Composition and degradation of organic matter in sediments from the Peru-Chile upwelling region

Dissertation
zur Erlangung des Doktorgrades
der Naturwissenschaften
- Dr. rer. nat. -

im Fachbereich Geowissenschaften
der Universität Bremen

vorgelegt von

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Bremen
April 2005

Tag des Promotionskolloquiums: 26. August 2005

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Man sieht nur mit dem Herzen gut.
Das Wesentliche ist für die Augen unsichtbar.

„Der kleine Prinz“
Antoine de Saint-Exupéry

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THESIS ABSTRACT

The Peru-Chile upwelling region is the largest coastal upwelling system of the world. As part of the projects “Peru-Upwelling” (RV Sonne cruise 147) and PUCK (RV Sonne cruise 156) sediments from the Peruvian and Chilean upwelling region have been investigated for organic geochemical composition and microbiological parameters. This thesis presents a biogeochemical characterization of surface sediments from the shelf and continental slope off Peru (9-14°S) and Chile (23°S and 36°S). Main objective was the characterization of sedimentary organic matter (OM) composition, with respect to sources and quality, and with special focus on early diagenetic degradation processes.

The general influence of depositional conditions on the accumulation and composition of sedimentary OM, and on the associated sedimentary processes, became evident from the comparison of sediments from two different depositional systems off Chile as well as from the examination of the spatial distribution of sediment characteristics off Peru. It could be shown that besides vicinity to actual upwelling centers and upwelling intensity, winnowing and redistribution by bottom currents in combination with effects of seafloor topography provide a major control on the sediment composition.

There were no indications for input of terrestrial OM to the investigated sediments. Elemental (C/N-ratio) and carbon isotopic compositions of the sedimentary OM were characteristic for a predominantly marine origin, and specific terrestrial biomarkers could not be identified. In particular, analysis of the molecular carbon isotopic composition revealed a non-terrestrial source for long-chain fatty acids, typically regarded as biomarkers for higher plant input. Lacking evidence for terrestrial OM in the sediments is in accordance with limited river discharge and small eolian input from the vegetation poor and extremely dry Atacama Desert that borders most of the investigated coastal area. Terrestrial input was also undetectable in sediments depositing near Concepción (36°S), where several rivers, draining the more humid hinterland of central Chile, enter the coastal Pacific. Here, an expected terrestrial signal was possibly concealed by the high marine input. Chlorin concentrations as a measure for input of phytoplankton detritus were on average a factor 10 higher in sediments off Peru than off Chile, partly reflecting higher annual primary production rates in the perennial upwelling region off Peru, whereas upwelling and productivity off Chile display strong seasonality. Characteristic biomarkers for diatoms (brassicasterol) and dinoflagellates (dinosterol) were abundant in sediments off Peru and highly correlated to OM concentrations, indicating that these phytoplankton organisms, typically dominating in highly productive

coastal upwelling areas, were major contributors to sedimentary OM.

Bacteria could be identified as an important source of sedimentary OM. In sediments off Chile, bacterial specific fatty acids (*iso*- and *anteiso* C_{14}-C_{17}) accounted for 12-34% of all identified fatty acids. Highest percentages were observed at the sediment surface of sites from the oxygen-minimum-zone, reflecting both, intense bacterial reworking at these shallow sites and accumulation of bacterial biomass in the absence of oxygen. Sediments from the oxygen-minimum-zone also displayed the highest concentrations of the fatty acid 10-methyl-16:0, indicative for the presence of sulfate- and/or iron-reducing bacteria of *Desulfobacter* and *Geobacter* species. In contrast, imprints of the large sulfur bacteria *Thioploca* on the OM composition could not be revealed, even though biomasses up to 250 g m^{-2} were observed off Peru. It could be shown that dead bacterial biomass accounts for a significant fraction of sedimentary OM. The amino sugar muramic acid uniquely found in bacterial cell walls was used to estimate bacterial cell numbers in sediments off Peru. These numbers were up to 500 times higher than cell counts reported for sediments in this area. It was further estimated that at most 5-36% of individual D-amino acids in Chilean sediments were associated with peptidoglycan of living cells.

Different parameters have been applied to assess the quality or freshness of the sedimentary OM. Water depth was the main factor controlling OM freshness at the sediment surface, e.g. the fractions of labile compounds such as chlorins, fatty acids, and amino acids decreased with increasing water depth. Since bottom water oxygen concentrations were closely related to water depths it was impossible to identify effects of oxygen availability on OM freshness. C/N-ratios, representing bulk OM quality, generally increased with increasing water depth and were highest at sites where refractory material accumulated. The amino acid based degradation index, derived from principal component analysis of the molecular amino acid composition, has successfully been applied to characterize OM freshness in sediments off central Chile, but did not reflect changes in the degradation state of sedimentary OM off northern Chile. A new parameter for OM freshness in sediments, the Chlorin Index, has been evolved and was routinely applied in this study. Low Chlorin Indices indicative for fresh OM were found in sediments from shallow water depth, whereas higher values characterized the more degraded state of sedimentary OM at greater water depths. Another quality parameter was derived from principal component analysis of the molecular fatty acid composition. This fatty acid index reflected OM alteration in water column and sediments off Chile and showed a good correspondence to other quality indicators applied in this study. Reactivities of bulk OM, chlorins, and individual fatty acids have been estimated from down-core decreasing

concentrations in dated sediments. The reaction rate constants for bulk OM decreased with increasing water depth, suggesting that water column degradation also affects long-term reactivity of sedimentary OM. Among the fatty acids, in accordance with findings of earlier studies, polyunsaturated were the most, long-chain saturated fatty acids the least reactive compounds.

Bacterial sulfate reduction was the quantitatively most important terminal electron acceptor process in the investigated sediments. Measured sulfate reduction rates (SRR) were therefore regarded to reflect the availability of sedimentary OM for microbial degradation. The SRR generally decreased with increasing water depth, following the water depth dependence of sedimentary OM quality. Overall, the SRR showed a good correspondence with the chemically defined parameters applied in this study to assess the quality of the sedimentary OM. The predominance of sulfate reduction for OM remineralization in anoxic marine sediments was stressed by the good correspondence of reaction rate constants, that were obtained for bulk OM on the one hand from measured SRR, and on the other hand from the down-core decrease in OM concentration. It could further be shown, that another important microbial degradation process in anoxic marine sediments, the anaerobic oxidation of microbially produced methane, is linked with the accumulation and burial of organic-rich sediments in the investigated region. Thus, biogeochemical processes in surface sediments influence amount and quality of substrates for methanogenesis deeper in the sediments.

KURZFASSUNG

Das peruanisch-chilenische Auftriebsgebiet ist das größte Küstenauftriebssystem der Welt. Im Rahmen der Projekte „Peru-Auftrieb“ (FS Sonne Ausfahrt 147) und PUCK (FS Sonne Ausfahrt 156) wurden Sedimente der peruanischen und chilenischen Auftriebsgebiete hinsichtlich ihrer organisch geochemischen Zusammensetzung und mikrobiologischer Parameter untersucht. Diese Arbeit präsentiert eine biogeochemische Charakterisierung von Oberflächensedimenten des Schelfs und Kontinentalhangs vor Peru (9-14°S) und Chile (23°S und 36°S). Hauptziel war die Charakterisierung der Zusammensetzung des organischen Materials (OM) im Hinblick auf Herkunft und Qualität, einen besonderen Schwerpunkt bildeten frühdiagenetische Abbauprozesse.

Der grundsätzliche Einfluss der Ablagerungsbedingungen auf die Akkumulation und Zusammensetzung von sedimentärem OM und die damit verbundenen sedimentären Prozesse wurde sowohl im Vergleich von Sedimenten aus zwei verschiedenen Ablagerungssystemen vor Chile als auch bei der Untersuchung der räumlichen Verteilung von Sediment-Eigenschaften vor Peru deutlich. Es konnte gezeigt werden, dass neben der räumlichen Nähe zu aktuellen Auftriebszentren und der Auftriebsintensität, Sortierung und Umverteilung durch Bodenströmungen - im Zusammenspiel mit Auswirkungen der Meeresbodentopografie - wesentliche Kontrollgrößen für die Sedimentzusammensetzung darstellen.

Es gab keine Hinweise auf Eintrag von terrestrischem OM in die untersuchten Sedimente. Elementare (C/N-Verhältnisse) und Kohlenstoff-isotopische Zusammensetzung des sedimentären OM waren charakteristisch für eine überwiegend marine Herkunft, und spezifische terrestrische Biomarker konnten nicht identifiziert werden. Insbesondere enthüllte die Analyse der molekularen Kohlenstoff-isotopischen Zusammensetzung eine nicht-terrestrische Quelle der langkettigen Fettsäuren, welche typischerweise als Biomarker höherer Pflanzen angesehen werden. Mangelnde Hinweise auf terrestrisches OM in den Sedimenten stehen in Einklang mit eingeschränktem Flusseintrag und geringem äolischen Eintrag aus der vegetationsarmen und extrem trockenen Atacama-Wüste, die an den größten Teil des untersuchten Küstenareals angrenzt. Auch nahe Concepción (36°S), wo mehrere Flüsse in den küstennahen Pazifik münden, die das feuchtere Hinterland Zentralchiles entwässern, war kein terrestrischer Eintrag in den Sedimenten feststellbar. Ein erwartetes terrestrisches Signal wurde hier möglicherweise von dem hohen marinen Eintrag überdeckt. Chlorin Konzentrationen, als ein Maß für den Eintrag von Phytoplanktondetritus, waren im Durchschnitt in Sedimenten vor Peru 10 mal höher als vor Chile. Teilweise spiegelt dies die

höheren jährlichen Primärproduktionsraten in dem ganzjährigen Auftriebsgebiet vor Peru wider, während Auftrieb und Produktivität vor Chile saisonal stark schwanken. Charakteristische Biomarker für Diatomeen (Brassicasterol) und Dinoflagellaten (Dinosterol) waren in Sedimenten vor Peru weit verbreitet und stark mit den Konzentrationen an OM korreliert, was darauf hindeutet, dass diese Phytoplankter, die typischerweise in hochproduktiven Küstenauftriebsgebieten dominieren, einen wesentlichen Beitrag zum sedimentären OM leisten.

Bakterien konnten als wichtige Quelle von sedimentärem OM identifiziert werden. In Sedimenten vor Chile machten bakterienspezifische Fettsäuren (*iso*- und *anteiso* C_{14}-C_{17}) 12-34% aller identifizierten Fettsäuren aus. Höchste Prozentsätze wurden an der Sedimentoberfläche von Stationen der Sauerstoff-Minimum-Zone beobachtet, was sowohl intensive bakterielle Überarbeitung an diesen flachen Stationen als auch Akkumulation bakterieller Biomasse in der Abwesenheit von Sauerstoff widerspiegelt. Sedimente der Sauerstoff-Minimum-Zone zeigten auch die höchsten Konzentrationen der Fettsäure 10-Methyl-16:0, was auf die Anwesenheit von Sulfat- und/oder Eisen-reduzierenden Bakterien der Gattungen *Desulfobacter* und *Geobacter* hindeutet. Im Gegensatz dazu konnten keine Spuren der großen Schwefelbakterien *Thioploca* in der Zusammensetzung des OM nachgewiesen werden, obwohl vor Peru Biomassen von bis zu 250 g m^{-2} beobachtet wurden. Es konnte gezeigt werden, dass abgestorbenes bakterielles Material einen wesentlichen Anteil des sedimentären OM ausmacht. Der Aminozucker Muraminsäure, der ausschließlich in bakteriellen Zellwänden vorkommt, wurde für eine Abschätzung bakterieller Zellzahlen in Sedimenten vor Peru herangezogen. Diese abgeschätzten Zellzahlen waren bis zu 500 mal höher als Ergebnisse direkter Zellzählungen, die für Sedimente dieses Gebiets vorliegen. Es wurde weiterhin abgeschätzt, dass höchstens 5-36% einzelner D-Aminosäuren in chilenischen Sedimenten mit Peptidoglykan lebender Zellen assoziiert waren.

Verschiedene Parameter wurden genutzt, um die Qualität oder Frische des sedimentären OM zu beurteilen. Wassertiefe war der Hauptkontrollfaktor für die Frische des OM an der Sedimentoberfläche, beispielsweise nahmen die Anteile labiler Verbindungen wie Chlorine, Fettsäuren und Aminosäuren mit zunehmender Wassertiefe ab. Da die Sauerstoffkonzentrationen des Bodenwassers eng mit der Wassertiefe verknüpft waren, war es nicht möglich, Auswirkungen der Sauerstoff-Verfügbarkeit auf die Frische von OM festzustellen. Die C/N-Verhältnisse, welche die Qualität des gesamten OM darstellen, stiegen allgemein mit zunehmender Wassertiefe an und waren am höchsten an Stationen, wo refraktäres Material akkumulierte. Der auf Aminosäuren basierende Abbau-Index, der aus

einer Hauptkomponentenanalyse der molekularen Aminosäurezusammensetzung abgeleitet wird, wurde erfolgreich eingesetzt, um die Frische des OM in Sedimenten vor Zentralchile zu charakterisieren, spiegelte jedoch nicht die Änderungen im Abbauzustand von sedimentärem OM vor Nordchile wider. Ein neuer Parameter für die Frische von OM in Sedimenten, der Chlorin Index, wurde entwickelt und in dieser Studie routinemäßig angewandt. Niedrige Chlorin Indizes, indikativ für frisches OM, wurden in Sedimenten aus geringer Wassertiefe gefunden, wohingegen höhere Werte den stärker degradierten Zustand von sedimentärem OM in größerer Wassertiefe charakterisierten. Ein weiterer Qualitätsindikator wurde aus einer Hauptkomponentenanalyse der molekularen Fettsäurezusammensetzung abgeleitet. Dieser Fettsäure-Index spiegelte die Veränderungen des OM in Wassersäule und Sedimenten vor Chile wider und zeigte eine gute Übereinstimmung mit anderen Qualitätsindikatoren, die in dieser Studie angewandt wurden. Die Reaktivitäten von gesamtem OM, Chlorinen und einzelnen Fettsäuren wurden jeweils aus den kernabwärts abnehmenden Konzentrationen in datierten Sedimenten abgeschätzt. Die Reaktionsgeschwindigkeitskonstanten für das gesamte OM nahmen mit zunehmender Wassertiefe ab, was darauf hindeutet, dass Abbau-Prozesse in der Wassersäule auch die längerfristige Reaktivität von sedimentärem OM beeinflussen. Unter den Fettsäuren waren, in Übereinstimmung mit früheren Studien, mehrfach-ungesättigte die am meisten, langkettige gesättigte die am wenigsten reaktiven Verbindungen.

Bakterielle Sulfatreduktion war der quantitativ wichtigste abschließende Elektronen-akzeptorprozess in den untersuchten Sedimenten. Gemessene Sulfatreduktionsraten (SRR) wurden daher als Maß für die Verfügbarkeit von sedimentärem OM für mikrobiellen Abbau angesehen. Die SRR nahmen allgemein mit zunehmender Wassertiefe ab, der Wassertiefen-Abhängigkeit der Qualität des sedimentären OM folgend. Insgesamt zeigten die SRR eine gute Übereinstimmung mit den chemisch definierten Parametern, die in dieser Studie zur Abschätzung der Qualität des sedimentären OM eingesetzt wurden. Die Vorherrschaft der Sulfatreduktion bei der Remineralisierung von OM in anoxischen marinen Sedimenten wurde durch die gute Übereinstimmung von Reaktionsgeschwindigkeitskonstanten unterstrichen, die für das gesamte OM einerseits aus gemessenen SRR und andererseits aus den kernabwärts abnehmenden Konzentrationen des OM abgeleitet wurden. Es konnte außerdem gezeigt werden, dass ein weiterer wichtiger mikrobieller Abbauprozess in anoxischen marinen Sedimenten, die anaerobe Oxidation mikrobiell produzierten Methans, mit der Akkumulation und Einbettung von organisch-reichen Sedimenten in der untersuchten Region verknüpft ist. Demnach beeinflussen biogeochemische Prozesse in den Oberflächensedimenten Menge und Qualität der Substrate für die Methanogenese tiefer in den Sedimenten.

Chapter 1

General Introduction

1. INTRODUCTION

This introduction sets the general frame for the studies presented in the following chapters. A closer examination of the global carbon cycle reveals the overall significance of biogeochemical processes in marine sediments. In order to provide some basic background knowledge and to give a general overview on contemporary state of research, processes that influence production and decomposition of marine organic matter are described, and basic theories on organic matter preservation mechanisms as well as models for sedimentary organic matter degradation are presented. Furthermore, parameters frequently used to characterize organic matter composition are summarized and general information on microbial degradation processes is given. The phenomenon of coastal upwelling is explained in detail and a general description of the investigated area off Peru and Chile is included.

THE GLOBAL CARBON CYCLE

The global carbon cycle can be described as consisting of a geochemical sub-cycle and a biologically mediated, biogeochemical sub-cycle (Fig. 1.1). By far the biggest fraction of carbon - 99% of combined lithospheric, atmospheric, and oceanic carbon - is fixed in sedimentary rocks, the huge geochemical reservoir, which therefore constitutes the main reservoir in the global carbon cycle (Hedges 1992). In steady state, in- and out-fluxes of individual reservoirs are balanced, e.g. the rate of carbon burial in sedimentary rocks equals the rate of rock erosion. Burning of fossil fuels is currently disturbing this steady state by increasing the carbon flux from the big geochemical reservoir to the relatively small atmospheric reservoir (Fig. 1.1). As a consequence, the atmospheric CO_2 concentration increased from pre-industrial values of 280 ppm to 365 ppm at present (in 1998), giving rise to global warming (Houghton et al. 2001).

The ratio of reservoir size and in- respectively out-flux determines the mean turnover time of a reservoir. Due to comparably smaller pool sizes and higher flux rates the biogeochemical sub-cycle acts more dynamically than the geochemical one. The ocean is the largest carbon reservoir in the biogeochemical sub-cycle. Exchange of atmospheric and oceanic CO_2 is limited to the oceans surface, where rapid equilibration occurs (Stuiver 1980). At high latitudes, cold and saline water sinks to the ocean interior, sequestering dissolved CO_2 from contact with the atmosphere (Broecker and Peng 1987; Krysell and Wallace 1988).

However, these water masses will return to the oceans surface by upwelling on average within the next 1000 years (Broecker and Peng 1982; Broecker 1991). The so-called physical carbon pump therefore provides a temporal sink rather than a real counter-pole for anthropogenic CO_2 liberation.

An important sink for atmospheric CO_2 is the build up of biomass, summing up to a net carbon flux of 100 Pg yr^{-1}. However, virtually all of the carbon annually fixed in terrestrial plants is released back to the atmosphere during decomposition in soils (Fig. 1.1). Whether terrestrial plants might profit from increased CO_2 concentrations and act as a short-term sink for anthropogenic carbon is still unclear (Falkowski et al. 2000). Carbon fixation by marine organisms is primarily limited to the euphotic zone of the oceans. Most of the carbon incorporated in organic tissues or carbonate shells is readily recycled in the water column (Suess 1980; see below) and of the small fraction reaching the sediments the biggest part is lost by organic matter degradation (Henrichs and Reeburgh 1987; see below) and carbonate dissolution. The tiny fraction of carbon that escapes remineralization in the sediment reenters the geochemical cycle, thereby providing a real counter-pole to carbon mobilization by fossil

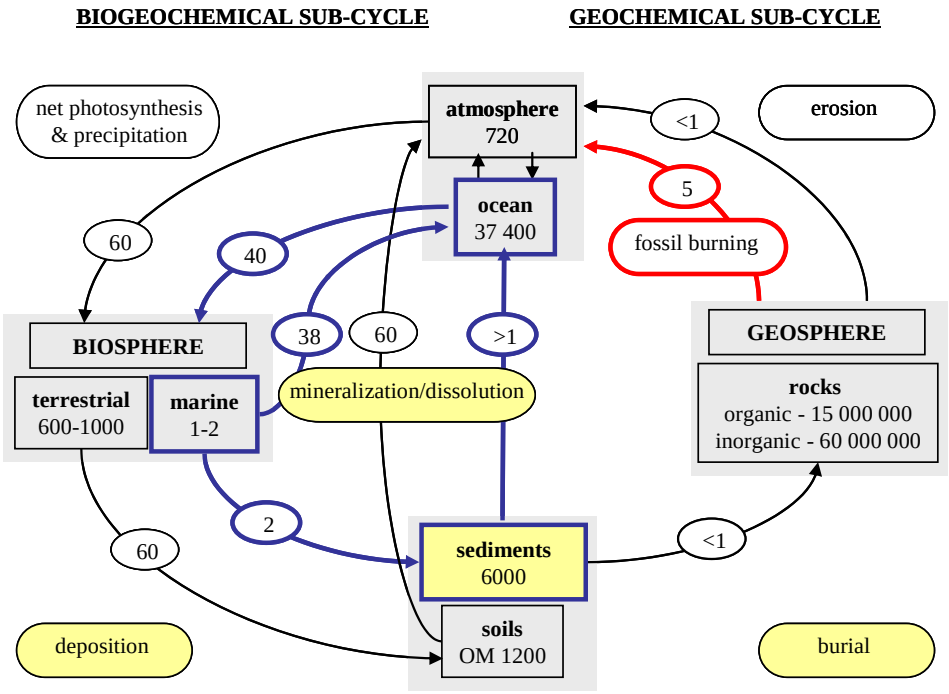

Figure 1.1. Simplified scheme of the global carbon cycle showing the most important reservoirs, fluxes, and processes. Reservoir sizes and annual fluxes are in Pg carbon, data from Killops and Killops (1993) and Falkowski et al. (2000). Blue: marine carbon cycle; red: site of anthropogenic disturbance; yellow: site and processes addressed in this thesis. Not included is the reservoir of marine dissolved organic matter (600 Pg C) with balanced in- and out-fluxes of 0.1 Pg C yr^{-1} (Williams and Druffel 1987).

burning. This means that carbon burial in sediments is the only effective long-term sink for atmospheric carbon and the only process that could over longer time scales balance anthropogenic CO_2 production. Understanding the processes that control rates and extent of remineralization and burial of organic carbon in marine sediments is therefore essential for understanding long-term global carbon cycles.

MARINE ORGANIC MATTER – PRODUCTION AND FATE

Marine organic matter predominantly derives from primary photosynthetic production by phytoplankton in the euphotic layer of the oceans. Other production processes like macro-algae photosynthesis in coastal areas (Smith 1981) and chemosynthesis at hydrothermal vents or in low oxygen environments (Karl et al. 1984; Taylor et al. 2001) might locally be important, but are negligible on global scales compared to phytoplankton photosynthesis, which accounts for 95% of global oceanic primary production (Killops and Killops 1993). Photosynthetic primary production rates are related to the availability of nutrients and light, hence ocean productivity varies spatially and temporally as a function of nutrient supply and insolation (Tab. 1.1; Fig. 1.2). High productivity in coastal areas is supported by river discharge of dissolved nutrients and eolian input of essential trace elements, and further profits from rapid nutrient recycling due to close coupling of benthic and pelagic systems in shallow, non-stratified water columns (Wollast 1991). In open ocean regions, advection of nutrient rich water from greater water depth stimulates high primary production rates, e.g. along the equatorial divergences and near the polar fronts (Broecker and Peng 1982; Fig. 1.2). High productivity in coastal upwelling regions also relies on advection of nutrient rich water. Occurrence and general characteristics of coastal upwelling will be explained in more detail below.

Table 1.1. Comparison of different marine environments. Data from Schlesinger (1997), percentages of global oceanic area, global annual primary production, and global annual new production are given in parentheses.

oceanic province	**global area** (10^6 km^2)		**primary production** (gC m^{-2} yr^{-1})		**new production**[a] (gC m^{-2} yr^{-1})	
open ocean	326	(90.0%)	130	(82.2%)	18	(79.2%)
coastal zone	36	(9.9%)	250	(17.5%)	42	(20.4%)
upwelling area	0.36	(0.1%)	420	(0.3%)	85	(0.4%)

[a]carbon flux at 100 m depth

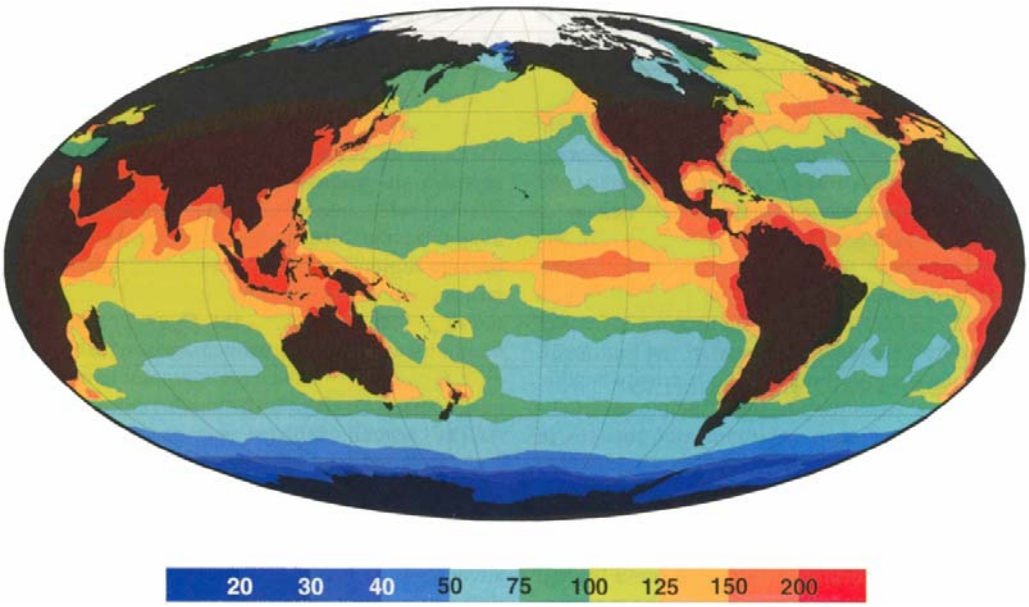

Figure 1.2. Global map showing the distribution of mean annual primary production. Among other parameters, the distribution of pigment concentration, surface-water temperature and surface irradiance were used for its construction. The representation is the result of model calculations. From Zabel et al. (2000), after Antoine et al. (1996).

Of the organic matter produced by phytoplankton in the surface ocean only a small fraction reaches the seafloor, generally this fraction is a function of primary production rate and water depth (Müller and Suess 1979; Suess 1980). Most of the primary production is readily recycled within the epipelagic zone and much of the particulate organic matter settling down the water column is remineralized before it reaches the seafloor (Fig. 1.3). In deep open ocean areas (>3000 m water depth), <1% of primary production escapes remineralization in the water column (Suess 1980), whereas up to 50% can reach the sediments in shallow coastal areas (Jørgensen et al. 1990). In the sediments organic matter degradation continues and finally, only <0.1% of the primarily produced organic matter will ultimately become buried in deep sea sediments (Berger et al. 1989). In coastal areas, this percentage is significantly higher, reaching up to >10% (Henrichs and Reeburgh 1987).

Organic matter degradation in water column and sediments is a predominantly biologically mediated process (Wakeham and Lee 1993). Heterotrophic organisms consume living and dead organic material mainly to sustain their energy needs. Some organic material is converted to new biomass, which in turn, together with excreted particulate and dissolved transformation products, might be exposed to heterotrophic alteration again. In summary, most organic matter is completely remineralized to CO_2 and nutrients, and the

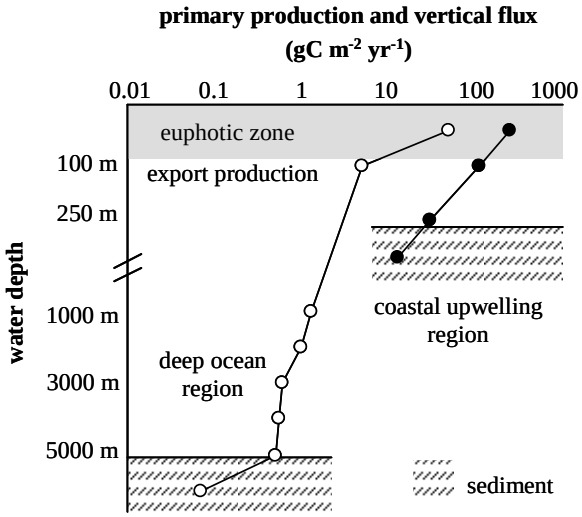

Figure 1.3. Schematic representation of primary production and organic matter flux in water column and sediments of open ocean and coastal upwelling regions (after Stein 1991).

residual fraction accumulating in sediments is mostly strongly altered compared to the original composition of freshly produced phytoplankton biomass (Wakeham and Lee 1989). This is because degradation and transformation processes change the structural and chemical composition of organic matter. Labile organic compounds are preferentially degraded and become selectively depleted in organic matter as diagenesis proceeds (Cowie and Hedges 1994; Wakeham et al. 1997a, b; Lee et al. 2000). Simultaneously the fraction of molecularly characterizable organic matter decreases from >80% in freshly synthesized to <20% in altered sedimentary organic material (Wakeham et al. 1997b; Fig. 1.4).

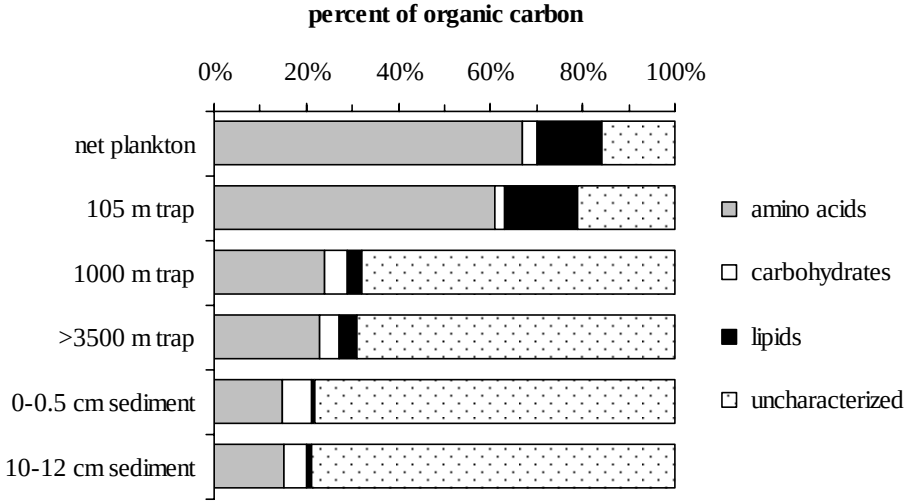

Figure 1.4. Cumulative biochemical class distributions (compound class carbon as percent of total carbon) for sites from the central equatorial Pacific (after Wakeham et al. 1997b).

CONTROLS ON ORGANIC MATTER DEGRADATION

Most of the factors influencing the extent of organic matter degradation can be summarized in two groups. Firstly, factors that determine the time available for degradation, e.g. water column depth (Suess 1980), sinking velocity depending on size, weight, and shape of organic matter particles (McCave 1975; Armstrong et al. 2002), sediment accumulation rate (Müller and Suess 1979), and sediment mixing (Aller 1982; Aller 1994). Secondly, factors that control rate and extent of degradation, e.g. organic matter composition with respect to sources (Hedges et al. 1988; Schubert and Stein 1996) and state of degradation (Westrich and Berner 1984), availability of electron acceptors - particularly oxygen - and prevailing degradation pathways (Canfield 1994), microbial community composition and function (Arnosti et al. 2005), and physical protection mechanisms (Keil et al. 1994; Mayer 1994).

The question of which variables dominantly control organic matter degradation in marine systems is one of the most complex and controversial issues in biogeochemical research. Particularly the importance of oxygen limitation for the accumulation of organic-rich sediments has been the subject of considerable debate (Canfield 1994 and references therein), resulting in the establishment of two general models. (1) The preservation model (Demaison and Moore 1980) is based on the assumption that organic matter degradation is less efficient under anoxic compared to oxic conditions. Absence of free oxygen is in this model regarded as a prerequisite for the deposition of organic-rich sediments. (2) The productivity model (Pedersen and Calvert 1990) on the other hand argues that high primary production is the principal factor controlling the accumulation of organic-rich sediments and that anoxic conditions develop as a consequence of high oxygen demand for the decomposition of settling organic matter. The integrative concept of oxygen exposure time as a major control on organic matter preservation includes several proposed variables, namely those that directly or indirectly affect oxygen penetration depth in the sediment and/or bulk sedimentation rate (Hartnett et al. 1998; Devol and Hartnett 2001). Oxygen exposure time has successfully been related to changes of organic matter content and composition, in that elongation of oxygen exposure results in reduced burial rate and enhanced state of degradation (Hartnett et al. 1998; Hedges et al. 1999).

A second important key concept generally regarded to affect organic matter preservation is that of physical protection (Keil et al. 1994; Mayer 1994). Organic matter adsorbed in mesopores of individual mineral particles or in intergranular areas might be

protected from enzymatic attack, since hydrolyzing exoenzymes cannot function within these small pores (Mayer 1994). A special case of physical protection is that of encapsulated compounds, e.g. specific amino acids in silicate or carbonate tests that are not released until the mineral phase dissolves (Hecky et al. 1973; Ingalls et al. 2003). Physical protection of organic material by association with mineral matrices provides a means for labile compounds to survive transit through the water column and become buried in sediments. It has been shown that organic matter sorbed to particles is mostly reversibly bound and once desorbed is easily degraded by microorganisms (Keil et al. 1994).

ORGANIC MATTER COMPOSITION

The chemical composition of organic matter provides information on its sources as well as on its degree of diagenetic alteration. Several elemental and molecular indicators are frequently applied to characterize origin and quality of organic matter. Some of these indicators are presented below, including general remarks on definition and constraints of applicability. Individual indicators are discussed in more detail in context with their application in the studies presented in the following chapters.

Source indicators (biomarkers)

The ideal indicator of organic matter source should exclusively derive from a specific organism or a group of organisms (Hedges and Prahl 1993). Ensuring the specificity of the signal is a general problem for the application of source indicators (e.g. Volkman 1986). Another problem arises from different stabilities of individual compounds, i.e. relative concentrations of specific indicators must not necessarily reflect relative contributions of the respective source organisms. Furthermore, assessing the quantitative composition of source communities is complicated as the molecular compositions of living organisms can change during their live cycles and along with environmental factors such as light levels and nutrient availability (Killops and Killops 1993).

The classical geochemical biomarker (molecular fossil) is sufficiently resistant to chemical and biological degradation to be traced in the geological record. This definition includes altered organic compounds, that based on their molecular structures can unambiguously be linked to particular biological precursor molecules, which in turn can be assigned to specific source organisms (Brassell 1993; Hedges and Prahl 1993). Biomarkers

applied to characterize community structures of living organisms are - in contrast to the geochemical definition - ideally rapidly degraded after death of the organism (Boschker and Middelburg 2002). In geochemical as well as in ecological studies, lipids are particularly suited as biomarkers, due to the high degree of structural complexity included in this compound class, together with the ease of analysis. Although not as species-specific as some lipid components, amino acids and carbohydrates can also provide useful source information (e.g. Ittekkot et al. 1984a, b). However, in general, specific molecules make up only a small fraction of bulk organic matter and direct source information is restricted to the molecularly characterizable fraction. Source information for the total organic matter pool, on the other hand, is provided by the elemental and isotopic composition of bulk organic matter.

Bulk terrestrial and marine indicators. Differences in the elemental composition of marine and terrestrial organic matter can be used to reveal possible terrestrial contributions to sedimentary organic matter (Meyers 1994). Dominated by nitrogen-poor macromolecules such as cellulose and lignin, terrestrial organic matter displays carbon to nitrogen ratios (C/N-ratios) of >20, whereas C/N-ratios of protein-rich marine organic matter range from 5-7 for freshly produced plankton material to 12 for degraded material (Hedges et al. 1986). Another parameter helpful to distinguish marine and terrestrial input is the carbon isotopic composition ($\delta^{13}C$) of bulk organic matter (Hayes 1993; Meyers 1994). Most photosynthetic plants use the C_3 Calvin pathway, producing a shift of ~-20‰ compared to the inorganic carbon source. Consequently marine phytoplankton incorporating dissolved bicarbonate with an isotopic value of ~0‰ typically has $\delta^{13}C$ values of -22‰ to -20‰, whereas terrestrial plants using atmospheric CO_2 with an isotopic value of ~-7‰ produce organic matter with an

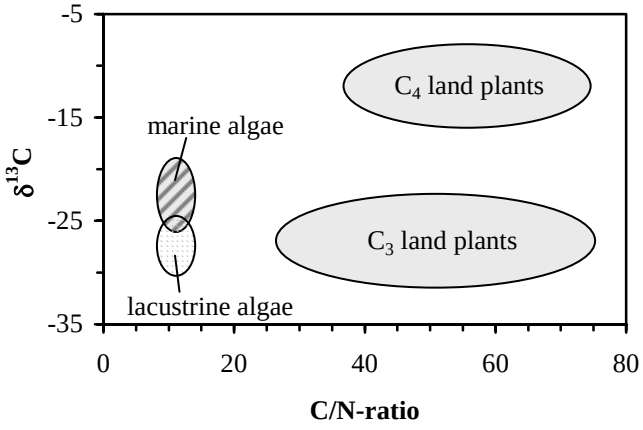

Figure 1.5. Elemental and isotopic source indicators of bulk organic matter. C/N-ratios (atomic) and $\delta^{13}C$-values of different terrestrial and marine source organisms plot in distinct areas (after Meyers 1994).

average $\delta^{13}C$ of ~-27‰. In contrast, the average carbon isotopic composition of organic matter derived from terrestrial C_4-plants is only ~-7‰ different from that of atmospheric CO_2, resulting in $\delta^{13}C$-values of ~-14‰, since C_4-plants, widely distributed in hot dry climates, use the C_4 Hatch-Slack pathway. A mixture of terrestrial organic matter from C_4- and C_3-plants might exhibit a $\delta^{13}C$ value similar to that of marine OM. The combination of carbon isotopic composition and C/N-ratio, however, in most cases provides a robust tool to identify terrestrial and marine contributions to bulk organic matter (Fig. 1.5).

Terrestrial biomarkers. Specific compound classes are indicative for input from higher plants. For example, lignin-derived phenols (Hedges and Parker 1976) and pentacyclic triterpenoids (ten Haven et al. 1992) are unique biomarkers for terrestrial plants. In contrast, most of the higher plant sterols often used as terrestrial biomarkers are rather unspecific with respect to their source, since they also occur in marine algae - sometimes as major constituents (Volkman 1986). Recent studies (e.g. Naraoka and Ishiwatari 2000) also demonstrated a marine origin of long-chain saturated fatty acids ($>C_{20}$), which are important constituents of plant waxes, and together with their transformation products long-chain *n*-alcohols and *n*-alkanes are widely used as indicators for land plant detritus (e.g. Meyers 1997). See chapter 4 for a detailed discussion of the origin of long-chain fatty acids in sediments off Chile.

Phytoplanktonic biomarkers. Although the primary signal is exposed to extensive alteration in the water column, some source indicators survive degradation providing information on the prevailing phytoplankton community (e.g. Schubert et al. 1998). Among the most frequently applied indicator compounds are the sterols brassicasterol (24β-methylcholesta-5,22E-dien-3β-ol) and dinosterol (4α,23,24-trimethyl-5α(H)-cholest-22-en-3β-ol), regarded to reflect input from diatoms (Volkman 1986) and dinoflagellates (Boon et al. 1979), respectively. Although brassicasterol is produced by a variety of other algae, it is suitable to trace diatom input particularly in high productivity areas where diatoms are the dominant phytoplankton (Volkman et al. 1987). In contrast, occurrence of 4-methyl sterols including dinosterol is mostly restricted to dinoflagellates (Volkman et al. 1998). Alkenones, long-chain ketones, are synthesized by prymnesiophytes which include another important group of phytoplankton, the coccolithophores (Volkman et al. 1980a). Polyunsaturated fatty acids abundant in fresh phytoplankton material are rapidly lost during early diagenesis and, except in shallow areas, are mostly absent from marine sediments (Wakeham et al. 1997b). Photosynthetic pigments, particularly chlorophylls and carotenoids, on the molecular level

can also reveal some source specificity. A recent compilation of microalgae biomarkers is provided by Volkman et al. (1998).

Bacterial biomarkers. The classical biomarkers for bacteria are branched-chain fatty acids such as *iso*- and *anteiso* C_{13}-C_{17} fatty acids (Kaneda 1991). Hopanes used by bacteria as membrane rigidifiers provide a stable highly specific biomarker (Rohmer et al. 1984). Information on living microbial communities can be derived from analysis of intact membrane lipids (Rütters et al. 2002; Sturt et al. 2004). The polar head-group of phospho- and glycolipids is rapidly lost after cell death; therefore intact molecules are indicative for living organisms (White et al. 1979). Intact membrane lipids also provide information on abundance and taxonomy of archaea (Sturt et al. 2004).

Bacterial cell walls contain peptidoglycan (Fig. 1.6), a structural polymer comprising polysaccharide chains that are cross-linked by amino acid chains. Recently, peptidoglycan has regained increased attention as a specific biomarker for bacterial cell wall material (e.g. Pedersen et al. 2001). The amino sugar muramic acid is uniquely found in peptidoglycan and the nonprotein amino acids D-alanine and D-glutamic acid are important constituents of this bio-polymer (Madigan et al. 2000). See chapter 5 and Lomstein et al. (subm.; see chapter 6B) for application and further discussion of peptidoglycan biomarkers.

Compound specific carbon isotopic signal. The carbon isotopic compositions of specific compounds provide a tool to distinguish contributions from sources significantly different in isotopic signal. Likewise bulk organic matter, compounds derived from terrestrial

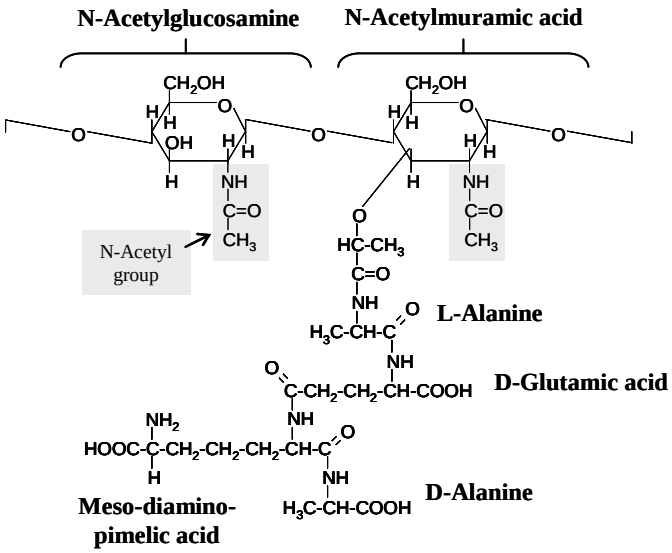

Figure 1.6. Structure of one of the repeating units of the bacterial cell wall polymer peptidoglycan (from Madigan et al. 2000).

C_3-plant material are easily distinguished from those originating from marine organisms. Biomass of autotrophic organisms, thriving on ^{13}C depleted carbon compounds derived from microbial remineralization processes, is typically depleted in ^{13}C compared to that of co-occurring heterotrophic organisms which incorporate the prevailing marine isotopic signal (Cowie et al. 1999). A special case is the strong ^{13}C depletion of prokaryotes associated with the process of anaerobic oxidation of methane (Elvert et al. 1999; Hinrichs et al. 1999), reflecting the uniquely negative $\delta^{13}C$ values of microbially formed methane (Whiticar 1999).

Quality indicators

The definition of quality indicators, describing the degree of diagenetic alteration, is based on observations that rates of quantitative and qualitative changes of organic matter decrease with ongoing degradation. Quality therefore describes the reactivity of organic matter with respect to diagenetic alteration. As freshly produced organic matter is more reactive than reworked sedimentary organic matter, quality in this context is synonymous to freshness. Quality indicators are also applied to assess bio-availability of organic matter (see below), assuming that reduced bio-availability going along with reduced quality explains lower rates of biologically mediated diagenetic alteration. The sensitivity of different quality indicators towards progressive diagenetic alteration might differ, restricting their applicability to a limited time span in degradation history each (Hedges et al. 1999).

C/N-ratio. Preferential degradation of nitrogen containing compounds during early diagenesis is reflected in increasing C/N-ratios. Whereas fresh marine organic matter has C/N-ratios of 5-7, values up to 12 characterize refractory organic matter (Hedges et al. 1986). The C/N-ratio provides information on the bulk organic matter composition including the molecularly uncharacterized fraction. However, the inherent difference in C/N-ratios of terrestrial and marine organic matter - as pointed out above - might bias the qualitative interpretation based on this rather crude parameter.

Labile compound classes. Selected compound classes are preferentially degraded compared to bulk organic matter (rf. Fig. 1.4). Hence, the fraction of TOC that is made up of labile compounds, such as amino acids, carbohydrates, fatty acids, and pigments, decreases with ongoing alteration (Cowie and Hedges 1992, 1994; Wakeham et al. 1997a, b; Lee et al. 2000). Likewise, ratios of more labile to more resistant compound classes decrease with ongoing degradation. For example, the ratio of total hydrolysable amino acids to total hydrolysable hexosamines decreases with increasing state of degradation (e.g. Gupta and Kawahata 2000), since hexosamines (amino sugars) protected in structural matrices are less

susceptible to degradation than amino acids which are mostly present as easily accessible proteinaceous material (Baas et al. 1995; Nagata et al. 2003).

Molecular composition. Principal component analysis (PCA) revealed, that changes in the degradation state of bulk organic matter are reflected in systematic changes in the molecular amino acid composition (Dauwe and Middelburg 1998). These changes are the base for the degradation index developed by Dauwe and Middelburg (1998) and Dauwe et al. (1999). In particular, glycine, serine, and threonine associated with structural compounds are enriched in more degraded material, whereas amino acids concentrated in the cell plasma such as tyrosine, phenylalanine, and glutamic acid tend to be depleted during degradation (Dauwe and Middelburg 1998). Furthermore, specific products of microbial activity become enriched in altered organic matter. The non-protein amino acids β-alanine (β-ala) and γ-aminobutyric acid (γ-aba) are decarboxylation products of aspartic acid (asp) and glutamic acid (glu), respectively. Consequently, mole percentages of β-ala and γ-aba increase with increasing degree of alteration, as well as the ratios β-ala/asp and γ-aba/glu (Lee and Cronin 1984; Cowie and Hedges 1992, 1994). Ornithine is a decomposition product of arginine and also accumulates with ongoing degradation (Lee and Cronin 1984). A detailed study of the amino acid composition in the sediments investigated off Chile, including stereochemistry and application of the amino acid degradation index, is given in Lomstein et al. (subm.; see chapter 6B).

In general, changes in concentrations of any specific source indicator might be used as quality indicator, in that increasing bacterial biomass indicates intense reworking, while high abundances of labile phytoplankton biomarkers represent fresh biomass. Very fresh organic matter is characterized by the presence of highly reactive compounds like poly-unsaturated fatty acids and intact chlorophylls which are rapidly lost from freshly produced organic matter and mostly absent from sediments (Wakeham et al. 1997b). The first steps of chlorophyll degradation include the loss of the central magnesium atom yielding pheaophytins and the hydrolytic cleavage of the phytol side-chain resulting in chlorophyllides that still contain Mg and pheaophorbides lacking Mg (Killops and Killops 1993). Molecular analysis of chlorophylls therefore can provide information on the degradation state during very early diagenesis. The lability of chlorins (chlorophyll and degradation products of chlorophyll) towards chemical treatment with hydrochloric acid is the base for the Chlorin Index (Schubert et al. 2005; see chapter 6A) which has been applied to characterize organic matter quality in sediments investigated off Chile (Chapter 2) and off Peru (Chapter 3).

The analytical window

The differentiation of characterized and uncharacterized fraction is mainly determined by the analytical methods applied to identify the composition of organic matter (Hedges et al. 2000). The so-called "analytical window" mostly focuses on the fractions of extractable lipids, extractable pigments, hydrolysable amino acids, and hydrolysable carbohydrates (e.g. Wakeham et al. 1997b). With respect to the scope of the studies presented in this thesis it is important to note that chemically uncharacterized is not synonymous to biologically recalcitrant (Lee et al. 2004).

