7.8	31.3	62.0
	9.6	120.1	0.03	0.06	22.5	0.2	89.8	0.006	0.58	0.6	66.8	74.4	14.0	2.8	5.6	22.5	44.3
	10.1	127.8	0.01	0.03	10.3	0.1	41.0	0.007	0.28	0.7	30.5	74.3	6.4	1.3	2.6	10.3	20.2
6	10.6	135.0	0.02	0.05	17.8	0.2	71.0	0.008	0.56	0.8	52.7	74.2	11.1	2.2	4.4	17.8	34.9

Chapter 6

Concluding Remarks

Concluding remarks

The primary objective of this study was to access the reactivity of organic carbon in continental margin sediments by the application of molecular organic carbon degradation indices and proxies.

We wanted to access the link between organic matter composition and mineralisation. Therefore we studied two major molecular carbon pools, pigments and proteins, as their molecular composition is subject to diagenetic changes: its reactivity (availability to microbial degradation) continuously decreases as degradation proceeds. Molecular compositional changes were indicated by molecular proxies, the chlorin-based CI and the protein-based DI.

One major issue of this work was to assess the time scales of these degradation indices. We could show that the different time spans on which the CI and DI correspond to degradation are highly associated with the chemical properties of pigments and proteins and mode of organic matter deposition in the investigated areas.

Diagenetic controls: BUS

Being highly sensitive to aerobic decay, high accumulation of organic carbon is promoted by a high primary productivity, high sedimentation rates that reduce its oxygen exposure time (Hartnett et al., 1998; Canfield, 1994; Calvert and Pedersen, 1992, Müller and Suess, 1979). High primary production associated with coastal upwelling was reflected by generally large amounts of fresher organic matter on the shelf that both decreased at greater water depths. Major influence of water column depth, thus reduced sedimentation, on organic matter amount and composition was consistent with applications of these indices in the Peru and Chile upwelling area (Niggemann, 2005), however in the Benguela upwelling system, sedimentation rate and the mode of carbon deposition were important additional controls on the molecular composition of organic material. In the central upwelling area, high accumulation of slightly less refractive organic matter (chlorins, proteins) at mid-slope depth, compared to the surrounding slope, characterized a large depocenter of organic carbon. Shelf depocenter sediments (mudbelt) were characterized by even higher carbon accumulation and contained more labile chlorin and protein matter. Anoxic organic carbon mineralisation was the process in shelf and slope sediments and directly related to chlorin concentrations. High sulfate reduction rates on the shelf decreased by three orders of magnitudes on the slope and could be primarily attributed to a decrease in total chlorin amounts. Refractive chlorin material promoted microbial mineralisation at both sites being slightly more labile (CI ~0.6) on the shelf than on the slope depocenter (CI ~0.75). Therefore we conclude for the Benguela upwelling system that at condition of high carbon supply, refractory organic matter features a greater availability to microbial mineralisation, promoting sulfate reduction.

Arctic Shelf (Spitzbergen)

In contrast to perennial high productivity in the BUS, Arctic primary production and coupled benthic activity are controlled by permanent cold temperatures, the seasonal changes of light and associated oceanographic conditions. Consistent with previous studies on the aerobic degradability of organic carbon in Spitzbergen shelf and slope sediments (Hulth et al., 1996), molecular proxies and their degradation indices revealed a similar regionalization of organic matter reactivity that was primarily related to seasonal ice coverage and the related productivity pattern. Earlier ice retreat and thus annually higher carbon supply by enhanced ice-edge productivity was reflected by increased deposition of refractive chlorin matter and characteristic phytoplankton pigments. Low amounts of labile (source-like) chlorin matter characterized sites of annually longer ice cover. In contrast protein content but less its composition decreased from largest amounts at sites of early ice retreat and affected by warm and nutrient-rich Atlantic water towards the northern permanent ice pack. We conclude that protein contents were tracing the average trend of the withdrawing marginal ice zone and represented a later time slice as well as differently preferred pathways of organic matter degradation. At high carbon supply, decomposing refractive chlorin matter mainly fueled sulfate reduction. From down core profiles at sites of low but very labile carbon supply we suggested, the reactive chlorin fraction was rapidly oxidized and proteins degradation continued with depth. This was in accord with Vandieken et al. (2006) who also emphasized organic carbon supply as major limiting factor of total mineralisation and sulfate reduction in particular.

Availability of molecular carbon pools to microbial degradation

To date chlorins and its degradation state (CI) have been mainly applied to characterize surface sediments that cover early diagenetic changes of organic matter over approximately 10 000 years (multicores). In order to define the sensitivity of the Chlorin Index and the protein-based DI to initial stages of organic matter supply and decomposition, we have performed anoxic sediment incubations of shelf and slope sediments. The overall result confirmed what the regional description of the BUS and Arctic suggested: inherent more refractive sedimentary matter enriched with fresh substrate from sites of higher carbon supply (MIZ, BUS slope) was easily available and at high rates utilized. In all incubations an initial delay of sulfate reduction rates was observed. Decreasing CI values and increased release of phytoplankton pigments (chlorophyll *a*, pheophytin *a*) indicated that hydrolytic breakdown of macromolecular matter took place. Subsequent to hydrolysis carbon mineralisation as measured by microbial sulfate reduction increased and bacteria could thrive on cleaved small compounds. In contrast to proteins, the CI proved most sensitive to the initial stages of degradation. Although this molecular proxy can not determine which of the small sized compounds fed microbial degradation, it clearly defines the time point (the rate-limiting step) of organic carbon compound availability.