MICROBIAL DEGRADATION PROCESSES

Organic matter degradation in marine sediments is mainly driven by microbial processes, a contribution of higher organisms is mostly limited to the uppermost oxic zone. In contrast to metazoans that are able to consume particulate organic matter, microorganisms can only take up small dissolved organic molecules of <600 daltons in size (Weiss et al. 1991). Therefore, the first step in organic matter degradation is the extracellular hydrolysis of complex macromolecular compounds, which is catalyzed by bacterial exoenzymes (Fig. 1.7). The range of organic substrates that can be respired to CO_2 by a single organism depends on the availability of suitable electron acceptors. The supply of dissolved electron acceptors (oxygen, nitrate, sulfate) is controlled by diffusive transport from the overlying bottom water. In addition, physical mixing might transport dissolved as well as solid oxidants (metal oxides) to deeper sediment horizons (Aller 1990).

Table 1.2. Terminal electron acceptor processes and methane production and their standard free energy yields ΔG^0 per mole organic carbon (from Jørgensen 2000). Note that ΔG^0 is for standard conditions (25°C, pH 7) and that substrate and product concentrations strongly influence ΔG.

pathway	stoichiometry of reaction	ΔG^0 (kJ mol^{-1})
oxic respiration	$CH_2O + O_2 \rightarrow CO_2 + H_2O$	-479
denitrification	$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$	-453
manganese reduction	$CH_2O + 3CO_2 + H_2O + 2MnO_2 \rightarrow 2Mn^{2+} + 4HCO_3^-$	-349
iron reduction	$CH_2O + 7CO_2 + 4Fe(OH)_3 \rightarrow 4Fe^{2+} + 8HCO_3^- + 3H_2O$	-114
sulfate reduction	$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$	-77
methane production	$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$	-136

Aerobic bacteria are able to respire a wide range of organic substrates. Oxic respiration is the energetically most favorable terminal electron acceptor process (Tab. 1.2), out-competing all other respiration pathways when oxygen is available. In deep sea sediments overlain by oxic bottom waters, the oxic zone might extend several dm deep into the sediment, whereas in shelf sediments, oxygen penetration is limited to the upper few mm (Glud et al. 1999). Sediments underlying oxygen-depleted to oxygen-free bottom waters, such as in the oxygen-minimum-zone off Peru and Chile, effectively lack an oxic zone (Glud et al. 1999).

In the absence of oxygen, microorganisms use other electron acceptors to oxidize organic matter, consecutively following the order of decreasing energy yield (Tab. 1.2). The different electron acceptors therefore become sequentially depleted with increasing sediment depth (Froelich et al. 1979). Nitrate concentrations are typically low in pore-water (<100 µmol l^{-1}) and nitrate reduction appears to play a minor role in organic matter remineralization, though its significance may be higher in areas with low oxygen and elevated nitrate concentrations in the bottom water (Canfield et al. 1993; Thamdrup and Canfield

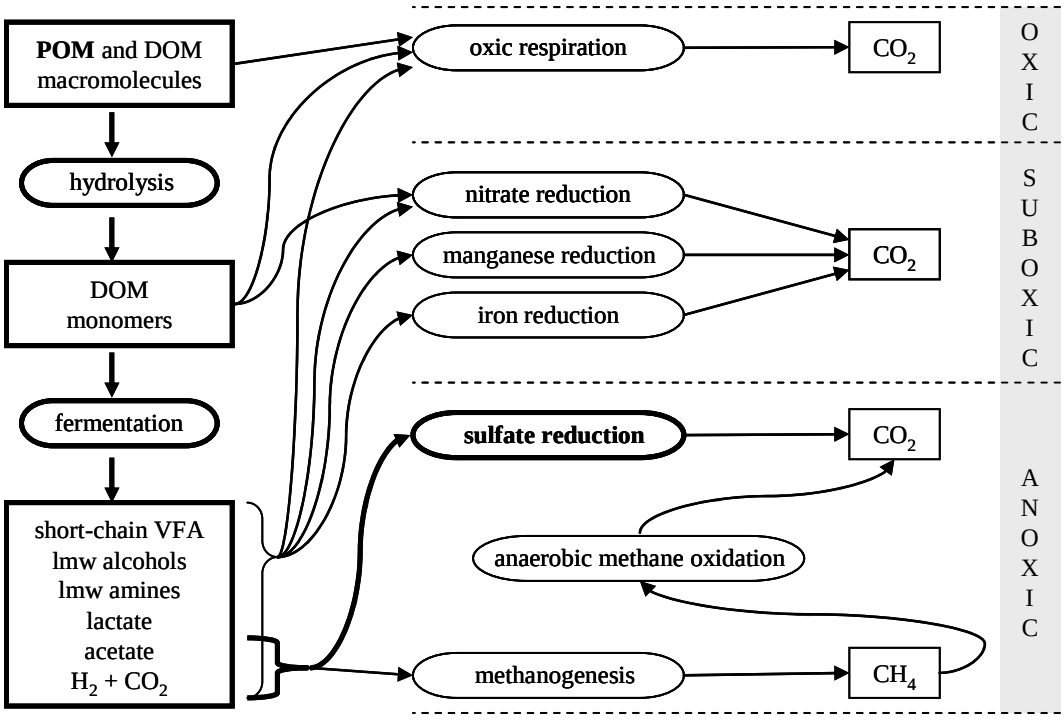

Figure 1.7. Simplified scheme of organic matter degradation in marine sediments. Adapted from Jørgensen (2000) after Fenchel and Jørgensen (1977). Bold lines illustrate pathways connecting substrate (POM) and process (sulfate reduction) investigated as part of this thesis. POM = particulate organic matter, DOM = dissolved organic matter, VFA = volatile fatty acids, lmw = low molecular weight.

1996). The importance of manganese and iron reduction strongly depends on the extent of physical mixing which transports the solid oxides to the depth of the reaction zone (Aller 1990). The quantitatively most important anaerobic remineralization pathway is sulfate reduction (Jørgensen 1982), which is supported by the high sulfate concentration in seawater (~28 mmol l^{-1}) - for comparison, oxygen saturated seawater displays oxygen concentrations of 200-500 µmol l^{-1} (Grasshoff et al. 1999).

In sediments where sulfate reduction is the dominant terminal electron acceptor process, measured rates of sulfate reduction reflect actual rates of carbon turnover, thereby providing a direct measure for the availability of sedimentary organic matter for microbial degradation (Westrich and Berner 1984). Sulfate reduction rates in sediments off Chile (Chapter 2) and Peru (Chapter 3) have been related to the organic matter composition in order to assess the applicability of different quality indicators for the characterization of the bio-availability of sedimentary organic matter (see below).

As the energy yield of bacterial metabolism becomes gradually smaller with increasing sediment depth, according to the sequence of oxidation pathways (Tab. 1.2), organisms become more restricted in the range of substrates they can use. Nitrate-, manganese-, and iron-reducers are still very versatile with respect to monomers they can respire, in contrast to sulfate reducers that rely on the activity of fermenting bacteria (Fig. 1.7). Main fermentation products are short-chain volatile fatty acids, lactate, low molecular weight alcohols and amines, acetate, H_2 and CO_2. Methanogens perform the last step in anoxic organic matter degradation converting acetate or H_2 and CO_2 to CH_4. Significant methane production is limited to the depth below the sulfate zone, since sulfate reducers successfully out-compete methanogens for common substrates (Zehnder 1988). Methane as the terminal product of anaerobic organic matter degradation accumulates in the methanogenic zone and diffuses upwards to the lower boundary of the sulfate reduction zone (Martens and Berner 1974). The sulfate-methane-transition zone is the site of anaerobic oxidation of methane by concomitant reduction of sulfate, according to the following net reaction (Barnes and Goldberg 1976):

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O$$

Anaerobic oxidation of methane in the sulfate-methane-transition zone integrates the whole degradation of organic matter buried below the sulfate reduction zone; including very deep sediment layers deposited thousands or millions of years ago. This way, the efficiency of degradation in former surface sediments is a major control on actual methane production in

the deep biosphere. Linking near surface organic matter composition and degradation to processes in the sulfate-methane-transition zone was part of a study on sediments from the Chilean margin (Treude et al. 2005; see chapter 6C).

ASSESSING BIO-AVAILABILITY

For a given degradation pathway, the organic matter composition determines rates and extent of microbial remineralization (Westrich and Berner 1984). In this context, composition includes chemical as well as structural properties such as packaging. Fresh organic matter is readily remineralized at similarly high rates under oxic and anoxic conditions (Westrich and Berner 1984; Cowie et al. 1992). For more refractory substrates, rates are higher in the presence of oxygen, reflecting that aerobic processes are more efficient and rapid in hydrolyzing structurally complex macromolecules (Kristensen et al. 1995). This might in part be due to the generation and utilization of highly reactive oxygen-containing radicals (e.g. $\cdot O_2^-$, $\cdot OH$, H_2O_2) during aerobic decomposition (Canfield 1994 and references therein).

Ongoing degradation decreases the susceptibility of the remaining organic matter to further microbial decomposition. The multi *G*-model describes the progressive decrease in organic matter reactivity towards degradation (Berner 1980; Westrich and Berner 1984). In this model the bulk organic matter is regarded to consist of a number of organic matter pools with decreasing reactivity, which become consecutively depleted as diagenesis proceeds. Based on the multi *G*-model, Middelburg (1989) developed the continuous *G*-model assuming a continuous spectrum of reactivities, which is more likely to describe natural organic matter composition.

Although there is broad consensus that freshness or quality of organic matter affects rate and extent of remineralization (e.g. Westrich and Berner 1984), no direct general relation of any parameter assessing organic matter quality and rates of microbial degradation has been established (Arnosti and Holmer 2003). The quality indicators describing organic matter composition are derived from chemical analysis, and it is likely that chemical and microbial definitions of organic matter quality differ significantly. Bacteria do not directly feed on particulate organic matter but rely on susceptibility of macromolecules to enzymatic hydrolysis, including chemical lability and structural accessibility (rf. Fig. 1.7). Bulk organic matter characteristics lack information on micro-scale spatial distribution, macromolecular structures, or possible physical protection (Arnosti 2004).

Nonetheless, quality indicators often show a good accordance with measured degradation rates (Dauwe et al. 1999), particularly in sediments characterized by fresh organic matter. On the other hand, organic matter dominated by highly refractory material and therefore denoted as low quality material might still support high degradation rates, since bacteria are able to thrive on a tiny fraction made up by fresh organic matter (Arnosti and Holmer 2003). Furthermore, deeply buried organic matter, that displays low quality characteristics and is regarded to be highly recalcitrant, still supports microbial live (Lee 1992; Parkes et al. 1994; Schippers et al. 2005).

In general, the applicability of a single quality indicator to assess the bio-availability of organic matter depends on the fraction of organic matter the respective parameter is based on. For example, bulk C/N-ratios might include highly recalcitrant organic matter resistant to microbial attack, which superimposes a possible small fraction of fresh reactive material (Arnosti and Holmer 2003). The degradation index that focuses on amino acid composition (Dauwe and Middelburg 1998) might include structural proteins that resist enzymatic attack but are hydrolyzed by chemical acid treatment. Furthermore, dissolution of carbonate tests might release encapsulated amino acids that also bias the interpretation based on the degradation index (Ingalls et al. 2003). The more specific a quality indicator is for fresh organic matter, and the higher its sensitivity is towards microbial degradation, the better is its applicability to assess bio-availability. One example of such a parameter is the Chlorin Index which is based on the degradability of labile chlorins (Schubert et al. 2005; see chapter 6A). The applicability of this quality indicator has been demonstrated by comparing it to measured sulfate reduction rates and other quality indicators (Schubert et al. 2005; see also chapters 2-4).

COASTAL UPWELLING

Coastal upwelling is a typical feature of the eastern boundary currents in the Pacific and the Atlantic Ocean, occurring as a wind-driven phenomenon at the west sites of North- and South America and North- and South Africa. Due to their characteristic high primary productivity, these regions can clearly be discerned on satellite images (Fig. 1.2). In the Arabian Sea coastal upwelling is associated with the monsoonal cycle. Driving force for coastal upwelling is the Ekman transport of surface water away from the coast (Fig. 1.8; Ekman 1905). Coastal upwelling regions are located in the trade wind region exposed to

constant wind fields that blow towards the equator. The Ekman spiral explains the interaction of wind stress and water movement (Fig. 1.8). In this model, the ocean is thought to consist of an infinite number of water layers. At the ocean surface wind directly interacts with the uppermost water layer and friction forces this water to move in wind direction. Coriolis forcing acts on moving water turning it left on the Southern hemisphere and right on the Northern hemisphere. The balance of the two acting forces - friction and Coriolis - determines the extent of deviation from the direction of wind and water mass movement. For the uppermost water layer the angle of deviation is 45° (Fig. 1.8). All deeper water layers are exposed to friction with the overlying water layer at their upper surface and with the underlying water layer at their lower surface. With increasing water depth, current speed decreases exponentially, at the lower boundary of the Ekman spiral, the friction depth, it is $^{1}/_{23}$ of the surface current speed. The angle of deviation to the direction of wind stress increases with water depth reaching 180° at friction depth. Integrated over the entire depth of the Ekman layer, which is typically 50-200 m, average wind-induced water movement is at right angle to the wind direction - on the Northern hemisphere to the right and on the Southern hemisphere to the left.

Surface water transported away from the coast towards the open ocean is replaced by water from greater water depth, typically 50-200 m. This upwelling water is characterized by high nutrient and CO_2 concentrations, low oxygen concentrations, and low temperatures. Nutrient and CO_2 enrichment and oxygen depletion reflect that upwelling waters originate from a depth of intense organic matter remineralization. Permanent nutrient supply fuels high primary production rates in coastal upwelling regions, favoring high burial rates of organic carbon and thereby providing a sink for atmospheric CO_2. On the other hand, upwelling

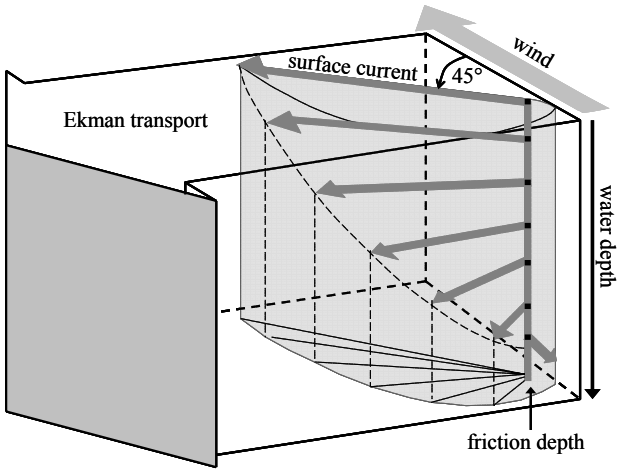

Figure 1.8. Schematic presentation of the Ekman spiral, adapted from Thurman and Trujillo (1999).

regions are also those regions in the world oceans where formerly fixed CO_2 is released from the ocean interior back to the atmosphere (Murray et al. 1994). Upwelling of cold water masses has an indirect effect on sediment composition. Evaporation of cold water is limited and furthermore, moisture of coastal air masses is trapped in coastal fogs (*camanchacas*) which precipitate above the coastal waters (Miller 1976). Therefore, the coastal atmosphere is generally dry in these regions and adjacent coastal areas comprise some of the driest deserts on Earth, e.g. the Atacama in South America and the Namib in South Africa. Due to limited precipitation, river runoff is usually small and eolian input of terrestrial organic matter from the vegetation poor hinterland is mostly negligible.

Several general characteristics of coastal upwelling regions are a consequence of the high primary production rates in the surface waters (Tab. 1.1). In the water column, decomposition of sinking organic detritus causes oxygen depletion at mid-water depth, and extended oxygen-minimum zones (OMZ) develop. Typically, the OMZ is defined for oxygen concentrations of <0.5 ml l^{-1} (Helly and Levin 2004). Where the OMZ intercepts the continental margin, sediments deposit under oxygen-depleted to oxygen-free bottom waters. Activity of bioturbating organisms is strongly reduced in these environments and laminated sediments might accumulate, which provide high resolution records for paleo-studies. Organic matter remineralization in OMZ-sediments mainly proceeds via anaerobic degradation pathways with sulfate reduction as the dominant terminal electron acceptor process (Thamdrup and Canfield 1996). A special feature of sediments from the OMZ is the occurrence of large filamentous sulfur bacteria *Thioploca* spp. (Fig. 1.9), *Beggiatoa* spp., and *Thiomargarita* spp. (Gallardo 1977; Schulz et al. 1999). These bacteria gain their energy from the oxidation of sulfide, the product of microbial sulfate reduction, most likely with nitrate as

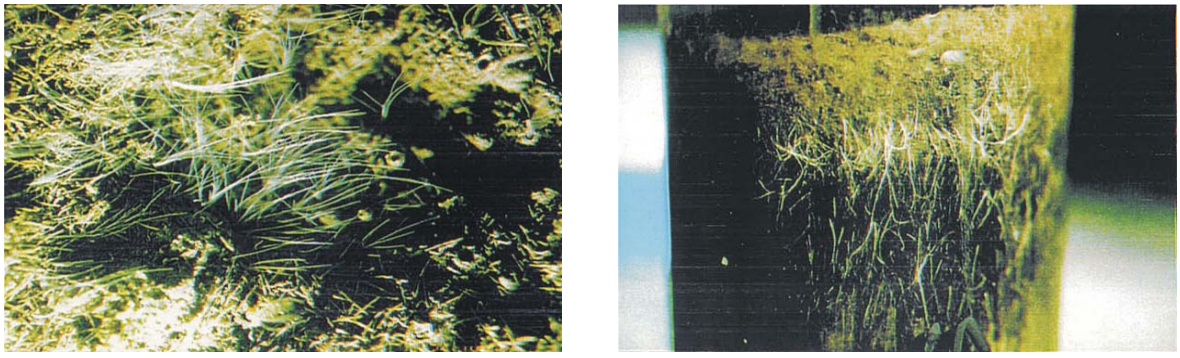

Figure 1.9. *Thioploca* from the shelf region off central Chile. Left: filaments extending from the sediment surface into the bottom water (frame is 15 mm wide), right: sheaths extending down-core into the sediment (core diameter is 8 cm). Pictures from Jørgensen and Gallardo (1999).

electron acceptor (Fossing et al. 1995). They can form dense mats at the sediment surface thereby affecting benthic community structures as well as sediment chemistry (Fossing et al. 1995). Occurrence and quantitative distribution of *Thioploca* have been examined in the investigated region off Peru in order to identify possible interactions with other sediment characteristics (Chapter 3).

THE PERU-CHILE UPWELLING REGION

The Peru-Chile upwelling region is the world's largest coastal upwelling regime, extending from 5°S in the north to 38°S in the south, bordering a coastline of ~5000 km length. Geologically this area is characterized by subduction of the Pacific plate under the South American continent, resulting in a steep continental rise with a generally very narrow shelf. The shelf break occurs at ~200 m water depth and from 12°S-33°S lies 10-20 km from the shoreline. Off northern Peru (6-10°S), the Chimbote platform extends up to 125 km away from the coast (ref. Fig. 3.1). South of 33°S the shelf gradually widens, reaching 50 km extension near 36°S. The seafloor topography along the South American coast exhibits specific for-arc basins and submarine canyons, which influence sediment transport and accumulation (Hebbeln et al. 2001; Reinhardt et al. 2002). The continental hinterland is mostly dominated by a hot and dry climate typical for tropical latitudes and adjacent coastal upwelling regions. Central Chile (31°S-37°S) is characterized by semi-arid Mediterranean climate with moderate winter precipitation brought by the South-Westerlies (Miller 1976). River discharge and terrigenous sediment delivery to the continental margin off Chile increase from north to south, following increasing precipitation rates (Lamy et al. 1998).

Present day oceanography in the coastal region is dominated by the equator-wards flowing Peru-Chile Current (PCC, Humboldt Current) and the underlying pole-ward flowing Gunther Undercurrent (Hill et al. 1998; Fig. 1.10). The PCC forms the eastern part of the south Pacific subtropical gyre and originates from the Antarctic Circumpolar Current (ACC) that diverges near 42°S into the northward flowing PCC and the south-eastward flowing Cape Horn Current (CHC). Flowing northwards, the PCC splits in a coastal and an oceanic branch, between these two branches the Peru-Chile Countercurrent (PCCC) transports subtropical water southwards. Exact position and general behavior of this surface current are not known in detail, particularly in the region off Chile (Strub et al. 1998), but it might extend southwards up to 35°S (Brandhorst 1971). At 5°S the PCC is deflected from the coast,

forming part of the westward flowing South Equatorial Current (SEC). The Gunther Undercurrent (GUC), flowing southwards at 100-400 m water depth, carries Equatorial Subsurface Water, which is saline, cold, oxygen-poor, and nutrient-rich (Shaffer et al. 1995). With few exceptions this is the source of water which is transported to the ocean surface by upwelling processes near the coast. Below 400-600 m water depth, Antarctic Intermediate Water flows towards the equator. At greater water depth, Pacific Deep Water sluggishly moves southwards (Shaffer et al. 1995).

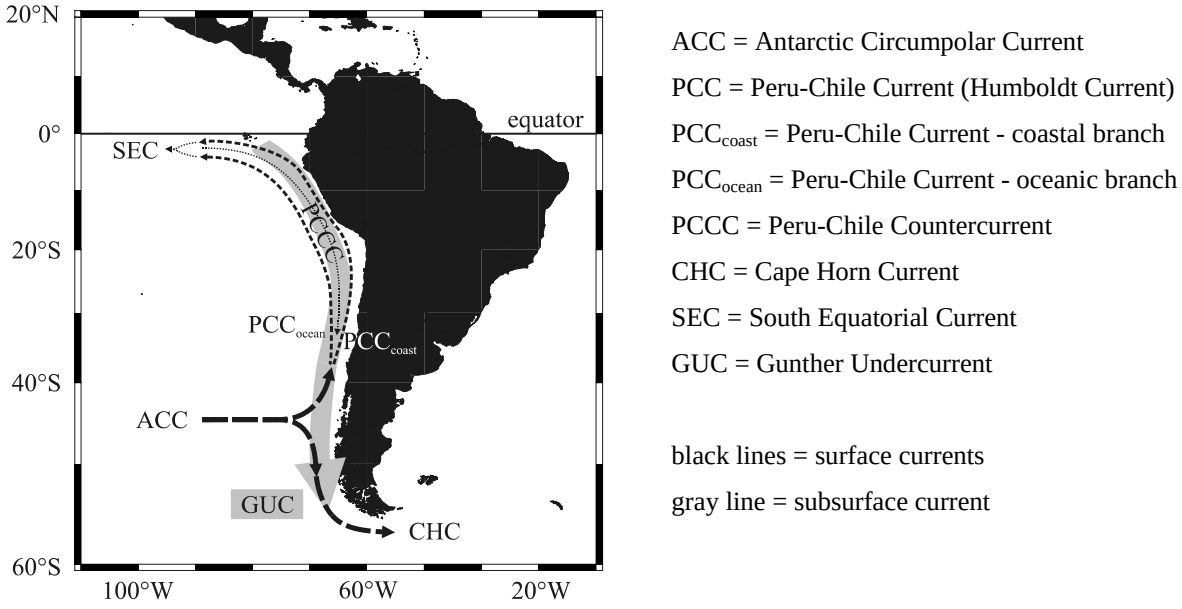

Figure 1.10. Simplified scheme of the modern oceanic current system in the south-east Pacific (after Strub et al. 1998). Longitudinal and latitudinal positions of plotted currents do not match exact oceanographic conditions.

Today, cells of intense upwelling are located near 7-8°S, 11-12°S, and 14-16°S off Peru (Zuta and Guillén 1970), and near 20°S, 23°S, 30°S, 33°S, and 37°S off Chile (Fonseca and Farías 1987). The position of persistent upwelling centers is controlled by seafloor topography and often related to the vicinity of capes. Upwelling off Peru and northern Chile is perennial, changes in intensity are related to seasonal variations in position and intensity of the trade winds (Shaffer 1982). Off central Chile, upwelling is limited to austral summer time, since upwelling favorable trade winds are replaced by northerly and north-westerly winds during austral winter (Ahumada et al. 1983). Detailed descriptions of hydrography and topography of the areas investigated in this thesis are given in the respective chapters.

A phenomenon inherently linked with coastal upwelling off South America is El Niño (Philander 1989). El Niño is closely connected with the climatic processes in the Pacific

region, wherefore this event is also known as ENSO (El Niño - Southern Oscillation). In periods of 5-10 years (Enfield 1989) upwelling ceases, accompanied by substantial disturbances of the climatic system in the Pacific region. Effects of El Niño ("Christ child") are strongest during summer time (Christmas). During El Niño pressure gradients over the Pacific Ocean are smaller than during normal times, in consequence trade winds weaken, there is no or only little surface water transport away from the coast, and upwelling breaks down. Ceasing of upwelling means cutoff of nutrient supply followed by mass dying of fish and seabirds (Arntz and Fahrbach 1991). Warmer surface waters cause more evaporation leading to catastrophic rainfalls, floods, and landslides (Wells 1990).

The sediments investigated as part of this thesis were sampled during non-El Niño times, 2-3 years after the El Niño of 1997-1998 (Levin et al. 2002). In principal, it is possible to trace the El Niño history in the sedimentary record, although signals of individual events might not be resolved and identification is mostly limited to periods of frequent and strong El Niño activity (McCaffrey et al. 1990; Wolf 2002). However, the sampling resolution chosen in the studies presented in this thesis corresponds to time intervals of at least 2-4 years - based on an assumed maximum sedimentation rate of 0.5 cm yr^{-1} - and is therefore too low to identify imprints of El Niño on the sediment composition.

2. OBJECTIVES AND OUTLINE OF THIS THESIS

The work presented in this thesis was part of the projects „Peru-Auftrieb“ (Peru upwelling, BMBF grant 03G0147A) and PUCK (Interrelationships between productivity and environmental conditions along the Chilean continental slope, BMBF grant 03G0156A). General objective of both projects was a better understanding of how present-day environmental conditions affect sedimentary processes in the Peru-Chile upwelling region (Kudrass 2000; Hebbeln et al. 2001). Knowledge of recent upwelling processes and their effects on the sediments provides a key for the reconstruction of paleo-environmental conditions in this important high-productivity region. The biogeochemical part of both projects included the geochemical characterization of sedimentary organic matter and the examination of bacterially mediated processes at the anoxic-suboxic sediment-water interface, with special focus on the influence of *Thioploca*.

The basic topics addressed in this thesis are (1) to identify the sources of the sedimentary organic matter, (2) to characterize the quality of the sedimentary organic matter, (3) to investigate the influence of depositional conditions on the accumulation and composition of sedimentary organic matter, and (4) to link the chemical description of sedimentary organic matter composition with its susceptibility to microbial degradation. In particular, the identification of organic matter sources focused on the detection of possible terrestrial contributions. Further aim was to trace bacterial biomass in the sediments and in more general, to elucidate the imprint of bacteria on organic matter composition. Different parameters were applied to characterize organic matter quality in order to determine the factors that control the quality or freshness of sedimentary organic matter and to quantify diagenetic changes in organic matter composition. An important question was how depositional conditions affect the accumulation and composition of sedimentary organic matter, thereby providing a dominant control on sedimentary processes. It was a major objective of this thesis to evaluate the relationship between organic matter composition as characterized by chemical analysis and its availability for microorganisms as assessed by directly measured sulfate reduction rates.

Chapter 2 deals with the accumulation and degradation of organic matter in sediments from two different depositional regimes in the Chilean upwelling region. It provides a general description of the investigated areas off Antofagasta (~23°S) and off Concepción (~36°S), including information on distribution of ^{210}Pb activity in the sediments, bulk organic matter composition, and sulfate reduction rates. The aim of this study was to characterize differences

in the depositional conditions and to investigate how these differences are reflected in sedimentary organic matter composition and carbon turnover rates.

Chapter 3 describes the spatial distribution of organic matter composition, sulfate reduction rates, and *Thioploca* biomass in surface sediments from the Peruvian upwelling region. Major goals of this study were to identify the factors controlling the actual distribution of sedimentary organic matter, to relate measured sulfate reduction rates to organic geochemical parameters, and to link occurrence and quantitative distribution of *Thioploca* with sediment characteristics.

Chapter 4 focuses on the biogeochemistry of fatty acids in sediments off Chile. Main objective of this study was the characterization of the fatty acid composition with respect to sources and reactivities. In addition, a fatty acid index was derived based on principal component analysis of the molecular fatty acid composition. This parameter was applied to trace diagenetic changes in the investigated sediments and further evaluated by relation to other frequently used quality indicators for organic matter.

Chapter 5 examines sources and fate of amino sugars in sediments from the Peruvian upwelling region, presenting the first sediment study exclusively focusing on amino sugars. One main intention therefore was to gain a general insight into abundance and distribution of amino sugars in sediments. A further aim was to evaluate the potential of amino sugars as source or quality indicators, with particular focus on the use of muramic acid as a tracer of bacterial bio- and/or necromass.

Chapter 6 presents the abstracts of three manuscripts that all address important aspects of this thesis. Chapter 6A presents basics and general applicability of the Chlorin Index, a new parameter for organic matter freshness in sediments (Schubert et al. 2005). The Chlorin Index is one of the parameters applied to characterize organic matter quality in the sediments from the Peru-Chile upwelling region. Chapter 6B deals with the biogeochemistry and stereochemistry of amino acids in sediments off Chile (Lomstein et al. subm.). The objectives of this study were to examine the degradation state of organic matter based on the concentration and molecular composition of amino acids, and to estimate the contribution of bacterial cell wall material to the sedimentary amino acid pool. Chapter 6C deals with anaerobic oxidation of methane and sulfate reduction in Chilean margin sediments (Treude et al. 2005). One intention of this study was to reveal the importance of composition and degradation of organic matter in surface sediments for microbial remineralization processes deeper in the sediments.

3. CONTRIBUTIONS TO PUBLICATIONS

This thesis includes the complete versions of four manuscripts that have been submitted for publication in international journals (Chapters 2-5). Further included are the abstracts of three manuscripts that are also part of this thesis but for reasons of length are not presented in full. Two of these articles are already published (Chapter 6A and 6 C).

Chapter 2 – full manuscript

Jutta Niggemann, Timothy G. Ferdelman, Bente Aa. Lomstein, Jens Kallmeyer, and Carsten J. Schubert

Accumulation and early diagenesis of sedimentary organic material in the Chilean coastal upwelling region

Sampling of sediments and analysis of organic parameters were carried out by Jutta Niggemann. Carsten J. Schubert measured δ^{13}C-values, Bente Aa. Lomstein contributed amino acid data. ^{210}Pb counting was performed by Jutta Niggemann and Timothy G. Ferdelman. Timothy G. Ferdelman and Jens Kallmeyer carried out sampling for sulfate reduction rate measurements. All data handling and evaluation including calculation of sulfate reduction rates and sediment accumulation rates were performed by Jutta Niggemann. Jutta Niggemann wrote the manuscript with editorial input from all co-authors. The manuscript has been submitted to *Geochimica et Cosmochimica Acta*.

Chapter 3 – full manuscript

Jutta Niggemann, Jens Kallmeyer, and Carsten J. Schubert

Spatial distribution of organic matter composition, sulfate reduction rates, and *Thioploca* biomass in surface sediments off Peru

This manuscript includes data acquired during RV Sonne cruise 147 by the participants from the MPI Bremen. Gabriele Klockgether carried out sediment sampling for organic parameters, Jens Kallmeyer sampled for sulfate reduction rate measurements, Elze Wieringa and Daniela Riechmann investigated *Thioploca* distribution. Organic parameters were determined by Jutta Niggemann; Carsten J. Schubert measured δ^{13}C- and δ^{15}N-values. All data handling and evaluation including calculation of *Thioploca* biomass and sulfate reduction rates were performed by Jutta Niggemann. Jutta Niggemann wrote the manuscript with editorial input from the co-authors. The manuscript has been submitted to *Marine Geology*.

Chapter 4 – full manuscript

Jutta Niggemann and Carsten J. Schubert

Fatty acid biogeochemistry of sediments from the Chilean coastal upwelling region: sources and diagenetic changes

Jutta Niggemann performed the analyses, evaluated the data, and wrote the manuscript with editorial input from Carsten J. Schubert. The manuscript has been submitted to *Organic Geochemistry*.

Chapter 5 – full manuscript

Jutta Niggemann and Carsten J. Schubert

Sources and fate of amino sugars in coastal Peruvian sediments

Jutta Niggemann performed the analyses, evaluated the data, and wrote the manuscript with editorial input from Carsten J. Schubert. The manuscript has been submitted to *Limnology and Oceanography*.

Chapter 6A – abstract only

Carsten J. Schubert, Jutta Niggemann, Gabriele Klockgether, and Timothy G. Ferdelman

Chlorin Index: A new parameter for organic matter freshness in sediments

This manuscript includes data of different studies. Gabriele Klockgether carried out initial analyses for the development of the Chlorin Index. Carsten J. Schubert and Timothy G. Ferdelman contributed data on organic matter composition and sulfate reduction rates, respectively, from the upwelling regions off Namibia and off Chile. Jutta Niggemann contributed data from the upwelling region off Peru and carried out HPLC-analyses for method approval. Carsten J. Schubert wrote the manuscript with input from Timothy G. Ferdelman and Jutta Niggemann. *Geochemistry, Geophysics, Geosystems* (2005) **6**, Q03005, doi:10.1029/2004GC000837.

Chapter 6B – abstract only

Bente Aa. Lomstein, Bo B. Jørgensen, Carsten J. Schubert, and Jutta Niggemann

Amino acid biogeo- and stereochemistry in coastal Chilean sediments

Bente Aa. Lomstein carried out amino acid analyses. Jutta Niggemann contributed data on sediment properties and bulk composition. Bente Aa. Lomstein wrote the manuscript with editorial input from the co-authors. Jutta Niggemann contributed parts on site description and explanation of PCA. This manuscript has been submitted to *Geochimica et Cosmochimica*

Acta.

Chapter 6C – abstract only

Tina Treude, Jutta Niggemann, Jens Kallmeyer, Paul Wintersteller, Carsten J. Schubert, Antje Boetius, and Bo B. Jørgensen

Anaerobic oxidation of methane and sulfate reduction along the Chilean continental margin

All sampling procedures and on-board measurements were performed in teamwork including Tina Treude, Jutta Niggemann, Jens Kallmeyer, and Paul Wintersteller. Rates of anaerobic oxidation of methane were measured by Tina Treude. Sulfate reduction rates and sulfate concentrations were measured by Jens Kallmeyer. Jutta Niggemann determined organic parameters and initiated the study on authigenic carbonates. Carsten J. Schubert determined $\delta^{13}C$-values. Tina Treude wrote the manuscript with input from Jutta Niggemann, Jens Kallmeyer, Carsten J. Schubert, Antje Boetius, and Bo B. Jørgensen. *Geochimica et Cosmochimica Acta* (2005) **69**, 2767-2779.

Chapter 2

Accumulation and early diagenesis of sedimentary organic material in the Chilean coastal upwelling region

Jutta Niggemann[a], Timothy G. Ferdelman[a], Bente Aa. Lomstein[b], Jens Kallmeyer[a,c], and Carsten J. Schubert[a,d]

submitted to *Geochimica et Cosmochimica Acta*

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ABSTRACT

In order to elucidate how depositional conditions and organic matter composition influence organic carbon turnover in sediments, we compared two different depositional systems in the Chilean coastal upwelling region: (1) at ~23°S off Antofagasta bordering the Atacama desert, and (2) at ~36°S off Concepción with a more humid hinterland. Eight sediment cores from water depths of 126-1350 m and core lengths up to 30 cm were investigated for excess ^{210}Pb activity, total organic and total inorganic carbon concentrations (TOC and TIC), C/N-ratios, organic carbon isotopic compositions (δ^{13}C), chlorin concentrations, Chlorin Indices (CI), and sulfate reduction rates (SRR). Sediment accumulation rates obtained from ^{210}Pb-analysis were similar in both regions, though vertical particle flux, as reflected in excess ^{210}Pb fluxes, and input of lithogenic terrestrial material, as reflected in dilution of autochthonous TOC and TIC, were higher at 36°S than at 23°S. Sampling of isolated deposition centers, that collect particles originally distributed over a much wider area and are dominated by reworked material, probably led to higher sediment accumulation rates in the northern area. Bioturbation was intense at 36°S even in sediments within the oxygen minimum zone (OMZ), whereas there were no indications for sediment mixing at 23°S, probably as a result of limited food supply. δ^{13}C-values and C/N-ratios were indicative for a predominantly marine origin of the sedimentary organic matter (OM) in both investigated areas. The extent of water column alteration was partly reflected in the surface sediments as chlorin concentrations decreased and C/N-ratios and Chlorin Indices increased with increasing water depth of the sampling site. Reaction rate constants derived from the depth profiles of TOC (k_{TOC}) decreased with increasing water depth, confirming the dominant control of water column degradation on the reactivity of sedimentary OM. Reactivity of chlorins quantified as $k_{chlorin}$ was generally higher than k_{TOC}, reflecting the preferential degradation of pigment material compared to bulk TOC. SRR were lower at 23°S than at 36°S partly due to the greater water depth of most of the sediments investigated in the northern region and consistent with a lower quality of the sedimentary OM at 23°S. Reaction rate constants for TOC degradation that were obtained from measured SRR (k_{SRR}) decreased with increasing water depth and showed a surprisingly good correspondence to k_{TOC}.

INTRODUCTION

In the present ocean, important regions of coastal upwelling are located along the western continental margins of North- and South America and North- and South Africa, as well as in the northwest Arabian Sea where this process is coupled to the monsoon-cycle. In coastal upwelling areas, advection of nutrient rich waters fuels primary production rates up to three orders of magnitude higher than the mean open ocean production (Ryther 1963). The permanent supply of freshly produced organic material (OM), overall high sedimentation rates, as well as oxygen depletion in the water column and at the sediment-water interface, and the shallow water depth of shelf and slope sediments favor the accumulation of organic-rich sediments (e.g. Thiede and Suess 1983; Stein 1991; Summerhayes et al. 1995).

Heterotrophic processes in water column and sediment reduce the total amount of sedimentary OM and change its molecular composition (Wakeham et al. 1997b). Ongoing early diagenesis decreases the availability of OM for further microbial decomposition, thus the reactivity of organic carbon is a function of its degree of alteration. Both in situ and laboratory studies have been carried out to assess the reactivity of sedimentary organic carbon, focusing on the fate of labile organic compounds such as fatty acids (Farrington et al. 1977; Haddad et al. 1992; Sun and Wakeham 1994; Canuel and Martens 1996; Sun et al. 1997; Camacho-Ibar et al. 2003), amino acids (Henrichs and Farrington 1987; Cowie and Hedges 1992), and chlorins (Stephens et al. 1997; Shankle et al. 2002). The reactivity of the organic compounds has been derived from degradation rates either observed in time series incubations (e.g. Sun et al. 1997) or calculated from concentration profiles in dated sediment cores (e.g. Farrington et al. 1977). These studies concluded that individual components are degraded at different rates and that the reactivity of sedimentary organic carbon is generally decreasing with increasing degree of alteration in water column and sediments.

Furthermore, the kinetic of organic carbon appears to be a function of the prevailing degradation pathways. Microbial degradation has been observed to be slower under anoxic than under oxic conditions, though the difference is smaller for fresh, easily hydrolysable, than for more refractory substrates (Henrichs and Farrington 1987; Lee 1992; Sun et al. 1993; Harvey et al. 1995; Kristensen et al. 1995; Sun et al. 1997; Lehmann et al. 2002). Oxygen deficient conditions have been shown to enhance organic carbon preservation, as an existing oxygen minimum zone in the water column allows a greater fraction of the export flux to reach the sediments and low bottom water oxygen concentrations decrease the efficiency of carbon oxidation in the sediment (Hartnett et al. 1998; Hartnett and Devol 2003). Bioturbation

might elongate the oxygen exposure time as mixing and burrowing activity transport particles towards the oxic zone and oxygen might penetrate deeper into the sediment (Aller 1994; Ziebis et al. 1996). In addition, macrofaunal organisms directly feed on the sedimentary OM and also stimulate microbial degradation (Aller 1982).

In the absence of dissolved oxygen, bacterial dissimilatory sulfate reduction is the quantitatively most important terminal electron acceptor process in most marine upwelling sediments (Jørgensen 1982; Canfield 1989; Ferdelman et al. 1999; Hartnett and Devol 2003). In sediments off central Chile (36°S), organic carbon mineralization rates determined by Thamdrup and Canfield (1996) indicated that sulfate reduction accounted for 100% of carbon oxidation in shelf sediments underlying oxygen-depleted bottom waters, and for at least 55% of carbon oxidation in slope sediments.

In a study on sediments from the Bay of Concepción and the adjacent shelf area off Chile, Schubert et al. (2000) linked the distribution of sulfate reduction activity and overall rates of sulfate reduction to the composition of sedimentary OM. They showed that the availability of labile marine OM as indicated by total protein and chlorin concentrations was correlated with higher sulfate reduction rates, whereas a dilution with less reactive terrestrially derived OM significantly altered the depth profiles of SRR. The suggestion of a two-component mixture of organic matter reactivities is consistent with a 2-G or multi-G model of OM reactivity, assuming that sedimentary OM consists of several pools with decreasing reactivity which are consecutively depleted with time and sediment depth (Jørgensen 1978, Westrich and Berner 1984, Jørgensen et al. 2001).

Schubert et al. (2000) hypothesized that variations in the regional distribution of marine OM (or variations in the amount of diluting terrestrial OM) determine the distribution of organic carbon degradation rates as measured by sulfate reduction. Beside differences in organic matter composition, depositional conditions should also affect the sedimentary carbon turnover. Here we test these hypotheses by comparing two sedimentary regimes in the Chilean upwelling region, both underlying important upwelling cells, but representing different depositional environments.

Observations of sea surface temperature (Fonseca and Farías 1987) and coastal zone color scanning recording pigment concentrations (Thomas 1999) along the Chilean coast identify areas of especially pronounced upwelling near 20°S, 23°S, 30°S, 33°S, and 37°S. Upwelling off central Chile occurs seasonally during austral summer months (Brandhorst 1971; Ahumada et al. 1983), at more northerly latitudes, attenuated upwelling also proceeds during winter (Morales et al. 1996; Blanco et al. 2001). For this study we concentrated on

sediments underlying the upwelling cells off Antofagasta (~23°S) in the North and off Concepción (~36°S) in the central region (Fig. 2.1). The two areas of investigation are located more than 1500 km away from each other and represent different climatic as well as depositional regimes.

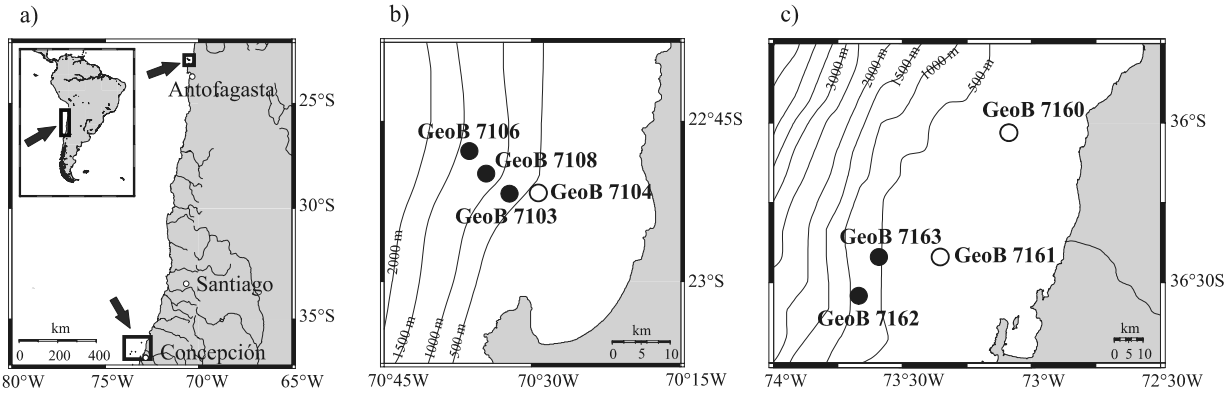

Figure 2.1. Investigation area (a) and location of sampling sites off Antofagasta (b) and off Concepción (c). OMZ-sites are marked by open circles. Note the different scales of the maps.

Near Antofagasta the sediments receive only small amounts of terrestrial material due to extremely low precipitation and prevailing alongshore winds that limit river discharge and eolian input (Lamy et al. 1998). The adjacent coastal hinterland consists of the hyper-arid Atacama Desert (18°S-30°S); the next closest river entering the coastal ocean in this region is the Loa River ~ 150 km further north. Strong bottom currents scour the narrow shelf and the steep slope off northern Chile and allow significant accumulation of sediments only in protected areas, e.g. local depressions or basins. Near Concepción the shelf is broader than off Antofagasta and annual precipitation in the Chilean coastal region increases from north to south, leading to enhanced river runoff and higher input of terrestrial material to the sediments (Hebbeln et al. 2000). Several rivers draining the humid central region of Chile enter the coastal ocean near 36°S: the Itata River north of the Bay of Concepción, the Andalién River flowing into the Bay, and the Bio-Bio River entering the Pacific south of the Bay.

The coastal area off Concepción and especially the Bay of Concepción have been the subject of numerous studies focusing on oceanographic conditions and fertility of prevailing waters (e.g. Ahumada et al. 1983; Arcos and Wilson 1984; Peterson et al. 1988), distribution and importance of mat-forming sulfur bacteria *Thioploca* and *Beggiatoa* (e.g. Gallardo 1977; Fossing et al. 1995; Schulz et al. 1996; Schulz et al. 2000; Graco et al. 2001), as well as

composition and mineralization pathways of sedimentary organic carbon (e.g. Farías et al. 1996; Thamdrup and Canfield 1996; Ferdelman et al. 1997; Glud et al. 1999; Schubert et al. 2000; Farías 2003; Pantoja and Lee 2003). For the investigation area near Antofagasta several studies are available on oceanographic conditions (e.g. Morales et al. 1996; Blanco et al. 2001; Marín et al. 2001; Sobarzo and Figueroa 2001; Escribano et al. 2004) and phytoplankton distribution (e.g. Rodriguez et al. 1991; Morales et al. 1996; Iriarte et al. 2000). However, information on sediment biogeochemistry in this region is lacking. Due to the narrow shelf and the steep slope off Northern Chile it is very difficult to recover sediment cores and sediment studies have been limited to the shallow area in the Bay of Mejillones (e.g. Ortlieb et al. 2000; Valdés et al. 2003; Valdés et al. 2004).

Here we present data characterizing (1) the depositional environment, (2) the bulk organic geochemical composition of the sedimentary OM, and (3) sedimentary organic carbon turnover as measured in part by sulfate reduction. We expected to find distinct differences between the depositional conditions near 23°S off Antofagasta and near 36°S off Concepción, that are partly reflected in differences in organic geochemical composition and turnover rates. Finally, we link these differences in OM composition to observed differences in sedimentary carbon turnover. In this context, we will demonstrate a general coupling of organic carbon reactivity as expressed in (1) remineralization rates linked with sulfate reduction and (2) the overall down-core decrease of TOC concentrations.

MATERIAL AND METHODS

Sampling and sample processing

Sampling was carried out during RV Sonne cruise SO-156 in April 2001. At that time, the oxygen minimum zone (OMZ) in the water column, with dissolved oxygen concentrations <22 µM, at 23°S extended from 30-50 m to 400 m water depth near the coast and from 70 m to 450-500 m water depth further offshore. At 36°S the OMZ was narrower than at 23°S, extending from 80-140 m water depth down to the seafloor at the shelf stations and from 70 m to 400 m water depth further offshore (Hebbeln et al. 2001). The narrowing of the water column OMZ from North to South is mainly due to the mixing of the southward flowing oxygen depleted Equatorial Subsurface Water with well-oxygenated Subantarctic Water above and Intermediate Antarctic Water below (Brandhorst 1971).

Table 2.1. Sampling sites with position, water depth, bottom water oxygen concentration, and location relative to position of water column OMZ.

station	latitude	longitude	water depth (m)	bottom water oxygen[a] (µmol l^{-1})	location relative to position of OMZ
GeoB 7103	22°51.99 S	70°32.54 W	891	45	below
GeoB 7104	22°52.00 S	70°29.42 W	307	7	within
GeoB 7106	22°48.00 S	70°36.70 W	1350	53	below
GeoB 7108	22°50.50 S	70°34.79 W	1007	n.d.[b]	below
GeoB 7160	36°02.33 S	73°04.39 W	367	7	within
GeoB 7161	36°25.51 S	73°23.32 W	126	0.4	within
GeoB 7162	36°32.52 S	73°40.02 W	798	105	below
GeoB 7163	36°25.55 S	73°35.71 W	536	103	below

[a]data from CTD-profiling (Hebbeln et al. 2001), [b]n.d. = not determined

Bottom water oxygen concentrations reported from CTD casts during the cruise ranged from 0.4 to 105 µM at the different stations (Hebbeln et al. 2001; Tab. 2.1). The lowest concentrations were found at GeoB 7104 (7 µM), GeoB 7160 (7 µM), and GeoB 7161 (0.4 µM), reflecting their location within the actual depth of the water column OMZ (Fig. 2.1b/c). The highest oxygen concentrations were measured in the bottom waters of the deeper sites GeoB 7106 (53 µM), GeoB 7162 (105 µM), and GeoB 7163 (103 µM). However, these latter concentrations were <35% oxygen saturation at the given temperatures and salinities.

Table 2.1 summarizes the characteristics of the sampling stations. At each station three multi-corer cores were sampled. For geochemical analyses the sediment cores were sliced in 1 cm intervals in the upper 6 cm and in 2 cm intervals below 6 cm. The samples were transferred to clean glass-vials and frozen at -25°C immediately after sampling. The sediment samples were later freeze-dried and homogenized by grinding in an agate mortar. Particulate material more than 0.5 cm in size, e.g. fish bones, shells, worm-tubes, and remains of worms, were excluded from the sediments.

For sulfate reduction rate incubations sub-cores were taken from individual multi-corer cores in two different ways: (1) For sampling in 1 cm resolution, 30 cm long Plexiglas core tubes (26 mm diameter) were used with silicone plugged holes every 1 cm. (2) For sampling in 5 cm intervals, 7 cm long glass tubes (10 mm diameter) made from a glass barrel were used, with a piston from a 5 ml plastic syringe on one side and sealed with a butyl rubber stopper on the other. All samples were immediately transferred into a dark incubator and stored close to in situ temperatures.

Additional samples were taken for the determination of porosity and wet density as well as for ^{210}Pb-counting. The cores were sliced into 1 or 2 cm intervals, transferred to Petri-dishes, sealed tightly with electric tape, and stored at 4°C until further analysis.

Elemental analysis

Total carbon (TC) and total nitrogen (TN) concentrations were determined on freeze dried samples by combustion/gas chromatography (Carlo Erba NA-1500 CNS analyzer) with a precision of ±0.7% for N and ±0.6% for C, respectively. Total inorganic carbon (TIC) was measured on a CM 5012 CO_2 Coulometer (UIC) after acidification with phosphoric acid (3 M). The precision for TIC was ±0.4%. Total organic carbon (TOC) was calculated as the difference of TC and TIC. The C/N-ratio was calculated as the molar ratio of TOC and TN. For the determination of the isotopic composition of TOC, samples were first treated with hydrochloric acid (3 M) to eliminate carbonates, rinsed three times with distilled water, and dried at 60°C (Schubert and Nielsen 2000). Depending on the TOC concentration, 0.2-1.1 mg of the decarbonated samples were combusted in a Thermo Quest elemental analyzer NC2500. The evolved CO_2 was passed to an Isoprime isotope-ratio mass spectrometer (Micromass, UK) in a continuous flow of helium. The results are reported in the δ notation relative to Vienna Pee Dee Belemnite (VPDB):

$$\delta^{13}\mathrm{C}(‰) = \left(\frac{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{sample}}}{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{s\,tan\,dard}}} - 1 \right) * 1000 \qquad (1)$$

Average standard deviation for four replicates was ±0.4‰.

Chlorins and Chlorin Index (CI)

For the determination of chlorins 100-200 mg of freeze dried sediment was extracted successively three times with 5 ml acetone (HPLC-grade, Roth, Germany) by sonication (10 min) and centrifugation (5 min, 1000 g). The samples were cooled with ice under low light conditions during extraction to prevent decomposition of the chlorins. The sediment extracts were measured on a Hitachi F-2000 fluorometer (λ_{ex}=428 nm, λ_{em}=671 nm) immediately after extraction. Chlorophyll *a* (Fluka), acidified with a few drops of pre-extracted hydrochloric acid (8 M) to yield phaeophytin *a*, was used as a standard. The

pigment concentration is given relative to phaeophytin *a*. The precision of the method was ±10%. In addition, the pigment extracts were acidified and measured again. Labile compounds are easily degraded by the acid treatment and the resulting molecules have different fluorescence properties than their precursors. The ratio of the fluorescence intensities (FI) of the acid-treated pigment extract and the untreated one has been shown to provide a measure for the degradability of the pigments. This ratio is defined as Chlorin Index (Schubert et al. 2005):

$$\text{Chlorin Index (CI)} = \frac{FI_{acidified\_extract}}{FI_{original\_extract}} \quad (2)$$

For intact chlorophyll *a* the CI is 0.2, highly degraded pigments approach a CI of 1 (Schubert et al. 2005).

Sulfate reduction rates (SRR)

Sulfate reduction rates were determined using the whole-core $^{35}SO_4^{2-}$ injection method. Details and caveats to the whole-core method are given in Jørgensen (1978) and Ferdelman et al. (1999). For the Plexiglas sub-cores ~5 µl of carrier-free $^{35}SO_4^{2-}$ (80 kBq μl^{-1}, Amersham) was injected through ports along the side, whereas in the glass-subcores, $^{35}SO_4^{2-}$ (~5-10 µl) was injected along the longitudinal axis. Incubation times varied between 6 and 42 hours. Bacterial activity was halted by transferring 1 cm slices of the sediment from the acrylic cores and the sediment extruded from the glass barrels, respectively, into 20 ml of 20% zinc acetate (20 g $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ per 100 ml solution) and freezing (-20°C). Blank controls were determined by fixing sediment in zinc acetate solution and subsequently adding $^{35}SO_4^{2-}$. Incorporation into total reducible inorganic sulfur (TRIS) was determined using the cold Chromium-II method (Kallmeyer et al. 2004). A Packard 2500 TR liquid scintillation counter (scintillation fluid Lumasafe Plus; Lumac LSC, Inc) was used to quantify the $^{35}SO_4^{2-}$ and $^{35}S_{TRIS}$ activities. Sulfate reduction rates were calculated according to Kallmeyer et al. (2004). Sulfate concentrations used in the calculations were assumed to be 28 mM as pore water measurements of sulfate using anion chromatography as per Ferdelman et al. (1997) from adjacent cores showed no significant depletion from seawater sulfate concentration (Kallmeyer, unpublished data).

For determination of porosity and density approximately 2-3 g of wet sediment were weighed into measuring cylinders, filled up with distilled water (Milli-Q) to an exact volume

of 10 ml, and reweighed to calculate the volume of the added water. The wet volume of the sediment aliquot is 10 ml minus the volume of the added water. Wet density is given as the ratio of wet weight and wet volume. The samples were dried at 60°C overnight and weighed again. The pore-water content was calculated as the difference of sediment wet weight and sediment dry weight. Porosity is the ratio of volume pore-water and volume wet sediment. For station GeoB 7163 no samples were available for porosity analysis. Therefore we determined the dry density of the freeze-dried samples and calculated porosity and density using the wet weight/dry weight ratio recorded during freeze-drying.

^{210}Pb-counting

For gamma-counting, dry sediments were homogenized by grinding in a mortar and 5-25 g transferred to polysulfone screw (diameter 45 mm) screw-top jars. Samples were kept for at least 20 days to reach secular equilibrium between the parent isotope ^{226}Ra and its short-lived daughter products ^{222}Rn, ^{214}Pb, and ^{214}Bi. Activities were then determined by non-destructive gamma spectrometry using an ultra-low-level germanium gamma detector (Canberra, EURISYS coaxial type N). Depending on the expected activity individual samples were counted for 1-4 days. Activities of the isotopes ^{210}Pb (46.4 keV), ^{214}Pb (295.2 and 352 keV), and ^{214}Bi (609.3 keV) were corrected for detector efficiency and intensity obtained from calibration with a uranium-thorium ore reference standard (DL-1a, Canadian Certified Reference Materials Project). ^{210}Pb self absorption in the sample was checked individually for every sample by the method of Cutshall et al. (1983), using a 10 kBq ^{210}Pb source (AEA Technology). Supported ^{210}Pb activity from the in situ decay of ^{226}Ra in the samples was determined as the activity of its short-lived daughter products ^{214}Pb and ^{214}Bi. Excess (unsupported) ^{210}Pb activity was calculated as the difference of total ^{210}Pb activity and ^{226}Ra activity.

Calculation of sediment accumulation rates

Sediment accumulation rates were calculated from the down-core changes of excess ^{210}Pb activity. To account for differences in sediment porosity excess ^{210}Pb was plotted versus cumulative sediment dry weight (Fig. 2.2) and sedimentation rates were derived from linear regression of ln excess ^{210}Pb in those parts of the sediments that appeared to be unaffected by mixing. Assuming constant excess ^{210}Pb flux and constant sedimentation over time,

sedimentation rates (r) were calculated from the slope (S) of the linear regression and the decay coefficient (λ), according to the constant activity model (Nittrouer et al. 1984):

$$r = \frac{\lambda}{S} \qquad \text{with} \qquad \lambda = \frac{\ln 2}{t_{1/2}} \qquad \text{(3.1 and 3.2)}$$

Half-life ($t_{1/2}$) of ^{210}Pb is 22.3 years. For each depth an age was calculated from cumulative dry weight and sedimentation rate (given in g cm^{-2} yr^{-1}). Accumulation rates (cm yr^{-1}) were then calculated from age and depth (Fig. 2.2) of the individual samples.

It should be noted here, that effects of bioturbation cannot be excluded for the apparently undisturbed sediments. Sediment accumulation rates calculated from profiles of excess ^{210}Pb often overestimate the actual accumulation rates, as gradually decreasing mixing efficiency with sediment depth might result in a depth profile indicating exponential decay which is falsely interpreted as undisturbed sediment accumulation.

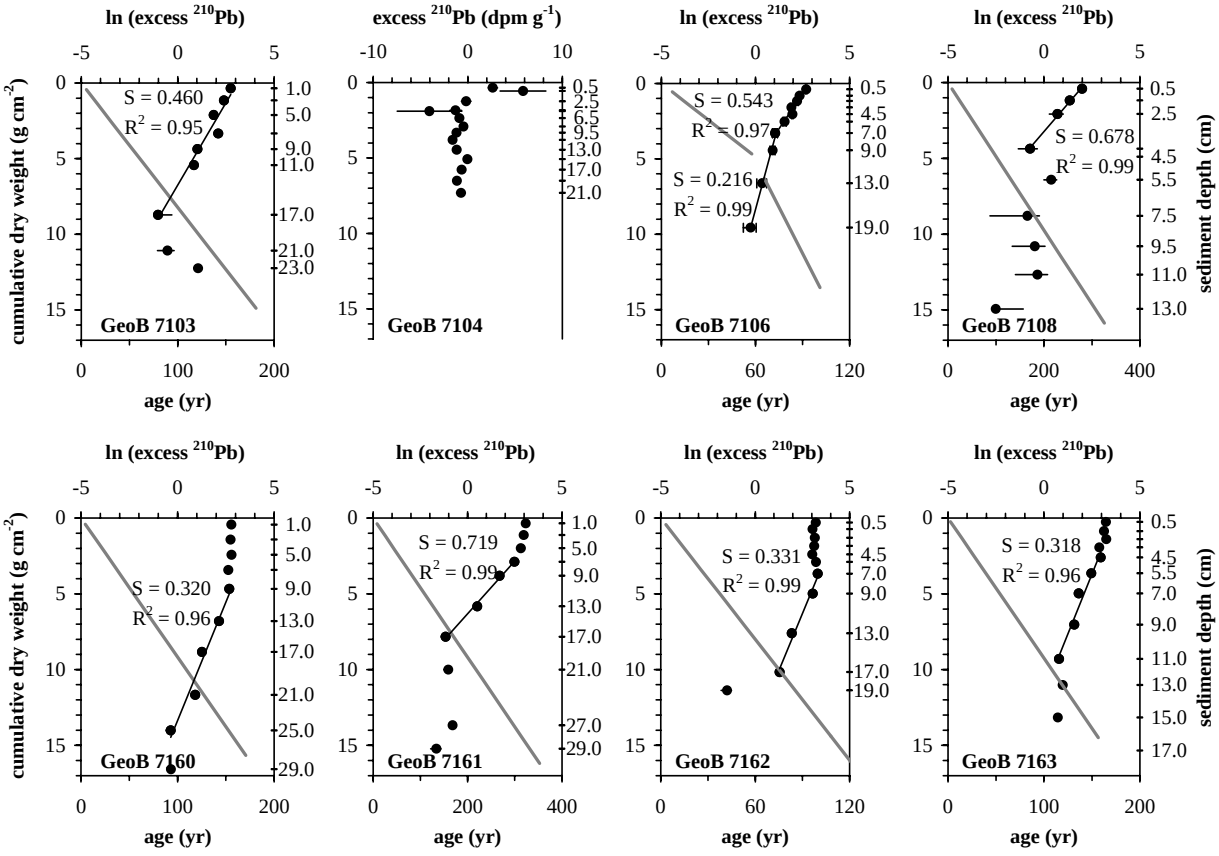

Figure 2.2. Profiles of excess ^{210}Pb activity (in dpm g^{-1} dry sediment) plotted as ln (except GeoB 7104) versus cumulative sediment dry weight (left axis), corresponding sediment depths are given (right axis). Error bars give ln of standard deviation (1 σ) for excess ^{210}Pb activity. Regression lines are plotted for the data points that indicate exponential decay. Grey lines give sediment age (lower axis) calculated from sedimentation rates.

RESULTS

General sediment characteristics

Near 23°S the sediments mainly consisted of sandy mud with surface porosities of ~0.7, whereas near 36°S hemipelagic mud dominated the sediments and porosities were higher (~0.8). The porosity profiles of GeoB 7161, GeoB 7162, and GeoB 7163 (not shown) reflect a change in sediment texture that was also observed during sampling: the lower part of the sediment (16-36 cm, 10-20 cm, and 6-18 cm, respectively) appeared stiffer than the softer upper part. A sharp transition in sediment texture from silt in the upper ~15 cm to clay below this depth was also reported by Thamdrup and Canfield (1996) and Ferdelman et al. (1997) for a sediment core from a site close to GeoB 7161.

For the northern area no direct information exists on living organisms in the sampled cores, with the exception of GeoB 7104 where several small worms and annelids were observed. The upper 50 cm of gravity cores taken at sites GeoB 7103, GeoB 7106, and GeoB 7108 showed no indications of bioturbation (Hebbeln et al. 2001). Furthermore, the freeze-dried samples did not reveal any remains of bioturbating infauna, and no *Thioploca* were reported for the investigated sites (Hebbeln et al. 2001). On the other hand we found numerous tests of benthic foraminifera in all sediments at 23°S, being especially abundant at GeoB 7104. Dominant species were of the family *Nonionidae* (T. Cedhagen, personal communication) which are particularly adapted to oxygen limited conditions (Bernhard et al. 1997).

At 36°S all stations were strongly bioturbated. Living organisms were found in the cores of GeoB 7160 and GeoB 7163, up to 16 cm and 12 cm sediment depth, respectively. At GeoB 7161 several worm tubes with vital worms escaped the sediment surface and at the deepest site in this area (GeoB 7162) a worm burrow was observed but no living organisms were found. The freeze-dried sediments of all stations from 36°S contained numerous remains of worms. *Thioploca* were present at all four stations. However, it was only at GeoB 7161 that a significant *Thioploca* biomass (5.2 g m^{-2}) was found (Hebbeln et al. 2001). At this site single filaments penetrated down to 18 cm sediment depth. Nevertheless, the observed *Thioploca* biomass was lower than the average value of 10 g m^{-2} reported for the Chilean shelf (Schulz et al. 1996).

Sediment mixing and accumulation rates

The cores from the southern area revealed nearly constant ^{210}Pb activity in the upper part of the sediments (Fig. 2.2), depicting the zone of effective sediment mixing most likely due to bioturbation. This well mixed zone penetrated deeper at GeoB 7160 and GeoB 7162 compared to GeoB 7161 and GeoB 7163, indicating a less effective mixing at the latter sites. There were no indications of sediment mixing in the sediments at 23°S from the depth profiles of excess ^{210}Pb, in accordance with the obvious lack of bioturbating organisms in the sediments from this region.

Average sediment accumulation rates as well as the observed ranges calculated from the ^{210}Pb-profiles are summarized in Table 2.2. Near Antofagasta, sediment accumulation rates were slightly lower compared to the region off Concepción. Samples of GeoB 7104 contained only very small amounts of excess ^{210}Pb indicating a lack of recent sedimentation at this site.

Total excess ^{210}Pb inventories were generally higher in sediments off Concepción than off Antofagasta, falling in the range 71-170 dpm cm^{-2} and 19-50 dpm cm^{-2}, respectively (Tab. 2.2). Accordingly, total excess ^{210}Pb fluxes calculated from these inventories by multiplying by λ were also higher off Concepción (2.2-5.3 dpm cm^{-2} yr^{-1}) than off Antofagasta (0.6-1.5 dpm cm^{-2} yr^{-1}).

Table 2.2. Depth interval of mixed zone, sediment accumulation rates ω derived from depth profiles of excess ^{210}Pb, inventories of total excess ^{210}Pb, and flux of total excess ^{210}Pb to the sediments. For every station the range of calculated ω is given in parentheses.

station	depth of mixed zone (cm)	ω (cm yr^{-1})	excess ^{210}Pb inventory (dpm cm^{-2})	excess ^{210}Pb flux (dpm cm^{-2} yr^{-1})
GeoB 7103	none	0.15±0.02 (0.19-0.13)	50	1.5
GeoB 7106	none	0.11±0.02 (0.13-0.07)	40	1.2
		0.26±0.01 (0.28-0.25)[a]		
GeoB 7108	none	0.04±0.01 (0.06-0.04)	19	0.6
GeoB 7160	10	0.19±0.02 (0.23-0.17)	124	3.9
GeoB 7161	8	0.10±0.01 (0.12-0.07)	71	2.2
GeoB 7162	10	0.17±0.01 (0.19-0.16)	170	5.3
GeoB 7163	5	0.15±0.03 (0.19-0.11)	111	3.5

[a]higher rates were observed in the deeper part of the sediment (8-20 cm)

Elemental composition

Total organic carbon and total inorganic carbon

TOC concentrations ranged from 1.6% to 12.4% sediment dry weight on the northern and from 1.5% to 4.2% on the southern transect (Fig. 2.3). Unexpectedly, TOC concentrations were generally (except at GeoB 7108) higher in the sediments at 23°S compared to 36°S.

The TOC profile at GeoB 7104 departed from those at the other investigated sites. The TOC concentration remained relatively constant (5.1-5.8%) within the upper 5 cm of the sediment, gradually increased to 12.4% at 9 cm depth, and then decreased to 6.4% at the end of the core. The depth distribution of TOC was partly reflected in the profiles of porosity and density, high TOC concentrations coincided with high porosity and low density. At GeoB 7103 and GeoB 7108 TOC concentrations ranged from 5.1% to 6.1% and from 1.6% to 2.0% sediment dry weight, respectively, showing an overall decrease with sediment depth. At GeoB 7106 the TOC concentrations exhibited strong scatter in the upper 10 cm and were relatively constant deeper in the sediment (4.1-4.5%).

At all stations in the southern region, TOC concentrations decreased with increasing sediment depth. GeoB 7162 and GeoB 7163 showed a constant decrease from the sediment surface throughout the core, from 2.6% to 2.3% and from 2.1% to 1.5% sediment dry weight, respectively. At GeoB 7160 the TOC concentration decreased from 3.1% at 3.5 cm depth to 2.5% at the end of the core. The strongest decrease was observed at GeoB 7161 from 4.1-4.2% in the upper 3 cm to 1.5% at the end of the core. A sharp minimum of 3.1% was present at 3.5 cm depth. The upper layer with TOC concentrations of ~4% coincided with the extension of the mixed zone, whereas the pronounced decrease towards the lowermost sample might reflect the change in sediment texture observed at this site.

TIC concentrations (data not shown) were generally higher at 23°S (up to 2.2% sediment dry weight) than at 36°S (<0.4%), probably due to the high abundances of calcareous foraminifera tests observed in the sediments off Antofagasta.

C/N-ratios

The C/N-ratios increased gradually with sediment depth at all sites of the southern transect (Fig. 2.3), reflecting the ongoing degradation of sedimentary OM and the preferential remineralization of nitrogen containing compounds (e.g. Meyers 1997). The observed increase was less pronounced at GeoB 7160 (9.8-10.7), GeoB 7163 (9.8-10.7), and GeoB 7162 (9.9-10.4) compared to GeoB 7161, which showed a strong increase from 9.3 at

the sediment surface to 11.0 at 21 cm sediment depth. The high C/N-ratio of 12.3 at the end of the core coincided with the change in sediment texture mentioned above.

Near 23°S constantly increasing C/N-ratios with sediment depth were observed at GeoB 7103 (10.3-11.5). C/N-ratios at GeoB 7104 increased strongly from 8.6 at the sediment surface (the lowest ratio observed in this study) to 12.2 at 7 cm depth. In the deeper part of the sediment C/N-ratios were high (>12), with a maximum of 12.8 at 15 cm depth (the highest ratio observed in this study). At GeoB 7108 the C/N-ratios fell in the range 9.6-10.2, without distinct depth pattern. C/N-ratios at GeoB 7106 ranged from 9.6 to 11.4, with ratios >10 in the upper 2 cm of the sediment and in the deeper part (11-21 cm) where they gradually increased. Maximum ratios were found at the end of the core but a section of constantly lower values (9.6-9.9) was observed at 2.5-9 cm.

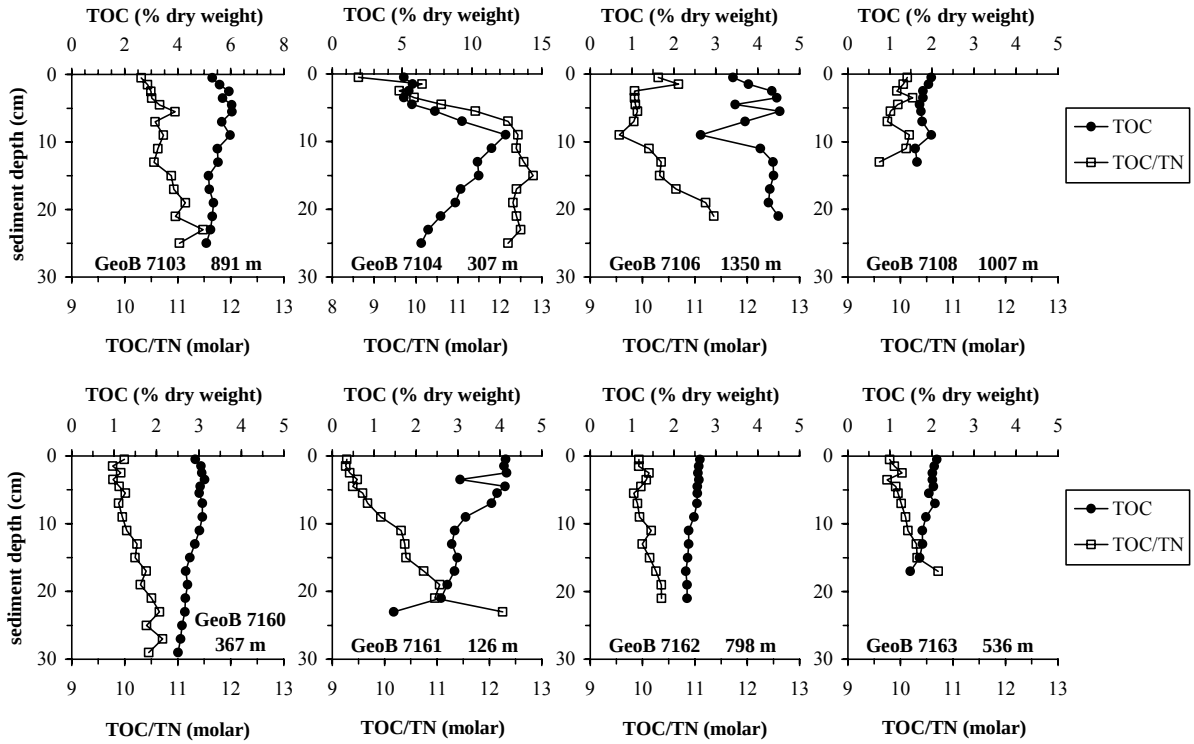

Figure 2.3. Depth profiles of TOC concentrations in % dry sediment weight (●) and C/N-ratios calculated from molar concentrations of TOC and TN (□). Note the different scales for GeoB 7104 (TOC and C/N) and GeoB 7103 (TOC).

Organic carbon isotopic composition

The organic carbon isotopic composition provides information on the organic carbon source. $\delta^{13}C$-values for marine OM are typically in the range -22‰ to -19‰, whereas terrestrial OM from C_3-plants varies from -28‰ to -26‰ (Fry and Sherr 1984). The

δ^{13}C-values observed in this study ranged from -20.1 to -24.5‰ and showed a clear separation between the northern and the southern transect (Fig. 2.4). With the exception of the light isotopic composition at GeoB 7161 at 2.5 cm depth (-22.7‰), all samples from 36°S fell in the narrow range -21.0 to -20.1‰, indicating a predominantly marine source of the sedimentary OM. At 23°S, the carbon isotopic composition was lightest at GeoB 7104 ranging from -24.5‰ to -22.6‰. All other δ^{13}C-values on the northern transect were between -23.4 and -21.4‰.

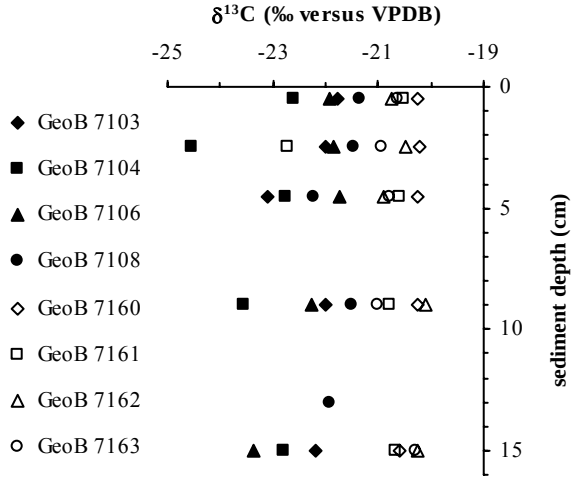

Figure 2.4. Depth distribution of organic carbon isotopic composition (δ^{13}C) in ‰ versus VPDB.

Total chlorins and Chlorin Index

Chlorins comprise a variety of degradation products of chlorophyll and provide a measure for the input of phytoplankton detritus. Total chlorin concentrations ranged from 4 to 24 µg g^{-1} dry sediment on the northern transect and from 7 to 31 µg g^{-1} dry sediment on the southern transect. With the exception of GeoB 7161, where the maximum concentration of 31 µg g^{-1} was found at 17 cm depth, highest concentrations always occurred in the uppermost cm (Fig. 2.5). At 36°S, surface concentrations decreased with increasing water depth, at 23°S, the highest surface concentration was found at GeoB 7103 (24 µg g^{-1}) whereas the surface value was lowest at GeoB 7108 (6 µg g^{-1}). At most stations the chlorin concentration showed an overall decrease with sediment depth, and, at all sites, the decrease was most extreme in the upper 3 cm, where 18-56% of the initial chlorin concentration was lost. The chlorin concentrations at GeoB 7104 and GeoB 7161 did not show a clear depth trend.

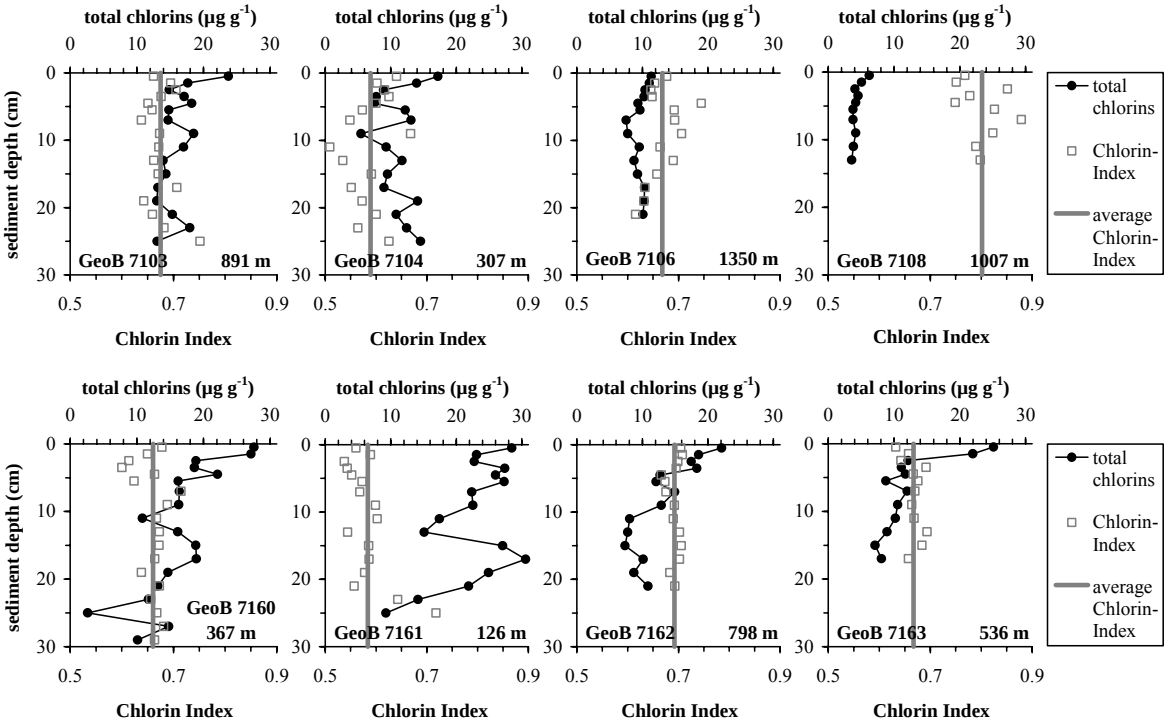

Figure 2.5. Depth profiles of total chlorin concentrations in µg g^{-1} dry sediment (●) and the Chlorin Index (□). Average Chlorin Index (all depth) is given by the grey lines.

The Chlorin Index (CI) at the sediment surface was lowest at the shallowest station GeoB 7161 (0.56) and highest at GeoB 7108 (0.77). The expected increase of CI with sediment depth could be observed at GeoB 7103, GeoB 7108, GeoB 7160, GeoB 7161, and GeoB 7163, where values at the end of the core were higher than at the sediment surface. The depth-averaged CI was lowest at the shallowest sites GeoB 7161 (0.58±0.04, including the high values at the end of the core), and GeoB 7104 (0.59±0.04), indicating that the phytodetritus was freshest at these sites. At GeoB 7108 an average CI of 0.80±0.04 characterized the pigment material to be the most degraded. At all other sites the average CI fell in the range 0.66 to 0.69, indicating the presence moderately altered chlorins.

Sulfate reduction rates

The depth distribution of sulfate reduction rates (SRR) is shown in figure 2.6, maximum SRR and the depth of the SRR peak at the different sites are summarized in Table 2.3. At GeoB 7103 SRR varied around 4 nmol cm^{-3} d^{-1} throughout the upper 15 cm. In the deeper part rates decreased slightly to values <1 nmol cm^{-3} d^{-1}. The depth distribution of SRR was similar to that at GeoB 7108 where rates ranged around 1 nmol cm^{-3} d^{-1} throughout

the core. The surface peak observed in the 1 cm sampling was not reflected in the 5 cm sampling (grey bars). GeoB 7104 showed a distinct surface peak of 11.4 nmol cm^{-3} d^{-1} and an exponential decrease to rates <1 nmol cm^{-3} d^{-1} at sediment depth >8 cm. The surface maximum at this site was even more strongly expressed in the 5 cm samples. At the deepest site (GeoB 7106) highest SRR were observed in the deeper part of the core (5-15 cm). SRR were <0.2 nmol cm^{-3} d^{-1} near the sediment surface and increased towards the maximum of 3.3 nmol cm^{-3} d^{-1} at 13 cm.

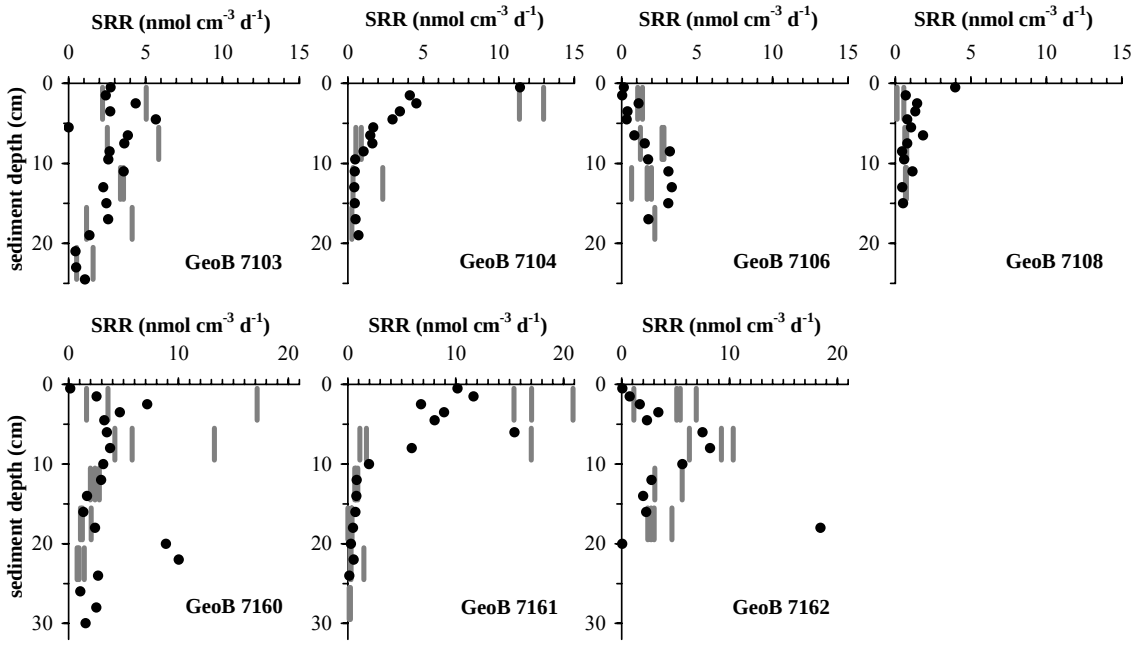

Figure 2.6. Depth profiles of sulfate reduction rates (SRR) in nmol cm^{-3} d^{-1}. Circles (●) mark 1 cm samples, grey bars mark 5 cm samples (1-4 parallels). Scales are different for the two transects.

At GeoB 7160 SRR were lowest at the sediment surface (<0.2 nmol cm^{-3} d^{-1}), indicating the dominance of respiratory processes other than sulfate reduction. In the detailed core, a subsurface peak of 7.2 nmol cm^{-3} d^{-1} was found at 2.5 cm depth. Down-core, SRR gradually decreased and showed a second peak of 8.9-10.0 nmol cm^{-3} d^{-1} at 20-22 cm depth. This well expressed maximum was not reflected in the 5 cm samples and thus appeared to show local heterogeneity, e.g. worm burrows with freshly introduced OM. At GeoB 7161 rates were high throughout the upper 6 cm. SRR derived from 1 cm sampling scattered in the range 6.8-15.5 nmol cm^{-3} d^{-1}, whereas those derived from 5 cm sampling were even higher (15.4-20.9 nmol cm^{-3} d^{-1}). A sharp down-core decrease to SRR <1 nmol cm^{-3} d^{-1} was observed at >10 cm depth, similar to the depth profiles reported by Thamdrup and Canfield (1996) and

Ferdelman et al. (1997) at a site close to GeoB 7161. These studies were carried out in March and revealed SRR significantly higher compared to the SRR we found towards the end of the upwelling season during the second half of April. However, high temporal variability of SRR should be limited to the shelf sites and is mainly due to seasonal changes in the availability of fresh organic carbon. Highest SRR at GeoB 7162 were found at 5-10 cm depth. SRR were <0.2 nmol cm^{-3} d^{-1} at the sediment surface, increased towards a maximum of 8.2 nmol cm^{-3} d^{-1} at 8 cm depth, and decreased further down-core. Like the deep peak at GeoB 7160, the peak observed at 18 cm (18.4 nmol cm^{-3} d^{-1}) was only resolved by high resolution sampling and not present in the 5 cm samples, and might be the result of sediment heterogeneity. Another possible explanation for the deep peaks is a disturbance during analysis: material might have become available that was protected from microbial degradation before sampling. We can exclude that the high SRR were caused by sulfate reduction coupled to the anaerobic oxidation of methane as (1) pore-water sulfate concentrations did not change significantly in the upper 30 cm of the investigated sediments and (2) in a gravity core retrieved at the position of GeoB 7162, Treude et al. (2005) located the zone of sulfate-methane transition at 320-450 cm sediment depth.

Generally, we found a good correspondence of SRR derived from the analysis of 1 cm and 5 cm intervals. Though the lower resolution did not resolve distinct peaks such as the surface maximum at GeoB 7104, in most cases the bigger intervals were in accordance with the shape of the SRR profile obtained from 1 cm sampling. The high variation found for the parallels in the upper 10 cm at GeoB 7160 and GeoB 7161, where the standard deviation was up to 111% of the average, probably reflects a greater heterogeneity at these sites. Redistribution of sediment particles by bioturbating organisms might create hot spots of elevated SRR.

Table 2.3. Depth integrated areal sulfate reduction rate (0-15 cm), near-surface maximum of SRR and depth of near-surface SRR peak, calculated reaction rate constant k_{SRR} at depth of SRR peak and average k_{SRR} (all depths).

station	areal SRR (mmol m^{-2} d^{-1})	maximum SRR (nmol cm^{-3} d^{-1})	SRR peak depth (cm)	k_{SRR} at peak depth (yr^{-1})	average k_{SRR} (yr^{-1})
GeoB 7103	0.53 ± 0.14	5.7	4.5	0.0017	0.0008 ± 0.0005
GeoB 7104	0.60 ± 0.19	11.4	0.5	0.0035	0.0009 ± 0.0013
GeoB 7106	0.24 ± 0.07	3.3	13	0.0013	0.0008 ± 0.0004
GeoB 7108	0.12 ± 0.03	4.0	0.5	0.0022	0.0004 ± 0.0003
GeoB 7160	0.78 ± 0.36	7.2	2.5	0.0040	0.0022 ± 0.0025
GeoB 7161	1.18 ± 0.28	11.7	1.5	0.0070	0.0033 ± 0.0042
GeoB 7162	0.82 ± 0.19	8.2	8	0.0047	0.0030 ± 0.0016

At most sites, subsurface or deep peaks of SRR indicated that other terminal electron acceptor processes account for part of carbon oxidation. In consequence, depth integrated SRR (0-15 cm) underestimate the TOC remineralization rate and rather provide a minimum estimate (Tab. 2.3). Areal SRR were higher in sediments at 36°S (0.78-1.18 mmol m^{-2} d^{-1}) than at 23°S (0.12-0.60 mmol m^{-2} d^{-1}). In both regions the depth integrated rates were highest at the shallowest sites. Overall, areal SRR decreased with increasing water depth.

DISCUSSION

Differences in depositional conditions off Antofagasta and off Concepción

Upwelling intensity and particle flux

The flux of excess ^{210}Pb to the sediments provides information on the upwelling intensity in the overlying water column. Two sources account for excess ^{210}Pb inventories in marine sediments: dry and wet deposition of atmospheric ^{210}Pb onto the ocean surface and production in the water column by the decay of ^{226}Ra. Dissolved ^{210}Pb is effectively scavenged on sinking particles and transported to the sediments. Consequently the flux of ^{210}Pb to the sediment is a function of supply in the water column and of particle flux. Upwelling supports both factors. Firstly, upwelling waters are fed by lateral inflow of open ocean water enriched in dissolved ^{210}Pb, and secondly, high nutrient concentrations fuel particle production in the euphotic zone.

Atmospheric deposition of ^{210}Pb accounts for an excess ^{210}Pb flux of 0.2 dpm cm^{-2} yr^{-1} to the sediments off Concepción (Muñoz and Salamanca 2003). We assume a similar contribution for the sediments off Antofagasta, although the lack of wet deposition might slightly lower the atmospheric input in this region. For the coastal ocean off California, Alexander and Venherm (2003) estimated a maximum flux of 0.37 dpm cm^{-2} yr^{-1} that is supported by in-situ decay for 800 m water depth. Assuming a similar ^{226}Ra concentration in the coastal Pacific waters off South America as off California and effective scavenging by sinking particles, in-situ decay might support an excess ^{210}Pb flux to the sediments of <0.1 dpm cm^{-2} yr^{-1} at the shallowest site and ~0.6 dpm cm^{-2} yr^{-1} at the deepest site. Thus, atmospheric supply and in-situ decay together account for <20% of the observed excess ^{210}Pb flux to sediments off Concepción, whereas off Antofagasta the fraction is >40%. The remaining flux is supported by the processes coupled to upwelling described above.

Excess ^{210}Pb fluxes are lower off Antofagasta than off Concepción indicating a reduced lateral inflow of dissolved excess ^{210}Pb and/or a smaller particle flux and therefore less effective scavenging of ^{210}Pb in the Antofagasta area. Upwelling off northern Chile (18°S-24°S) is limited to a narrow region close to the coast (Morales et al. 1996), whereas further South upwelling reaches a wider extension towards the ocean (Thomas 1999). The locally restricted upwelling near Antofagasta might be less effective in sustaining lateral inflow of ^{210}Pb enriched water into the coastal region. Primary productivity dependent on nutrient supply is also limited to the inshore area (Morales et al. 1996) and thus enhanced particle fluxes are more likely to occur close to the coast.

Near Concepción excess ^{210}Pb fluxes increase with increasing water depth, i.e. distance to coast, and no relation to sediment accumulation rates exists. Approaching the coast, the upwelling water becomes more depleted in dissolved ^{210}Pb as high particle fluxes extending far offshore effectively scavenge the imported ^{210}Pb. Obviously, the supply of radioisotopes controls ^{210}Pb fluxes to the sediments near 36°S. Accordingly, sediments from shallower water depth in the adjacent Bay of Concepción receive a reduced ^{210}Pb flux of 0.9 dpm cm^{-2} yr^{-1} at the bay mouth and of 0.2 dpm cm^{-2} yr^{-1} within the bay, respectively (Muñoz and Salamanca 2003).

Off Antofagasta excess ^{210}Pb fluxes show no relation to water depth, i.e. distance to coast, but are positively correlated with sediment accumulation rates. The loading of sedimentary particles with ^{210}Pb appears to be similar for all investigated sites indicating that the water column particle flux is the controlling factor on ^{210}Pb fluxes in this region. ^{210}Pb is probably not limited in the water column and is equally scavenged on all particles settling down the water column off Antofagasta. This means that the overall vertical particle flux in the Antofagasta region is not very large, especially when compared to the region off Concepción, where pelagic sedimentation exceeds ^{210}Pb supply.

Sediment mixing (bioturbation)

The prevailing bottom water oxygen concentrations fail to explain the obvious absence of bioturbating macrofauna in the region at 23°S, as oxygen concentrations determined off Antofagasta (7-53 μM) do not fall below the range observed off Concepción (0.4-105 μM). Furthermore, as we observed living organisms at the time of sampling, we can exclude that mixing in the OMZ-sediments near Concepción occurs only occasionally during periods of oxygenation in the non-upwelling season or during El Niño events.

Oxygen effects on intensity and depth of bioturbation have been proposed to occur at

the aerobic-dysaerobic boundary between 13 and 45 µM (Savrda and Bottjer 1991; Levin et al. 2000). In a study on sediments across the OMZ of the Arabian Sea, low bottom water oxygen concentrations have been shown to result in a decrease of the mixed layer thickness, whereas the mixing intensity did not reveal significant differences under suboxic (<9 µM) and oxic (>89 µM) conditions (Smith et al. 2000). In this context it is worth to note the extension of the mixed layer in sediments from the OMZ off Concepción. Under suboxic conditions at GeoB 7160 (7 µM) an effectively mixed layer reached down to 10 cm sediment depth and the profile of excess ^{210}Pb resembled that of the well oxygenated site GeoB 7162. A shallower mixed layer was found at GeoB 7161 where the bottom water oxygen concentration was only 0.4 µM, nevertheless, it still reached 6 cm sediment depth.

Limited food supply may impede effective bioturbation off Antofagasta. Although TOC concentrations were higher in the sediments off Antofagasta than off Concepción (Fig. 2.3), this material was probably of very low nutritional value. Chlorin concentrations at the sediment surface, which reflect the input of phytoplankton detritus - ergo food - from the water column, were higher at 36°S than at 23°S (Fig. 2.5). Consequently, sediment mixing appears to be primarily controlled by input fluxes of fresh OM which in turn depend on rates of primary productivity and extent of water column degradation.

Sediment accumulation

Sediment accumulation rates obtained from ^{210}Pb analyses were only slightly lower off Antofagasta compared to those off Concepción (Tab. 2.2). Based on the obviously limited sources for terrestrial input at 23°S and considering earlier studies from this region that report increasing sediment accumulation rates from North to South (Lamy et al. 1998; Hebbeln et al. 2000), we expected the sediment accumulation rates at 36°S to be significantly higher than at 23°S. Sediment accumulation rates for the late Holocene obtained from ^{14}C-dating of deep-sea cores (2500 m and 800 m water depth, respectively) showed the expected latitudinal trend, ~16 cm kyr^{-1} at 24°S (Mohtadi and Hebbeln 2004) and ~128 cm kyr^{-1} at 36°S (D. Hebbeln, personal communication).

The higher sediment accumulation rates observed in our study might reflect that input from upwelling induced productivity is higher closer to the coast than further offshore at deep sea sites. Furthermore, in the region near 23°S, the sampling strategy might explain the unexpectedly high sediment accumulation rates. Strong bottom currents and the steep slope off Antofagasta limit sediment accumulation to locally restricted depositional centres. Those areas that were specifically chosen for coring probably collect sedimentary material that was

originally distributed over a much larger area. Therefore, the obtained sediment accumulation rates might not be representative for the overall area off Northern Chile but represent isolated depositional centers. This scenario of sediment accumulation is consistent with the overall small vertical particle flux observed at 23°S.

The lower TOC and TIC concentrations observed in the sediments at 36°S compared to those at 23°S result from a stronger dilution with lithogenic terrestrial material in the southern region and partly reflect the different sedimentation regimes. Aeolian input is the prevailing source of terrestrial debris off northern Chile (Lamy et al. 1998), whereas the terrestrial detritus near Concepción is mainly delivered by the rivers Bio-Bio and Itata, as indicated by the inorganic geochemical composition at GeoB 7162 (M. Grunwald, personal communication).

In summary, the depositional conditions at 23°S are characterized by small vertical particle fluxes and little dilution with terrestrial material. However, sediment accumulation rates in this region are large, but only in locally restricted depositional centers, representing a relatively small area of the continental margin at 23°N. Furthermore, the rapidly accumulating sediments in these basins must principally consist of reworked, radiochemically (^{210}Pb) dead material, as the overall fluxes of ^{210}Pb are low, and evenly distributed over all water depths. A predominance of reworked material is consistent with the lack of bioturbation in the northern region. In the southern region near Concepción, direct pelagic sedimentation of particles from the water column accounts for a larger fraction of the accumulating sediments. Consequently, though the total amount of OM in these sediments is lower than at 23°S, they contain a larger fraction of fresh organic material providing the food for bioturbating organisms. As we will see, the differences in the depositional environment are strongly reflected in the organic carbon composition of the sediments at 36°S and 23°S, even though both sedimentary regimes may be characterized as upwelling dominated.