With respect to the CI being sensitive to the initial stages of degradation and the DI responding to later organic matter decay, the question arose if molecular indices may as well reflect geological time scales and thus could be applied to reconstruct organic carbon flux and burial? We have estimated past sulfate reduction rates based on chlorin deposits and then estimated total organic carbon flux and burial. The results were supported by paleoceanographic implications based on molecular carbon pools and their composition in Benguela continental slope sediments (2000m wd). They revealed that large amounts of refractive chlorin organic matter were buried during the last glacial maximum. Smaller amounts of more labile organic matter were deposited during interglacial upwelling events. Different availability of organic matter was most likely associated with the mode of carbon deposition. During the LGM particle resuspension and sorption of refractive chlorin matter to suspended clayey particles was most probably associated with the lowered sea level, leading to enhanced organic matter sedimentation and burial rates. At interglacial periods phytodetrititus aggregates accumulated comparatively undiluted. This resulted in burial of fresher matter (as indicated by high THAA amounts and DI values) probably incorporated within aggregates or complexes of refractory bacterial biomass.

Based on these different modes of chlorin and protein carbon deposition, the basic model that we introduced could be further refined to reconstruct past carbon fluxes that apparently depend on the mode of carbon supply and burial.

Future research in the BUS and other high-productivity regions should consider and quantify the relative contribution of depositional processes, in particular for estimates of past carbon fluxes. Deposition conditions strongly impact the availability of molecular organic matter to microbial degradation that may last even until today as observed from slow mineralisation rates (SRR) in chlorin deposits of the LGM.

Contributions to manuscripts

Chapter 2

Diagenetic controls on pigment - and protein - based organic carbon degradation indices

The concept of the study was developed by A. Ahke and T.G. Ferdelman. Sampling, performance of experiments and analysis of organic parameters was carried out by A. Ahke. C. Schubert provided facilities for THAA measurements and carried out amino acid analysis. Calculation of the DI was conducted by A. Ahke. Sulfate reduction rate data from the Namibian continental slope and shelf were contributed by T.G. Ferdelman and V. Brüchert. A. Ahke wrote the manuscript that will be prepared for submission to *Geochimica et Cosmochimica Acta* with co-authors T.G. Ferdelman and C.J. Schubert.

Chapter 3

Organic matter composition of the Benguela shelf and slope depocenters: A characterization by productivity proxies and molecular degradation indices

The concept of the study was developed by A. Ahke, T.G. Ferdelman and C.J. Schubert. Sampling, analysis and evaluation of organic parameters was carried out by A. Ahke. C. Schubert provided facilities for THAA measurements and amino acid analysis. Calculation of the DI was conducted by A. Ahke. A. Ahke wrote the manuscript with editorial input from T.G. Ferdelman and C.J. Schubert. The manuscript is in preparation for submission to *Deep-Sea Research* with co-authors T.G. Ferdelman, C.J. Schubert, V. Brüchert and M. Zabel.

Chapter 4

Organic carbon reactivity of Arctic sediments (Spitzbergen Shelf) characterized by molecular degradation indices of two major carbon pools, pigments and proteins

The concept of the study was developed by A. Ahke, T.G. Ferdelman and B. B. Jørgensen. Sampling, analysis and evaluation of organic parameters was carried out by A. Ahke. C. Schubert provided facilities and support for THAA measurements and amino acid analysis. Calculation of the DI was conducted by A. Ahke. M. Nickel assisted sampling and contributed sulfate reduction rate data. She also provided sediment samples from West Spitzbergen fjords and eastern stations X, XII and VIII. A. Ahke wrote the manuscript. A manuscript based on this chapter will be prepared for submission to *Continental Shelf Research* with co-authors M. Nickel, T.G. Ferdelman, C.J. Schubert and B.B. Jørgensen.

Chapter 5

Paleoenvironmental implications from molecular productivity proxies and degradation indices on the Benguela continental slope (GeoB 8425)

The concept of the study was developed by A. Ahke and T.G. Ferdelman. M. Zabel enabled the author's participation on the Meteor 57/2 cruise and was responsible for coring and stratigraphy. This included access to the gravity core (GeoB 8425) and allocation of sulfate data. Analysis and evaluation of organic parameters was carried out by A. Ahke. T.G. Ferdelman carried out sampling for organic parameters and sulfate reduction rate measurements; A. Ahke performed analysis and calculations of sulfate reduction rates. C. Schubert performed amino acid analysis. Calculation of the DI was done by A. Ahke. A. Ahke wrote the manuscript. A manuscript based on this chapter will be prepared for submission to *Marine Geology* with co-authors T.G. Ferdelman, C.J. Schubert and M. Zabel.

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