Sedimentary organic carbon composition

Organic carbon source

Overall, the observed C/N-ratios are consistent with a predominantly marine source of the sedimentary OM. Due to its higher protein content marine OM has significantly lower C/N-ratios than terrestrial OM. Terrestrial material dominated by nitrogen-free bio-macromolecules such as cellulose and lignin displays C/N-ratios of 20-500, whereas freshly

produced plankton material shows C/N-ratios of 5-7 (Hedges et al. 1986). Degradation of marine OM during early diagenesis results in ratios up to 12 (Meyers 1997). As shown by the profiles in Fig. 2.3, the C/N-ratio in the investigated sediments is primarily controlled by ongoing preferential degradation of N-containing compounds and therefore not applicable to identify a possibly small contribution of terrestrial OM.

The carbon isotopic composition of the sedimentary OM at 36°S can clearly be assigned to a marine source (Fig. 2.4). The shift to generally more negative $\delta^{13}C$-values at 23°S is unlikely to result from an enhanced contribution of terrestrial OM, as (1) terrestrial input in this region is generally low, (2) the C/N-ratio is in the typical range for marine OM. Analysis of sedimentary fatty acids also revealed a predominantly marine origin of the OM deposited at 23°S (Niggemann and Schubert, chapter 4).

The observed difference in $\delta^{13}C$-values between the sedimentary OM near 23°S and near 36°S might reflect differences in the extent of diagenetic alteration. Early diagenetic alteration can result in a slightly lighter carbon isotopic composition of the residual OM (Lehmann et al. 2002), most probably due to the preferential degradation of carbohydrates and proteins that are generally enriched in ^{13}C compared to total plant tissue. However, such an early diagenetic change in isotopic composition should be expressed in all investigated sediments and besides make up <1‰ of the initial composition (Freudenthal et al. 2001). A contribution of isotopically light OM produced by chemoautotrophic bacteria might also explain a ^{13}C depletion of the sedimentary TOC (Cowie et al. 1999). However, a significant contribution is more likely to occur in the sediments at 36°S with higher organic carbon degradation rates and abundant *Thioploca*.

We suggest that differences in the initial isotopic composition of the marine OM account for most of the observed differences in the $\delta^{13}C$-values of the sedimentary OM. Most of the factors affecting the carbon isotopic composition of phytoplankton, e.g. water temperature, dissolved CO_2 concentration, growth rate, and species composition (see review: Popp et al. 1997), are influenced by upwelling of cold, nutrient-rich waters. Equatorial Subsurface Water of the Gunther Undercurrent is the source of upwelled waters off Northern (e.g. Morales et al. 1996) and off Central Chile (e.g. Brandhorst 1971), but differences in the strength and seasonality of upwelling might account for differences in the prevailing surface water. The diatom assemblages reported for the surface sediments indicate an influence of southern, cold waters near 36°S, although the assemblages in both regions are similar and characteristic for upwelling conditions (Romero and Hebbeln 2003).

Extent of water column degradation

The degradation of OM starts immediately after the death of cells and continues during its settling through the water column, thus the OM reaching the sediment surface normally has already undergone varying degrees of initial remineralization (e.g. Cowie and Hedges 1994). The extent of water column degradation is partly reflected in the C/N-ratios observed at the sediment surface of the investigated sites. Except at GeoB 7104 where the lowest C/N-ratio was found, C/N-ratios increased linearly with water depth of the sampling site (Fig. 2.7a) reflecting the preferential loss of nitrogen containing compounds during early remineralization.

Chlorin concentrations provide information on the amount of phytoplankton detritus reaching the sediment and are a function of surface productivity and extent of water column degradation (Harris et al. 1996). Near Concepción, chlorin concentrations at the sediment surface slightly decreased with increasing water depth (Fig. 2.7b) reflecting the ongoing degradation of settling plankton material. The effect of water depth is less expressed off

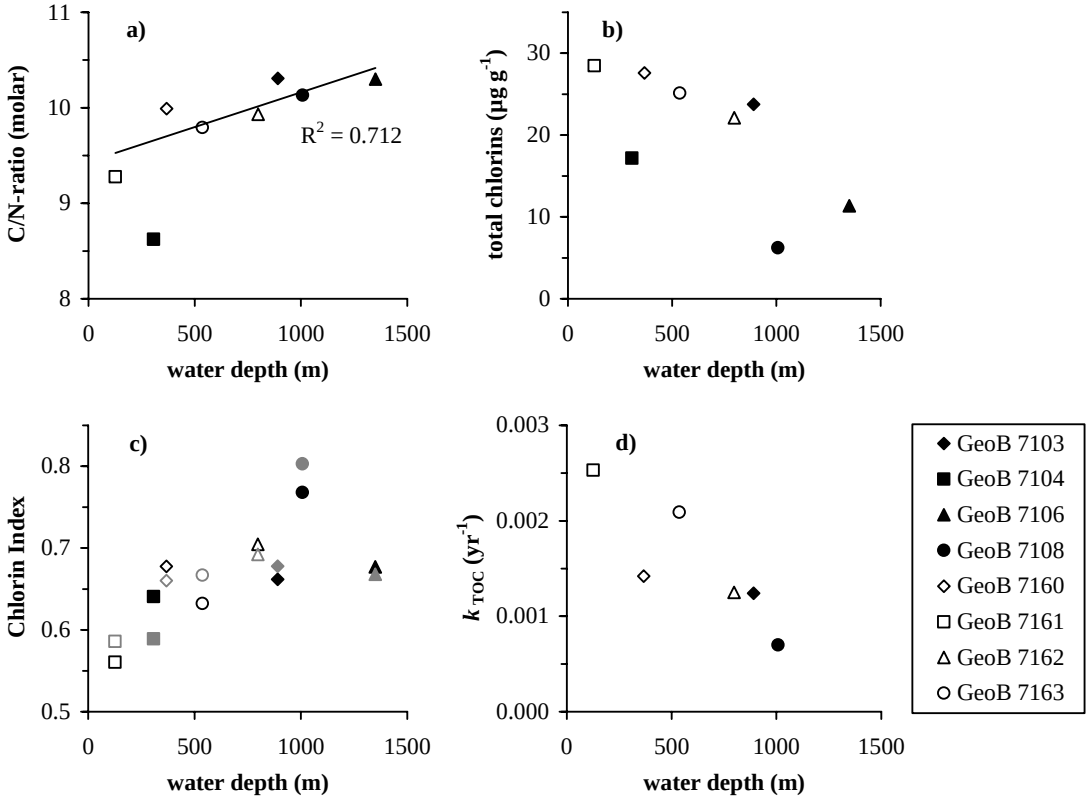

Figure 2.7. Water depth dependence of sedimentary organic matter characteristics. C/N-ratios (a), total chlorin concentrations in µg g^{-1} dry weight (b), Chlorin Index (c), and reaction rate constants of TOC (k_{TOC}) (d). Data points represent surface sediments (0-1 cm), except k_{TOC} that describes down-core degradation. The depth-averaged Chlorin Index is given in grey symbols (c). GeoB 7104 is not included in regression (a).

Antofagasta, but lowest chlorin concentrations were found at the deepest sites (>1000 m). Pigments belong to the labile fraction of sedimentary organic compounds and are selectively degraded during the earliest stages of OM transformation in the water column (Wakeham et al. 1997b; Lee et al. 2000). Shankle et al. (2002) found a log-dependence of chlorin concentrations and water depth for surface sediments from the Arabian Sea. Our results do not reveal such a strict relation of chlorin concentrations and water depth (Fig. 2.7b), indicating that in the investigated areas off Chile other depositional factors than water depth also affect the chlorin concentration in surface sediments. This is particularly true for shelf sediments as chlorin concentrations reported for sediments from shallower water depth (34-87 m) near Concepción (Schubert et al. 2000) fall in the same range we observed at greater water depth.

We can only speculate about possible effects of oxygen availability on the extent of chlorin degradation as oxygen concentration is closely related to water depth (Tab. 2.1). The highest chlorin concentration found at the sediment surface at GeoB 7161 might be explained by the shallow water depth (126 m) as well as by the low bottom water oxygen concentration (0.4 µM). There is strong evidence that oxygen limitation favors the preservation of OM (Hartnett et al. 1998; Hartnett and Devol 2003), and Sun et al. (1993) reported lower degradation rates for chlorophyll *a* in the absence than in the presence of oxygen. On the other hand, labile organic compounds have been shown to degrade at equal rates under oxic and anoxic conditions (e.g. Hulthe et al. 1998; Lehmann et al. 2002). Shankle et al. (2002) excluded a direct effect of oxygen concentration on the degradation of chlorins and suggested that "the presence of oxygen at even very low concentrations (6 µM) was sufficient to stimulate oxic degradation" of sedimentary chlorins.

Surface concentrations of total fatty acids (Niggemann and Schubert, chapter 4) and total hydrolysable amino acids (Lomstein et al. subm.) analyzed from the same samples investigated in this study also showed an overall decrease with increasing water depth, consistent with an increased degradation status of sedimentary OM at greater water depth.

Quality of the sedimentary organic material

Earlier studies indicated that the rate of organic carbon degradation can be a function of quality rather than of quantity of sedimentary OM (Hedges et al. 1988; Lee 1994). The Chlorin Index (CI) provides information on the freshness of the pigment material entering the sediments as phytoplankton detritus (Schubert et al. 2005). The CI indicated that sedimentary chlorins were freshest at GeoB 7161 and GeoB 7104, consistent with the shallow water depth

and the low bottom water oxygen concentration at these sites, as both factors are considered to favor the deposition of labile compounds. Despite only slightly greater water depth and equal oxygen concentration, the CI was higher at GeoB 7160 compared to GeoB 7104, and in the range of most other deeper sites investigated in this study. Possibly this is due to the intense bioturbation at GeoB 7160 that might have enhanced organic carbon alteration (Aller 1982). The most refractory chlorins were found at GeoB 7108, where the CI was significantly higher than at all other sites. GeoB 7108 showed the lowest sediment accumulation rate, thus the high CI reflects the advanced degradational state of this comparably old sediment. All in all, both the CI at the sediment surface and the CI averaged over sediment depth increased with increasing water depth (Fig. 2.7c), pointing at a dominant control of water column alteration on the quality of sedimentary OM.

We compared the CI to other frequently applied indicators for OM quality, the amino acid based degradation index (DI) established by Dauwe and Middelburg (1998) and Dauwe et al. (1999) and C/N-ratios. On both transects, the DI given in Lomstein et al. (subm.) is correlated with the CI (Fig. 2.8a), r^2=0.92 for both regressions. Low CI indicating fresh pigment material coincide with high DI reflecting fresh THAA. We already showed that the C/N-ratio is highly correlated with sediment depth and sediment age (Fig. 2.3, see above), therefore it is reasonable to expect a high CI and a low DI when the C/N-ratio is high, i.e. when the sedimentary OM is old and degraded. Off Concepción, both CI and DI showed the expected relation to the C/N-ratio, r^2=0.85 and r^2=0.90, respectively (Fig. 2.8b/c). In contrast, off Antofagasta, CI and DI were inversely related to the C/N-ratio and are obviously not

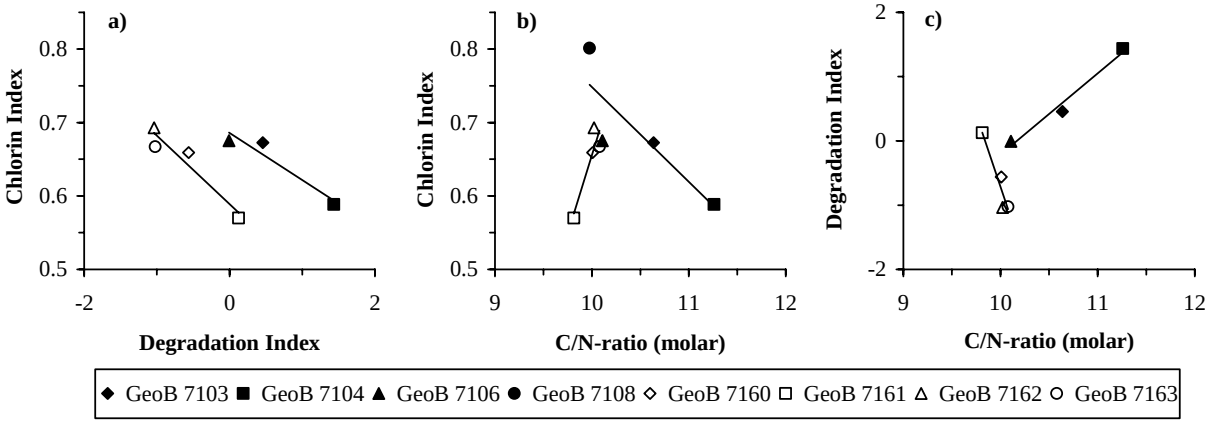

Figure 2.8. Comparison of OM quality indicators. a) Chlorin Index (CI) versus amino acid degradation index (DI, data from Lomstein et al. (subm.)), b) CI versus C/N-ratio, c) DI versus C/N-ratio. Plotted are average values (0-18 cm sediment depth).

representative for the entire TOC pool in these sediments. As the C/N-ratio includes all compound classes present in the sediment, a big pool of highly refractory N-depleted OM might conceal a smaller pool of fresh material that is assessed by CI and DI.

The CI focuses on the pigment material that makes up a small fraction of the total OM pool, <0.1% in the investigated samples. While the chlorin concentration strongly decreased within the uppermost sediment layer (0-3 cm), at most sites the CI changed only slightly throughout the core (Fig. 2.5). These depth distributions suggest that part of the chlorins was protected against degradation within the sediment and that the quality of this remaining small pool stayed unchanged. Shankle et al. (2002) also report relatively little down-core changes in the relative concentrations of the different pigment groups. Probably the labile chlorins were preserved within their original organic matrices or through adsorption to minerals as proposed by Keil et al. (1994).

The DI has been used as a measure for the quality of the bulk sedimentary organic carbon pool (Dauwe et al. 1999). Surprisingly, the DI indicate that the sedimentary OM off Antofagasta is fresher than that off Concepción (Lomstein et al. subm.). This finding is neither reflected in the CI, nor in the C/N-ratio, nor in the SRR (Tab. 2.3). Apparently, the DI does not distinguish between the influence of source and degradation on the amino acid composition in the sediments deposited near 23°S (for discussion see Lomstein et al. subm.).

We conclude that due to alteration in the water column, the quality of depositing OM decreases with increasing water depth. Off Concepción where pelagic sedimentation predominates, C/N-ratio, Chlorin Index, and amino acid based degradation index are suitable to assess bulk OM freshness. In contrast, off Antofagasta, the predominance of reworked material conceals a possibly small contribution of fresh OM.

Organic matter degradation in the sediments

Compositional changes and degradation rates of organic matter

Generally, the extent of organic carbon remineralization in sediments is related to the availability for microbial degradation. We already showed that water depth at the sampling site affects the quality of the deposited OM and it is well known that selective degradation consecutively reduces the pool of reactive compounds (e.g. Westrich and Berner 1984; Wakeham et al. 1997b). The preferential degradation of labile relative to more resistant compounds results in qualitative changes of the sedimentary organic carbon pool, expressed

in down-core decreasing contributions of labile OM to the TOC pool. At the end of the core, chlorins and THAA (data from Lomstein et al. subm.) generally constitute a smaller fraction of TOC than at the sediment surface (Fig. 2.9). The only exception is at GeoB 7161, where changes in sediment texture indicate variations of input over time. The different reactivities of chlorins and TOC can be quantified by calculating reaction rate constants from the down-core decrease of both parameters.

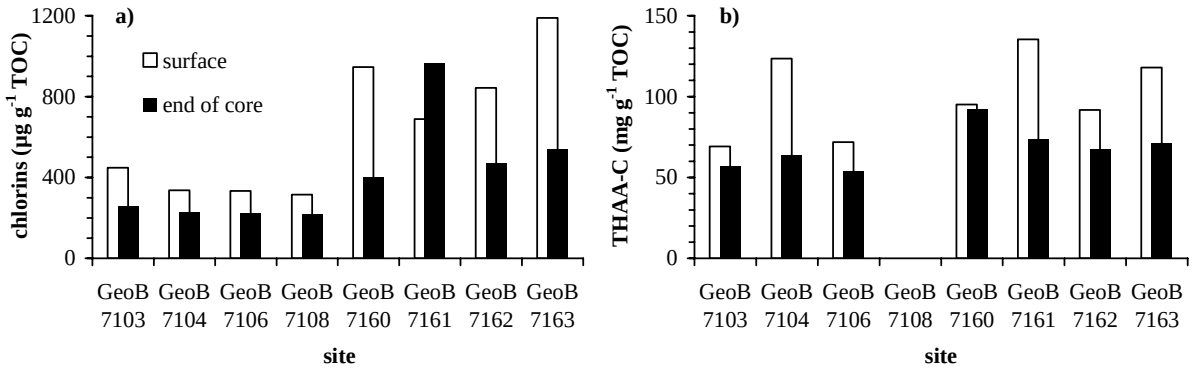

Figure 2.9. Fraction of TOC made up by chlorins (a) and THAA (b) at the sediment surface (0-1 cm) and at the end of the core. THAA data are from Lomstein et al. (subm.).

Assuming steady state conditions, i.e. constant input and degradation of OM as well as undisturbed sedimentation, the degradation rate R and the reaction rate coefficient *k* can be calculated based on a first-order degradation kinetics (Canuel and Martens 1996):

$$R = \frac{c_0 - c_1}{t_1 - t_0} \qquad \text{and} \qquad k = \frac{-\ln(c_1 / c_0)}{(t_1 - t_0)} \qquad (4.1 \text{ and } 4.2)$$

with c_0 being the initial concentration at the time of deposition (t_0) and c_1 being the concentration at greater depth corresponding to time t_1. Concentration was plotted versus sediment age as determined from excess ^{210}Pb and degradation rates were obtained from the slope of a linear regression, reaction rate constants from the slope of a logarithmic (ln) fit.

The assumption of steady-state may not hold, especially for the sediments at GeoB 7104 and GeoB 7106 and partly at GeoB 7161, where down-core variations of the TOC concentration indicate changes in OM input over time. However, the constant decrease of TOC concentration with sediment depth observed at the other sites reflects constant ongoing degradation. For the calculation of TOC degradation rates (R_{TOC}) and reaction rate constants (k_{TOC}) we did not include the upper 0-3.5 cm at GeoB 7103, where TOC concentrations

increased slightly. Further we excluded the data point at 9 cm depth at GeoB 7108 and the two distinct peaks at 3.5 cm and at the core end of GeoB 7161 (Fig. 2.3).

R_{TOC} is highest at GeoB 7161 (7.2 µmol g^{-1} yr^{-1}), in accordance with the prevailing deposition of comparably fresh OM at this shallow site. At the other sites, R_{TOC} ranging from 1.1 µmol g^{-1} yr^{-1} at GeoB 7108 to 5.8 µmol g^{-1} yr^{-1} at GeoB 7103 (Tab. 2.4) are clearly related to the TOC concentration of the sediments - the higher the concentration of organic carbon, the higher the absolute degradation rate. k_{TOC} provides more specific information on the reactivity of the sedimentary organic carbon as it considers differences in the total amount of organic carbon that is exposed to degradation. The reaction rate constants decrease with increasing water depth at the sampling site (Fig. 2.7d), again indicating that the quality of the sedimentary organic carbon - here measured as reactivity - is a function of water depth and that water column alteration strongly affects sedimentary processes.

In general, R_{TOC} and k_{TOC} determined off Chile cover a similar range as those values reported for the Northern Gulf of California (Camacho-Ibar et al. 2003). However, for a sediment at 2100 m water depth in the Black Sea, Sun and Wakeham (1994) calculated a k_{TOC} of 0.015 yr^{-1}, which is on average an order of magnitude higher than the k_{TOC} observed off Chile. The apparently lower reaction rate constants off Chile might in part be the result of disturbed depth profiles due to the mixing of bioturbating organisms. Particularly the *k*-values estimated for the bioturbated sediments near Concepción probably underestimate the true values, as sediment mixing attenuates changes in the depth profiles of TOC, thereby obscuring the real extent of degradation. Differences in bioturbation activity might also explain the lower k_{TOC} at GeoB 7160 and GeoB 7162 compared to GeoB 7161 and GeoB 7163 (Tab. 2.4), where sediment mixing was less intense (Fig. 2.2).

Calculating the reaction rate constants for the sedimentary chlorins ($k_{chlorin}$), we considered two pools of different reactivity, a labile fraction and a more refractory fraction (Stephens et al. 1997). From the strong decrease in the upper 0-2.5 cm we calculated values for the labile pool ($k_{chlorin\ I}$), and from the slight decrease further down-core values for the refractory pool ($k_{chlorin\ II}$). At GeoB 7103 we did not include the lowermost samples (21-25 cm), at GeoB 7160 the minimum peak at 25 cm was excluded, and at GeoB 7161 we only considered the upper 13 cm of the sediment (Fig. 2.5). We calculated values in the range 0.0117-0.0719 yr^{-1} for $k_{chlorin\ I}$ and in the range 0.0013-0.0105 yr^{-1} for $k_{chlorin\ II}$ (Tab. 2.4). Although we used a very simple approach, our results are similar to those of Shankle et al. (2002) who applied a two-layer steady state model to study chlorin degradation in sediments from the Arabian Sea. They came out with *k*-values of 0.0024-0.1000 yr^{-1} for the labile and

0.0004-0.0057 yr^{-1} for the refractory pool.

The reaction rate constants of both chlorin pools showed no general difference between the investigated regions at 23°S and 36°S, nor a clear relation to water depth. This might in part be due to changes in pigment input over time as well as to occasional mixing of fresh chlorins to greater sediment depth. In addition, following the scenario of consecutively degrading pools with decreasingly reactive compounds (Jørgensen 1978, Westrich and Berner 1984), remineralization of chlorins might be less effective - and $k_{chlorin}$ lower - when more reactive compounds are still available. Nonetheless, the calculated reaction rate constants $k_{chlorin}$ and k_{TOC} manifest the generally higher reactivity of chlorins compared to bulk TOC. In the upper sediment layer $k_{chlorin\ I}$ is higher than k_{TOC} by a factor 6-35 (Tab. 2.4). The observed difference is less expressed at GeoB 7108 and GeoB 7162, consistent with a reduced reactivity of the initially deposited chlorins at these deep sites. The more refractory fraction of the chlorins represented by $k_{chlorin\ II}$ is still a factor 2-8 more reactive than the TOC pool (Tab. 2.4). $k_{chlorin\ II}$ is highest at GeoB 7160 and GeoB 7162 where intense bioturbation mixes fresh labile phytodetritus to deeper sediment layers.

In conclusion, what do the *k*-values tell us? The *k*-values quantify the average long-term reactivity of OM: the higher the *k*-value, the bigger the fraction of the total OM pool that is degraded per time interval. For bulk TOC (k_{TOC}) this fraction is lower at 23°S than at 36°S, reflecting the predominance of reworked, less-reactive material at 23°S. The higher $k_{chlorin}$ compared to k_{TOC} substantiate the generally higher reactivity of chlorins relative to bulk TOC, implying that the degradation of chlorins accounts for a significant fraction of TOC remineralization.

Table 2.4. Organic carbon degradation rates (R_{TOC}) and reaction rate constants (*k*) for a steady state first order degradation kinetics applied to the depth profiles of TOC and total chlorins. $k_{chlorin\ I}$ and $k_{chlorin\ II}$ represent the labile and refractory pool of chlorins, respectively.

station	R_{TOC} (µmol g^{-1} yr^{-1})	k_{TOC} (yr^{-1})	$k_{chlorin\ I}$ (yr^{-1})	$k_{chlorin\ II}$ (yr^{-1})
GeoB 7103	5.8	0.0012	0.0416	0.0044
GeoB 7108	1.1	0.0007	0.0117	0.0013
GeoB 7160	3.6	0.0014	0.0486	0.0066
GeoB 7161	7.2	0.0025	0.0161	0.0061
GeoB 7162	2.6	0.0013	0.0243	0.0105
GeoB 7163	3.1	0.0021	0.0719	0.0045

Reaction rate coefficient k_{SRR}

The reactivity of sedimentary organic carbon has also been estimated from SRR (Westrich and Berner 1984; Schubert et al. 2000). The first step in anaerobic remineralization is the hydrolytic breakdown of macromolecular OM by fermenting bacteria. This step is thought to be the slow, rate limiting step in OM remineralization, whereas the second step, the final oxidation of low-molecular fermentation products and H_2 is fast and operates near equilibrium. In sediments where sulfate reduction is the dominant terminal electron acceptor process, SRR provide a direct measure for the reactivity of the sedimentary organic carbon. Given that pore-water sulfate is not limited, the rate of carbon remineralization through bacterial sulfate reduction is a function of the availability of reactive organic compounds and can be construed to follow pseudo-first order kinetics (Berner 1980; Westrich and Berner 1984):

$$\frac{\mathrm{dG}}{\mathrm{dt}} = -k * [\mathrm{G}] \tag{5}$$

Based on this equation where dG/dt is the rate of organic carbon remineralization and [G] is the organic carbon concentration, and according to the stoichiometry of bacterial sulfate reduction

$$\mathrm{SO_4^{2-}} + 2\mathrm{CH_2O} \rightarrow \mathrm{H_2S} + 2\mathrm{HCO_3^-} \tag{6}$$

a reaction rate coefficient k_{SRR} can be calculated as

$$k_{\mathrm{SRR}} = \frac{2 * \mathrm{SRR}}{[\mathrm{TOC}]}. \tag{7}$$

We assumed sulfate reduction to be the dominant process at sediment depths where SRR were maximum. Only at the shallowest sites GeoB 7104 and GeoB 7161, SRR were highest right at the sediment surface (Fig. 2.6, Tab. 2.3), in accordance with the low bottom water oxygen concentration at these two sites. At all other sites, subsurface or deep peaks of SRR indicated that other terminal electron acceptor processes account for part of carbon oxidation.

For the SRR peaks we calculated the lowest k_{SRR} of 0.0013 $\mathrm{yr^{-1}}$ at the deepest site GeoB 7106 and the highest k_{SRR} of 0.0070 $\mathrm{yr^{-1}}$ at the shallowest site GeoB 7161 (Tab. 2.3). Note that the observed difference can partly be explained by a general decrease of organic carbon reactivity with sediment depths as OM deeper in the sediment is already in an

advanced state of degradation. Further, k_{SRR} calculated from peak rates deeper in the sediments is not representative for the reactivity of initially deposited OM. However, the generally lower k_{SRR} observed at 23°S are in accordance with a reduced OM reactivity in the sediments at 23°S compared to 36°S and the influence of water depth alteration is reflected in decreasing k_{SRR} with increasing water depth (Tab. 2.3). For sediments from the Bay of Concepción, Schubert et al. (2000) calculated k_{SRR} in the range 0.0008-0.0300 yr^{-1} for sulfate reduction peak rates following the same approach applied in our study. The higher values observed in the bay sediments are consistent with the shallower water depth.

Depth-averaged values, including k_{SRR} at all sediment depths, ranged from 0.0004 yr^{-1} at GeoB 7108 to 0.0033 yr^{-1} at GeoB 7161. Like the peak rate k_{SRR} they were generally lower in the sediments near 23°S compared to 36°S (Tab. 2.3), and with the exception of GeoB 7104 and GeoB 7162 decreased with increasing water depth (Fig. 2.10a). We compared the bulk organic carbon reactivity as assessed by k_{SRR} with the Chlorin Index describing the freshness of sedimentary pigments (Fig. 2.10b). The lowest CI coincided with the highest k_{SRR} (GeoB 7161) and the highest CI with the lowest k_{SRR} (GeoB 7108), but we found no general relation of fresh chlorins (low CI) and high reactivity (high k_{SRR}), and refractory chlorins (high CI) and low reactivity (low k_{SRR}). It has been shown that sedimentary micro-organisms might thrive on a small highly reactive fraction that is not reflected in bulk OM parameters (Arnosti and Holmer 2003). Therefore, a small portion of reactive OM might fuel high SRR although most of the chlorins are already old and degraded. On the other hand, reactive fresh pigments might be protected from degradation by sediment bacteria (Keil et al. 1994), but manifest themselves in a low CI.

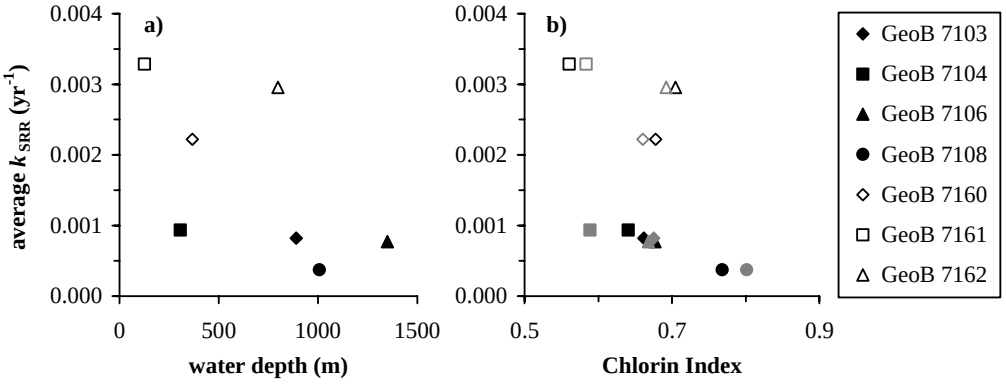

Figure 2.10. Reaction rate constant k_{SRR} (depth-averaged values), derived from sulfate reduction rates and TOC concentrations, versus water depth at sampling site (a) and Chlorin Index (b). Chlorin Indices of surface sediments (0-1 cm) are marked by black symbols, depth-averaged values by grey symbols.

Linking k_{SRR} and k_{TOC}

The reaction rate constants k_{TOC} calculated from the depth profiles of TOC concentrations show a surprisingly good correspondence to the reaction rate coefficients k_{SRR} that describe TOC remineralization coupled to sulfate reduction (Fig. 2.11). Although the two coefficients are calculated based on different approaches, the obtained values fall in the same range: 0.0004-0.0033 yr^{-1} for k_{SRR} and 0.0007-0.0025 yr^{-1} for k_{TOC}, respectively, and for both parameters highest values were found at GeoB 7161 and lowest at GeoB 7108.

The overall good relation for the different approaches is remarkable. While k_{TOC} describes the result of several years of sedimentary organic carbon degradation that is imprinted in the depth profiles of TOC, k_{SRR} is considered to reflect the actual reactivity of the sedimentary organic carbon at the time of sampling. At least at the shelf sites, where SRR display high temporal variability, k_{SRR} calculated from a single sampling should not be representative for the long term reactivity of bulk sedimentary organic carbon assessed by k_{TOC}. Other factors also influence the parameters used to calculate k_{TOC} and k_{SRR}. Bioturbation might attenuate the TOC decrease depicted in the depth profile and lead to an underestimation of the organic carbon reactivity obtained as k_{TOC} - a possible reason why k_{TOC} in the bioturbated sediments at 36°S is lower than k_{SRR}. On the other hand, k_{SRR} might also underestimate the actual organic carbon reactivity, when other pathways of organic carbon oxidation account for part of the total TOC degradation - which is a likely explanation why k_{SRR} at 23°S is lower than k_{TOC}.

In spite of all these caveats, the good correspondence of k_{TOC} and k_{SRR} observed in this study could have been expected. Though it may in part be based on the combined effect of several compensating parameters, in general, a coupling of the two coefficients is consistent

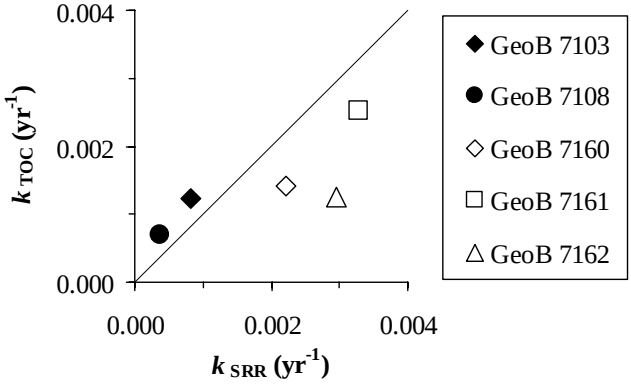

Figure 2.11. Comparison of the reaction rate constants derived from depth profiles of TOC (k_{TOC}) and measured sulfate reduction rates (k_{SRR}). The 1:1-line is plotted.

with the predominance of bacterial sulfate reduction for organic carbon remineralization in anoxic marine sediments (Jørgensen 1982; Canfield 1989).

CONCLUSIONS

We could show that depositional conditions affect sedimentary carbon turnover by controlling organic matter input and composition. Although both investigated regions represent characteristic upwelling systems, the depositional conditions differ substantially. At 23°S the vertical particle flux is much lower than at 36°S, and particles accumulating in isolated deposition centers in the northern region are mostly old and reworked. Bioturbation is intense at 36°S but lacking at 23°S, further, input of terrestrially derived clastic material is higher in the humid central region than off northern Chile. However, these differences are not visible from sediment accumulation rates, which are similar in both investigated regions.

Although sedimentary OM in both regions is predominantly of marine origin - which is a typical feature of sediments in coastal upwelling regions - this material is fresher at 36°S compared to 23°S. The differences in sedimentary OM composition are consistent with a generally more reworked state of the sediments at 23°S, but might also reflect the greater water depth of most sites sampled off Antofagasta. Most parameters describing OM freshness reflect the influence of water column alteration on sedimentary OM composition: With increasing water depth, chlorin concentrations decrease and C/N-ratios and Chlorin Index increase. In general, oxygen availability might play an important role in OM preservation but possible effects might be concealed as bottom water oxygen concentration is closely related to water depth. Decreasing degradation rate constants k_{TOC} with increasing water depth suggest that water column degradation also affects the long-term reactivity of sedimentary OM. Finally, the differences in OM freshness are reflected in SRR that decrease with increasing water depth and are generally lower at 23°S than at 36°S.

The depositional environment is a dominant control on organic matter content, composition, and turnover, and leaves its imprint in the sedimentary record. This has major implications for paleo-environmental reconstructions that are based on bulk sediment descriptions. Our findings show that sediments deposited in the same general upwelling regime (e.g. Chile) might display significant differences in organic matter content, composition, and turnover that are independent from water column productivity and vertical particle flux.

Acknowledgements. We thank the officers, crew, and shipboard scientific party of RV Sonne cruise SO-156 for their help and cooperation, particularly Dierk Hebbeln (University of Bremen) for logistical support. We are grateful to Gabriele Klockgether and Kirsten Imhoff (MPI Bremen) for help in the home laboratory. Furthermore, we thank Peter Berg (University of Virginia) for interpretation of ^{210}Pb data and Tomas Cedhagen (University of Aarhus) for identification of foraminifera. This work was part of the project PUCK (Interrelationships between productivity and environmental conditions along the Chilean continental slope, grant 03G0156A) supported by the BMBF (Federal Ministry of Education and Research, Germany). Further support was given from the Max Planck Society, Germany, and the Danish Natural Science Research Council (grant 21-01-0475). Part of this manuscript was written during a stay of Jutta Niggemann at the University of Aarhus made possible by a scholarship of SOAS (School of Aquatic Sciences, Denmark).

Chapter 3

Spatial distribution of organic matter composition, sulfate reduction rates, and *Thioploca* biomass in surface sediments off Peru

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submitted to *Marine Geology*

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ABSTRACT

In order to reveal possible impacts of organic matter (OM) composition on rates of microbial sulfate reduction and *Thioploca* distribution in shelf and slope sediments off Peru, sediments from a total of 34 sites, covering 50-1400 m water depths, were investigated for total organic carbon (TOC), total inorganic carbon, C/N-ratios, $\delta^{13}C$ of TOC, $\delta^{15}N$ of total nitrogen, total chlorins, Chlorin Index, lipid biomarkers, bottom water oxygen concentrations, sulfate reduction rates (SRR), and *Thioploca* biomass. C/N-ratios (7.7-10.7) and $\delta^{13}C$-values (-21.1 to -19.7‰ vs. VPDB) were indicative for a predominantly marine origin of the sedimentary OM. $\delta^{15}N$-values (up to 12.6‰ vs. air) reflected upwelling of ^{14}N-depleted water from the oxygen minimum zone, a region known for intense denitrification. Spatial distribution of OM character was strongly determined by bottom currents and seafloor morphology, hence sediment composition was mainly uncoupled from surface water productivity. A band of TOC-rich sediments (>12% dry weight) characterized by high C/N-ratios (>10), indicating a dominance of altered OM, was found at mid-water depth coinciding with extended mud-wave fields. Highest SRR were measured in shelf sediments where sedimentary OM was freshest as indicated by low Chlorin Indices (<0.75), low C/N-ratios (<9), and high contributions of chlorins and fatty acids to bulk OM. *Thioploca* were absent at water depths below 360 m and the patchy distribution showed no relation to any parameter describing OM composition, bottom water oxygen concentration, or SRR. Even though biomasses of up to 250 g m^{-2} were observed, imprints of *Thioploca* on the composition of sedimentary OM, including previously proposed biomarkers, could not be identified.

INTRODUCTION

Sediments underlying the highly productive waters in coastal upwelling regions are typically enriched in organic carbon compared to non-upwelling regions (Romankevich 1984). The Peruvian upwelling region has been the subject of intense and repeated studies on oceanographic, geochemical, and biological topics (e.g. Thiede and Suess 1983; Suess and Thiede 1983), but comprehensive studies that directly address the interaction of sediment chemistry and microbiology are lacking.

Sediment studies near 12°S off Peru revealed a coupling of meiofaunal distribution and organic matter (OM) availability, characterized by the concentration of labile organic compounds, i.e. proteins, carbohydrates, and lipids (Neira et al. 2001; Levin et al. 2002). In the absence of oxygen, OM degradation is limited to anaerobic microbial processes, and in marine sediments, sulfate reduction is the quantitatively most important terminal electron acceptor process (Jørgensen 1978). For sediments from the oxygen minimum zone (OMZ, oxygen concentration <22 µmol L^{-1}) near 15°S off Peru, Fossing (1990) reports areal sulfate reduction rates (SRR) that are much higher than SRR in sediments from similar water depth in non-upwelling regions. He further estimates that sedimentary sulfate reduction accounts for remineralization of 9-29% of the total primary production in the investigated area.

In the upwelling region off central Chile, SRR have successfully been related to the composition of sedimentary organic carbon, in that a dilution of the predominating fresh marine OM with more refractory terrestrial OM resulted in altered SRR profiles and overall lower degradation rates (Schubert et al. 2000). We therefore expected that compositional differences in the sedimentary OM off Peru were reflected in the distribution of SRR. The present distribution of OM on the Peruvian continental margin has been attributed to interactions of the prevailing current system with the shelf-slope morphology (Reimers and Suess 1983). Reinhardt et al. (2002) showed the dominant influence of the pole-ward undercurrent on the general sediment deposition pattern.

Another special feature of sediments in coastal upwelling regions is the occurrence of large sulfur bacteria (Gallardo 1977; Fossing et al. 1995; Schulz et al. 1999). *Thioploca* spp. has frequently been reported in the coastal region off Peru (Rosenberg et al. 1983; Henrichs and Farrington 1984; McCaffrey et al. 1989; Neira et al. 2001; Levin et al. 2002), but studies on the spatial distribution and quantification of biomass in this region are lacking. Paleo-environmental studies would benefit from reliable indicators of ancient *Thioploca* communities, as their distribution indicates oxygen limited conditions. Cyclolaudenol has been proposed as specific lipid biomarker for *Thioploca* (McCaffrey et al. 1989), but to our knowledge, this indicator has not yet been applied to assess recent or ancient *Thioploca* distribution.

The aim of this study is (1) to map the actual distribution of sedimentary OM in the region 9-14°S and to identify the controlling factors, (2) to relate sulfate reduction rates measured in the sediments to organic geochemical parameters, and (3) to link occurrence and quantitative distribution of *Thioploca* with sediment characteristics.

REGIONAL SETTING

The hydrography in the coastal region off Peru is dominated by two major currents, the equator-wards flowing Peru-Chile-Current at the surface (up to 200 m water depth) and the pole-ward flowing Peru Undercurrent underneath (Hill et al. 1998). The latter transports oxygen-poor, nutrient-rich water, which is brought to the euphotic zone by upwelling processes. Perennial upwelling off Peru is driven by persistently blowing southerly winds. Today, cells of intense upwelling are located near 7-8°S, 11-12°S, and 14-16°S, where average primary production rates reach 1-3 g C m^{-2} d^{-1} (Zuta and Guillén 1970). Remineralization of sinking OM causes an extended OMZ at ~50-650 m water depth over shelf and slope (Emeis et al. 1991; Lückge and Reinhardt 2000). High primary production, high sedimentation rates, shallow water depth, and oxygen limitation in water column and sediments favor the accumulation of organic-rich sediments. The sedimentary OM is predominantly of marine origin, as input from the dry coastal area is limited to a small eolian input of clastic debris.

The investigated region off Peru reached from 9.5°S to 13.5°S latitude and included a wide area of shelf and slope sediments (Fig. 3.1). Compared to other continental margins the shelf is relatively narrow (<50 km near 11°S and 13°S), except in the Northern part of the investigated area where the Chimbote platform extends up to 100 km from the coast. The morphology of the shelf is characterized by a coast-parallel rise at ~200 m water depth, the outer shelf high (Thornburg and Kulm 1981). This morphologic feature captures the sediments on the upper shelf in two coastal basins, the Salaverry Basin in the North (~9-11°S) and the Pisco Basin in the South (~12-14°S).

The seafloor morphology affects the prevailing currents, e.g. the Peru Undercurrent accelerates upon the broad, shallow Chimbote platform (Shaffer 1982) and sweeps the exposed seafloor. Sediment accumulates primarily in regions that are protected from the bottom currents. One important setting is the “mud-lens” off Callao (~12°S), located in a lee position of the Peru Undercurrent, where sediments are deposited up to 40 m thick in undisturbed layers (Reinhardt et al. 2002). Extended mud-wave fields at mid-water depth (250-400 m) reflect the actual position of the undercurrent (Reinhardt et al. 2002).

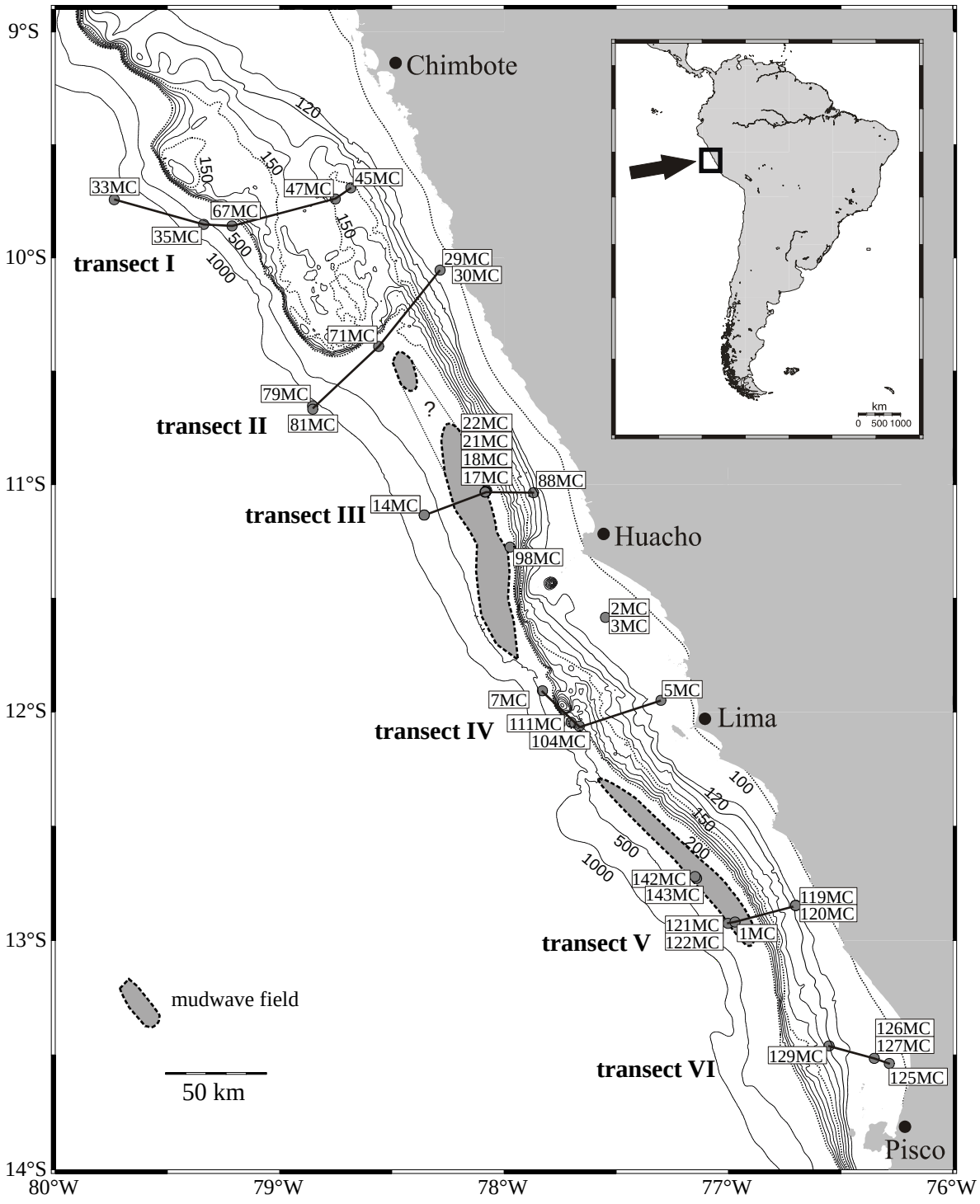

Figure 3.1. Map of investigated area with bathymetry (modified from Reinhardt et al. 2002). Sampling sites and transects of geochemical study are plotted.

MATERIAL AND METHODS

Sampling

During RV Sonne cruise 147 in June 2000 sediment cores from a total of 34 sites were sampled for various geochemical and biological analyses (Fig. 3.1 and Tab. 3.1-3.3). Surface sediments were retrieved by multicorer sampling in order to keep an undisturbed sediment-water interface.

Geochemical analyses

For geochemical analyses the upper 0-1 cm interval of the sediment cores was transferred to clean glass-vials and frozen at –25°C immediately after sampling. The samples were freeze-dried and homogenized by grinding in an agate mortar.

TOC, TIC, TN, and C/N-ratio. Total carbon (TC) and total nitrogen (TN) concentrations were determined by combustion/gas chromatography (Carlo Erba NA-1500 CNS analyzer) with a precision of ±0.7% for N and ±0.6% for C, respectively. Total inorganic carbon (TIC) was measured on a CM 5012 CO_2 Coulometer (UIC) after acidification with phosphoric acid (3 mol L^{-1}). The precision for TIC was ±0.4%. Total organic carbon (TOC) was calculated as the difference of TC and TIC. The C/N-ratio was calculated as the molar ratio of TOC and TN.

$\delta^{13}C$ and $\delta^{15}N$. For the determination of the isotopic composition of TOC, samples were first treated with hydrochloric acid (3 N) to eliminate carbonates, rinsed three times with distilled water, and dried at 60°C (Schubert and Nielsen 2000). For the determination of the nitrogen isotopic composition, samples were used without further pre-treatment. Depending on the TOC concentration 0.1-1.1 mg of the samples were combusted in a Thermo Quest elemental analyzer NC2500. The evolved CO_2 and N_2 gas, respectively, was passed to an Isoprime isotope-ratio mass spectrometer (Micromass, UK) in a continuous flow of helium. The results are reported in the δ notation relative to Vienna Pee Dee Belemnite (VPDB) and air, respectively. Average standard deviation for four replicates was 0.15‰ for organic carbon and 0.12‰ for total nitrogen measurements.

Total chlorins and Chlorin Index. For the determination of chlorins 10 mg of freeze-dried sediment were extracted successively four times with acetone by sonication (10 min) and centrifugation (5 min). The samples were cooled with ice under low light conditions during extraction to prevent decomposition of the chlorins. The sediment extracts were measured on a Hitachi F-2000 fluorometer (λ_{ex}=428 nm, λ_{em}=671 nm) immediately after extraction. It was checked by dilution series that absorption did not attenuate the fluorescence yield of colored extracts. The pigments measured by this method comprise intact chlorophylls and several of their degradation products. Chlorophyll *a* (Fluka), acidified with a few drops of hydrochloric acid (8 N) to yield phaeophytin *a*, was used as a standard, and the pigment concentration is given relative to phaeophytin *a*, assuming that phaeophytins were the prevailing sedimentary pigments. The precision of the method was ±5%. In addition, the pigment extracts were acidified and measured again. Labile compounds are easily degraded by the acid treatment and the resulting molecule has different fluorescence behavior than its precursor. The ratio of the fluorescence intensities (FI) of the acid-treated and the untreated pigment extract has been shown to provide a measure for the degradability of the pigments. This ratio is defined as Chlorin Index (Schubert et al. 2005):

$$\text{Chlorin Index (CI)} = FI_{\text{acidified extract}}/FI_{\text{original extract}}$$

For intact chlorophyll *a* the CI is 0.2, highly degraded pigments approach a CI of 1 (Schubert et al. 2005).

Lipid analysis. Methanol (Me-OH), dichloromethane (DCM), and hexane used for extraction and sample preparation were HPLC grade (Roth, Germany). MilliQ-water (KCl 0.5% w/v) and HCl (8 N) were extracted with DCM (3x) before use. According to the TOC concentration of the sample, 0.5-3 g of freeze-dried homogenized sediment were ultrasonically extracted (20 min, ice cooling), successively with 10 ml Me-OH, Me-OH/DCM (1:1), and DCM. Internal standards added prior to extraction were nonadecanoic acid, C_{36}-*n*-alkane, and 5α-cholestane. The extracts were combined in a separation funnel containing 10 ml of milliQ-water. The DCM fraction was collected and the aqueous phase extracted with 10 ml DCM again. The combined DCM-fraction was volume-reduced by rotary evaporation and treated with N_2 to dryness before 5 ml of methanolic KOH (6% w/w) were added. Saponification was carried out for 3 h at 80°C. After addition of 2 ml milliQ-water, neutral lipids were extracted with hexane (4x2 ml). The remaining extract was then acidified (8 N HCl) to pH 1 and fatty acids (FA) were extracted

with hexane (4x2 ml). The solvent was subsequently removed by rotary evaporation and under a stream of N_2. FA were derivatized to methylesters by the use of 1 ml boron-trifluoride methanol (14%, Sigma) for 1 h at 60°C. After the addition of 1 ml milliQ-water, FA methylesters were extracted with hexane (4x2 ml). The neutral fraction was treated with BSTFA (N,O-Bis(trimethylsilyl)trifluoroacetamide) for 10 min at 60°C prior to gas chromatographic (GC) analysis to yield the more volatile trimethylsilyl-derivatives of alcohols and sterols.

GC analysis was performed on a Hewlett Packard (HP) 5890 Series II instrument equipped with split-splitless-injector, HP5 column (50 m length, 0.32 mm I. D., 0.17 µm film thickness), and flame ionization detector. Carrier gas was helium (2 ml min^{-1}), splitless mode was run for 1 min after injection. The oven temperature program was set to an initial temperature of 60°C (1 min), heating rates were 10°C min^{-1} to 150°C and 4°C min^{-1} to 310°C, the final temperature was kept for 10 min. For quantification, peak areas were compared to the peak area of the internal standard. Identification of compounds was done by comparison of retention times with standard substances and by analysis of mass spectra (MS). GC-MS analysis was carried out on a Finnigan Trace MS coupled to a Thermoquest Trace GC that was equipped with the same column described above and the temperature program used was the same as for GC-analysis.

Sulfate reduction rates

A detailed description of the sampling and analysis procedure, as well as calculation of SRR is given in Böning et al. (2004). They also present areal SRR integrated for some sites included in this study. However, the values of Böning et al. (2004) include the 0-20 cm depth interval. For the purpose of our study we integrated SRR down to 16 cm depth, the minimum length of all investigated cores, in order to ensure comparability for different sites. Since sulfate reduction activity was mostly limited to the upper 10-15 cm of the sediments, areal SRR presented here are only slightly lower than those presented by Böning et al. (2004).

Biomass of nitrate-storing sulfur bacteria

To estimate the biomass of the filamentous *Thioploca* spp., sub-cores were taken from the multi-corer core with plexiglas tubes (3.6 cm inner diameter, 30 cm length). The sediment in each core was extruded from the tube and placed on a slightly tilted surface. The silt

between the sheaths (bundles of *Thioploca*-trichomes) was then washed away carefully with seawater from a squirt bottle, starting at the top of the core. After one centimeter of the sediment had been washed away, the number of exposed sheaths was counted using a stereolupe. At each depth 5-8 randomly chosen sheaths were cut off and inspected with a microscope. The number of sheaths per square centimeter multiplied by the average number of trichomes per sheath, the average diameter of trichomes (which is species dependent), and the average sheath length in the one centimeter interval gave the biovolume of trichomes per sediment volume at a given depth (Schulz et al. 1996; Schulz et al. 2000). The average sheath length was calculated by a given factor depending on the orientation of the sheaths per sediment depth (Schulz et al. 1996). The biomass of trichomes was calculated from the biovolume assuming that the *Thioploca* trichomes had a density of 1 g cm^{-3}.

Bottom water oxygen

Bottom water for the determination of oxygen concentrations was taken directly from the overlying water in the multi-corer immediately after retrieving of sediments. Bottom water oxygen concentrations were determined by Winkler titration (Hansen 1999).

Data division into classes

In order to achieve a suitable visualization of the spatial distribution of selected parameters, the range of observed data was divided into five classes each. The number of classes is approximately equal to the square root of the number of samples (19-31), following a common method to derive an appropriate number of classes (Swan and Sandilands 1995). For most parameters the total range was divided in equal intervals (Tab. 3.4). To account for the skewness of the data set of *Thioploca* biomass and to include information of *Thioploca* absence, class 1 was defined for zero biomass, class 2 for low biomasses of <1 g m^{-2}, and biomasses >1 g m^{-2} were divided in the remaining three classes using the respective logarithmic values.

RESULTS

General sediment characteristics

Bottom water oxygen. Oxygen concentrations in the bottom water were generally low (<30 µmol L^{-1}) independent of the water depth at the sampling site (Tab. 3.2). With the exception of 30MC and 129MC, oxygen concentrations fell within the range characteristic for OMZ (<22 µmol L^{-1}). At all investigated sites oxygen was detectable in the bottom water with a minimum concentration of 4 µmol L^{-1} at 5MC. No free hydrogen sulfide could be detected in the bottom waters. At the deepest sites sampled for bottom water oxygen (79MC at 1179 m and 14MC at 654 m), concentrations were 15 µmol L^{-1} and 10 µmol L^{-1}, respectively.

TOC. Total organic carbon concentrations ranged from 1.9% to 20.2% sediment dry weight (%dw; Tab. 3.1). A band of high TOC concentrations (>12%dw) was found at mid-water depths (230-360 m), and extended to the shelf sites 45MC on transect I in the north (14.1%dw) and 129MC on transect VI in the south (11.1%dw; Fig. 3.2a). At the shallow sites near the coast (<~130 m) and at the deeper sites on the lower slope (>500 m), TOC concentrations were in the range 1.9-7.8%dw and 3.3-6.4%dw, respectively.

TIC. Total inorganic carbon concentrations ranged from <0.1%dw at 88MC to 5.7%dw at 14MC (Tab. 3.1). The shelf stations contained less than 1%dw of TIC, whereas at the deepest sites (>1000 m), TIC made up 1.3-1.7%dw (Fig. 3.2b). Highest concentrations of 4.7-5.7%dw were found at the slope sites 35MC (598 m), 67MC (270 m), and 14MC (654 m). Assuming that calcium carbonate is the predominant form of TIC, the sediments contained up to 48%dw of $CaCO_3$.

C/N-ratios. C/N-ratios ranged from 7.7 to 10.7 and exhibited a slight north-south trend with ratios >9.6 on transects V and VI in the south (Tab. 3.1, Fig. 3.2c). One exception was the shallowest site 125MC (transect VI) with a ratio of 7.9. In the northern part of the investigated area (9-12°S), C/N-ratios were <9 near the coast and in slope sediments at 598 m (35MC) and 654 m (14MC) water depth. Higher ratios were found at mid-water depth (150-300 m) and at the deepest sites 33MC and 81MC.

Table 3.1. Summary table of bulk geochemical parameters of surface sediments (0-1 cm) including core number with latitude, longitude, and water depth. Total organic carbon (TOC) and total inorganic carbon (TIC) concentrations in % sediment dry weight, C/N-ratio as molar ratio of TOC and total nitrogen, isotopic composition of organic carbon ($\delta^{13}C$) versus VPDB, isotopic composition of total nitrogen ($\delta^{15}N$) versus air, total chlorin concentrations in µg g^{-1} sediment dry weight and normalized to TOC, and Chlorin Index (CI).

station	latitude	longitude	depth (m)	TOC (%dw)	TIC (%dw)	C/N	$\delta^{13}C$	$\delta^{15}N$	total chlorins (µg gdw^{-1})	total chlorins (µg $gTOC^{-1}$)	CI
1MC	12°55.21 S	76°58.25 W	321	20.2	1.0	10.4	-20.1	7.7	157	779	0.73
5MC	11°56.95 S	77°18.04 W	96	3.7	0.1	8.7	-19.8	7.5	243	6658	0.67
7MC	11°54.36 S	77°49.73 W	282	12.9	0.6	10.3	-20.9	7.9	157	1216	0.69
14MC	11°08.00 S	78°21.33 W	654	6.1	5.7	8.6	-20.5	6.2	31	509	0.81
17MC	11°01.63 S	78°04.72 W	252	12.2	0.5	9.1	-20.0	7.9	228	1866	0.75
29MC	10°03.28 S	78°17.10 W	102	4.9	0.1	8.2	-19.7	11.4	332	6845	0.63
33MC	9°44.56 S	79°44.22 W	1369	5.7	1.4	10.0	-20.7	4.7	22	386	0.83
35MC	9°51.15 S	79°20.32 W	598	6.4	4.7	7.7	-20.5	6.3	51	798	0.77
45MC	9°41.47 S	78°40.99 W	153	14.1	0.5	9.1	-19.9	8.0	254	1803	0.74
67MC	9°51.52 S	79°12.74 W	270	5.6	5.3	7.9	n.d.	6.7	38	679	0.81
71MC	10°23.42 S	78°33.51 W	238	14.3	2.8	10.1	-20.3	7.7	138	964	0.75
79MC	10°39.17 S	78°51.17 W	1174	3.7	1.3	9.1	n.d.	4.6	14	383	0.75
81MC	10°40.04 S	78°51.15 W	1278	3.3	1.7	9.1	-20.6	4.5	13	389	0.78
88MC	11°01.56 S	77°52.35 W	127	7.8	0.0	7.8	-19.9	12.6	408	5244	0.71
104MC	12°03.68 S	77°39.84 W	185	5.2	0.5	7.9	-20.3	9.5	366	7079	0.71
119MC	12°50.79 S	76°42.05 W	115	7.3	0.1	9.6	-19.8	8.7	247	3407	0.66
121MC	12°55.54 S	77°00.12 W	360	16.4	1.5	10.3	-20.1	8.0	131	799	0.75
125MC	13°32.19 S	76°16.97 W	50	1.9	0.3	7.9	-21.1	7.2	85	4474	0.73
127MC	13°30.87 S	76°21.03 W	86	4.7	0.2	10.7	-20.1	7.1	112	2409	0.74
129MC	13°28.05 S	76°33.13 W	123	11.1	0.1	9.8	-20.1	7.8	180	1622	0.73

n.d. = not determined

Table 3.2. Summary table of biological parameters and oxygen concentration in the bottom water. Sulfate reduction rates (SRR) are given for the surface sediment (0-1 cm) and as depth integrated areal sulfate reduction rates (0-16 cm). SRR profile shapes are classified according to depth of maximum SRR: S = surface (0-1 cm), SS = subsurface (1-5 cm), D = deep (>5 cm). *Thioploca* biomass was calculated from the sediment surface to the maximum penetration depth of filaments. Ranges are given for duplicate measurements.

station	latitude	longitude	depth (m)	SRR (nmol cm^{-3} d^{-1})	areal SRR (mmol m^{-2} d^{-1})	SRR shape	*Thioploca* biomass (g m^{-2})	*Thioploca* penetration	oxygen (µmol L^{-1})
1MC	12°55.21 S	76°58.25 W	321	3.3±0.3	0.3±0.1	SS/SS	0	0 cm	16
2MC	11°34.97 S	77°33.08 W	86	180.8±27.6	9.2±2.4	SS/SS	194	16 cm	8
3MC	11°35.04S	77°32.89 W	86	197.9	6.9	S	n.d.		19
5MC	11°56.95 S	77°18.04 W	96	103.3±43.6	3.9±1.3	S/S	<1	5 cm	4
7MC	11°54.36 S	77°49.73 W	282	9.6±4.6	1.1±0.7	S/SS	n.d.		n.d.
14MC	11°08.00 S	78°21.33 W	654	0.9±0.3	0.2±0.0	SS/SS	n.d.		10
17MC	11°01.63 S	78°04.72 W	252	18.3	1.5	SS	12	13 cm	10
18MC	11°01.82 S	78°04.83 W	255	64.5	1.9	S	n.d.		n.d.
21MC	11°01.86 S	78°04.99 W	257	182.2	3.4	S	n.d.		n.d.
22MC	11°01.87 S	78°05.00 W	258	280.7	3.4	S	28	12 cm	n.d.
30MC	10°03.24 S	78°17.10 W	102	28.8	5.9	SS	193±78	9 cm	28
33MC	9°44.56 S	79°44.22 W	1369	0.0±0.0	0.4±0.2	SS/SS	n.d.		n.d.
35MC	9°51.15 S	79°20.32 W	598	4.4	0.2±0.2	S/SS	0	0 cm	10
45MC	9°41.47 S	78°40.99 W	153	44.1±40.4	3.0±0.5	SS/SS	250	12 cm	22
47MC	9°44.36 S	78°45.10 W	155	157.9±119.6	2.8±0.7	S/SS	69	6 cm	15
67MC	9°51.52 S	79°12.74 W	270	13.1±4.6	0.5±0.3	S/S	<1	<1 cm	n.d.
71MC	10°23.42 S	78°33.51 W	238	26.1±16.0	0.5±0.1	S/S	96	21 cm	14
79MC	10°39.17 S	78°51.17 W	1174	<d.l.	<d.l.	<d.l.	0	0 cm	15
81MC	10°40.04 S	78°51.15 W	1278	3.4±3.4	0.3±0.2	S/D	0	0 cm	n.d.
88MC	11°01.56 S	77°52.35 W	127	464.9±114.5	10.9±3.8	S/S	184±2	20 cm	20

Table 3.2. continued.

station	latitude	longitude	depth (m)	SRR (nmol cm^{-3} d^{-1})	areal SRR (mmol m^{-2} d^{-1})	SRR shape	*Thioploca* biomass (g m^{-2})	*Thioploca* penetration	oxygen (µmol L^{-1})
98MC	11°16.50 S	77°58.40 W	218	25.6±10.8	0.8±0.1	S/S	0	0 cm	n.d.
104MC	12°03.68 S	77°39.84 W	185	196.4	3.2	S	0	0 cm	n.d.
111MC	12°00.55 S	77°40.70 W	179	n.d.	n.d.	n.d.	19	6 cm	15
119MC	12°50.79 S	76°42.05 W	115	<d.l.	6.1	D	48	9 cm	n.d.
120MC	12°50.77 S	76°42.06 W	115	n.d.	0.9	S	n.d.		n.d.
121MC	12°55.54 S	77°00.12 W	360	9.4	0.2	S	<1	9 cm	n.d.
122MC	12°55.54 S	77°00.15 W	364	6.3	0.1	S	n.d.		n.d.
125MC	13°32.19 S	76°16.97 W	50	80.0±77.5	3.4±1.4	S/D	n.d.		n.d.
126MC	13°30.86 S	76°21.03 W	85	553.9	11.4	S	n.d.		n.d.
127MC	13°30.87 S	76°21.03 W	86	21.4	4.8	D	60	9 cm	7
129MC	13°28.05 S	76°33.13 W	123	63.3	1.1	S	5	12 cm	26
142MC	12°43.67 S	77°08.52 W	365	21.7±16.6	0.5±0.2	S/S	n.d.		10
143MC	12°43.93 S	77°07.96 W	359	4.0±0.9	0.1±0.0	S/S	n.d.		11

n.d. = not determined, <d.l. = below detection limit

δ^{13}C. The organic carbon isotopic composition fell in the range –21.1 to –19.7‰ (Tab. 3.1). With the exception of 125MC where the lightest isotopic composition was found, δ^{13}C-values indicated less ^{13}C-depletion near the coast (>–19.9‰). The slight decrease of δ^{13}C-values with increasing water depth most probably reflects the preferential degradation of isotopically heavier compounds like amino acids and sugars compared to isotopically lighter biomass during early diagenesis (Lehmann et al. 2002).

δ^{15}N. The isotopic composition of total nitrogen ranged from 4.5 to 12.6‰ (Tab. 3.1). The lightest isotopic composition was found at the deepest sites (>1000 m; Fig. 3.2d). Nitrogen in most shelf and upper slope sediments was depleted in ^{14}N by >7‰ compared to air, depletion was strongest at 29MC and 88MC (δ^{15}N>10‰).

Organic carbon composition

Total chlorins and Chlorin Index. Total chlorin concentrations ranged from 13 to 408 µg gdw^{-1} (Tab. 3.1), and were highest at the shelf stations (>200 µg gdw^{-1}), except on transect VI, where an opposite trend was observed (Fig. 3.2e). At sites from >600 m water depth, chlorin concentrations were 13-51 µg gdw^{-1}, with lowest values at the deepest sites 33MC and 81MC. Normalized to the TOC concentration of the sediments, on all transects, chlorin concentrations decreased with increasing water depth (Tab. 3.1).

The CI increased with increasing water depth (Tab. 3.1, Fig. 3.2f). All shelf and upper slope sites showed values <0.75, whereas the sediments from the lower slope (>500 m) exhibited CI of up to 0.83. The lowest value (0.63) indicating the freshest pigments was found at 29MC (102 m), whereas the deepest station 33MC showed the highest CI (0.83), pointing to more refractory chlorins.

Phytoplankton biomarkers. At all shelf sites, except 29MC, the phytol concentration was >1 mg gTOC^{-1} (Tab. 3.3). Lower concentrations were found in the slope sediments. Concentrations of brassicasterol (24β-methylcholesta-5,22E-dien-3β-ol) were highest (>80 µg gdw^{-1}) at mid-water depth (230-360 m), and lowest (<25 µg gdw^{-1}) at the deepest sites (>500 m) as well as at the near-coastal sites 125MC, 127MC, and 5MC (Tab. 3.3, Fig. 3.2g). The distribution of dinosterol (4α,23,24-trimethyl-5α(H)-cholest-22-en-3β-ol) was

similar to that of brassicasterol, with highest concentrations (>45 µg gdw^{-1}) at mid-water depth and lowest concentrations (<15 µg gdw^{-1}) at the deeper sites and at 125MC (Tab. 3.3). High dinosterol concentrations of >50 µg gdw^{-1} were also observed at the shelf sites 45MC and 88MC. Normalized to the TOC concentration of the sediments, brassica- and dinosterol concentrations were highest in shelf and upper slope sediments and on most transects decreased with increasing water depth to lowest concentrations at the deepest sites.

Fatty acids. The sum of all identified FA (ΣFA) was by far highest at 5MC and 88MC (>15 mg $gTOC^{-1}$), and generally decreased with increasing water depth of the sampling site (Tab. 3.3). The fraction of ΣFA that is made up by saturated *n*-FA with chain-length C_{21}-C_{28} (Σlong-chain FA) increased with increasing water depth and was highest at the deepest site (Tab. 3.3). The sum of 16:1ω7 and 18:1ω7 made up 4-25% of ΣFA and did not reveal a distinct distribution pattern (Tab. 3.3).

Table 3.3. Selected lipid compounds in surface sediments (0-1 cm). Brassicasterol and dinosterol in µg g^{-1} sediment dry weight, phytol in µg $gTOC^{-1}$, and sum of fatty acids (ΣFA) in mg $gTOC^{-1}$. Sum of long-chain FA (ΣLC-FA) and sum of 16:1ω7 and 18:1ω7 in % ΣFA.

station	brassicasterol (µg gdw^{-1})	dinosterol (µg gdw^{-1})	phytol (µg $gTOC^{-1}$)	ΣFA (mg $gTOC^{-1}$)	ΣLC-FA (% ΣFA)	16:1ω7+18:1ω7 (% ΣFA)
1MC	133	63	695	2.3	6	18
5MC	16	21	2851	25.9	1	14
7MC	97	56	967	4.7	4	20
14MC	19	11	959	1.7	9	15
17MC	82	51	1638	6.2	4	20
29MC	41	36	578	9.0	3	13
33MC	10	9	454	1.1	15	17
35MC	21	13	606	2.0	8	25
45MC	64	52	1342	4.9	5	20
67MC	35	13	593	4.5	4	21
71MC	93	48	222	1.3	7	4
81MC	1	1	53	0.8	8	25
88MC	65	57	4277	15.7	3	23
104MC	34	24	3065	7.4	5	23
119MC	32	34	1580	5.4	5	18
121MC	108	56	470	2.7	6	21
125MC	6	9	4732	9.9	5	14
127MC	14	19	2425	3.7	8	19
129MC	46	42	1954	2.5	9	16

Biological parameters

Sulfate reduction rates (SRR). At most investigated sites, SRR were highest at or near the sediment surface (Tab. 3.2). Highest volumetric rates at 0-1 cm sediment depth were found at 126MC (554 nmol cm^{-3} d^{-1}) and for one parallel at 88MC (579 nmol cm^{-3} d^{-1}). Volumetric rates and profile shapes of parallel cores from one site partly exhibited strong deviations. Likewise, depth integrated rates from parallel cores of some sites deviated up to 100% from the average (Tab. 3.2). Nonetheless, inter-site variability of both volumetric and areal SRR was higher than those of parallel cores from a single site. Areal SRR were <1 mmol m^{-2} d^{-1} in all sediments from >300 m water depth (Tab. 3.2, Fig. 3.2h). Except for 67MC, all shelf and upper slope sediments displayed rates >1 mmol m^{-2} d^{-1}. Maximum areal rates of >9 mmol m^{-2} d^{-1} were found at sites 126MC, 88MC, and 2MC.

Thioploca. 121MC at 360 m water depth was the deepest site where *Thioploca* was found (Tab. 3.2, Fig. 3.2i). At the deeper sites 35MC, 79MC, and 81MC, no *Thioploca* were present in the sediments. The biomass of *Thioploca* was highest at the shallow shelf sites (up to 250 g m^{-2}) and decreased with increasing water depth. Apparently, the *Thioploca* biomass was higher in shelf and upper slope sediments from the northern part of the investigated area compared to transects V and VI in the south. The downward extension of single *Thioploca* filaments varied from <1 to 21 cm sediment depth. The species composition based on filament diameters summarized by Jørgensen and Gallardo (1999) was dominated by *T. chileae* (12-20 µm) and *T. araucae* (30-43 µm), followed by *T. marina* (3-6 µm) and a so far undescribed species with filament diameters between 50 and 80 µm.

Table 3.4. Ranges of defined classes for selected parameters.

parameter	class 1	class 2	class 3	class 4	class 5
TOC (%dw)	1.50-5.32	5.32-9.14	9.14-12.96	12.96-16.78	16.78-20.60
TIC (%dw)	0.0-1.2	1.2-2.4	2.4-3.6	3.6-4.8	4.8-6.0
C/N-ratio	7.55-8.21	8.21-8.87	8.87-9.53	9.53-10.19	10.19-10.85
$\delta^{15}N$ (vs. air)	4.50-6.12	6.12-7.74	7.74-9.36	9.36-10.98	10.98-12.60
total chlorins (µg gdw^{-1})	0-85.5	85.5-171.0	171.0-256.5	256.5-342.0	342.0-427.5
Chlorin Index	0.625-0.667	0.667-0.709	0.709-0.751	0.751-0.793	0.793-0.835
brassicasterol (µg gdw^{-1})	0.0-26.8	26.8-53.6	53.6-80.4	80.4-107.2	107.2-134.0
areal SRR (mmol m^{-2} d^{-1})	0.05-2.33	2.33-4.61	4.61-6.89	6.89-9.17	9.17-11.45
Thioploca biomass (g m^{-2})	0	<1	4.5-17.8	17.8-70.8	70.8-281.8
accumulation rate (cm yr^{-1})	0.0-0.1	0.1-0.2	0.2-0.3	0.3-0.4	0.4-0.5

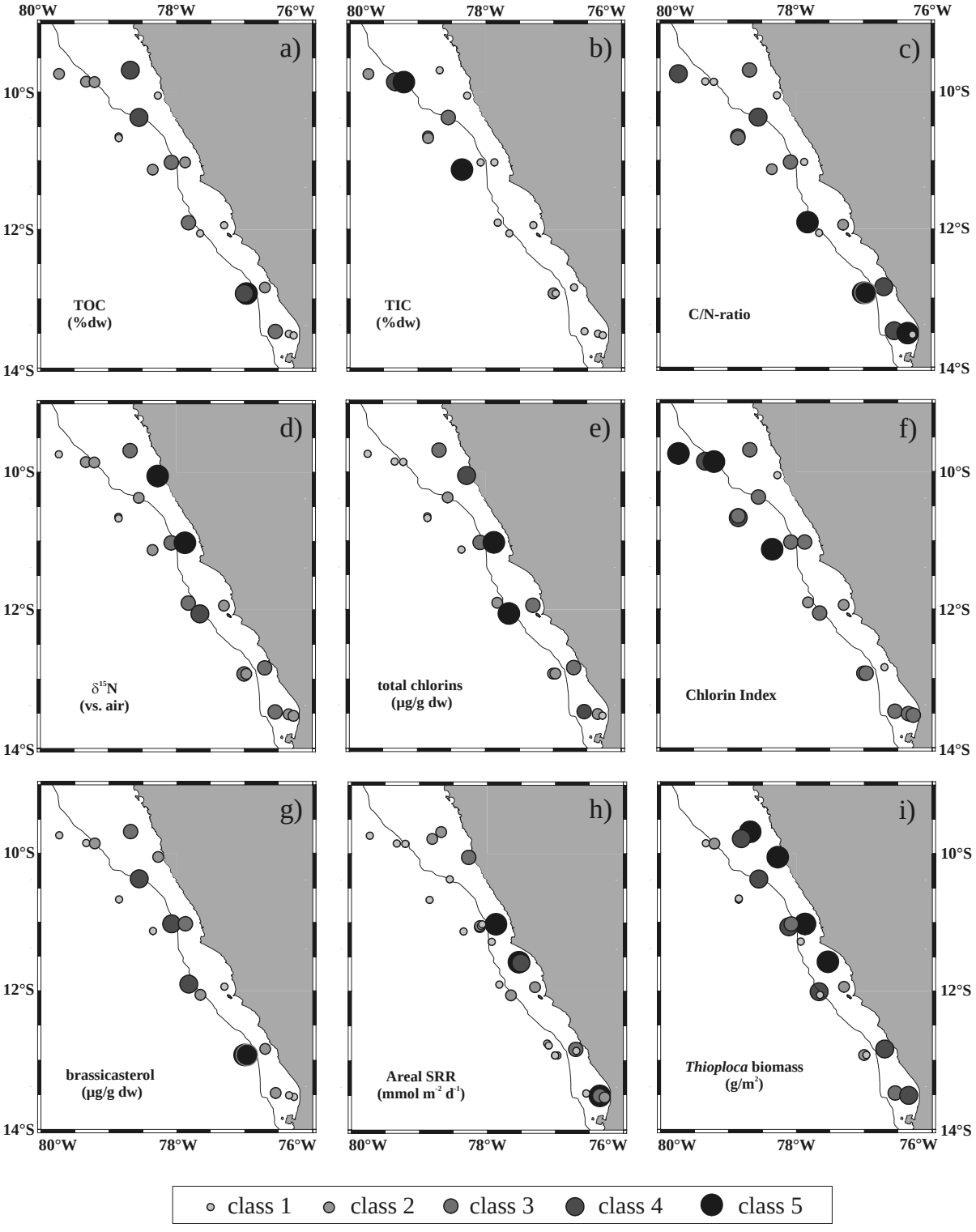

Figure 3.2. Spatial distribution of geochemical and biological parameters. Surface values (0-1 cm) are given for TOC (a), TIC (b), C/N-ratio (c), $\delta^{15}N$ (d), chlorins (e), Chlorin Index (f), and brassicasterol (g). Areal SRR (h) is integrated from 0-16 cm, *Thioploca* biomass (i) considers total interval of penetration depth. For class assignments see Table 3.4.

DISCUSSION

Factors controlling the spatial distribution of sediment composition

Three major factors have been proposed to determine the distribution of TOC concentrations in continental margin sediments off Peru (Reimers and Suess 1983): 1) Rates of primary production determine the rates of OM input to the sediments. 2) Oxygen limitation in the water column and at the sediment surface limits aerobic degradation processes. 3) Prevailing currents and seafloor topography determine regions of preferential sediment deposition.

Effects of currents and seafloor topography

The observed distribution of TOC matches that reported by Reimers and Suess (1983), who compiled data from a total of 88 surface sediments in the region 3-17°S off Peru (Fig. 3.2a and 3.3a). The band of high TOC concentrations at mid-water depths corresponds to the upper slope mud lens also described by Krissek et al. (1980). Results of high resolution echo-sounding studies revealed extended mud-wave fields within the 250-400 m depth interval (Fig. 3.1) as a direct result of the pole-ward flowing undercurrent (Reinhardt et al. 2002). The fine-grained sediments forming the mud-waves accumulate organic material resulting in high TOC concentrations. Lower TOC concentrations found at the shelf sites near the coast can be explained by dilution of OM with clastic terrigenous material delivered by small rivers or as eolian dust (Scheidegger and Krissek 1982).

Following this argumentation it becomes clear that the occurrence of maximum TOC concentrations in the center of the water column OMZ (200-400 m) is due to the geological and oceanographic setting and not primarily due to oxygen limitation. Additionally, bottom water oxygen concentrations showed that all investigated sediments were deposited under oxygen limited conditions (Tab. 3.2) and therefore oxygen exposure was mostly restricted to the duration of particle settling through the oxygenated part of the water column.

Slope sediments from ~500-1500 m water depth are exposed to reworking and winnowing by enhanced bottom currents, reflected in high abundances of calcareous foraminifera tests and elevated TIC concentrations. Sedimentological studies revealed that at these sites the coarse fraction (>63µm) made up >18%dw (Wolf 2002). The predominance of coarse material in mid-slope sediments was also observed by Reimers and Suess (1983), and further supported by high zirconium/aluminium-ratios (Zr/Al-ratios) reported by Böning et al.

(2004). Since zirconium is typically enriched in the heavy mineral fraction, high Zr/Al-ratios point to an enhanced contribution of coarse-grained material.

The co-occurrence of high TOC concentrations and smaller grain-size is consistent with an enhanced preservation potential of OM that is associated with mineral surfaces (e.g. Keil et al. 1994), and provides support that grain size distribution is a principal determinant of TOC concentrations in Peru margin sediments as proposed by Bergamaschi et al. (1997). Alternatively, the observed co-occurrence might simply reflect similar hydraulic properties of particulate OM and fine grained material.

Differences in C/N-ratios originate from varying degrees of degradation of the sedimentary OM, as preferential degradation of N-containing compounds during early diagenesis results in increasing C/N-ratios (Meyers 1997). Low C/N-ratios at shallow shelf sites reflect reduced water column degradation and rapid burial due to high sediment accumulation rates (Reimers and Suess 1983). High C/N-ratios in the mud-wave sediments indicate that a big fraction of the sedimentary OM is already in an advanced state of degradation, consistent with a reworked state of these sediments. Previous petrographical studies revealed a poor preservation of initial structures of particulate OM in Peruvian margin sediments as an effect of strong reworking (Lückge et al. 1996). Accumulation of reworked sediments might also explain the high C/N-ratios observed in shelf sediments of transects V and VI.

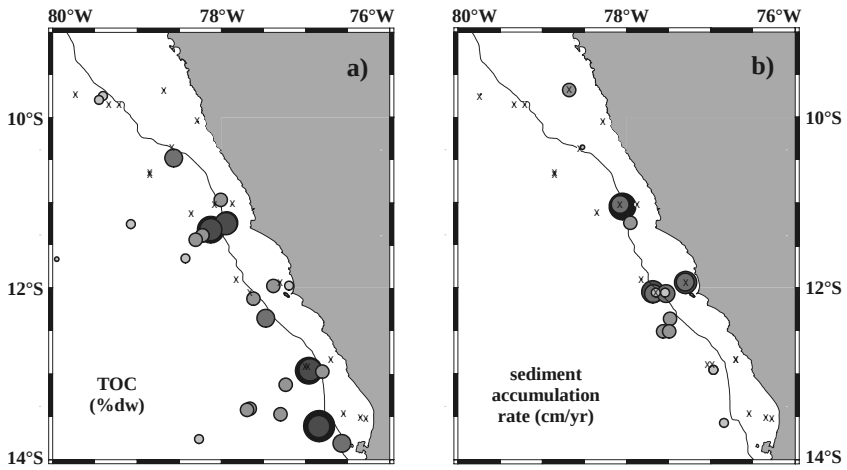

Figure 3.3. Compilation of literature data. a) TOC concentrations from Reimers and Suess (1983), b) sediment accumulation rates from DeMaster (1979, cited in Reimers and Suess (1983)), Koide and Goldberg (1982), Reimers and Suess (1983), Kim and Burnett (1988), McCaffrey et al. (1990), Levin et al. (2002), Kriete et al. (2004), Böning et al. (2004), Rein et al. (2005). Crosses mark position of sites (transects) investigated in this study. Legend like in Fig. 3.2, for class assignments see Table 3.4.

Organic matter input to the sediments

Carbon isotopic composition and C/N-ratios indicate a predominantly marine source of the sedimentary OM (Tab. 3.1). Previous studies of land plant specific lignin compounds in sediments off Peru revealed that even in close proximity to the coast, terrestrial OM contributes only a small, highly degraded fraction (Bergamaschi et al. 1997). Concentrations of typical terrestrial lipid biomarkers, including various triterpenoids that are reported for the region at 15°S (Volkman et al. 1987), were mostly below the detection limit of the analysis procedure applied in this study (data not shown). Long-chain *n*-FA (LC-FA) frequently used as indicator of land-plant material (Meyers 1997) are common in marine algae (e.g. Volkman 1998) and bacteria (e.g. Volkman et al. 1988; Ratledge and Wilkensen 1988) and therefore not applicable to unequivocally detect terrestrial input. In the investigated sediments, the fraction of LC-FA among the ΣFA increased with increasing water depth (Tab. 3.3), reflecting the preferential preservation of LC-FA relative to most other FA. A similar trend has been observed in sediments off Chile (Niggemann and Schubert, chapter 4).

Chlorin concentrations provide a measure for the amount of phytoplankton detritus that is reaching the sediment and have successfully been applied as productivity indicator (e.g. Harris et al. 1996; Schubert et al. 1998). The observed chlorin concentrations were on average a factor 10 higher compared to those found in sediments from the coastal upwelling regions off Namibia (C. J. Schubert, unpublished results) and off Chile (Schubert et al. 2000; Niggemann et al., chapter 2). Seasonal upwelling off Chile (Ahumada et al. 1983; Morales et al. 1996) leads to reduced annual primary production rates and consequently lower input of phytoplankton detritus to the sediments, compared to the region of perennial upwelling off Peru. In addition, lower chlorin concentrations off Namibia and Chile reflect enhanced water column degradation due to the greater water depths of the investigated sediments.

Ongoing degradation of settling particles results in a decrease of chlorin concentrations with increasing water depth, e.g. Shankle et al. (2002) found a logarithmic relation of water depth and chlorin concentrations in surface sediments from the Arabian Sea. In general, the observed chlorin concentrations followed the expected depth trend, most probably dilution with clastic material masks higher chlorin concentrations in the shelf sediments from the southernmost transects (Tab. 3.1, Fig. 3.2e). Chlorin accumulation rates would be suitable to trace the total input of phytodetritus, but as sediment accumulation rates reported for the investigated area display a patchy distribution (Fig. 3.3b), it would be highly speculative to derive chlorin accumulation rates based on the existing data.

The concentrations of fatty acids (r^2=0.76) and phytol (r^2=0.68) were correlated with

those of chlorins, indicating that the spatial distribution of these compounds was also mainly determined by phytoplankton input and water column degradation. In contrast, there was no relation of chlorin and TOC concentrations, consistent with a varying contribution of reworked OM to the sediments.

Imprint of upwelling activity

Phytoplankton communities in the center of upwelling cells are predominated by diatom species (e.g. Blasco et al. 1980). Brassicasterol has repeatedly been used as biomarker for input of diatom material, as it makes up >90% of total sterols in some diatom species (Volkman 1986 and references therein). However, it has been shown that not all diatoms produce brassicasterol (e.g. Barrett et al. 1995) and that some dinoflagellates and haptophytes also contain significant amounts of this sterol (e.g. Goad et al. 1983; Volkman et al. 1998). Nevertheless, brassicasterol provides a suitable measure for the input of diatom detritus to the sediments, as it makes up 12% of the sterol fraction of *Chaetoceros* sp. (Lin et al. 1983), the predominant diatom species in the Peruvian upwelling region (Rojas de Mendiola 1981; Schuette and Schrader 1981; Sellner et al. 1983).

Brassicasterol was highly correlated to TOC (r^2=0.94, Fig. 3.4a), indicating that diatoms were the dominant producers of sedimentary OM, and also reflecting a higher preservation potential of sterols compared to chlorins, phytol, and fatty acids, that are more strongly affected by water column degradation. Highest brassicasterol concentrations were not found at the shelf and upper slope sites directly underlying the productive center of the

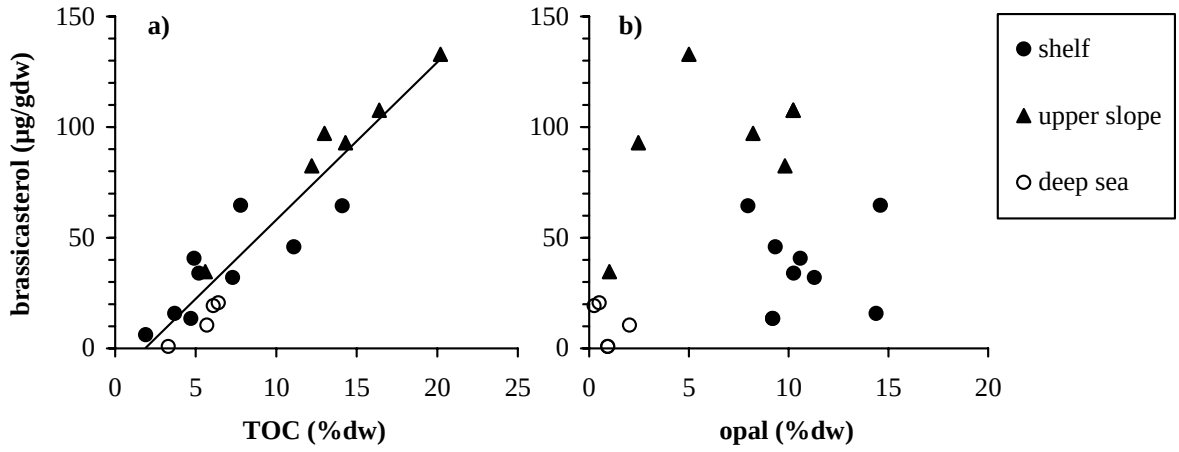

Figure 3.4. Concentration in surface sediments (0-1 cm) of brassicasterol versus (a) TOC and (b) opal. Opal data are from Wolf (2002). Water depth assignments of sites are as follows: shelf at <200 m, upper slope at 200-500 m, and deep sea at >500 m.

upwelling cell at 11-12°S (Reimers and Suess 1983), but in the mud-wave sediments located further south (1MC, 121MC). The uncoupling of water column productivity and composition of the underlying sediment is consistent with a predominant control of currents and seafloor topography on the sediment distribution. Accordingly, the high brassicasterol concentrations of the upper slope sites (7MC, 17MC, 71MC) coincide with the accumulation of TOC-rich sediments. In contrast, high opal concentrations indicate that diatom tests accumulate in the shelf sediments directly underlying the near-coastal upwelling (Wolf 2002). Apparently, redistribution by the prevailing currents is less effective for the heavier opal tests than for the associated diatom OM (Fig. 3.4b).

Dinosterol indicative for input from dinoflagellates (e.g. Boon et al. 1979), followed the distribution of brassicasterol (r^2=0.91) and was also highly correlated with TOC (r^2=0.85). The close coupling of dinosterol and brassicasterol and the similar range of concentrations (Tab. 3.3) point to a general contribution of dinoflagellates to the production of marine OM in the upwelling region off Peru, also reported by Huntsman et al. (1981). However, as the spatial distribution of dinosterol should also be affected by currents and seafloor topography, it probably does not directly reflect dinoflagellate abundances in the overlying water column.

The nitrogen isotopic composition of sedimentary OM has been used to reconstruct paleo-productivity (e.g. Francois et al. 1992; Altabet and Francois 1994; Higginson et al. 2003). In case of abundant nutrients, i.e. permanent replenishment of nitrate, preferential assimilation of $^{14}NO_3^-$ leads to comparably light phytoplankton biomass. In contrast, under nutrient limitation, complete utilization of the available NO_3^- is reflected in $\delta^{15}N$-values of the produced particulate OM which record the isotopic composition of the N-source. Perennial upwelling off Peru creating nutrient-replete conditions, i.e. physical supply of NO_3^- is greater than biological assimilation, should therefore be reflected in ^{15}N depleted OM compared to the nutrient source.

Water upwelling in the coastal region off Peru originates from the depth of the OMZ, a site of intense denitrification (Codispoti and Christensen 1985; Codispoti et al. 1986). During this process ^{14}N is preferentially lost, leaving the remaining nitrate enriched in ^{15}N (Cline and Kaplan 1975). Phytoplankton growing on this ^{15}N enriched nutrient source incorporates the heavy isotopic signal, e.g. particulate OM in the Equatorial Tropical Pacific has average $\delta^{15}N$ values of 11.7‰ compared to 4.5-5‰ in most other oceanic regions (Liu and Kaplan 1989).

It is likely that the higher $\delta^{15}N$ values near the coast reflect the ^{15}N enriched nutrient pool of the upwelled waters, whereas lower values at the deeper sites indicate a nutrient

source with typical marine nitrogen isotopic composition. In the upwelling region off Chile, Hebbeln et al. (2000) observed an increase of $\delta^{15}N$-values with increasing distance to the coast and assumed a consecutive depletion in $^{14}NO_3^-$ when surface waters move away from the near-coastal upwelling center. However, the shallowest sediment sampled off Chile was at 471 m water depth and no data for shelf sites was available.

As pelagic sedimentation is overprinted by reworking and redistribution of sediments, $\delta^{15}N$ values, like other OM characteristics, should be decoupled from processes in the overlying water column. Diagenetic alteration in the sediments might account for part of the observed differences in the nitrogen isotopic composition of the OM, as degradation under anoxic conditions has been shown to result in $\delta^{15}N$ values about 3‰ lower than the initial value (Lehman et al. 2002).

Linking sediment geochemistry and sulfate reduction rates

Quality of sedimentary organic matter

The quality of OM determines its availability for microbial decomposition and therefore constitutes a dominant control on rates and extent of OM remineralization (e.g. Westrich and Berner 1984). Different proxies based on the composition of particulate OM have been applied to assess the quality of sedimentary OM, such as amino acid and carbohydrate contribution to TOC (Cowie and Hedges 1994), or amino acid composition (Dauwe et al. 1999).

Like amino acids and carbohydrates, chlorins, phytol, and fatty acids are preferentially degraded compared to bulk TOC during early diagenesis (Wakeham et al. 1997b; Lee et al. 2000). Thus, TOC-normalized concentrations can be used to assess the labile fraction of the sedimentary OM that is still available for microbial degradation. Water depth appears to be the main factor controlling the distribution of labile compounds in the sediments as the fraction of chlorins, phytol, and ΣFA decreased with increasing water depth (Fig. 3.5a-c).

The Chlorin Index provides a measure for the freshness of the pigment material. The low CI in shelf and upper slope sediments indicate a predominance of fresh undegraded chlorins, whereas at the deeper sites most sedimentary chlorins were already in an advanced state of degradation (high CI, Fig. 3.5d and 3.2f).

The C/N-ratio has often been applied to assess the degradational state of OM (e.g.

Stevensen and Cheng 1972; Meyers and Eadie 1993). This parameter gives the average elemental composition of the sedimentary OM including a possibly highly recalcitrant fraction, and therefore is not generally applicable to evaluate the bioavailability of the sedimentary OM. Sedimentary micro-organisms might thrive on a small, but highly reactive fraction that is not reflected in the C/N-ratio (Arnosti and Holmer 2003). However, for the sites at <600 m water depth, chlorin concentrations were slightly correlated to C/N-ratios (r^2=0.68): High chlorin concentrations indicating a large pool of relatively fresh phytodetritus coincided with low C/N-ratios reflecting predominance of undegraded OM, and vice versa.

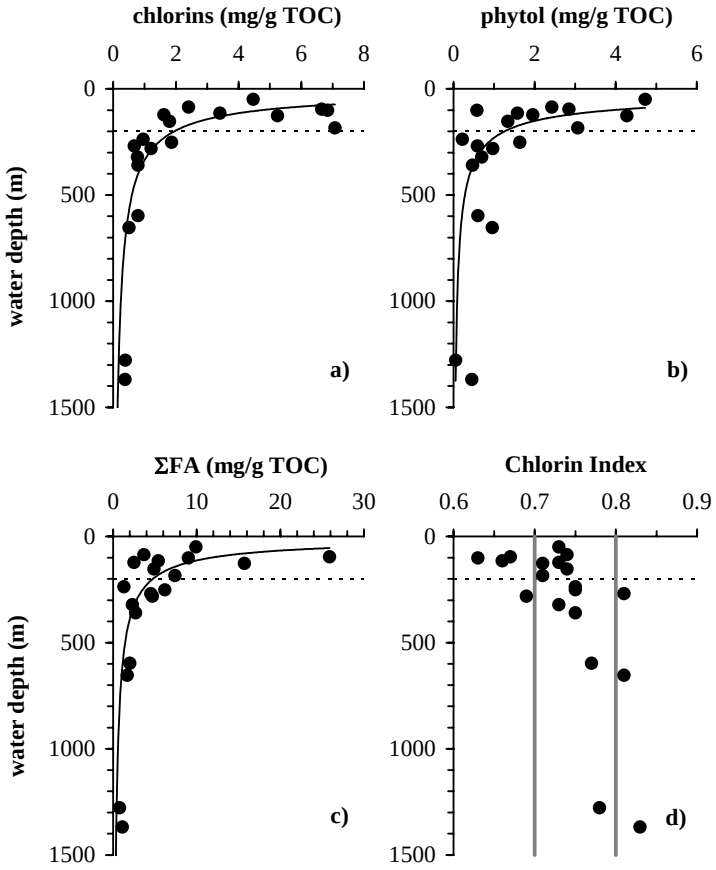

Figure 3.5. Water depth dependence of parameters describing organic matter freshness. TOC-normalized concentration in surface sediment (0-1 cm) of chlorins (a), phytol (b), and sum of fatty acids (c), and Chlorin Index (d). Dotted lines mark depth of shelf edge (200 m).

Controls on sulfate reduction rates

Assuming that sulfate reduction is the dominant terminal electron acceptor process in the degradation of sedimentary OM, SRR can be regarded as a direct measure for the bioavailability of sedimentary OM. Other oxidation pathways might account for part of OM

remineralization, especially at those sites were SRR displayed subsurface and deep peaks (Tab. 3.2). Oxygen itself was probably less important for carbon oxidation as the bottom water oxygen concentration was low at most sites (<28 µmol L^{-1}). Apparently, oxygen availability did not markedly affect the spatial distribution of SRR, e.g. the highest SRR found at 88MC coincided with comparably high bottom water oxygen concentrations (Tab. 3.2).

In sediments from the upwelling region off Chile, sulfate reduction accounts for 100% of carbon oxidation in shelf sediments underlying oxygen-depleted bottom waters and for at least 55% of carbon oxidation in slope sediments, where oxygen, nitrate, and manganese reduction together make up 15% and Fe reduction up to 29% of total carbon oxidation (Thamdrup and Canfield 1996). Fe reduction off central Chile is favored by intense bioturbation which promotes recycling of reduced Fe at the sediment surface (Aller and Yingst 1980). There is no information on bioturbation in the sediments investigated in this study, so we can only speculate about the role of Fe reduction in sedimentary carbon oxidation.

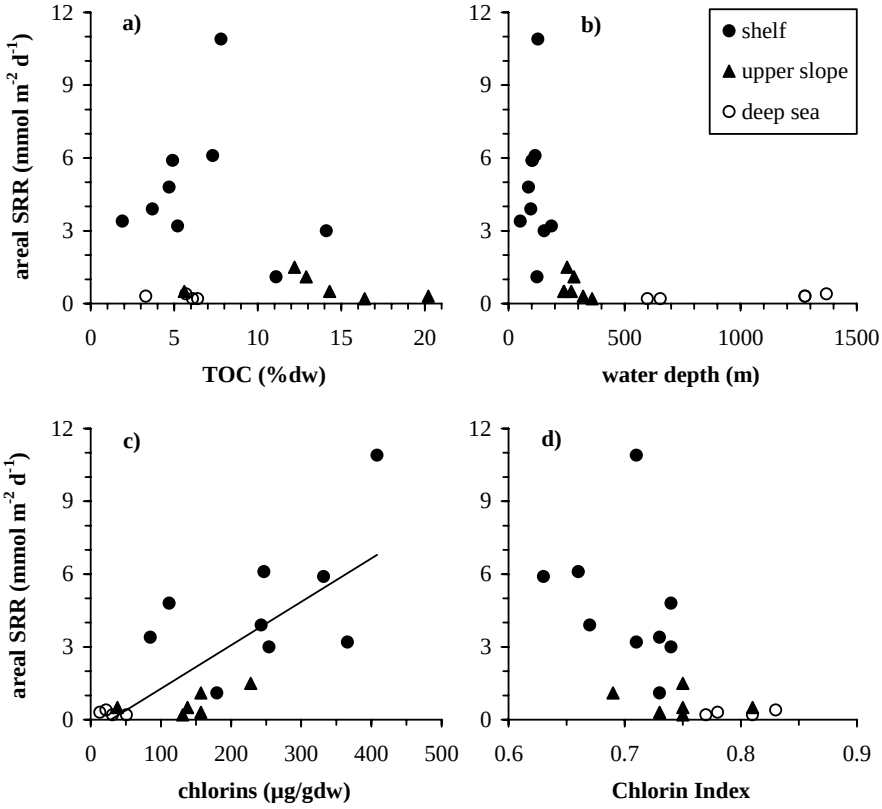

Figure 3.6. Areal SRR versus TOC (a), water depth (b), chlorins (c), and Chlorin Index (d). Compositional parameters describe surface sediment (0-1 cm), water depth assignments as in Fig. 3.4.

The spatial distribution of surface SRR as well as of areal SRR showed no relation to the total amount of sedimentary OM (Fig. 3.6a), consistent with the finding that the organic-rich sediments from mid-water depth are dominated by refractory OM. In contrast, we observed a strong relation of SRR and water depth (Fig. 3.6b and 3.2h), reflecting the water depth dependence of OM quality. Chlorin concentration and CI, applied to quantitatively assess the quality of sedimentary OM, are related to both surface and areal SRR, in that high SRR coincided with high chlorin concentrations and low CI, and vice versa (Fig. 3.6c/d). These findings are in accordance with results of earlier studies off Chile (Schubert et al. 2000; Niggemann et al., chapter 2) and off Namibia (Schubert et al. 2005).

Sediment geochemistry and *Thioploca* distribution

Controls on Thioploca distribution

The exact metabolism of *Thioploca* spp. is still unknown, most likely it is based on the oxidation of sulfide by reduction of internally stored nitrate (Fossing et al. 1995; Schulz et al. 1996). The occurrence of *Thioploca* has mainly been related to the absence of oxygen and the availability of hydrogen sulfide (Gallardo 1977; Nelson 1989; Fossing et al. 1995; Schulz et al. 1996; Huettel et al. 1996). At all sites investigated off Peru, the redox environment was similar, oxygen-limited but not sulfidic, and there was no general relation of bottom water oxygen concentrations and *Thioploca* biomass (Tab. 3.2).

Figure 3.7 shows the depth penetration of *Thioploca* and pore-water sulfide (from Böning et al. 2004) at 17MC, 29/30MC, and 45MC. No free sulfide that is produced by sulfate reduction was detected in the pore-water of the upper sediment layer, where *Thioploca* occurred. It is still unclear whether the oxidizing activity of *Thioploca* is the controlling factor on sulfide distribution, or whether *Thioploca* only penetrate to the depth of free sulfide and other oxidation mechanisms account for the absence of sulfide (Ferdelman et al. 1997).

As the metabolism of *Thioploca* relies on the availability of hydrogen sulfide, OM quality determining rates of sulfate reduction and thus sulfide production should have an indirect effect on the distribution of *Thioploca*. There was a slight relation of areal SRR and *Thioploca* biomass in that high SRR and high Thioploca biomass coincided in shelf and upper slope sediments. But none of the parameters describing either quantity or quality of sedimentary OM was related to the distribution of *Thioploca*. This is in accordance with findings of Henrichs and Farrington (1984) in sediments near 15°S, where the occurrence of

Thioploca filaments showed no relation to any feature of sediment or pore-water chemistry measured. Although we have no direct evidence, it is likely that the availability of fresh OM also influenced the distribution of *Thioploca* biomass by providing dissolved metabolites as carbon source. In general, the patchy distribution of *Thioploca* that is manifested in deviations of parallel cores and neighboring sites (Tab. 3.3; Fig. 3.2i) points to small scale controlling factors.

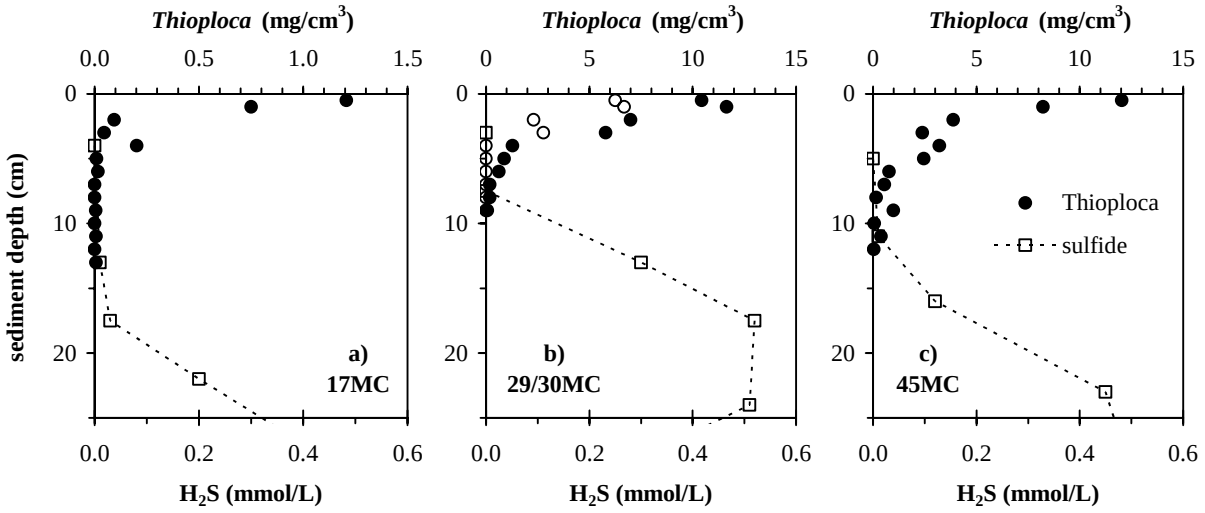

Figure 3.7. Sediment depth profiles of *Thioploca* biomass and pore-water sulfide at 17MC (a), 29/30MC (b), and 45MC (c). Open circles in (b) represent parallel core. Sulfide data from Böning et al. (2004).

Imprint of Thioploca on sediment geochemistry?

The lipid composition of *Thioploca* has been described by McCaffrey et al. (1989), who suggested cyclolaudenol as a sterol biomarker for *Thioploca*. However, repeated analysis of *Thioploca* did not reveal any sterol compounds (C. J. Schubert, unpublished results; J. Peckmann, K.-U. Hinrichs, personal communication), consistent with the general view that bacteria typically lack the ability of sterol synthesis (Ourisson et al. 1979). Accordingly, studies on sterol composition of sediments from the Peruvian upwelling region, where widespread occurrence of *Thioploca* has been described (e.g. Gallardo 1977), did not report a contribution of cyclolaudenol (Smith et al. 1983a; Volkman et al. 1987).

As *Thioploca* biomass may contribute up to 80% of total biomass in the sediments (Gallardo 1977), these organisms should also make up a significant fraction of sedimentary OM. We tested whether *Thioploca* occurrence might be traced by enhanced concentrations of its most abundant fatty acids 16:1ω7 and 18:1ω7 (McCaffrey et al. 1989; C. J. Schubert,

unpublished results; J. Peckmann, personal communication). We did not find any relation to the actual distribution of *Thioploca* - a result that could have been expected as both FA are ubiquitous in marine organisms and therefore a possible contribution from *Thioploca* is indistinguishable from the input background. Furthermore, the distribution of these two FA is strongly affected by diagenetic alteration. From these results we conclude that *Thioploca* lipids do not provide a specific and diagenetically stable biomarker.

CONCLUSIONS

We showed that the spatial distribution of sediments in the coastal region off Peru is mainly determined by prevailing currents and seafloor topography. High TOC concentrations were found in mud-wave fields at mid-water depths, whereas high TIC concentrations occurred at sites opposed to intensive bottom currents.

The sedimentary OM was predominantly of marine origin, there were no indications for a significant terrestrial contribution. Due to the controlling effect of current activity and seafloor topography, sediment composition was largely uncoupled from productivity of surface waters. Brassicasterol and dinosterol were highly correlated with TOC, indicating that diatoms and dinoflagellates, both known to be the predominant phytoplankton in upwelling waters, are the main source of sedimentary OM.

Sulfate reduction rates showed a good correspondence with parameters assessing the quality of the sedimentary OM, i.e. concentrations of chlorins and phytol, and the Chlorin Index describing the freshness of the chlorin pool. Both SRR and freshness parameters were related to water depth, reflecting the decrease of OM quality with ongoing water column degradation. We were unable to link the spatial distribution of *Thioploca* biomass to geochemical characteristics, which might in part be due to the patchy occurrence of *Thioploca*. Attempts to trace *Thioploca* biomass in the sedimentary lipid composition were also unsuccessful.

In summary, our results show that for a better understanding of the sediment biogeochemistry it is important not only to combine geochemical and biological findings but also to include information on the geophysical and oceanographic setting. The larger scale situation in the upwelling region off Peru is quite well known, but the microscale physicochemical situation at the seafloor probably displays high variability, leading to a patchy distribution of biological niches that in turn also affect the sediments.

Acknowledgements. We thank the officers, crew, and shipboard scientific party of RV Sonne cruise SO-147. We are grateful to Gabriele Klockgether (MPI Bremen) for sampling and help in the home laboratory. Elze B. A. Wieringa and Daniela Riechmann (MPI Bremen) contributed data on *Thioploca* distribution and bottom water oxygen concentration. Thanks to André Preisler (MPI Bremen) for fruitful discussions on *Thioploca* data. Lutz Reinhardt (BGR Hannover) kindly provided an electronic version of the bathymetric map from the investigation area. This work was part of the project “Peru-Auftrieb” (grant 03G0147A) supported by the BMBF (Federal Ministry of Education and Research, Germany). Further support came from the Max Planck Society, Germany.

Chapter 4

Fatty acid biogeochemistry of sediments from the Chilean coastal upwelling region: sources and diagenetic changes

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submitted to *Organic Geochemistry*

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ABSTRACT

Sediments from two different depositional regions off Northern (23°S) and off central Chile (36°S) covering water depths from 126 to 1350 m were analyzed for their fatty acid (FA) composition. Highest total FA concentrations were found at the shallowest sites from the oxygen minimum zone and total organic carbon (TOC) normalized concentrations were generally higher at 36°S (1.8-4.9 mg g^{-1} TOC) than at 23°S (0.8-1.6 mg g^{-1} TOC). Reaction rate constants *k*, calculated from the down-core decrease of total and individual FA were related to sediment accumulation rates, reflecting decreasing reactivity with advancing time since deposition. Polyunsaturated FA were the most, long-chain saturated *n*-FA (LC-FA) the least reactive compounds. Carbon isotopic compositions of individual LC-FA (-27.1±1.9‰ vs. VPDB) were similar to those of mid-chain saturated *n*-FA (-25.1±1.8‰) and bacterial FA (-26.1±3.0‰), indicating a non-terrestrial source for most LC-FA. Principal component analysis was applied to reveal information on the main factors that control the FA composition in the sediments off Chile. The first component that explained 48% of the total variance in the data set was assigned to compositional changes during early diagenesis. Calculated site scores were defined as FA degradation index and showed a good correspondence with other FA based quality indicators and C/N-ratios of bulk organic matter. The FA index revealed diagenetic alteration that was only partly reflected in the pigment based Chlorin Index and not visible from the amino acid based degradation index.

INTRODUCTION

Fatty acids (FA) constitute an important fraction of the lipid pool in living and dead organic material. Their abundance in living organisms, the source specificity of individual compounds, and their relative lability make FA suitable to trace sources and diagenetic changes of organic material in water column and sediments.

Numerous studies used the source information provided by FA to estimate the relative contributions of terrestrial, algal or planktonic, and bacterial FA to the total FA pool of marine sediments (e.g. Volkman et al. 1980b; Smith et al. 1983b; Prahl et al. 1989; Gong and Hollander 1997; Wakeham et al. 1997a; Budge and Parrish 1998; Canuel 2001; Zimmerman and Canuel 2001; Camacho-Ibar et al. 2003). Although most FA are not unique to one source, major differences in the FA composition of individual or grouped source organisms allow for

assignment to predominating sources. Analysis of the organic carbon isotopic composition provides support for the source assignments. Corresponding to the ^{13}C depletion of C_3-plant derived terrestrial compared to marine organic material (Meyers 1997; references therein), terrestrial FA from C_3-plants are isotopically lighter than marine FA. Bacterial sedimentary FA have been assigned to a common source based on their similar isotopic composition (Gong and Hollander 1997).

Diagenetic alteration changes both the absolute amount and the relative contribution of individual FA. Some general trends in the relative reactivity of FA have been described, e.g. unsaturated FA degrade faster than saturated FA (e.g. Farrington et al. 1977; Haddad et al. 1992; Sun and Wakeham 1994). These differences in reactivity have mostly been related to different sources, in that planktonic are more reactive than terrestrial FA (e.g. Canuel and Martens 1996; Camacho-Ibar et al. 2003), and association with protective matrices rather than differences in molecular structure has been suggested to account for the greater stability of terrestrial FA (e.g. Haddad et al. 1992; Canuel and Martens 1996). Recently, Gong and Hollander (1997) estimated that part of the long-chain FA traditionally assigned to terrestrial sources are in situ products of bacterial reworking and Naraoka and Ishiwatari (2000) suggest a marine source for long-chain FA in sediments from the open Pacific.

Coastal upwelling regions are characterized by high plankton productivity, oxygen depletion in the water column, and organic carbon rich sediments with predominantly marine organic material. The exact mechanism leading to the accumulation of organic carbon rich sediments is still under debate, but most likely is a combination of several factors including high productivity (Calvert and Pedersen 1992), extent of water column degradation (Jahnke 1990), oxygen limitation (Demaison and Moore 1980; Paropkari et al. 1992; Hartnett et al. 1998), and high sedimentation rates (Müller and Suess 1979).

Attempts to link sedimentary FA composition and the availability of oxygen revealed a selective enrichment of individual FA under oxygen-limited conditions. Gong and Hollander (1997) were able to trace a higher contribution of bacterial FA in sediments from the anoxic depocenter than in oxic sediments from the periphery of Santa Monica Basin. In sediments from the Arabian Sea, bacterial and terrestrial FA were enriched in sediments within the oxygen-minimum-zone (OMZ), whereas *n*-FA concentrations showed no relation to the OMZ (Schulte et al. 2000). However, a comparison of the FA pools in anoxic sediments from the Peruvian upwelling region (Smith et al. 1983b; McCaffrey et al. 1989) and those in sediments underlying oxygenated bottom waters in the deep Pacific (Wakeham et al. 1997a), does not reveal major compositional differences, with the exception of those that

are related to more effective water column degradation at the deeper sites.

In this study we provide the first description of the FA composition in sediments from the coastal upwelling region off Chile. Results from different depositional regimes off Northern (23°S) and off central Chile (36°S) are compared and discussed with respect to sources and reactivities of grouped and individual FA. Principal component analysis was used in order to identify the main factors that control the FA composition in the sediments off Chile. We show that the factor accounting for the maximum variance can be ascribed to FA degradation. According to the amino acid based degradation index established by Dauwe and Middelburg (1998) and Dauwe et al. (1999), we defined a FA index evaluated by relating it to other frequently used quality indicators for organic carbon.

MATERIAL AND METHODS

Study area and sampling

The coastal Pacific off Chile is part of the Peru-Chile Current upwelling system, one of the most productive oceanic regions in the world (Berger et al. 1987). Over its wide latitudinal extension (>40°), duration and intensity of upwelling change, as well as the climatic regime of the hinterland, prevailing currents, and seafloor morphology. Each of these factors influences the deposition of particles on the seafloor and thus accounts for differences in sediment composition (Lamy et al. 1998; Hebbeln et al. 2000).

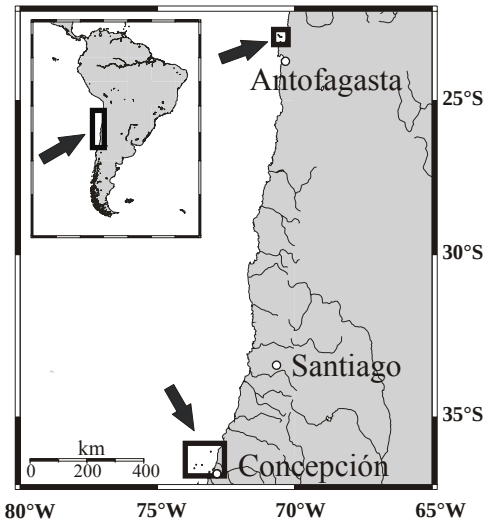

Figure 4.1. Location of the investigated areas off Antofagasta and off Concepción.

For this study we chose two areas of investigation that represent different depositional regimes in the Chilean coastal upwelling region: in the North at 23°S off Antofagasta and in the central region at 36°S off Concepción (Fig. 4.1). Off Antofagasta, the steep slope and strong bottom currents limit sediment accumulation to isolated depositional centers. The adjacent Atacama Desert is one of the driest regions in the world and eolian input is the prevailing source of terrigenous material (Lamy et al. 1998). Upwelling off Northern Chile is concentrated close to the coast and attenuated during winter times (Morales et al. 1996; Blanco et al. 2001). Primary production rates are high throughout the year and reach values of up to 11 mg C m^{-3} h^{-1} (Iriarte et al. 2000). In contrast, upwelling displays strong seasonality off central Chile (Brandhorst 1971; Ahumada et al. 1983), with high primary production rates of up to 57 mg C m^{-3} h^{-1} in summer months (Peterson et al. 1988). Continental shelf and slope off Concepción extend further offshore than off Antofagasta and are more favorable for sediment accumulation. Several rivers, mainly the Itata, Bio-Bio, and Andalién River, drain the coastal region near Concepción, supplying terrestrial detritus to the adjacent sediments.

The study sites covered a wide range of water depths and bottom water oxygen concentrations (Tab. 4.1). The shallowest sites, namely GeoB 7104, GeoB 7160, and GeoB 7161, were located within the actual depth of the water column OMZ (<0.5 ml O_2 l^{-1}). A detailed description of the study sites is given in Niggemann et al. (Chapter 2), including information on the distribution of ^{210}Pb activity in the sediments, bulk sediment composition (total organic and inorganic carbon, total nitrogen, C/N-ratios, $\delta^{13}C$ of TOC, chlorins, Chlorin Index), and sulfate reduction rates.

Table 4.1. Sampling sites with position, water depth, bottom water oxygen concentration, sediment accumulation rate, and extension of mixed layer.

station	latitude	longitude	water depth (m)	bottom water O_2[a] (ml l^{-1})	sediment accumulation rate[b] (cm yr^{-1})	mixed layer[b] (cm)
GeoB 7103	22°51.99 S	70°32.54 W	891	1.00	0.15	none
GeoB 7104	22°52.00 S	70°29.42 W	307	0.15	n.d.[c]	n.d.[c]
GeoB 7106	22°48.00 S	70°36.70 W	1350	1.18	0.11	none
GeoB 7108	22°50.50 S	70°34.79 W	1007	n.d.[c]	0.04	none
GeoB 7160	36°02.33 S	73°04.39 W	367	0.16	0.19	0-10
GeoB 7161	36°25.51 S	73°23.32 W	126	0.01	0.10	0-8
GeoB 7162	36°32.52 S	73°40.02 W	798	2.36	0.17	0-10
GeoB 7163	36°25.55 S	73°35.71 W	536	2.30	0.15	0-5

[a]data from CTD-profiling (Hebbeln et al. 2001), [b]data from Niggemann et al. (Chapter 2), [c]n.d. = not determined

Sampling was carried out during RV Sonne cruise SO-156 in April 2001. Multicorer cores were sliced in 1 cm intervals in the upper 6 cm and in 2 cm intervals below 6 cm depth. The samples were transferred to clean glass-vials and frozen at -25°C immediately after sampling. Sediment samples were later freeze-dried and homogenized by grinding in an agate mortar. Particulate material more than 0.5 cm in size, e.g. fish bones, shells, worm-tubes, and remains of worms were excluded from the sediments. Depth intervals chosen for FA analyses were 0-1, 2-3, 4-5 cm at all sites and additionally 6-8, 10-12, 14-16, 18-20, 22-24 cm at the shallowest (GeoB 7104, GeoB 7161) and deepest sites (GeoB 7106, GeoB 7162) of each transect. Carbon isotopic composition of individual FA was determined for the surface samples (0-1 cm) from all sites and for all samples at GeoB 7104 and GeoB 7161.

Fatty acid analysis

Methanol (Me-OH), dichloromethane (DCM), and hexane used for extraction and sample preparation were HPLC grade (Roth, Germany). MilliQ-water (KCl 0.5% w/v) and HCl (25% v/v) were extracted with DCM (3x) before used. Based on the total organic carbon (TOC) concentration of the sample, 0.5-3 g of freeze-dried homogenized sediment were ultrasonically extracted (20 min, ice cooling), successively with 10 ml Me-OH, Me-OH/DCM (1:1), and DCM. Nonadecanoic acid (19:0) was added as an internal standard prior to extraction. The extracts were combined in a separation funnel containing 10 ml of milliQ-water. The DCM fraction was collected and the aqueous phase extracted with 10 ml DCM again. The combined DCM-fraction was volume-reduced by rotary evaporation and treated with N_2 to near dryness before 5 ml of methanolic KOH (6% w/w) was added. Saponification was carried out for 3 h at 80°C. After addition of 2 ml milliQ-water, neutral lipids were extracted with hexane (4x2 ml). The remaining extract was then acidified (25% HCl) to pH 1 and FA were extracted with hexane (4x2 ml). The solvent was subsequently removed by rotary evaporation and under a stream of N_2. FA were derivatized to methylesters by the use of 1 ml boron-trifluoride methanol (14%, Sigma) for 1 h at 60°C. After the addition of 1 ml milliQ-water, FA methylesters were extracted with hexane (4x2 ml).

Gas chromatographic (GC) analysis was performed on a Hewlett Packard (HP) 5890 Series II instrument equipped with a split-injector, a HP5 column (50 m length, 0.32 mm I. D., 0.17 µm film thickness), and a flame ionization detector. The carrier gas was helium (2 ml/min), and splitless mode was run for 1 min after injection. The oven temperature program was set to an initial temperature of 60°C (1 min), heating rates were 10°C/min to

150°C and 4°C/min to 310°C, and the final temperature was maintained for 10 min. For quantification, peak areas were compared to the peak area of the internal standard. Identification of compounds was done by comparison of retention times with standard substances and by analysis of mass spectra (MS). GC-MS analysis was carried out on a Finnigan Trace MS coupled to a Thermoquest Trace GC. Analysis of carbon isotopic compositions of individual FA was performed using a GC (HP 6890 Series) attached to a Delta^{plus} isotope-ratio (ir) MS (Thermoquest, Finnigan) via a combustion interface (GC Combustion III, Finnigan). For calibration a CO_2 standard was injected at the beginning and at the end of each analysis. GCs coupled to MS and irMS were equipped with the column described above and the temperature program used was the same as for GC-analysis. Isotopic compositions are reported in the δ notation relative to Vienna Pee Dee Belemnite (VPDB):

$$\delta^{13}C\ [‰] = (((^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{standard})-1)*1000 \quad (1)$$

Calculation of rate constants

Following the approach applied by Canuel and Martens (1996) we assumed that FA are degraded by first-order kinetics. In that case concentration changes during degradation can be described by a simple decay equation according to Berner (1980):

$$\frac{\Delta c}{\Delta t} = \frac{c_1 - c_0}{t_1 - t_0} = -kc \quad (2)$$

where Δc is the change in concentration of a given compound during the time interval Δt, with c_0 being the initial concentration at time t_0 and c_1 being the concentration at greater depth corresponding to time t_1. The first order rate constant *k* describes the proportion of a given concentration c that is degraded per time. Considering steady state, *k* can be calculated as follows:

$$k = \frac{-\ln(c_1 / c_0)}{(t_1 - t_0)} \quad (3)$$

Sediment ages were obtained from ^{210}Pb dating (Niggemann et al., chapter 2). As sediment mixing attenuates changes in the depth profiles of total and individual FA concentrations, *k*-values calculated for the sediments deposited off Concepción probably underestimate real FA reactivity, thus they provide minimum estimates.

Principal component analysis

The FA data set was analyzed statistically using JMP version 3 (SAS Institute). A total of 30 individual FA quantified in 42 samples were included in a principal component analysis (PCA). PCA was used to reduce the dimensionality of the data set in order to reveal the dominant factors that determine the FA distribution in the investigated sediments. A detailed description of mathematics and interpretation of PCA is given in Meglen (1992). Principal components are the orthogonal axes of a multidimensional space identified by PCA that has fewer dimensions than the original data. The maximum variance of the data set is found on the first axis. Factor loadings are the correlation coefficients between the original variable and the principal components, thus providing information on the extent a single variable is affected by the environmental factors reflected in the principal component. Site scores include the position of all variables of a sample, quantifying the relationship of the sample and the principal component, and allowing to rank the samples according to the influence of the environmental factor that is represented by the principal component.

RESULTS AND DISCUSSION

Total fatty acid concentrations

Surface concentrations

Total fatty acid (TFA) concentrations at the sediment surface (0-1 cm) ranged from 20 to 203 μg g^{-1} dry weight. The concentration was highest at the shallowest site GeoB 7161 and <100 μg g^{-1} dry weight at all other sites from >300 m water depth (Tab. 4.2). Differences between the two investigated areas become apparent when comparing the TOC-normalized concentrations. Off Antofagasta surface concentrations were generally lower (0.8-1.6 mg g^{-1} TOC) than off Concepción (1.8-4.9 mg g^{-1} TOC).

For a surface sediment from 2094 m water depth in the Black Sea, Sun and Wakeham (1994) report a TFA concentration of 1.8 mg g^{-1} TOC. Reduced degradation efficiency due to the mostly anoxic water column might explain the comparably high surface concentration at this deep site. In a study on sediments from the Santa Monica Basin, Gong and Hollander (1997) found surficial TFA concentrations of 0.8 mg g^{-1} TOC at an oxic site and of 2.8 mg g^{-1} TOC at an anoxic site, pointing to enhanced FA preservation in the absence of

oxygen. Off Chile, TFA concentrations were also highest in the sediments underlying the oxygen-depleted bottom waters of the water column OMZ, namely GeoB 7104 off Antofagasta and GeoB 7160 and GeoB 7161 off Concepción. However, as these three stations were also the shallowest sites sampled, we cannot distinguish whether the higher concentrations are a consequence of reduced degradation due to limited oxygen availability or a consequence of less efficient water column degradation due to shallower water depth.

Table 4.2. Total fatty acid (TFA) concentration in surface sediments (0-1 cm) and reaction rate coefficient *k* for TFA degradation in the surface layer (0-1 to 2-3 cm).

station	TFA (µg g^{-1} dw)	TFA (mg g^{-1} TOC)	*k* (yr^{-1})
GeoB 7103	63	1.2	0.078
GeoB 7104	83	1.6	n.d.[a]
GeoB 7106	29	0.8	0.030
GeoB 7108	20	1.0	0.026
GeoB 7160	58	2.0	0.029
GeoB 7161	203	4.9	0.028
GeoB 7162	55	2.1	0.064
GeoB 7163	38	1.8	0.041

[a]n.d. = not determined

During early diagenesis FA are preferentially degraded compared to the bulk organic carbon pool (e.g. Wakeham et al. 1997b). Numerous studies provide evidence that shallow water depths (<50 m) favor high TFA concentrations in surface sediments, e.g. 14 mg g^{-1} TOC in Buzzard Bay (Farrington et al. 1977), 3.4-22 mg g^{-1} TOC in Cape Lookout Bight (Haddad et al. 1992; Canuel and Martens 1996), and up to 35.7 mg g^{-1} TOC in Chesapeake Bay (Zimmerman and Canuel 2001). The latter study also revealed the seasonality of TFA concentrations in that highest concentrations coincided with algal bloom events in the overlying surface water. A similar effect was reported by Gogou and Stephanou (2004) for sediments from the Eastern Mediterranean Sea at 100-940 m water depth. We cannot exclude that the surface sediments investigated in our study show a similar seasonality of TFA concentrations as high productivity in the coastal waters off Chile is coupled to upwelling of nutrient-rich water masses. Sampling was carried out in April towards the end of the upwelling period. We therefore assume that the surface TFA concentrations reported in this study represent a transitional situation between possibly higher values during times of strongest upwelling and possibly lower values during winter time when this process is less effective.

In the coastal ocean off Peru upwelling is strong year-round. Smith et al. (1983b) reported a TFA concentration of 22.3 mg g^{-1} TOC for a surface sediment at 145 m water depth, a value 4-5 times higher than the maximum concentration found off Chile at 126 m water depth. Apart from seasonal effects or a generally higher input off Peru, the sampling strategy might account for the observed differences. When comparing surface concentrations it is generally important to consider the depth interval denoted as "surface sediment". While Smith et al. (1983b) analyzed the upper 0-0.3 cm, the sediments investigated in our study integrated over the uppermost cm. Organic matter degradation is very effective near the sediment-water interface and TFA concentrations decrease strongly within the uppermost sediment layer. For example, in the equatorial Pacific Ocean, TFA concentrations in the floc layer were up to 2.5 times higher than those in the upper 0-0.5 cm of the underlying sediment (Wakeham et al. 1997a). Consequently, at least part of the differences listed in this discussion might also derive from unconformity of sampling procedures.

Depth profiles

The depth profiles of TOC-normalized TFA concentrations showed a similar shape as those given per sediment dry weight, except at GeoB 7104 where TOC concentrations exhibited strong down-core variations (Fig. 4.2). At all investigated sites TFA concentrations decreased strongly within the uppermost sediment layer and reached background values at ~5 cm off Antofagasta and at ~10 cm off Concepción (Fig. 4.2). The discontinuity in the TFA profiles at GeoB 7161 and GeoB 7162 separating the decrease in the upper 8 cm and the constant values below, reflects the extension of the mixed layer at these sites (Tab. 4.1).

According to the reaction rate constants *k* calculated for the surface decrease of TFA, the bulk FA pool at the sediment surface was most reactive at GeoB 7103 and least reactive at GeoB 7108 (Tab. 4.2). In contrast to the TFA surface concentrations that showed an overall decrease with increasing water depth (see above), there was no relation of *k*-values and water depths. Instead *k*-values were slightly related to sediment accumulation rates, indicating that degradation processes in the sediment rather than in the water column determine the reactivity of the sedimentary FA.

Canuel and Martens (1996) showed that degradation rate constants are highest near the sediment-water interface soon after deposition and that the reactivity of a given lipid compound decreases over time, describing a log-log dependence of reaction rate constant and time since deposition. In our study, the initial concentration c_0 was set the concentration of a given constituent integrated over the uppermost sediment layer (0-1 cm) corresponding to

3-9 years of sediment deposition. Thus, c_0 most likely did not represent the FA concentration of freshly deposited organic matter and also included a bigger fraction of more refractory, less reactive compounds. The same holds for c_1 (2-3 cm) that corresponded to an age of 12-45 years depending on the sediment accumulation rate. Consequently, the rate constants calculated in this study do not reflect the initial reactivity of sedimentary FA. As a result of their short-term study Canuel and Martens (1996) stated that "steady state diagenetic models underestimate rates of degradation at or near the sediment-water interface by an order of magnitude." For TFA they reported *k*-values of 12.0-1.5 yr^{-1} (0.033-0.004 d^{-1}) for time spans of 31-144 days, i.e. 10-500 times higher than the *k*-values observed in our study. Reaction rate constants calculated for the total down-core decrease of TFA integrated over up to 112 years yielded in values of 0.015-0.023 yr^{-1} (data not shown), similar to those reported by Camacho-Ibar et al. (2003) for sediments from the Northern Gulf of California. Camacho-Ibar et al. (2003) averaged over individual *k*-values of different depth intervals in up to 170 cm sediment depth, reaching ages up to 800 years.

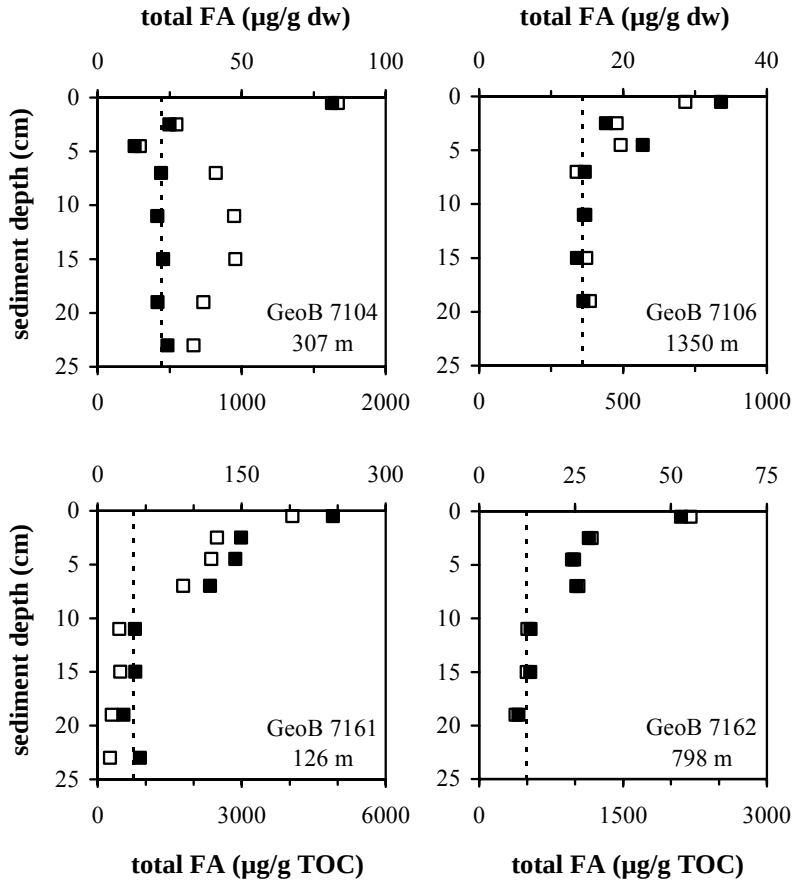

Figure 4.2. Depth profiles of total fatty acid (TFA) concentrations in µg/g sediment dry weight (□) and in µg/g TOC (■). Background concentrations (dotted line) are given in µg/g TOC.

Assuming a constant pool of refractory TFA that is represented as background concentration in the deeper part of the sediment (Fig. 4.2), we calculated reaction rate constants for the degradation of the labile fraction of TFA (labile FA = TFA – refractory FA). These values were up to 2.8 times higher (data not shown) than those of the bulk TFA pool, but still much lower than the reactivities reported by Canuel and Martens (1996) for freshly deposited FA. In a study on lipid degradation in the upper 2 cm of a Black Sea sediment, Sun and Wakeham (1994) applied two different models to estimate reaction rate constants. The one-component model assuming a single pool of equal reactivity yielded a *k*-value of 0.039 yr^{-1} for TFA degradation, the two-component model based on a labile and a refractory pool yielded a *k*-value of 0.048 yr^{-1} for the degradation of labile FA. Both rate constants fall towards the lower end of values observed off Chile, partly reflecting the sediment age (2 cm correspond to a time span of >100 years), but probably also a result of differences in depositional conditions, e.g. lower primary productivity, greater water depth, and permanently anoxic water column at the Black Sea site.

In the absence of oxygen a contribution of bioturbating organisms to organic matter degradation can be excluded. Bioturbation supports degradation both directly by active consumption of sedimentary organic carbon and indirectly by stimulating microbial activity (Aller 1982), and thus might effectively increase degradation rates. On the other hand, sediment mixing accompanied with bioturbating activity attenuates down-core changes in concentration profiles, which might be interpreted as reduced reactivity of a given compound.

Fatty acid composition

We identified FA in the range C_{12} to C_{28} and 17β(H),21β(H)-bishomohopanoic acid. At the sediment surface the composition of the FA pool was similar to that reported in previous studies on sediments from the deep Equatorial Pacific Ocean (Wakeham et al. 1997a) and the Peruvian upwelling region (Smith et al. 1983b; McCaffrey et al. 1989), with 16:0 (16-20% TFA), 16:1ω7 (10-23% TFA), and 18:1ω7 (8-15% TFA) being the major individual FA. At greater sediment depth (18-20 cm), 16:0 (25-31% TFA), 14:0 (9-11% TFA), and 18:0 (5-7% TFA) dominated the TFA pool. All in all, there were no major compositional differences between the two investigated areas off Antofagasta and off Concepción.

The individual FA were grouped in five classes:

1) **m**id-**c**hain saturated *n*-**FA** (MC-FA): chain-length C_{12}-C_{20}
2) **l**ong-**c**hain saturated *n*-**FA** (LC-FA): chain-length C_{21}-C_{28}
3) **m**ono**u**nsaturated *n*-**FA** (MUFA): 16:1, 18:1, and 24:1
4) **p**oly**u**nsaturated *n*-**FA** (PUFA): 20:5, 20:4, and 22:6
5) bacterial FA: branched-chain (*iso* and *anteiso*, 10-me-16:0) and 17β(H),21β(H)-bishomohopanoic acid

The relative contributions of the different compound classes to the TFA pool are illustrated in Fig. 4.3.

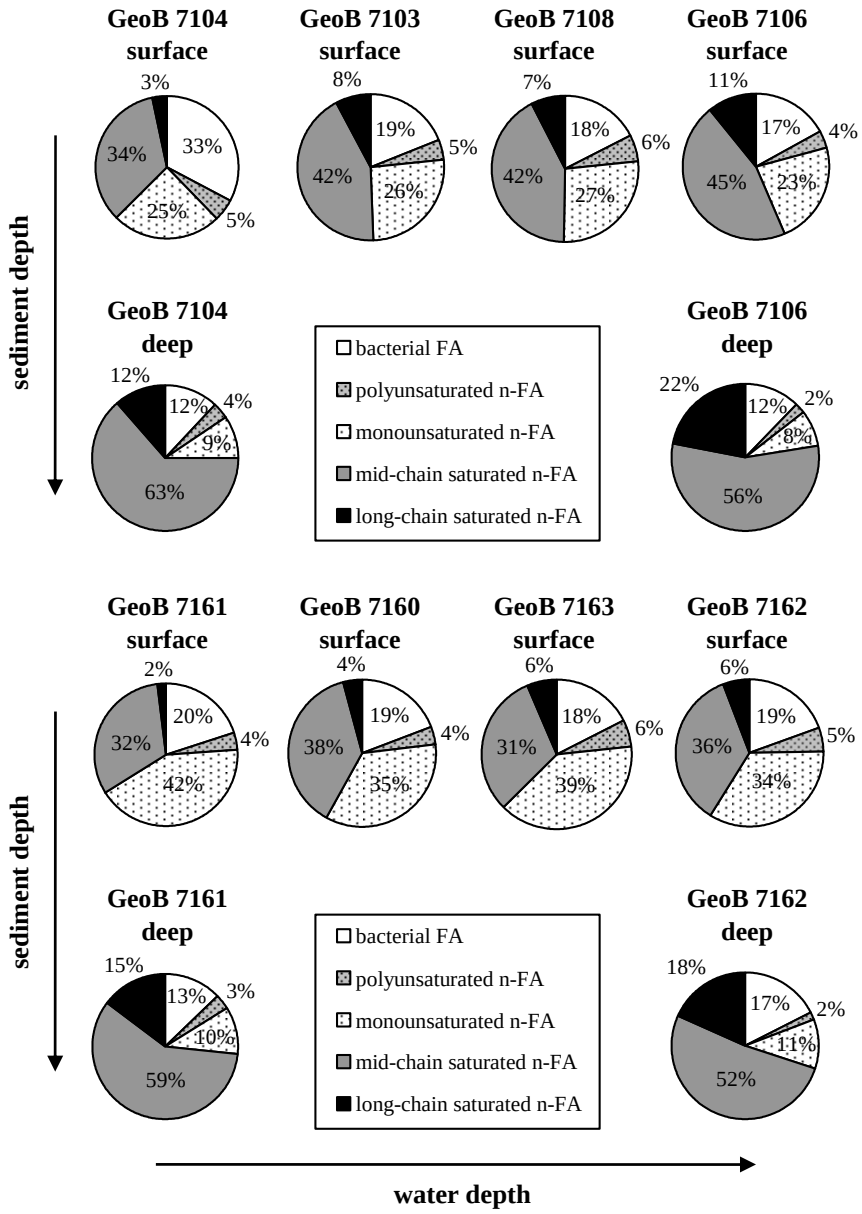

Figure 4.3. Composition of the fatty acid pool at the sediment surface (0-1 cm) and at 18-20 cm sediment depth. See text for group assignments.

Saturated n-fatty acids. Independent of chain-length the relative concentrations of all saturated *n*-FA increased with increasing water depth and increasing sediment depth (Fig. 4.3). Whereas MC-FA are mostly unspecific, i.e. derive from various sources, LC-FA are widely used as an indicator for land plant detritus (e.g. Meyers 1997). Assuming a uniquely allochthonous source of the LC-FA, the observed relative increase with ongoing degradation in water column and sediment reflects a preferential preservation of terrestrial FA as it has previously been reported (e.g. Haddad et al. 1992; Meyers and Eadie 1993; Canuel and Martens 1996; Camacho-Ibar et al. 2003). The increasing fraction of MC-FA however, can also be explained by in-situ production of sedimentary organisms (Cranwell 1984; Gong and Hollander 1997).

The carbon isotopic composition of individual FA allows for a more detailed source assignment. In most samples, LC-FA (Fig. 4.4, open symbols) were only slightly depleted in ^{13}C compared to MC-FA (black symbols) and/or bacterial FA (gray symbols), indicating that the LC-FA were at least partly derived from marine or bacterial rather than from terrestrial sources. A predominantly non-terrestrial source of the FA is in accordance with source assignments based on bulk compositional parameters like C/N-ratio and $\delta^{13}C$ of TOC (Niggemann et al., chapter 2).

Terrestrial LC-FA of C_3-plants fall in the range -35‰ to -30‰ PDB (Naraoka and Ishiwatari 2000). Assuming an isotopic composition for marine material given by the average $\delta^{13}C$ of the most abundant MC-FA (14:0, 16:0, and 18:0) and considering a terrestrial end-member with an average $\delta^{13}C$ of -32.5‰, we calculated the fraction of terrestrially derived LC-FA (Tab. 4.3). This fraction was higher for the sediments at 36°S than at 23°S, in accordance with the lack of terrestrial organic carbon sources off Northern Chile. Teece et al. (1999) noted that isotopically depleted FA may be falsely attributed to a terrestrial origin when a possible bacterial contribution is ignored. The marine end-member assumed for our estimates includes isotopic shifts attributable to secondary production as an admixture of FA from bacteria should affect the MC-FA to a similar degree as the LC-FA. On the other hand, an admixture of LC-FA from C_4-plants would shift the isotopic composition of the LC-FA pool to less negative values. Organic material of C_4-plants is on average 13‰ less depleted in ^{13}C than that of C_3-plants (Meyers 1994) and as C_4-plants are adapted to hot dry climates they might be abundant in the desert region at 23°S.

At GeoB 7104, the ranges of $\delta^{13}C$ for MC-FA and LC-FA fell closely together throughout the core (Fig. 4.4b) and the maximum terrestrial contribution estimated was 24% at 2-3 cm depth (Tab. 4.3). Down-core, most FA became enriched in ^{13}C, only the isotopic

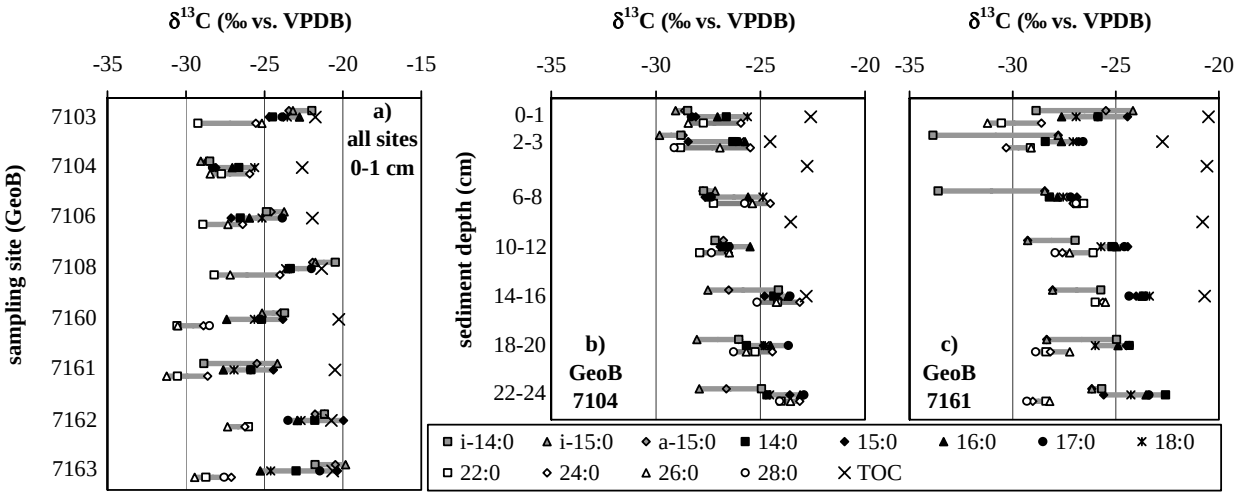

Figure 4.4. Carbon isotopic composition ($\delta^{13}C$) of individual fatty acids: a) at the sediment surface (0-1 cm) of all sites, b) down-core profile at GeoB 7104, c) down-core profile at GeoB 7161. Grey bars mark the range of grouped FA (bacterial, MC, LC). $\delta^{13}C$ of TOC (from Niggemann et al., chapter 2) is given for comparison.

composition of some bacterial FA did not follow this trend (Fig. 4.4b). These findings are in accordance with laboratory studies showing a ^{13}C enrichment for individual FA during decomposition of up to 7‰ relative to the algal input (Sun et al. 2004), and a similar ^{13}C enrichment accompanying diagenetic changes of plant derived *n*-alkanes (Nguyen Tu et al. 2004). The ^{13}C depletion of bacterial FA deeper in the core is consistent with a contribution of isotopically light FA from secondary production under anaerobic conditions (Teece et al. 1999). Generally, the narrow ranges of isotopic composition are consistent with a reworked state of the organic material at GeoB 7104.

At GeoB 7161 (Fig. 4.4c), the light isotopic composition of *i*-14:0 (-39.9‰ at 6-8 cm) might point to a contribution from chemoautotrophic bacteria using ^{13}C depleted carbon derived from remineralization processes in the sediment (Freeman et al. 1990; Freeman et al. 1994; Cowie et al. 1999). Autotrophy is likely to occur in sediments with high organic carbon degradation rates and Ferdelman et al. (1997) observed high numbers of autotrophic acetogenic bacteria in shelf sediments off central Chile. At GeoB 7161 bacterial FA became less depleted in ^{13}C deeper in the core, which is in accordance with elevated sulfate reduction rates being limited to the mixed layer (Niggemann et al., chapter 2).

The isotopic ranges of LC-FA and MC-FA were clearly separated throughout the core, with LC-FA being on average 1.8‰ to 5.3‰ lighter than MC-FA. The estimated contribution of terrestrial LC-FA is given in Table 4.3. From these percentages we calculated depth profiles of terrestrial and non-terrestrial LC-FA at GeoB 7161 (Fig. 4.5). According to our

source assignments terrestrial LC-FA were replaced by non-terrestrial LC-FA during degradation in the upper 0-8 cm. This implies in situ production of ^{13}C enriched LC-FA which in turn is inconsistent with a ^{13}C depletion relative to the carbon source expected for FA derived from secondary production (Teece et al. 1999). Our approach neither considers changes in the isotopic composition of the end-members that occur during diagenesis as the residual FA pool becomes less depleted in ^{13}C (Sun et al. 2004), nor those that might coincide with changes in sediment input over time. Below 10 cm, corresponding to the lower boundary of the mixed layer, non-terrestrial LC-FA decreased (Fig. 4.5), indicating that degradation was more effective than production, whereas terrestrial LC-FA slightly increased. This increase might be explained by changes in sediment deposition since sediment texture (Niggemann et al., chapter 2; Thamdrup and Canfield 1996) and inorganic composition (P. Böning, personal communication) show clear differences between the upper ~15 cm and the lower part of the sediments deposited at this site.

Table 4.3. Average isotopic composition of LC-FA (22:0, 24:0, 26:0, 28:0) and MC-FA (14:0, 16:0, 18:0) and estimated contribution of LC-FA derived from terrestrial sources.

station	sediment depth (cm)	average $\delta^{13}C$ LC-FA (‰)	average $\delta^{13}C$ MC-FA (‰)	terrestrial LC-FA[a] (% LC-FA)
GeoB 7103	0-1	-26.7	-23.6	34
GeoB 7104	0-1	-27.4	-26.4	15
GeoB 7106	0-1	-27.5	-25.9	25
GeoB 7108	0-1	-26.5	-23.5	33
GeoB 7160	0-1	-29.6	-26.1	55
GeoB 7161	0-1	-30.1	-26.8	58
GeoB 7162	0-1	-26.5	-22.5	41
GeoB 7163	0-1	-28.2	-24.3	48
GeoB 7104	2-3	-27.6	-26.0	24
GeoB 7104	6-8	-25.7	-26.0	0[b]
GeoB 7104	10-12	-27.1	-26.3	12
GeoB 7104	14-16	-24.2	-24.1	1
GeoB 7104	18-20	-25.4	-25.0	6
GeoB 7104	22-24	-23.7	-24.1	0[b]
GeoB 7161	2-3	-29.5	-27.7	38
GeoB 7161	6-8	-26.9	-27.9	0[b]
GeoB 7161	10-12	-27.2	-25.3	27
GeoB 7161	14-16	-25.7	-23.6	24
GeoB 7161	18-20	-28.2	-25.1	42
GeoB 7161	22-24	-28.7	-23.5	58

[a]assumed terrestrial end-member of -32.5‰, [b]MC-FA more depleted in ^{13}C than LC-FA

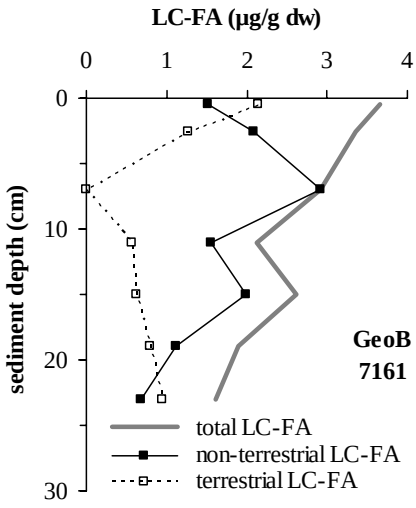

Figure 4.5. Down-core profiles of summed up LC-FA and estimated contribution of marine and terrestrial LC-FA at GeoB 7161 in µg/g dry weight. LC-FA included are 22:0, 24:0, 26:0, and 28:0.

Unsaturated n-fatty acids. Monounsaturated *n*-FA were highly abundant in all investigated surface sediments (Fig. 4.3). 16:1ω7 (40-54%), 18:1ω7 (33-36%), and 18:1ω9 (10-23%) accounted for most of this compound class, whereas 24:1 (0-2%) was a minor contributor. C_{16} and C_{18} MUFA are common in algae (e.g. Volkman et al. 1980b; Volkman et al. 1989), bacteria (e.g. Volkman et al. 1980b), zooplankton (e.g. Lee et al. 1971), and benthic fauna (Farrington et al. 1973). 24:1 might be of zooplanktonic origin as it accumulates in sinking particles in mid-water depth (Wakeham et al. 1997a). In accordance with observations of earlier studies (e.g. Haddad et al. 1992; Sun and Wakeham 1994; Canuel and Martens 1996; Sun et al. 1997), the fraction of MUFA decreased with increasing sediment depth (Fig. 4.3) pointing to a generally more labile character of these compounds compared to their saturated relatives.

Polyunsaturated *n*-FA are major components of phytoplankton (e.g. Volkman et al. 1989; Wakeham 1995), but also common in zooplankton (Lee et al. 1971), benthic fauna (Farrington et al. 1973), and some, mostly extremophilic, bacteria (Russell and Nichols 1999). In the sediments investigated in this study PUFA made up 4-6% of TFA at the sediment surface and accounted for 2-4% of TFA deeper in the sediment (Fig. 4.3). PUFA are highly abundant in fresh plankton material and rapidly lost with ongoing degradation in water column and sediment (e.g. Wakeham et al. 1997a; Budge and Parrish 1998). We therefore conclude that most of the originally produced PUFA were lost before the particles reached the sediment.

Bacterial fatty acids. *Iso*- and *anteiso*-FA are abundant constituents of bacteria and commonly ascribed to bacterial sources (Parkes and Taylor 1983; Kaneda 1991), although they are not unique to bacteria and not all bacteria produce them. In the investigated sediments *a*-15:0 was the predominant branched FA, accounting for 17-43% of all bacterial FA.

10-methyl-16:0 was especially abundant at the sediment surface of GeoB 7104 and in the mixed layer of GeoB 7161, making up 10-11% and 22-31% of all bacterial FA, respectively. These two sites were located within the actual depth of the OMZ and showed the highest sulfate reduction rates of the respective transect (Niggemann et al., chapter 2). As 10-methyl-16:0 has been reported for sulfate- and iron-reducing bacteria of *Desulfobacter*- and *Geobacter*-species (Taylor and Parkes 1983; Lovley et al. 1993; Zhang et al. 2003), it is likely that *Desulfobacter* accounted for at least part of the organic carbon remineralization coupled to sulfate reduction in these sediments. Thamdrup and Canfield (1996) report the dominance of sulfate- and iron-reduction in shelf and slope sediments off central Chile. The general occurrence of 10-methyl-16:0 in the sediments investigated in our study indicates that *Desulfobacter*- and/or *Geobacter*-species might be involved in either of these processes.

17β(H),21β(H)-bishomohopanoic acid is an early diagenetic product of bacteriohopanetetrol common in bacterial membranes (Ourisson et al. 1984; Rohmer et al. 1984) and the most abundant hopanoic acid in recent and ancient sediments (Farrimond et al. 2002). 17β(H),21β(H)-bishomohopanoic acid made up 2-33% of all bacterial FA, and was least abundant in the mixed layer of GeoB 7161 and most abundant in the deeper part of GeoB 7104. Its carbon isotopic composition ranged from -28.5‰ to -21.3‰, being on average less depleted in ^{13}C (-24.0‰±2.0‰) than branched FA (-26.1‰±3.0‰). Gong and Hollander (1997) found light isotopic compositions of up to -45‰ and proposed an autotrophic origin for sedimentary 17β(H),21β(H)-bishomohopanoic acid. For recent sediments from the open Pacific Ocean, Naraoka et al. (2000) reported $\delta^{13}C$-values ranging from -23.8 to -19.4‰ and suggested production by heterotrophs using marine organic carbon. Based on the similar isotopic composition of all bacterial FA in our study, we also assume a non-autotrophic source for 17β(H),21β(H)-bishomohopanoic acid.

Together the bacterial FA accounted for 17-20% of TFA in the surface sediments, except at GeoB 7104 where they made up 33% of TFA (Fig. 4.3). The high bacterial contribution at this site from the OMZ might indicate intense bacterial reworking favored by the absence of grazing organisms. A higher contribution of bacterial FA to the sedimentary

organic carbon pool of anoxic sediments was also reported for the Arabian Sea, where branched 15:0 and 17:0 were enriched in surface sediments from the OMZ compared to sediments outside the OMZ by a factor up to 3 (Schulte et al. 2000). In sediments from the anoxic depocenter of the Santa Monica Basin, bacterial FA (including odd-numbered *n*-FA in the range C_{12}-C_{21}) accounted for ~40% of TFA at the sediment surface, whereas in the sediment from the oxic periphery this fraction was only ~20% (Gong and Hollander 1997).

The fraction of bacterial FA slightly decreased with increasing water depth and was generally less abundant deeper in the sediment (Fig. 4.3), indicating net loss of bacterial FA with ongoing degradation. The wide range of percentages bacterial FA make up of TFA (Fig. 4.3) together with the wider range of carbon isotopic composition (Fig. 4.4) partly reflect the high dynamic of this FA pool. Sedimentary bacterial biomass comprises both bacterioplankton that deposited from the water column and biomass that is produced in-situ by sedimentary bacteria. The FA pool of surface sediments from Chesapeake Bay contained 4-22% branched FA and displayed seasonal variations of up to 62% (standard deviation) at individual sites (Zimmerman and Canuel 2001).

Reactivity of individual fatty acids

The reactivities of individual FA showed the same site distribution as the reactivities calculated for the TFA pool, with highest *k*-values at GeoB 7103 and lowest at GeoB 7108 (Tab. 4.4). The calculated reaction rate constants fall in between the lower range of values reported for sediments from the Black Sea (Sun and Wakeham 1994), from Buzzard Bay (Farrington et al. 1977), and from the Northern Gulf of California (Camacho-Ibar et al. 2003), and the higher values observed in short-time studies for <1 year by Canuel and Martens (1996) and Sun et al. (1997) and for about 10 years by Haddad et al. (1992). The order of reactivity observed off Chile and the distribution pattern shown in various studies show that like the TFA reactivity, individual FA reactivity decreases with increasing time since deposition (Tab. 4.4).

To account for differences in initial FA composition and the effects of uncertainty in age assignments, we calculated relative reactivities for the individual FA at each site. Using this approach we could also include data of GeoB 7104 where sediment age was not available. At most sites PUFA were the most reactive compounds, 20:5 at GeoB 7103, GeoB 7108, GeoB 7161, and GeoB 7162, 20:4 at GeoB 7163, and 22:6 at GeoB 7160. At GeoB 7104

(*i*-15:0) and GeoB 7106 (*i*-17:0), bacterial FA displayed the highest *k*-values. Averaged relative reactivities of all sites showed the expected order with PUFA being the most and LC-FA being the least reactive compounds (Fig. 4.6). The wide range of reactivities observed for individual MC-FA, MUFA, and bacterial FA reflects the combination of degradation and production in the sediments. The effect of in situ production is most strongly expressed at GeoB 7104 where high concentrations of bacterial FA at the sediment surface constitute a pool of highly reactive compounds.

Within the different FA classes there were some general trends in reactivity. The *k*-values of individual LC-FA decreased with increasing chain length (Fig. 4.6). This finding is in contrast to results of Sun et al. (1997) who postulated that large size differences were required to see an effect of chain length on reactivity. The decrease observed in our study however, might reflect a general relation of substrate chain length and availability for bacterial metabolism (Gillan and Johns 1986). Haddad et al. (1992) argued against such a relation as they found an abrupt change in reactivity from MC-FA to LC-FA and no consistent chain length trends within either of these two compound groups. In the sediments investigated off Chile, the reactivities of MC-FA did not display a chain length pattern either, most likely due to in situ production of bacterial FA that affected the calculation of *k*-values. The generally observed lower reactivity of LC-FA compared to MC-FA that is also evident in the sediments off Chile has been attributed to an association with protecting matrices like

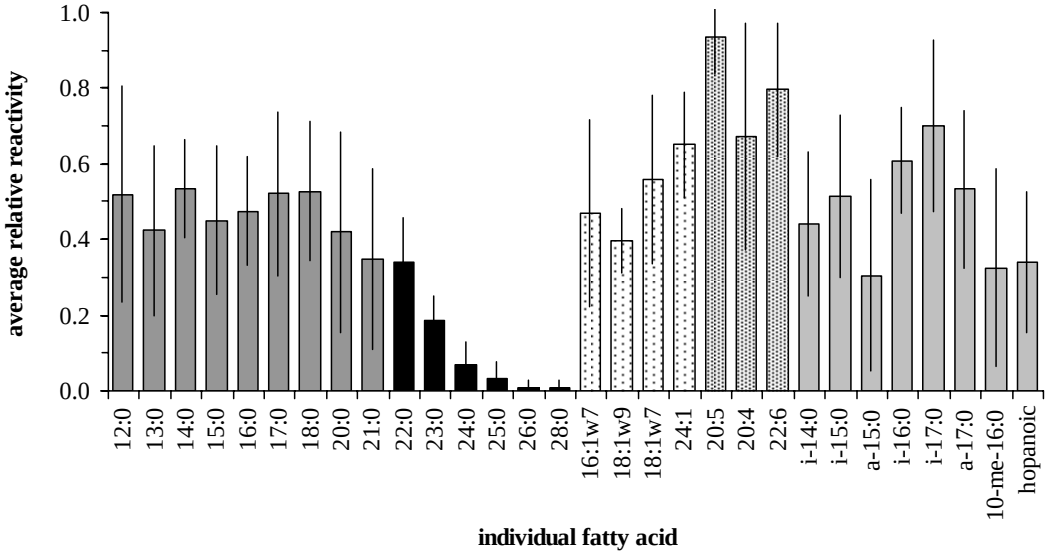

Figure 4.6. Relative reactivity of all identified fatty acids averaged over all investigated sites. Dark grey bars = mid-chain saturated *n*-FA, black bars = long-chain saturated *n*-FA, light-dotted bars = monounsaturated *n*-FA, strongly dotted bars = polyunsaturated *n*-FA, Light grey bars = bacterial FA. See text for group assignments.

Table 4.4. Degradation rate constants *k* for individual fatty acids in sediments investigated in this study and values reported in previous studies. Water depth of sampling site and considered time interval are given.

site/ oceanic region	water depth (m)	time since deposition (yr)	14:0 *k* (yr^{-1})	16:0 *k* (yr^{-1})	18:0 *k* (yr^{-1})	24:0 *k* (yr^{-1})	16:1ω7 *k* (yr^{-1})	PUFA[h] *k* (yr^{-1})	*i*-15:0 *k* (yr^{-1})
GeoB 7103	891	14	0.091	0.095	0.110	0.010	0.087	0.169	0.077
GeoB 7106	1350	20	0.052	0.041	0.049	n.d.[a]	0.024	0.055	0.036
GeoB 7108	1007	45	0.029	0.029	0.028	0.001	0.035	0.060	0.029
GeoB 7160	367	12	0.033	0.031	0.039	n.d.[a]	0.020	0.063	0.038
GeoB 7161	126	22	0.042	0.030	0.037	0.010	0.020	0.099	0.041
GeoB 7162	798	14	0.075	0.065	0.072	0.024	0.070	0.162	0.070
GeoB 7163	536	14	0.051	0.038	0.030	0.016	0.049	0.119	0.034
Gulf of California[b]	69-460	66-850	0.000-0.059	---	0.002-0.062	0.000-0.029	---	0.008-0.050[i]	0.003-0.034
Black Sea[c]	2094	up to 150	0.027	0.035	---	0.056	0.049	---	0.042[k]
Buzzard Bay[d]	17	34	0.015	0.014	0.011	---	0.086	---	---
Cape Lookout Bight[e]	<20	10	1.1	1.1	0.85	0.15	---	---	---
Cape Lookout Bight[f]	<20	0.08-0.39	2.6-14.2	1.5-11.0	8.8-18.6	1.5-2.9	1.8-18.3	2.6-13.9[j]	3.7-16.4
Lab incubations[g]	---	0.22	29-44	22-91	---	---	18-26	73	---

[a]n.d. = not determined, [b]Camacho-Ibar et al. (2003), [c]Sun and Wakeham (1994), [d]Farrington et al. (1977), [e]Haddad et al. (1992), [f]Canuel and Martens (1996), [g]Sun et al. (1997), [h]20:5 if not indicated differently, [i]combined pool of 20:5, 20:4, 22:6, and 22:5, [j]combined pool of 20:5 and 20:4, [k]combined pool of *i*- and *ai*-15:0

lignin structures or waxy coatings of higher plants (e.g. Haddad et al. 1992; Wakeham et al. 1997a). This explanation does not hold for LC-FA of algal and microbial origin and thus limited bioavailability (solubility) is a more probable reason (Gillan and Johns 1986).

Among the bacterial FA, *a*-15:0, 10-me-16:0, and 17β(H),21β(H)-bishomohopanoic acid displayed the lowest reactivity whereas *i*-16:0 and *i*-17:0 showed the strongest decrease (Fig. 4.6). Different reasons account for the low reactivity of individual bacterial FA. Due to their polycyclic structure hopanoids are generally more resistant to degradation than acyclic compounds (Farrimond et al. 2002). Most probably 10-me-16:0 is produced in situ by sulfate- and/or iron-reducing bacteria (see above). Accordingly, FA with relatively low *k*-values like *a*-15:0 might be major components of in situ produced bacterial biomass, whereas the ratio of production and degradation is probably lower for FA with higher *k*-values like *i*-16:0 and *i*-17:0.

Principal component analysis

Principal component analysis (PCA) has been used previously to determine factors that control the FA composition in particulate organic material, revealing factors that could be ascribed to different sources (Reemtsma and Ittekkot 1992) and environmental processes (Canuel 2001). Including parameters on bulk organic matter composition and additional lipid biomarker in a PCA, Zimmerman and Canuel (2001) were able to assess seasonal and spatial variability in the organic matter composition of surface sediments. All these studies concentrated on relatively fresh material with well preserved source information.

With ongoing degradation the fatty acid composition changes, following some general pattern. The fractions of PUFA and MUFA decrease whereas those of MC-FA and LC-FA increase (see Fig. 4.3). These trends have been reported in numerous studies (see discussion above for references) and can be used to describe the actual state of degradation of the FA pool and also the bulk organic carbon pool as FA comprise an important fraction of sedimentary organic material. PCA provides the possibility to identify individual components as well as groups of components that account for the biggest part of the total variance in a data set. As this method is based on a comparison of relative differences between concentrations of individual components in different samples, PCA has the advantage to reveal changes of minor components that might play an important role in the identification of the degradational state.

Principal components

Two factors explained 64% of the total variance of the data set. Factor 1 accounted for 48% of variance and had positive loadings for all saturated *n*-FA and negative loadings for most of the bacterial FA and MUFA (Fig. 4.7). Factor 2 accounted for only 16% of variance and had positive loadings for all PUFA and negative loadings for all LC-FA (Fig. 4.7). According to this distribution, factor 1 appears to reflect the compositional changes accompanied with diagenetic alteration that are mainly characterized by the preferential accumulation of saturated *n*-FA (most positive loadings) and preferential loss of MUFA (most negative loadings). The high positive loadings for 24:1 and 17β(H),21β(H)-bishomohopanoic acid point to a preferential accumulation of these components with ongoing degradation. We already discussed the relative stability of the hopanoid hydrocarbon skeleton and also noted the unexpected low reactivity of 24:1 compared to the other MUFA. Factor 2 might be interpreted as an indicator for the ratio of input and in situ production. PUFA commonly assigned to phytoplankton sources and 24:1 from zooplankton production were most positively loaded, together with individual bacterial FA and MC-FA. Accordingly, negative

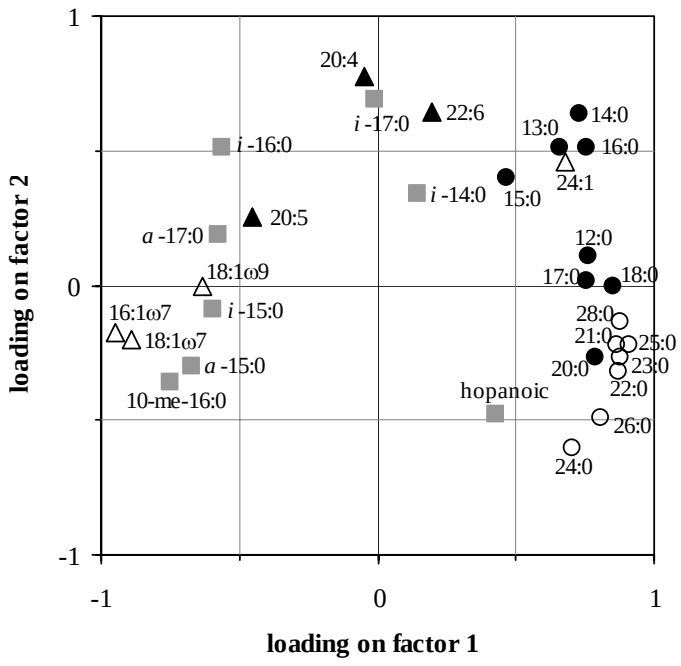

Figure 4.7. Factor loadings of individual fatty acids for the first two principal components identified by PCA. Black circles = mid-chain saturated *n*-FA, open circles = long-chain saturated *n*-FA, open triangles = monounsaturated *n*-FA, black triangles = polyunsaturated *n*-FA, grey squares = bacterial FA. See text for group assignments.

loadings on factor 2 reflect a predominance of in situ production. The negative loading for all LC-FA is consistent with our interpretation that the long-chain FA are predominantly of autochthonous origin. However, most of the variance included in the long-chain FA data was explained by changes occurring during degradation (factor 1) rather than reflecting in situ production (factor 2).

Site scores

In order to include a maximum of information on the state of degradation that is present in the FA data set we followed the same approach Dauwe and Middelburg (1998) used to derive the amino acid based degradation index. For every sample a site score (FA-Index) was calculated from the factor coefficients of factor 1, the mole percentages of the individual FA (FA_i), and its means and standard deviations (stdv) in the data set:

$$\text{FA} - \text{Index} = \sum_i \frac{\text{FA}_i - \text{mean FA}_i}{\text{stdv FA}_i} * \text{factor coefficient FA}_i \qquad (4)$$

The mole percentages of individual FA that were positively loaded on factor 1 increased with increasing FA-Index whereas those with negative loadings decreased (Fig. 4.8). Samples from the sediment surface (0-1 cm, open symbols) generally plotted in the more negative range of the FA-Index and were characterized by low mole percentages of saturated *n*-FA and high mole percentages of MUFA and selected bacterial FA. Deeper in the sediments (closed symbols), the FA-Index was higher coinciding with higher mole percentages of saturated *n*-FA and lower mole percentages of MUFA (Fig. 4.8). These trends nicely reflect the changes associated with FA degradation in the sediments and support the applicability of the FA-Index as indicator for the quality of the sedimentary organic matter.

The depth profiles of the FA-Index (Fig. 4.9) provide information on the FA biogeochemistry that is not obvious from the depth profiles of FA concentrations alone. The strong linear increase in the upper sediment layer at GeoB 7104 is consistent with the slow sediment accumulation and the lack of bioturbation reported for this site (Tab. 4.1). Ongoing degradation effectively alters the FA composition in the upper 8 cm, below the FA composition does not change markedly. At GeoB 7161, the FA-Index remains relatively constant in the upper 8 cm indicating a similar state of degradation for the FA pool in this layer corresponding to the zone of intense sediment mixing (Tab. 4.1). Below the bioturbated

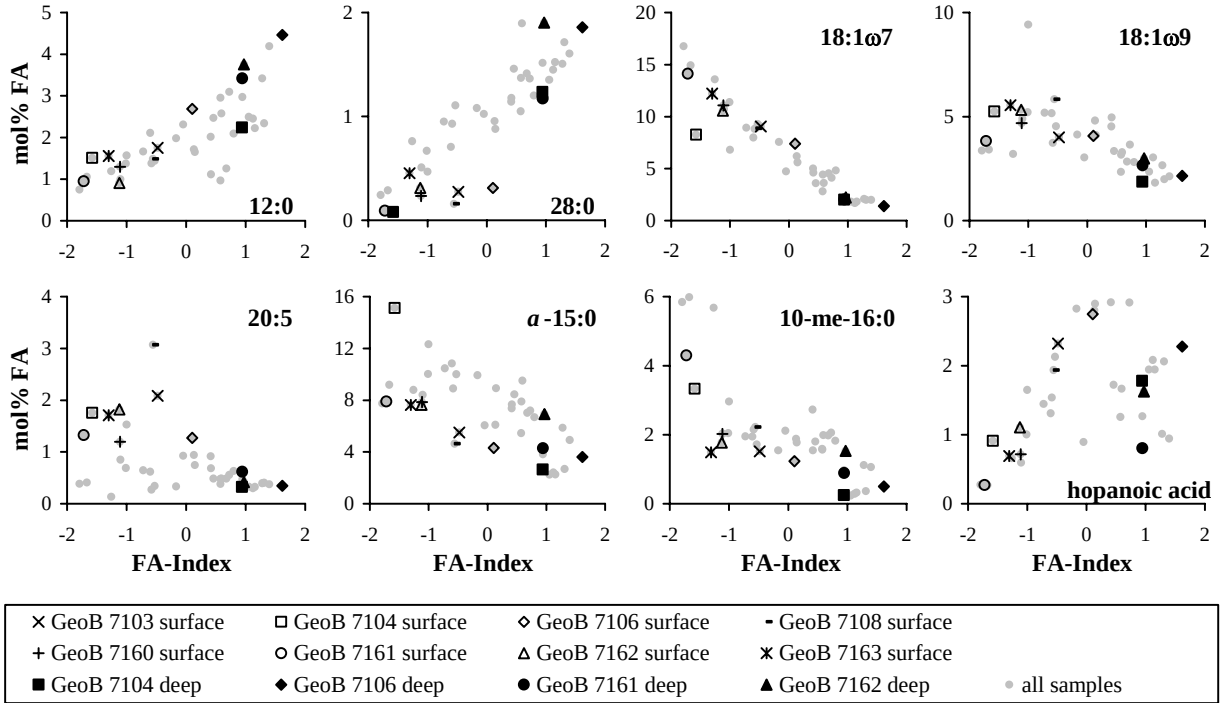

Figure 4.8. Mole percentages of selected individual fatty acids versus site scores defined as Fatty-Acid-Index (FA-Index).

zone ongoing degradation results in an increase of the FA-Index. Effects of sediment mixing on the FA-Index are less strongly expressed at GeoB 7162 than at GeoB 7161, but still there is a clear separation of lower values (<0) in the mixed layer and higher values (>0) deeper in the core. The FA-Index does not change in the upper sediment layer at GeoB 7106 as it could be expected because there was no mixed layer at this site (Tab. 4.1). The clear separation of constant values in the upper 0-3 cm and increasing values below might point to an occasional input of less degraded organic material to the upper subsurface layer. Unlike the other sites investigated in this study, GeoB 7106 displayed strong down-core scatter of TOC concentrations (Niggemann et al., chapter 2). Changes of organic carbon input over time might have been accompanied by changes in organic carbon quality. It is also possible that occasional bioturbation was not reflected in the ^{210}Pb profiles.

The FA-Index was also suitable to assess the extent of water column degradation. Values at the sediment surface (0-1 cm) increased with increasing water depth (r^2=0.90) depicting the initial degradation in the water column. Earlier studies showed that major compositional changes during water column degradation include the preferential loss of phytoplankton derived PUFA (Wakeham et al. 1997a). Including these early diagenetic changes in the data set of sedimentary FA composition used for PCA should result in high

negative loadings on factor 1 for PUFA. We therefore propose that for a more ubiquitous application of the FA-Index as quality indicator, data from a broader range of organic matter freshness should be included. On the other hand, including sediments from different depositional regions, varying water depths, bottom water oxygen contents, sedimentation rates, and sediment mixing, we could show that this approach is suitable to reveal and quantitatively assess differences in sedimentary FA composition and relate these differences to the state of organic matter degradation.

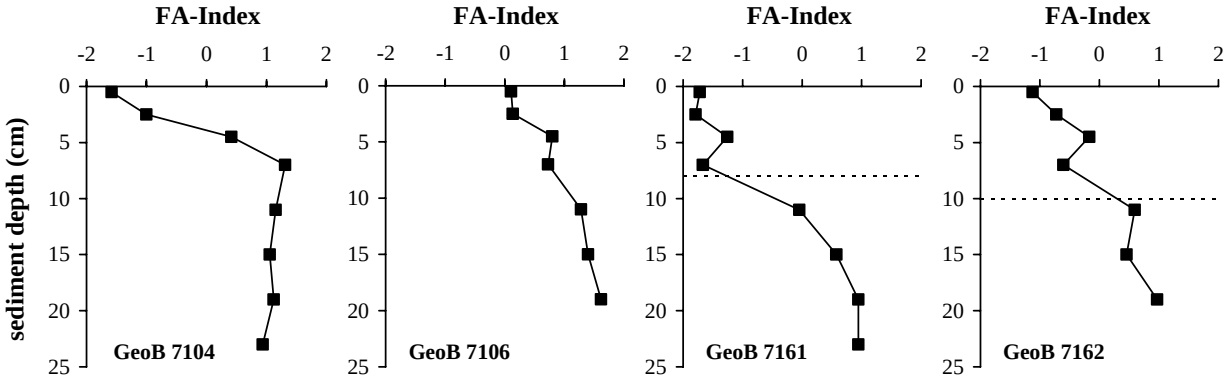

Figure 4.9. Fatty-Acid-Index (FA-Index) versus sediment depth. The mixed layer depth is plotted for GeoB 7161 and GeoB 7162.

Evaluation of the FA-Index

Numerous indicators for the quality of organic matter based on different compounds and compound classes have successfully been applied to various samples. The FA-Index showed a good correlation with other FA derived quality indicators, e.g. the fraction of TFA that is made up by long-chain fatty acids and the ratio of saturated to unsaturated FA (Fig. 4.10a/b). Both parameters increased with increasing FA-Index reflecting the preferential preservation of long-chain FA compared to TFA and of saturated FA compared to unsaturated FA, respectively. The ratio of 18:1ω7 and 18:1ω9 has been used to trace bacterial reworking of plankton material (e.g. Wakeham et al. 1997a) as 18:1ω7 is a major FA of bacteria, whereas 18:1ω7/18:1ω9 ratios of planktonic material are usually <1 (Camacho-Ibar et al. 2003). There was an inverse relation of FA-Index and 18:1ω7/18:1ω9 ratio (Fig. 4.10c) indicating that the influence of bacterial biomass was strongest in the recently deposited material near the sediment surface and that the bacterially derived 18:1ω7 was preferentially

lost down-core compared to 18:1ω9. Wakeham et al. (1997a) reported low 18:1ω7/18:1ω9 ratios for sinking organic material and high ratios for sediments but they also found a decrease from the sediment surface (>1) to 10-12 cm sediment depth (<1).

The FA-Index was linked to the bulk organic carbon composition in that a high fraction of TFA coincided with low FA-Indices indicating fresh material (Fig. 4.10d). Fatty acids compose a labile fraction of the organic carbon pool and are preferentially lost during degradation (e.g. Wakeham et al. 1997b), therefore the fraction of TOC that is made up by FA decreases with ongoing degradation.

Other frequently applied indicators for organic matter quality are less well related to the FA-Index (Fig. 4.11). The amino acid based degradation index established by Dauwe and Middelburg (1998) and Dauwe et al. (1999) showed only little down-core and inter-site variation and was not applicable to trace differences in organic matter freshness in the samples investigated in our study (Lomstein et al. subm.). Especially the high DI in the deeper part of the sediment at GeoB 7104 indicating fresh material are in contrast to the high FA-Indices found at that depth that point to highly degraded material (Fig. 4.11a). With the

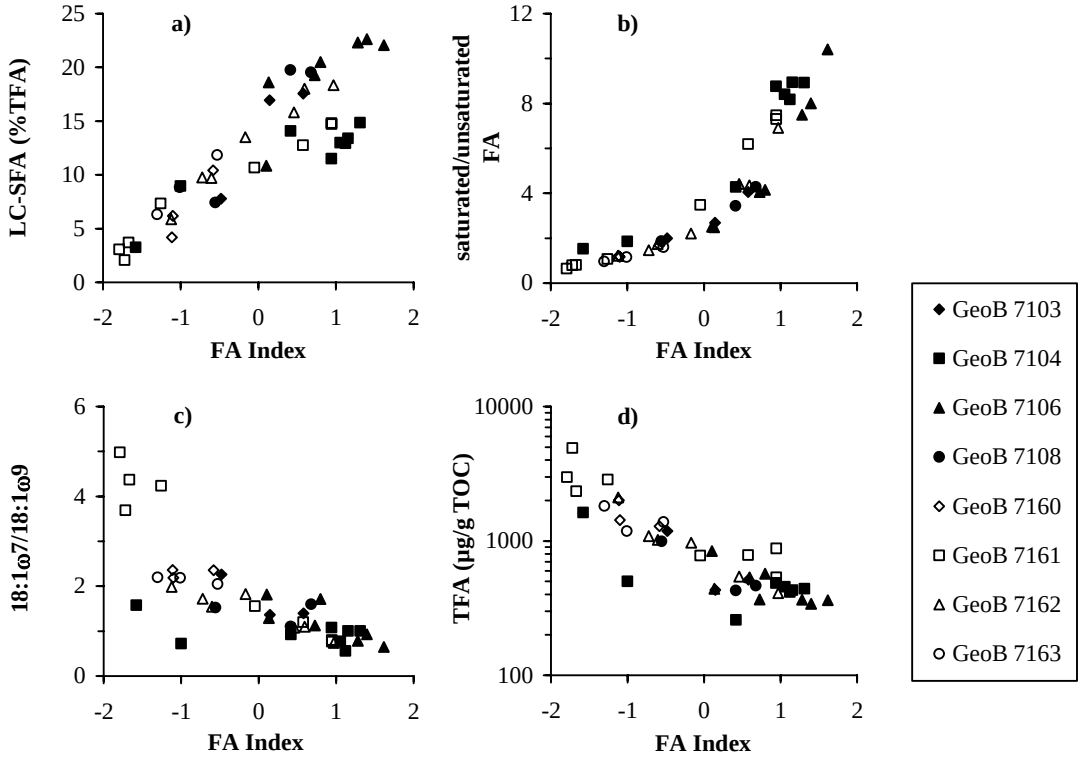

Figure 4.10. Fatty-Acid-Index (FA-Index) versus fatty acid based indicators for organic matter quality, a) long-chain saturated *n*-FA (C_{21}-C_{28}) in % total FA, b) ratio of monounsaturated (16:1ω7, 18:1ω7, 18:1ω9) and saturated (C_{12}-C_{28}) *n*-FA, c) ratio of 18:1ω7 and 18:1ω9, d) total fatty acids in µg g^{-1} TOC.

exception of very high C/N-ratios in the deeper part of GeoB 7104 and at the core end of GeoB 7161, the FA-Index was slightly correlated (r^2=0.51) with the C/N-ratio (Fig. 4.11b). All samples with a FA-Index <-0.5 were positively correlated with the Chlorin Index (r^2=0.58, Fig. 4.11c), whereas there was no relation of the two parameters at the deep sites GeoB 7106 and GeoB 7162 as well as in the deeper parts of the shallow sites GeoB 7104 and GeoB 7161. Obviously, the FA-Index is more sensitive than the Chlorin Index in detecting diagenetic alteration when the organic material reached an advanced state of degradation. Most likely this difference is due to the focus on labile degradable pigment material in case of the Chlorin Index (Schubert et al. 2005), whereas the FA-Index covers a bigger range of individual components and includes changes in molecular composition.

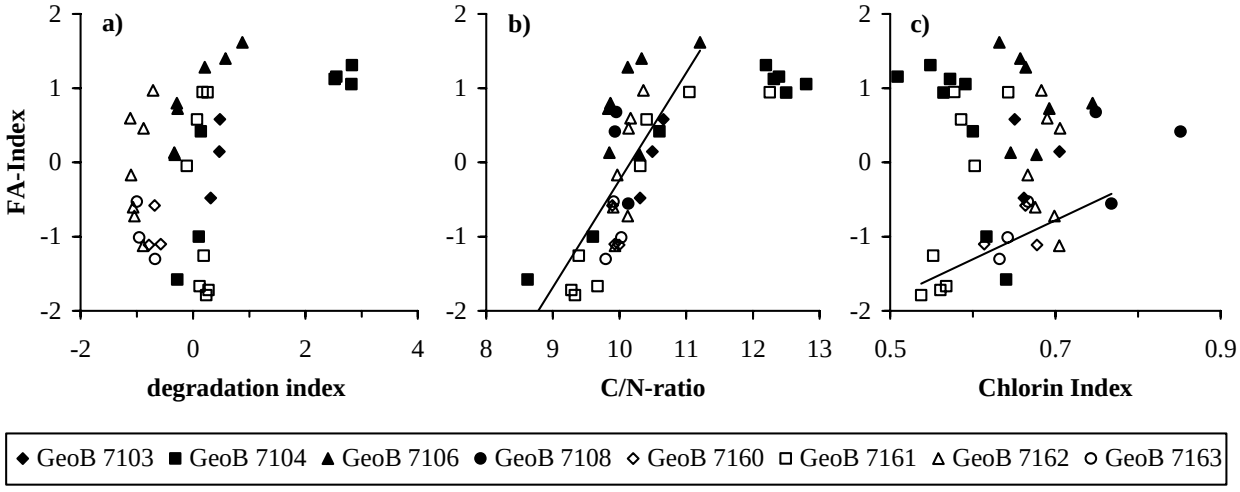

Figure 4.11. Fatty-Acid-Index (FA-Index) versus different indicators for organic matter quality, a) amino acid based degradation index (Lomstein et al. subm.), b) C/N-ratio, c) Chlorin Index (Niggemann et al., chapter 2).

CONCLUSIONS

Water depth was the most important factor determining TFA concentrations in surface sediments from the Chilean coastal upwelling region. As bottom water oxygen concentration and water depth co-varied, we were unable to identify an effect of oxygen availability on TFA concentration. There were no major compositional differences of the FA pool between the individual sites, except a significantly higher contribution of bacterial FA in the surface sediment at GeoB 7104, a site located within the actual depth of the water column OMZ.

All identified FA could be assigned to predominantly marine and bacterial sources and

the carbon isotopic composition revealed a non-terrestrial origin for most LC-FA. Reactivities of total and individual FA, calculated from the surface decrease in concentration, showed no relation to water depth but an overall decrease with time since deposition. In accordance with previous studies, PUFA were the most and LC-FA the least reactive compounds.

PCA revealed that diagenetic alteration is the main factor accounting for the variability of the FA data. The site scores (FA-Index) reflect ongoing degradation in water column and sediment, revealing changes that are not reflected in the amino acid based DI and being more sensitive than the C/N-ratio and the Chlorin Index that focuses on the pigment pool.

Acknowledgements. We thank the officers, crew, and shipboard scientific party of RV Sonne cruise SO-156 for their help and cooperation, particularly Dierk Hebbeln (University of Bremen) for logistical support. We are grateful to Gabriele Klockgether (MPI Bremen) for sampling during leg 1 and help in the home laboratory. Furthermore, we thank Bente Aa. Lomstein (University of Aarhus) for fruitful discussions on PCA. This work was part of the project PUCK (Interrelationships between productivity and environmental conditions along the Chilean continental slope, grant 03G0156A) supported by the BMBF (Federal Ministry of Education and Research, Germany). Further support was given from the Max Planck Society, Germany.

Chapter 5

Sources and fate of amino sugars in coastal Peruvian sediments

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submitted to *Limnology and Oceanography*

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ABSTRACT

Amino sugars are involved in the marine carbon and nitrogen cycles and comprise an important fraction of marine organic matter (OM). However, existing information on abundance and distribution of these compounds in marine sediments is scarce. Three sediment cores (<50 cm) from the coastal region off Peru were investigated for glucosamine (GlcN), galactosamine (GalN), mannosamine (ManN), and muramic acid (MA). The sum of the four amino sugars accounted for 1.0-2.4% of organic carbon and 1.5-3.9% of nitrogen in the sediments. Down-core decreasing concentrations indicated preferential degradation of amino sugars compared to bulk sedimentary OM. Constantly high concentrations of refractory OM depositing at a site from the oxygen minimum zone were related to an accumulation of recalcitrant bacterial biomass. GlcN (44-56 mol%) and GalN (33-42 mol%) were the dominant amino sugars in all investigated samples, ManN (6-14 mol%) and MA (1-5 mol%) were less abundant. MA was predominantly associated with cell wall remains rather than living bacteria, since bacterial abundances estimated based on MA concentrations were up to 500 times higher than cell counts reported for sediments from this area. GlcN/GalN-ratios (1.1-1.7) indicated that chitin, a polymer of GlcN, was not a major contributor to the amino sugar pool of the investigated sediments. Likewise, GlcN/MA-ratios (13-68) argued against a predominant role of peptidoglycan, which exhibits a 1:1-ratio. Specific sources for the majority of sedimentary amino sugars remain unidentified. However, similar amino sugar compositions observed in the sediments and the close association of GlcN and GalN indicate a homogenization during OM degradation, which is interpreted as an imprint of bacterial OM.

INTRODUCTION

Amino sugars constitute an important fraction of living and dead marine organic material (OM). They are widely distributed as building blocks of abundant biopolymers, particularly glucosamine (GlcN) in chitin, a structural polymer in many marine invertebrates, fungi, and algae (Gooday 1990), and GlcN and muramic acid (MA) in peptidoglycan, a major constituent of bacterial cell walls (Madigan et al. 2000). Amino sugars are derivatives of monosaccharides with one hydroxy- being substituted by an amino- functional group. As nitrogen-containing organic compounds amino sugars are involved in both, the marine carbon as well as the marine nitrogen cycle.

Most studies on amino sugars, also denoted as hexosamines, in the marine realm were limited to the analysis of GlcN and galactosamine (GalN) (Ittekkot et al. 1984a, b; Müller et al. 1986; Haake et al. 1993; Gupta et al. 1997; Dauwe and Middelburg 1998; Jennerjahn and Ittekkot 1999; Jennerjahn et al. 1999; Gupta and Kawahata 2000). Ratios of GlcN and GalN have been used to identify OM sources, with high values being characteristic for high abundances of chitin-rich zooplankton (e.g. Müller et al. 1986; Gupta and Kawahata 2000). Due to their association with structural polymers, amino sugars are on average more stable than amino acids (Baas et al. 1995; Nagata et al. 2003), and THAA/THHA-ratios ((total hydrolysable amino acids)/(total hydrolysable hexosamines)) have successfully been applied as an indicator for OM freshness, with higher values indicating fresh and lower values more degraded material (e.g. Gupta and Kawahata 2000).

Recently, additional data are available on abundance and distribution of mannosamine (ManN) and muramic acid (MA) in marine OM, but this information is mostly limited to particulate (POM) and dissolved OM (DOM) in the water column (Kaiser and Benner 2000; Benner and Kaiser 2003). Relatively low MA concentrations in marine DOM indicate that peptidoglycan remnants are minor constituents of this pool. In contrast, abundance and surprisingly constant proportions of GlcN and GalN indicate a major prokaryotic source of marine DOM.

In soil science amino sugars are routinely used to characterize microbial community structures, namely to estimate relative contributions of fungi and bacteria (e.g. Kandeler et al. 2000; Amelung 2001; Glaser et al. 2004). Amino sugars are stabilized in soils and persist after the death of cells, they therefore provide an indicator for microbial necromass rather than for living biomass (Glaser et al. 2004).

Historically, there have been attempts to establish MA analysis for estimating bacterial abundances in marine POM and sediments (e.g. King and White 1977; Moriarty 1977; Mimura and Romano 1985) and some studies revealed a good correspondence of estimated and counted bacterial numbers (e.g. Mimura and Romano 1985). However, using MA concentrations to derive bacterial numbers is based on the assumption that peptidoglycan of dead cells is rapidly degraded, a prerequisite that might not hold particularly for anoxic environments, where meiofaunal grazing is inhibited (Gillan and Johns 1986).

Sediments from the coastal upwelling region off Peru deposit under oxygen-deficient to anoxic conditions and dead bacterial biomass has been proposed to accumulate with ongoing burial (Parkes et al. 1993). The sediments investigated in this study are characterized by high organic carbon concentrations, a dominance of marine OM originating from the

highly productive overlying water masses, and high rates of bacterial remineralization which also indicate high abundances of active sedimentary bacteria (Niggemann et al., chapter 3). For the purpose of this study we chose sediments that represent different depositional conditions with respect to water depth, bottom water oxygen concentration, and physical hydrographical impact (Reinhardt et al. 2002; Böning et al. 2004). As sedimentation rates are typically high in the investigated region (Reimers and Suess 1983), the sediments provide a high resolution record of OM input and OM degradation.

The aim of this study is (1) to broaden the data base on abundance and distribution of amino sugars in marine sediments, (2) to evaluate the potential of amino sugars to trace sources and diagenetic changes of marine OM, and (3) to relate muramic acid and peptidoglycan concentrations in sediments to bacterial bio- and/or necromass.

MATERIAL AND METHODS

Sampling

Sampling was carried out during RV Sonne cruise 147 in June 2000. The sampling area and the positions of the investigated sites are shown in Figure 5.1. A detailed description of the sampling area and the geochemistry of individual sites is given in Böning et al. (2004) and Niggemann et al. (Chapter 3). At the time of sampling, the oxygen minimum zone (OMZ) in the water column extended from 50-650 m and the sediment at 29MC and 71MC was covered by oxygen-depleted bottom water. 29MC represents a typical shallow near-coastal site with dominance of fresh OM, high sulfate reduction rates (SRR), and high *Thioploca* biomass. 71MC is characteristic for mud-wave field sediments that exhibit high organic carbon concentrations dominated by refractory OM. Although SRR were low at this site, high *Thioploca* biomass was observed. 81MC was chosen as a deep sea reference, with low organic carbon concentrations and dominance of altered OM. SRR were low at this site and *Thioploca* were absent.

Sediments were retrieved by multi-corer coring to keep the surface undisturbed. The sediment cores were sliced in 1 cm intervals in the upper 6 cm and in 2 cm intervals below 6 cm. Samples were transferred to clean glass-vials and frozen at -25°C immediately after sampling. The sediment samples were freeze-dried and homogenized by grinding in an agate mortar.

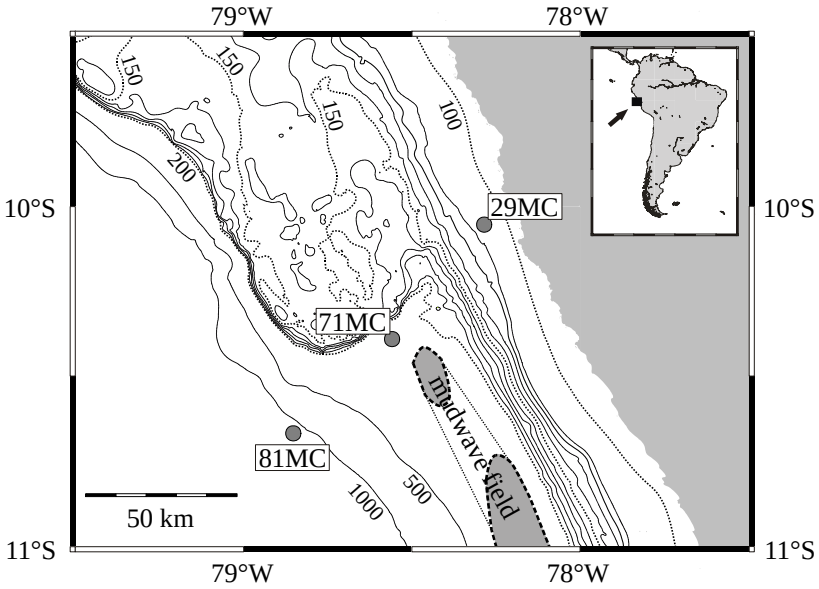

Figure 5.1. Map of investigated area with bathymetry (adopted from Reinhardt et al. 2002) and location of sampling sites 29MC (102 m water depth; 10°03.28 S, 78°17.10 W), 71MC (238 m; 10°23.42 S, 78°33.51 W), and 81MC (1278 m; 10°40.04 S, 78°51.15W).

Analyses

Total carbon (TC) and total nitrogen (TN) concentrations were determined on freeze dried samples by combustion/gas chromatography (Carlo Erba NA-1500 CNS analyzer) with a precision of ±0.7% for N and ±0.6% for C, respectively. Total inorganic carbon (TIC) was measured on a CM 5012 CO_2 Coulometer (UIC) after acidification with phosphoric acid (3 mol L^{-1}). The precision for TIC was ±0.4%. Total organic carbon (TOC) was calculated as the difference of TC and TIC. The C/N-ratio was calculated as the molar ratio of TOC and TN.

Amino sugars (glucosamine (GlcN), galactosamine (GalN), mannosamine (ManN), muramic acid (MA)) were determined following the procedure of Zhang and Amelung (1996). According to the nitrogen concentration of the sample, 50-250 mg of freeze-dried sediment was hydrolyzed with 10 ml of 6 N HCl for 8 h at 105°C. The hydrolysate was neutralized with 1.5 N KOH and desalted by dilution in methanol. Conversion of amino sugars to aldononitrile acetate derivatives was carried out according to the method of Guerrant and Moss (1984). Gas chromatographic analysis was performed on a Hewlett Packard (HP) 5890 Series II instrument equipped with a flame ionization detector and a HP5 column (50 m length, 0.32 mm I. D., 0.17 µm film thickness), carrier gas was helium. The oven temperature

program was set to an initial temperature of 120°C (held for 1 min), heating rates were 10°C min^{-1} to 250°C (2.5 min) and 20°C min^{-1} to 270°C (2 min). For quantification, the ratio of amino sugar peak and internal standard (myo-inositol) peak in the sample were compared to peak area ratios of standard samples with known concentrations.

The analysis procedure of Zhang and Amelung (1996) has been developed and approved for determination of amino sugars in soil samples. We checked by repeated dilution in methanol that the purification step was successful in removing all salts from the sediment hydrolysates. Reported recoveries of amino sugars for the applied analysis procedure are >90% for GlcN, GalN, and ManN, and >80% for MA (Zhang and Amelung 1996). Average standard deviation for duplicates in this study was 7, 10, 18, and 33% of the average for GlcN, GalN, ManN, and MA, respectively.

RESULTS

Total amino sugar concentrations

In general, amino sugar concentrations were strongly correlated with TOC and TN concentrations of the sediment samples. Total amino sugar concentrations (sum of GlcN, GalN, ManN, and MA; data not shown) were highest at 71MC (27-43 µmol gdw^{-1}), where organic carbon concentrations were significantly higher than at the other sites (Tab. 5.1). Lowest amino sugar concentrations were found at 81MC (4-9 µmol gdw^{-1}) and in the deeper part of 29MC (2-5 µmol gdw^{-1}), coinciding with comparably low TOC concentrations of 2.7-3.8%dw and 1.0-2.1%dw, respectively. As down-core changes of total amino sugar concentrations were also mostly determined by changes in TOC concentrations, data are presented as TOC- and TN-normalized amino sugar concentrations.

In all investigated samples, the four amino sugars together made up a similar fraction of TOC and TN, irrespective of water depth of the sampling site and presumed differences in the degradational state of the sedimentary OM, and accounted for 1.0-2.4% of TOC and for 1.5-3.9% of TN (Fig. 5.2). At 29MC and 81MC the percentages were highest near the sediment surface and decreased with increasing sediment depth, from 2.4 to 1.2% TOC and 3.4 to 1.5% TN at 29MC, and from 2.0 to 1.3% TOC and 3.3 to 2.1% TN at 81MC, respectively. At 71MC the percentages remained relatively constant down-core, 1.9±0.1% TOC and 3.3±0.3% TN.

Table 5.1. Concentrations of glucosamine (GlcN), galactosamine (GalN), mannosamine (ManN), and muramic acid (MA) in sediment samples. TOC concentrations and C/N-ratios are given.

Site,	TOC	C/N	Amino sugar (µmol $gTOC^{-1}$)			
Depth (cm)	(%dw)	molar	GlcN	GalN	ManN	MA
29MC, 0-1	4.8	7.0	72.3	43.4	13.7	2.1
29MC, 2-3	6.1	7.6	54.8	36.8	6.7	2.7
29MC, 4-5	6.4	7.9	57.0	47.3	7.2	1.2
29MC, 6-8	6.1	7.7	37.0	35.2	9.5	2.7
29MC, 10-12	5.1	8.2	54.1	40.6	8.5	3.6
29MC, 14-16	6.0	8.5	53.9	43.9	6.1	0.7
29MC, 18-20	4.8	8.2	51.4	37.9	6.7	2.2
29MC, 22-24	5.3	7.9	51.4	37.5	6.7	2.1
29MC, 26-28	2.1	7.9	45.6	36.1	7.0	2.1
29MC, 30-32	2.1	8.2	40.6	33.0	7.6	2.4
29MC, 34-36	2.0	7.8	36.4	30.3	6.3	2.1
29MC, 38-40	1.0	7.1	34.3	26.0	6.1	2.2
71MC, 0-1	14.3	8.7	62.9	40.3	11.6	1.9
71MC, 1-2	15.0	8.7	49.8	33.4	12.3	2.1
71MC, 2-3	16.4	9.5	54.6	36.4	12.1	1.9
71MC, 4-5	15.1	9.4	60.2	43.0	9.5	1.0
71MC, 6-8	16.8	9.3	54.3	36.6	10.8	2.1
71MC, 10-12	17.2	9.3	48.5	32.8	11.0	3.6
71MC, 14-16	16.9	9.4	48.0	34.1	9.2	3.4
71MC, 18-20	10.7	8.5	48.0	35.9	13.9	1.7
71MC, 22-24	14.3	9.0	51.0	33.2	10.1	4.5
71MC, 26-28	12.8	9.3	54.8	38.4	11.4	1.5
71MC, 30-32	12.7	9.4	47.4	35.5	11.0	1.5
71MC, 34-36	14.8	9.5	48.7	39.1	11.9	1.5
71MC, 38-40	12.3	8.5	45.6	35.0	12.1	1.4
71MC, 42-44	10.2	7.8	52.1	40.9	14.4	2.2
71MC, 46-48	13.7	8.6	60.6	42.2	8.5	1.2
81MC, 0-1	3.3	7.8	63.3	38.6	9.4	0.9
81MC, 1-2	3.4	8.8	43.8	28.7	11.2	1.9
81MC, 2-3	2.6	7.2	35.2	22.2	7.2	1.7
81MC, 4-5	2.2	7.8	53.9	35.6	5.6	1.5
81MC, 6-8	3.8	9.9	28.1	19.3	5.6	1.4
81MC, 10-12	3.0	9.0	32.1	22.0	3.6	1.4
81MC, 14-16	2.7	7.8	37.9	26.5	7.2	1.7

Individual amino sugars

Glucosamine was the most abundant amino sugar in all investigated samples (Tab. 5.1), making up 44-56 mol% of the analyzed amino sugars, followed by galactosamine accounting for 33-42 mol%. Mannosamine and muramic acid were minor contributors, making up 6-14 mol% and 1-5 mol%, respectively. Down-core and inter-core variability of all individual amino sugars partly reflected differences in TOC concentrations. TOC-normalized concentrations of GlcN and GalN were higher at 71MC (52±5 and 37±3 µmol $gTOC^{-1}$) and 29MC (49±11 and 37±6 µmol $gTOC^{-1}$) than at 81MC (42±13 and 27±7 µmol $gTOC^{-1}$). At 29MC and 81MC they decreased with increasing sediment depth, whereas 71MC revealed no down-core trend (Tab. 5.1). TOC-normalized concentrations of ManN were on average lower at 29MC (7.7±2.2 µmol $gTOC^{-1}$) and 81MC (7.1±2.6 µmol $gTOC^{-1}$) compared to 71MC (11.3±1.6 µmol $gTOC^{-1}$). At 29MC and 81MC, ManN concentrations decreased in the upper part of the sediment and remained rather constant below (Tab. 5.1). At 71MC concentrations of ManN were generally less variable, without distinct down-core trend. For MA lowest and comparably constant concentrations were found at 81MC (1.5±0.3 µmol $gTOC^{-1}$), whereas at 29MC and 71MC concentrations were higher and more scattered, 2.2±0.7 and 2.1±1.0 µmol $gTOC^{-1}$, respectively.

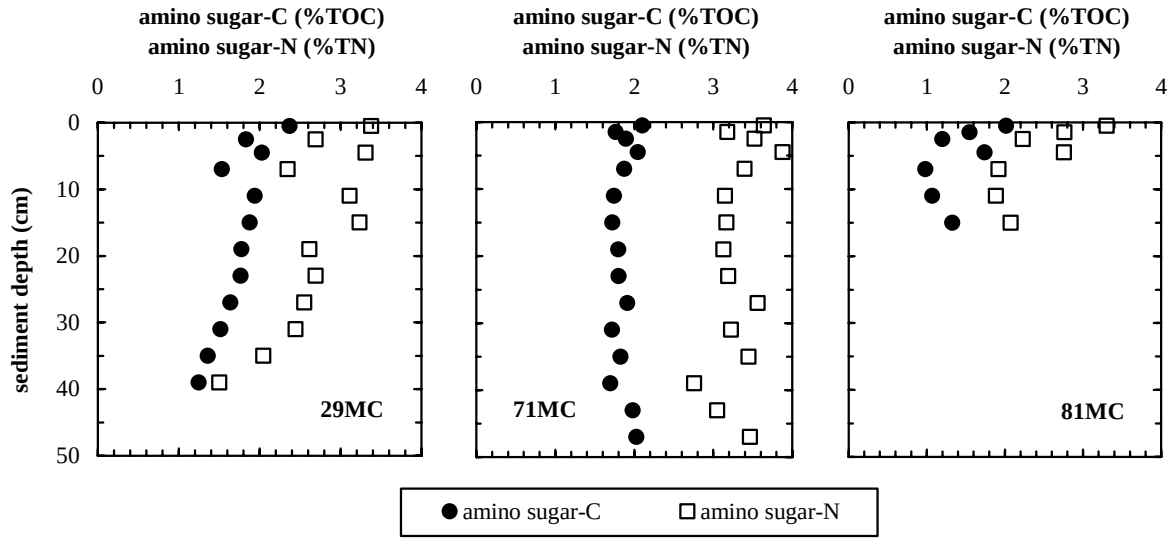

Figure 5.2. Depth profiles of amino sugar carbon (in %TOC) and nitrogen (in %TN) concentrations at 29MC, 71MC, and 81MC.

Amino sugar ratios

Molar ratios of glucosamine and galactosamine (GlcN/GalN) covered a narrow range (1.1-1.7), with an average value of 1.4±0.1 for all investigated samples (Fig. 5.3). Inter-core variations were small, average ratios for the different sites were 1.3±0.2 at 29MC, 1.4±0.1 at 71MC, and 1.5±0.1 at 81MC. At all sites, highest GlcN/GalN ratios occurred in the uppermost cm (1.7 at 29MC, 1.6 at 71MC and 81MC) and in general, GlcN/GalN ratios were higher near the sediment surface than deeper in the cores. But only at 81MC a continuous down-core decrease was observed. The molar ratios of glucosamine and mannosamine (GlcN/ManN, data not shown) ranged from 3.5 to 10.0, and showed strong scatter in the upper part of all sediment cores, whereas they distinctly decreased deeper in the cores at 29MC and 71MC. In general, GlcN/ManN ratios were higher at 29MC (6.6±1.5) and 81MC (6.2±2.2) than at 71MC (4.7±1.0). The molar ratios of glucosamine and muramic acid (GlcN/MA) fell in the range 13-68 and showed strong scatter throughout the cores (Fig. 5.3). At 29MC, the depth profile of GlcN/MA roughly followed that of GlcN/GalN. GlcN/MA ratios were on average slightly higher at 71MC (32±14) and 81MC (32±16) than at 29MC (29±16).

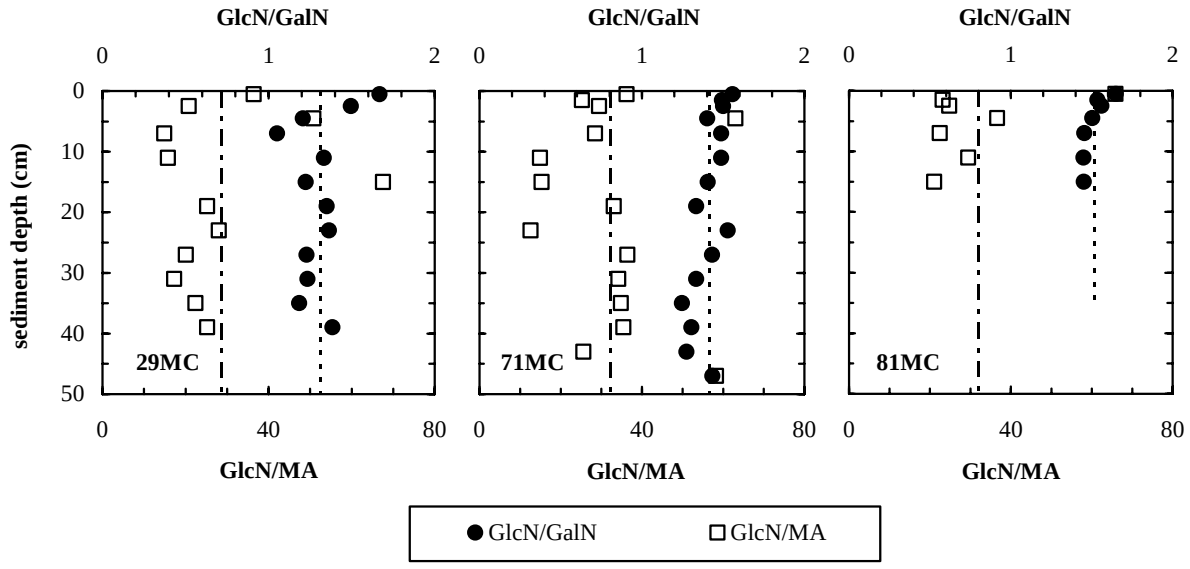

Figure 5.3. Molecular ratios of glucosamine and galactosamine (GlcN/GalN) and glucosamine and muramic acid (GlcN/MA) versus sediment depth at 29MC, 71MC, and 81MC. Dotted lines give average GlcN/GalN, broken lines average GlcN/MA-ratios at the respective sites.

DISCUSSION

Contribution of amino sugars to sedimentary organic carbon and nitrogen

The fraction of TOC and TN that is made up by amino sugar carbon and nitrogen in the sediments off Peru falls within the range of values previously reported for sediments from different oceanic regions, and various water and sediment depths (Fig. 5.4). Although most published amino sugar studies were limited to the analysis of GlcN and GalN, these two compounds provide a good estimate for the total amino sugar concentration as MA and ManN together contribute a maximum of 16% to the total amino sugar pool of sediments (this study; Liebezeit 1993) and marine POM (Benner and Kaiser 2003).

The down-core decrease of amino sugar carbon and nitrogen contributions observed at 29MC and 81MC (Fig. 5.2), indicates a preferential degradation of amino sugars compared to bulk sedimentary OM. The relatively constant concentrations at 71MC are consistent with a dominance of reworked, homogenized material at this site, and might also reflect sediment mixing either by bioturbation, or by suspension and redeposition due to exposure to bottom currents. Accordingly, amino sugar concentrations of bioturbated sediments from the North Sea also showed no down-core trend in the upper 15 cm (Dauwe and Middelburg 1998).

Over a 12 m long core from the Bransfield Strait, Liebezeit (1993) observed strong variations in the amino sugar concentration. Lower concentrations (amino sugar-C: 0.5-1.1% of TOC) coincided with turbidite sequences and most likely reflect that the turbidite OM was

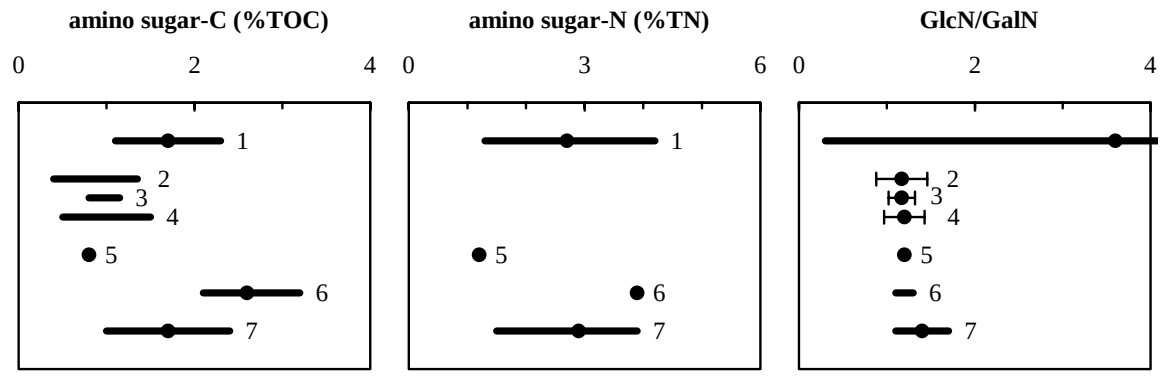

Figure 5.4. Amino sugar carbon (in %TOC) and nitrogen (in %TN) concentrations and GlcN/GalN-ratios reported for sediments from different oceanic regions and water depths. (1) Dauwe and Middelburg (1998), maximum GlcN/GalN-ratio: 16.3; (2-4) Liebezeit (1993); (5) Gupta et al. (1997); (6) Jennerjahn and Ittekkot (1999); (7) this study.

dominated by reworked material impoverished in amino sugars. As also obvious from the down-core trends at 29MC and 81MC, ongoing degradation in the sediments results in decreased amino sugar fractions (Fig. 5.2). The comparably high amino sugar concentrations at 71MC appear to be inconsistent with a reworked state of the material accumulating at this site. How can we explain this discrepancy? 71MC is located in the center of the water column oxygen minimum zone. Oxygen exposure for OM that accumulates at this site - both from pelagic sedimentation as well as laterally imported resuspended material - is limited to the short transit time from the euphotic zone to the upper boundary of the OMZ. Under oxygen deficient conditions degradation is left to anaerobic bacteria and grazing on bacterial biomass by higher organisms is limited. We therefore assume that refractory bacterial biomass makes up a significant fraction of the reworked OM accumulating at 71MC and accounts for the unexpectedly high and constant amino sugar concentrations.

Amino sugars as source and quality indicators

In the coastal upwelling region off Peru primary production rates are high year-round (e.g. Zuta and Guillén 1970) supplying a constantly high rain of fresh organic material dominated by phytoplankton detritus. In general, freshly produced OM is characterized by low amino sugar concentrations, e.g. amino sugar carbon and nitrogen account for 0.1-0.5% of TOC and 0.1-0.6% of TN in phototrophic algae, and for 0.3-1.2% of TOC and 0.3-0.9% of TN in natural populations of heterotrophic bacteria (Benner and Kaiser 2003). Higher concentrations of amino sugars in marine POM are mostly due to a contribution of chitin-rich material from zooplankton biomass. Amino sugar concentrations reported for POM from different oceanic regions and water depths are summarized in figure 5.5. High surface water productivity is reflected in lower contributions of amino sugar carbon and nitrogen to TOC and TN of bulk POM, as phytoplankton increases relative to zooplankton biomass (Müller et al. 1986). Accordingly, the contributions of amino sugar carbon and nitrogen to TOC and TN in the investigated sediments off Peru fall towards the lower range of values reported for marine POM (Fig. 5.2 and 5.5).

The molecular amino sugar composition provides further evidence that chitin was not a major contributor to the amino sugar pool in the sediments. Chitin is a polymer of GlcN and high chitin concentrations are reflected in high GlcN/GalN-ratios as reported for zooplankton-rich POM (Müller et al. 1986; Gupta et al. 1997; Gupta and Kawahata 2000). The ratios

observed in the sediments off Peru are similar to those reported for small-size, zooplankton-poor POM (Benner and Kaiser 2003), and fall within the range of values previously observed in sediments (Fig. 5.4). Slightly lower GlcN/GalN-ratios prevail in sediments from greater water depth (Liebezeit 1993; Gupta et al. 1997; Jennerjahn et al. 1999), whereas ratios >10 were found in shallow coastal waters (<5 m water depth; Dauwe and Middelburg 1998). Decreasing GlcN/GalN-ratios with increasing water depth reflect the rapid degradation of chitin in the water column. Chitin is relatively resistant to decay when complexed with protein in invertebrate cuticles (Baas et al. 1995), but once this protecting coating is lost, the polysaccharide is easily broken down by enzymatic hydrolysis (Gooday 1990). Ongoing degradation of remaining chitinaceous material might also explain the slight down-core decrease of GlcN/GalN-ratios in the sediments (Fig. 5.3).

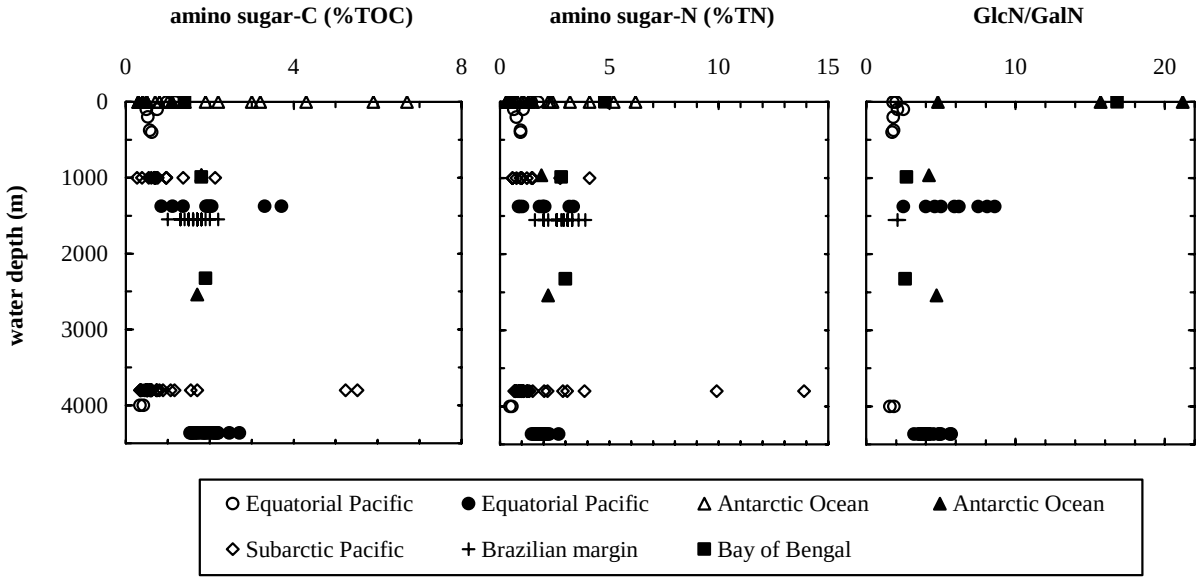

Figure 5.5. Amino sugar carbon (in %TOC) and nitrogen (in %TN) concentrations and GlcN/GalN-ratios reported for particulate organic matter (POM) from different oceanic regions and water depths plotted versus water depth. Equatorial Pacific (open circles: Benner and Kaiser 2003; closed circles: Gupta and Kawahata 2000), Antarctic Ocean (Müller et al. 1986; open triangles: 75-150 µm POM, closed triangles: >150 µm POM), Subarctic Pacific (Haake et al. 1993), Brazilian margin (Jennerjahn et al. 1999), Bay of Bengal (Gupta et al. 1997).

ManN is common in bacterial products (Kenne and Lindburg 1983) and widely distributed in membrane glycolipids as a building block of sialic acids. Reported GlcN/ManN-ratios are 2-46 for bacteria and 8-18 for algae, respectively (Benner and Kaiser 2003; Glaser et al. 2004). We can only speculate on the sources of ManN in the investigated sediments. The

high ManN concentrations at 71MC point to an association with reworked material and decreasing GlcN/ManN-ratios in the deeper part of the sediments indicate a preferential preservation during OM degradation of ManN compared to GlcN. The strong down-core decrease of ManN concentrations in the upper part at 29MC and 81MC might be explained by rapid decomposition of a highly reactive pool of ManN that either originates from freshly deposited plankton detritus or from in situ produced bacterial biomass. However, the ManN/MA-ratios ranging from 2.4 to 9.9 indicate that living bacteria which are characterized by ManN/MA-ratios of 0.6-1.6 (Benner and Kaiser 2003; Glaser et al. 2004) are not the major source of ManN in the investigated sediments.

Bacterial contribution to living and dead sedimentary OM

Based on the concentrations of MA, which occurs in a 1:1-ratio with GlcN in peptidoglycan, this bacterial cell wall polymer accounted for 4.3±1.8 mol% of the total amino sugar pool and 4.2±1.8% of total GlcN. Peptidoglycan is the only known source for MA, which therefore is a specific biomarker for bacterial cell wall material. For sediment bacteria Moriarty (1977) suggested a MA concentration of 60 nmol mgC^{-1} assuming a predominance of Gram-negative bacteria, a value similar to MA concentrations reported for cultivated soil bacteria (61±25 nmol mgC^{-1}; Glaser et al. 2004). With an average carbon content for pelagic coastal marine bacteria of 30.2 fg $cell^{-1}$ (Fukuda et al. 1998), we calculate an average bacterial MA concentration of 1.8 amol $cell^{-1}$, which is very close to MA concentrations of cultivated sediment bacteria (1.9-2.1 amol $cell^{-1}$, Mimura and Romano 1985). If all analyzed MA was associated with intact bacterial cells, the observed MA concentrations would reflect bacterial abundances of 0.02-0.79x10^{12} cells gdw^{-1}, which equals 0.04-1.34x10^{12} cells cm^{-3} wet sediment (with a dry weight/wet volume ratio of 1.7). These numbers are up to 500 times higher than bacterial counts in surface sediments off Peru (~3x10^{9} cells cm^{-3}; Parkes et al. 1993), indicating that most MA was not associated with living bacteria but with cell wall remains. Bacterial abundance estimates that are based on the non-protein amino acid D-Ala, which is also associated with peptidoglycan, came out with similar discrepancies of estimated and counted numbers (Pedersen et al. 2001; Grutters et al. 2002). Obviously, peptidoglycan persists in the sediments for a long time after the death of the cells. Hence, MA concentrations in sediments are an indicator for bacterial necromass rather than for bacterial biomass. Bacterial necromass has been suggested as a main component of refractory OM in sediments

(e.g. Parkes et al. 1993) and there is growing evidence that cell wall remains make up a significant fraction of sedimentary OM (Pedersen et al. 2001, Grutters et al. 2002). Bacterial remains and particularly peptidoglycan have also been suggested to be a major component of refractory DOM in the ocean (Boon et al. 1998; McCarthy et al. 1998; Benner and Kaiser 2003).

In living Gram-negative bacteria the majority of GlcN is not associated with peptidoglycan, and yields of MA in natural and cultivated bacterial assemblages are 2-15-fold lower than that of GlcN (Benner and Kaiser 2003; Glaser et al. 2004). High GlcN/MA-ratios should therefore be indicative for living cells, whereas a dominance of dead cells, i.e. empty cell sacks, should lower this ratio approaching the 1:1-ratio of peptidoglycan, which is presumed to be more stable than e.g. (lipo-) polysaccharides that are the main source of GlcN in living bacteria (Kenne and Lindburg 1983). Even the lowest GlcN/MA-ratios observed in this study are by far higher than the peptidoglycan ratio (Fig. 5.3), reflecting that although bacterial cell walls and their remnants make up an important fraction of sedimentary OM they account for a minor fraction of sedimentary amino sugars.

The remaining mystery of sedimentary amino sugars

So what are the main constituents comprising the sedimentary amino sugars? Obviously, the most prominent amino sugar polymers chitin and peptidoglycan cannot explain abundances and distribution of amino sugars in the investigated sediments. Low GlcN/GalN-ratios are inconsistent with chitin being a major contributor and high GlcN/MA-ratios argue against a predominant role of peptidoglycan. Further, partly due to the lack of existing data, we have no unambiguous explanation for abundance and distribution of ManN.

The interpretation of amino sugar data would profit from a more clear definition of the analytical window of amino sugar analysis. Hydrolysis conditions are optimized to maximize amino sugar yields and reported recoveries are limited to pure substances, i.e. simple biopolymers without association with protecting matrices (Zhang and Amelung 1996; Kaiser and Benner 2000). We do not know whether the hydrolysis conditions chosen completely hydrolyze all fresh OM and whether they also successfully attack refractory OM. Compound specific isotopic analysis might help to identify different pools and further elucidate the biogeochemistry of amino sugars in sediments.

In general, OM degradation appears to result in a rather homogenous amino sugar pool. Beside the narrow ranges covered by TOC- and TN-normalized sedimentary amino sugar carbon and nitrogen concentrations, the ratio of the dominating amino sugars GlcN and GalN indicates a similar composition of the altered amino sugar pool (Fig. 5.3). A close association of GlcN and GalN in marine OM was also observed by Benner and Kaiser (2003) who report surprisingly narrow ranges of GlcN/GalN-ratios in POM and UDOM (1-2, average 1.5) and interpret them as indication for a dominant prokaryotic source. The molecular character of this presumably prokaryotic OM remains further unrevealed - in DOM as well as in sedimentary POM.

Acknowledgments We thank the officers, crew, and shipboard scientific party of RV Sonne cruise SO-147, particularly Gabriele Klockgether (MPI Bremen) for sampling. Special thanks to Xudong Zhang and Wulf Amelung (University of Bayreuth) for teaching the analysis procedure for amino sugars. This work was part of the project “Peru-Auftrieb” (grant 03G0147A) supported by the BMBF (Federal Ministry of Education and Research, Germany). Further support came from the Max Planck Society, Germany.

Chapter 6A

Chlorin Index: A new parameter for organic matter freshness in sediments

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Geochemistry Geophysics Geosystems **6**, Q03005
doi:10.1029/2004GC000837

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ABSTRACT

Total chlorins, comprising degradation products of chlorophyll, have been used recently to reconstruct paleoproductivity from marine sediment cores. Here, we report on a new index, the Chlorin Index (CI), that proves to be a helpful tool for rapidly estimating organic matter freshness in marine sediments. The CI is a ratio between the fluorescence intensity of a sediment extracted with acetone and treated with hydrochloric acid and the original sediment extract. It represents the ratio of chlorophyll and its degradation products deposited in the sediments that could still be chemically transformed and those that are inert to chemical attack. The ratio is lower in sediments that include freshly deposited phytoplankton material and higher in older, more degraded sediments. We measured this new parameter on surface sediments, and sediments from several short and a long sediment core from different oceanic settings. CI values range from 0.2 for chlorophyll *a* to 0.36-0.56 for fresh material deposited on the shelf off Namibia to values around 0.67 in sediments off Chile and Peru to values up to 0.97 for sediments in a deep core from the northeastern slope of the Arabian Sea. We have compared the CI to rates of bacterial sulfate reduction, as a direct measure of organic matter reactivity and to other degradation indices based on amino acid composition. We conclude that the CI is a reliable and simple tool for the characterization of organic material freshness in sediments in respect to its degradation state.

Chapter 6B

Amino acid biogeo- and stereochemistry in coastal Chilean sediments

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submitted to *Geochimica et Cosmochimica Acta*

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ABSTRACT

The spatial distribution of total hydrolysable amino acids (THAA) and amino acid enantiomers (D- and L- forms) was investigated in sediments underlying two contrasting Chilean upwelling regions: at ~23°S off Antofagasta and at ~36°S off Concepción. The contribution of amino acids to total organic carbon and total nitrogen in surface sediments decreased with increasing water depth (from 126 to 1350 m) indicating an increased degradation status of organic matter in surface sediments at greater water depth. In accordance with this, a conservative estimate of THAA mineralization showed that sedimentary amino acid reactivity decreased with increased water depth and thus, progressive degradation status of the organic matter that was incorporated into the sediment. Reactivity of organic matter in the sediment was also assessed using Principal Component Analysis (PCA) and the Degradation Index (DI) developed by Dauwe and Middelburg (1998). *Sensu* Dauwe and Middelburg (1998) more negative DI reflect more degraded organic matter and positive DI values suggest fresher organic matter. Off Concepción, PCA was successfully applied to indicate on the degradation status of organic matter in sediment at different water depths. However, off Antofagasta DI increased with sediment depth and surface DI values did not reflect variations in the water depth. The contribution of peptidoglycan amino acids to THAA was estimated from the concentrations of D-aspartate, D-glutamic acid, D-serine and D-alanine. The results indicate that peptidoglycan amino acids accounted for a progressively larger fraction of surface THAA at increased water depths. Further, the contribution of peptidoglycan amino acids to THAA increased with increased depth and age of the sediments (up to 288 yr old). Independent estimates based on enumerated bacteria and the concentrations of the respective D-amino acids indicate that most of the measured D-amino acids originated from cell wall remains.

Chapter 6C

Anaerobic oxidation of methane and sulfate reduction along the Chilean continental margin

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Geochimica et Cosmochimica Acta **69**, 2767-2779

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ABSTRACT

Anaerobic oxidation of methane (AOM) and sulfate reduction (SR) were investigated in sediments of the Chilean upwelling region at three stations between 800 and 3000 m water depth. Major goals of this study were to quantify and evaluate rates of AOM and SR in a coastal marine upwelling system with high organic input, to analyze the impact of AOM on the methane budget, and to determine the contribution of AOM to SR within the sulfate-methane transition zone (SMT). Furthermore, we investigated the formation of authigenic carbonates correlated with AOM. We determined the vertical distribution of AOM and SR activity, methane, sulfate, sulfide, pH, total chlorins, and a variety of other geochemical parameters. Depth-integrated rates of AOM within the SMT were between 7 and 1124 mmol m^{-2} a^{-1}, effectively removing methane below the sediment-water interface. Single measurements revealed AOM peaks of 2 to 51 nmol cm^{-3} d^{-1}, with highest rates at the shallowest station (800 m). The methane turnover was higher than in other diffusive systems of similar ocean depth. This higher turnover was most likely due to elevated organic matter input in this upwelling region offering significant amounts of substrates for methanogenesis. SR within the SMT was mostly fuelled by methane. AOM led to the formation of isotopically light DIC ($\delta^{13}C$: -24.6‰ VPDB) and of distinct layers of authigenic carbonates ($\delta^{13}C$: -14.6‰ VPDB).

Chapter 7

Concluding Remarks and Perspectives

CONCLUDING REMARKS AND PERSPECTIVES

This thesis provides a significant contribution to the existing data base on organic matter composition and degradation in coastal marine sediments. Thereby, the results of this thesis constitute an important additional contribution to the general understanding of biogeochemical processes in marine sediments. In particular, the findings emphasize the general influence of depositional conditions on sediment distribution and composition. Dependence and influence of bacterial degradation processes on the composition of sedimentary organic matter could be further elucidated. Moreover, new insights could be gained into the role of bacterially derived organic matter for the composition and preservation of sedimentary organic matter.

In the following, the most important results of this thesis are summarized and discussed with respect to their significance for related studies. Furthermore, some general implications for basic topics in geological and paleo-environmental research are addressed. Also included are discussions on perspectives and possible aspects of future research.

TERRESTRIAL VS. MARINE ORGANIC MATTER

A basic aim of this thesis was to characterize the sources of the sedimentary organic matter. It could be shown that there is presently no significant input of terrestrial organic matter to the sediments depositing in the investigated areas of the Peru-Chile upwelling region. Since the largest part of the investigated areas borders the dry and vegetation poor Atacama Desert this finding could have been expected. On the other hand, it is remarkable that even in the area off central Chile, with high river discharge and seasonally reduced primary production, sedimentary organic matter is predominantly derived from marine sources. This observation has implications for paleo-environmental reconstructions in that, solely based on relative contributions of terrestrial and marine organic matter in the sediments, the climatic and hydrographic situation presently characterizing the central Chilean region can not be distinguished from that presently found in the regions of Northern Chile and Peru. However, the stronger dilution of marine material with land-derived clastic debris in the sediments accumulating off central Chile provides evidence for generally higher riverine input in this more humid region.

The predominance of marine organic matter is a general characteristic of sediments

accumulating in coastal upwelling regions (e.g. Calvert and Price 1983; Schulte et al. 2000), and is finally reflected in the hydrogen-rich kerogen (type I and II) of black shales originating from former sites of highly productive coastal upwelling (Tissot and Welte 1984). Furthermore, the lack of terrestrial organic matter is of significance for the discussion of sedimentary organic matter reactivity and preservation. In general, contributions of terrestrial organic matter are regarded to enhance organic matter burial fluxes, since material derived from vascular plants is intrinsically more resistant to chemical and microbial degradation than material derived from marine organisms (Hedges et al. 1988). This thesis provides further evidence that for sediments accumulating in highly productive coastal upwelling areas terrestrial contributions can be ruled out as a factor explaining enhanced preservation of organic matter.

DEPOSITIONAL CONDITIONS AND SEDIMENT COMPOSITION

In coastal upwelling regions, high primary production rates, high sedimentation rates, shallow water depth, and reduced oxygen availability create depositional conditions that favor the accumulation of organic rich sediments (Thiede and Suess 1983). In the investigated areas, high primary production rates are reflected in a strong phytoplankton signal in the underlying sediments, and a generally high quality of sedimentary organic matter, which points to a permanent supply of freshly produced phytodetritus. Water depth could be shown to have a strong effect on organic matter quality in the sediments. This means that degradation and transformation processes during transit through the water column dominantly control organic matter composition and this way also influence carbon turnover processes in the sediments. However, the exact reasons for the strong water column effect remain unrevealed, one likely explanation are differences in settling times. As part of this thesis, it was not possible to identify effects of oxygen availability on the composition and degradation of sedimentary organic matter. The investigated sites were located within and below the actual depth of the water column oxygen-minimum-zone and increases in bottom water oxygen concentrations were closely related to increasing water depth. In order to distinguish effects of water depth and oxygen availability, future studies should also include sediments depositing above the depth of the water column oxygen-minimum-zone.

The observed spatial variability of sediment characteristics stresses the general influence of seafloor topography and bottom currents on the distribution of sediments.

Winnowing and redistribution of sedimentary material result in the uncoupling of sediment composition from processes in the overlying water column. In particular, it could be shown that differences in organic matter accumulation rates do not necessarily reflect differences in primary productivity in the overlying surface waters. These findings have major implications for paleo-environmental interpretations of sedimentary records in areas where bottom currents and seafloor topography dominantly influence the distribution of sediment characteristics.

BACTERIAL ORGANIC MATTER

With respect to the characterization of organic matter sources, production and fate of bacterial biomass in marine sediments are of crucial importance. Three pools of bacterial organic matter can be distinguished in marine sediments: 1) the living bacteria, 2) the remains of dead bacteria that can be molecularly characterized, and 3) the fraction of uncharacterized organic matter that derives from bacterial biomass or bacterial products. Further efforts are needed to quantify the different pools and to elucidate rates and mechanisms of organic matter transfer between these pools. Recently, new analytical methods have been developed to chemically characterize the fraction of living bacteria, e.g. the analysis of intact membrane lipids clearly separates the living fraction and furthermore provides the possibility to characterize microbial community structures (Rütters et al. 2002; Sturt et al. 2004). The analyses of compounds specifically derived from the bacterial cell wall polymer peptidoglycan, in particular the amino sugar muramic acid and individual D-amino acids, proved to be useful to estimate the contribution of living and dead cell wall material (Pedersen et al. 2001; Benner and Kaiser 2003). As part of this thesis, it could be shown that most of the bacterial organic matter associated with peptidoglycan is present as non-living organic matter. Still, it remains a big challenge to identify bacterial contributions to the refractory, so far uncharacterized fraction of sedimentary organic matter (Hedges et al. 2000).

Isotopic labeling studies might help to elucidate the transfer of living bacterial biomass to the refractory pool, thereby focusing on those transformation processes that occur at an early diagenetic stage. On the other hand, the inherent isotopic signal of selected compound classes might also be suitable to trace the fate of bacterial organic matter. In this respect, compounds specifically associated with peptidoglycan might be of particular interest, due to their ubiquitous occurrence in bacteria, their high source specificity, and their well known structural association. However, for bacterially derived D-amino acids information on carbon

isotopic composition is limited (McCarthy et al. 2004) and so far nothing is known on the isotopic composition of amino sugars in general. Further important information on sedimentary processes involving bacterial organic matter might be revealed by the characterization of compound-specific nitrogen isotopic signals of individual D-amino acids and amino sugars.

ORGANIC MATTER QUALITY AND BIOAVAILABILITY

Another important aspect of this thesis was to characterize the quality of sedimentary organic matter and to assess its availability for microbial degradation processes. In general, the parameters applied to characterize organic matter quality reflect an overall decrease of organic matter freshness with increasing water depth. Rates of bacterial sulfate reduction measured in the sediments also decrease with increasing water depth. Since sulfate reduction is the dominant terminal electron acceptor process in the investigated sediments, sulfate reduction rates are used as a direct measure for the bioavailability of sedimentary organic matter. The concurrent decrease of sulfate reduction rates and chemically defined organic matter quality with increasing water depth demonstrates that in the investigated areas, changes in the bioavailability of sedimentary organic matter are related to changes in its chemical composition. However, some basic constraints concerning the general applicability of chemically defined parameters for the evaluation of organic matter susceptibility towards microbial degradation should be outlined here.

First, although a generally good accordance is observed for some quality indicators and depth integrated sulfate reduction rates, in most cases down-core changes of sulfate reduction rates are not reflected in corresponding down-core trends of parameters describing organic matter composition. At most sites, sulfate reduction rates strongly decreased with increasing sediment depth, though chemical analyses revealed excess availability of sulfate, sufficient amounts of organic carbon, and sufficient reservoirs of chemically labile organic matter throughout the core. Obviously, most quality indicators do not appropriately describe down-core changes in organic matter availability. One reason for the observed discrepancies is that reactive organic matter that is inaccessible for microbial degradation in the sediment might be released during chemical analysis and is therefore included in the interpretation of organic matter freshness. One such example is the acid dissolution of carbonate tests and the liberation of encapsulated amino acids (Ingalls et al. 2003). More generally, all those organic

molecules that are physically protected from enzymatic attack, e.g. by adsorption in mesopores or intergranular areas (Keil et al. 1994; Mayer 1994), might be released by chemical treatment. A special case of physical protection from microbial degradation is the sequestration of diatom chloroplasts by some benthic foraminifera (Bernhard and Bowser 1999). The activity of these foraminifera, that were also identified in sediments investigated in this thesis, provides an active transport mechanism for fresh plankton material in non-bioturbated sediment and might lead to the occurrence of unexpectedly fresh organic matter at greater sediment depth (up to several cm deep; T. Cedhagen, personal communication). Furthermore, as long as algae biomass is incorporated in living foraminifera it is protected from microbial degradation. It is a general problem for the evaluation of organic matter bioavailability that chemical analysis does not retain information on physical protection, association with macromolecular structures, or micro-scale spatial distribution (Arnosti 2004).

In some cases, high rates of microbial remineralization are observed though the sedimentary organic matter is characterized as being of low quality. This finding reflects that small fractions of highly reactive organic matter might drive high rates of microbial degradation and that bulk sediment characteristics do not account for sediment heterogeneity, where niches of high activity might exist. In this context, it is worth to note that most parameters used to describe organic matter quality are based on the chemical composition of the molecularly characterized fraction - in the sediments investigated as part of this thesis this fraction makes up <25% of the sedimentary organic matter. However, being chemically uncharacterized is not synonymous with being unavailable for microbial organisms and there are clear indications that bacteria do feed on the refractory organic matter pool (Arnosti and Holmer 2003). Furthermore, the term uncharacterized includes those compound classes that are not analyzed routinely but might be important substrates for microbial communities, e.g. extracellular polymeric substances rich in amino sugars and transparent exopolymer particles likely to contain significant amounts of sugar alcohols (Lee et al. 2004).

In conclusion, it has do be kept in mind that organic matter quality as assessed by chemical analysis is not synonymous to bioavailability. Quality indicators are useful tools to estimate organic matter freshness, and in sediments accumulating fresh organic matter they can provide valuable information on the susceptibility of sedimentary organic matter towards microbial degradation. However, in view of all the constraints outlined above, it appears to be generally impossible to predict rates and extent of microbial remineralization solely based on the chemical description of the organic matter composition - irrespective of how comprehensive this description might be.

Chapter 8

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DANKSAGUNG

Zunächst danke ich Herrn Prof. Dr. Bo Barker Jørgensen für die Begutachtung der Arbeit und die freundliche Unterstützung meiner wissenschaftlichen Aktivitäten während meiner Zeit am Max-Planck-Institut. Herrn Prof. Dr. Kai-Uwe Hinrichs danke ich für die Übernahme des Zweitgutachtens.

Carsten Schubert danke ich ganz herzlich für die vertrauensvolle Zusammenarbeit, für die offene Wertschätzung meiner Arbeit, für seine ständige Bereitschaft zur Diskussion - trotz zuletzt großer räumlicher Entfernung - und die vielen aufmunternden Worte. Danke auch für die aufgebrachte Geduld und die gewährten Freiheiten, auch wenn es oftmals schwer war nachzuvollziehen, was ich denn nun schon wieder, noch besser machen wollte...

Ein besonderer Dank geht an Tim Ferdelman für die zahlreichen anregenden Diskussionen und die überaus bereichernde Zusammenarbeit. Bente Aagard Lomstein danke ich für den intensiven und konstruktiven Ideenaustausch und die schöne Zeit in Aarhus - mange tak! An dieser Stelle möchte ich auch der Arbeitsgruppe Mikrobiologie der Universität Aarhus für die freundliche Aufnahme während meines Aufenthalts in Dänemark danken.

Nicht unerwähnt bleiben sollen die wissenschaftlichen Kollegen und die Crew von FS Sonne Fahrt SO-156, in erster Linie Dierk Hebbeln als Fahrtleiter und Projektkoordinator. Für die freundschaftliche Zusammenarbeit in den Projekten PUCK und Peru-Auftrieb danke ich insbesondere Tina Treude, Jens Kallmeyer und Philipp Böning.

Vielen Dank an Gabriele Klockgether, Kirsten Imhoff und Swantje Lilienthal für die technische Unterstützung im Labor und die nette Arbeitsatmosphäre. Ich danke meinen zeitlängsten Bürokollegen Marcus Elvert und Nina Knab für die gemeinsame Zeit, für die permanente Bereitschaft zum Gedankenaustausch und die zahlreichen auch über die wissenschaftliche Arbeit hinausgehenden Gespräche. In diesem Zusammenhang geht mein Dank auch an Niko Finke, Sandra Ehrenhauss, Solveig Bühring, Verona Vandieken, Helge Niemann, André Preisler und Marcel Kuypers. Besonders danken möchte ich Jochen Nüster für seine überspringende Lebensfreude und seinen nahezu grenzenlosen Optimismus und Paul Wintersteller, der für mich einfach zur richtigen Zeit am richtigen Ort war.

Stellvertretend für alle weiteren Mitarbeiter des Max-Planck-Instituts, die meine Arbeit in verschiedenster Weise unterstützt haben, geht mein Dank an Ulrike Tietjen für ihre zuverlässige Unterstützung bei Reiseplanungen und anderen organisatorischen Dingen, sowie an Bernd Stickforth für seine wertvolle Hilfe in allen bibliothekarischen Angelegenheiten.

Außerdem möchte ich meinen Freundinnen danken, die mir helfen, nicht den Blick für die wesentlichen Dinge des Lebens zu verlieren - insbesondere Yvonne & Daniela und Sandra & Rita. Mein Dank gilt auch meinen Mitspielerinnen vom SF Wüsting und FSV Westerstede, die mich wiederholt für Dienstreisen und Spätschichten freigestellt haben.

Ich danke meiner Freundin Anke, dass sie immer da ist und meine Hand hält. Danke für den dicken Carlos und die verrückte Luna.

Und ich danke meinen Eltern Ludger und Urte. Ich kann meine Dankbarkeit nicht in Worte fassen. Es ist Eure Liebe, die mich bei jedem meiner Schritte begleitet.