Distribution, composition, flux and variability of organic carbon in Fram Strait/Yermak Plateau (Arctic Ocean) and (palaeo) environmental significance.

Verteilung, Zusammensetzung, Fluss und Variabilität von organischem Kohlenstoff in der Framstraße / Yermak Plateau (Arktischer Ozean) und die Bedeutung für (Paläo)- Umweltrekonstruktionen.

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Abstract

Surface sediments and selected sedimentary records from the Fram Strait/Yermak Plateau were studied using organic-geochemical bulk parameters as well as detailed biomarker lipid analysis. The origin of organic carbon in surface sediments, composed of a complex mixture of ice-rafted, current-transported and primary/secondary produced organic matter, was investigated. From literature data and stable carbon isotope analysis of specific biomarker compounds (fatty acids, *n*-alkanes, *n*-alkanols) a classification in three lipid pools was established.

Marine organic matter amounts up to 50 % in most surface samples, being in concurrence with results from studies in the Arctic Ocean, where a higher contribution of terrestrial-derived organic matter was found. The biomarker lipid results exceeded bulk parameter values (> 70 %). These results are not unusual in open water zones and in the vicinity of the MIZ, where increased primary productivity and an effective export of marine organic matter to the seafloor was described from other studies. In the ice-covered and low productive Yermak slope area, an increased percentage of marine organic matter was found. A complex system of vertical and lateral transport processes close to the MIZ and within Atlantic waters of the Yermak Slope Current (YSC) towards north enables a lateral advection of particulate matter, resulting in elevated amounts of marine organic matter in sediments. A lateral transport over more than 200 km is provided in the YSC (Rutgers van der Loeff et al., 2002).

The lateral transport and enhanced preservation of particulate organic matter played an important role during certain periods in the last 30,000 years. Accumulation rates determined in several sediment cores showed increased preservation of organic carbon in areas influenced by current transport and close to probable sea-ice edges in three time slices. Maximum accumulation of organic carbon was found where elevated TOC and biomarker concentrations have been reported in surface sediments. A palaeoenvironment reconstruction was established from the temporal and spatial distribution of TOC in sediments.

In addition, a sediment core from the Yermak slope with an extraordinarily high temporal resolution has been investigated in detail. A coupled organic-geochemical and sedimentological approach was conducted to reconstruct near-bottom current conditions (sedimentology) in relation with surface water conditions (organic geochemistry). Short-term fluctuations and variations in deposition of biomarkers in sediments were obtained in the Bølling-Allerød, representing the major warming and deglaciation in Europe. In such periods, described as TOC-Events I-V, elevated concentrations of marine biomarkers were found. The biomarker and sedimentology records are in concert with climate reconstructions obtained from the Greenland Ice Core GISP2. Only the Younger Dryas period must be discussed controversial with a decoupling of the bottom water from the surface water signal. A regional characteristic due to special wind conditions might have been responsible for higher productivity and preservation of marine organic matter in the Younger Dryas period. Cold, glacial-like conditions were reported from entire Europe, with the exception of terrestrial records of western Svalbard and a recently published study of lake

sediments in southern Greenland, where warm and dry conditions were suggested in summer (Björck et al., 2002).

Kurzfassung

Oberflächensedimente und Sedimentkerne aus der Framstrasse und vom Yermak Plateau wurden detailliert auf organisch-geochemische Basisparameter und Lipidbiomarker hin untersucht. Die Herkunft von organischem Kohlenstoff in Oberflächensedimenten, welcher aus einer komplexen Mischung aus eis-, strömungstransportiertem und primär-/sekundär-produziertem Material zusammengesetzt ist, wurde untersucht. Anhand von bisher bekannten Informationen über Biomarker und der zusätzlichen Analyse von stabilen Kohlenstoffisotopen an spezifischen Biomarkerkomponenten (Fettsäuren, *n*-Alkane, *n*-Alkanole) wurde eine Klassifikation in drei Lipidgruppen durchgeführt.

Im Gegensatz zu Ergebnissen aus früheren Studien aus dem Arktischen Ozean, in denen ein höherer Anteil an terrestrischem organischem Material gemessen wurde, beträgt der Anteil an marinem organischem Material in den meisten Oberflächenproben dieser Arbeit bis zu 50%. Die Ergebnisse aus Biomarkern ergaben sogar einen Anteil von > 70%. Diese Ergebnisse sind nicht überraschend in offenem Wasser und in der Nachbarschaft von Eiskanten. Aus anderen Arbeiten wurde dort eine erhöhte Primärproduktion und ein effektiver Transport zum Meeresgrund festgestellt. Am eisbedeckten und wenig produktiven Hang des Yermak Plateaus wurden erhöhte Anteile an marinem organischem Material festgestellt. Ein komplexes System von vertikalen und lateralen Transportprozessen in der Nachbarschaft von Eisrandlagen und innerhalb der nach Norden fliessenden Atlantischen Wassermasse des Yermak Slope Current (YSC) ermöglicht eine laterale Advektion von partikulärem Material, was zu erhöhten Mengen an marinem organischem Material in Sedimenten führt. Ein lateraler Transport über Entfernungen von mehr als 200 km wird innerhalb des YSC ermöglicht (Rutgers van der Loeff et al., 2002).

Der laterale Transport und eine dadurch verbesserte Erhaltung von partikulärem organischem Material spielte in einigen Abschnitten der letzten 30,000 Jahre eine wichtige Rolle. Akkumulationsraten aus drei verschiedenen Zeitabschnitten zeigen eine verbesserte Erhaltung von organischem Kohlenstoff in Gebieten, die von Strömungen beeinflusst waren und / oder in der Nähe von vermuteten Eiskanten lagen. Die höchsten Akkumulationsraten von organischem Kohlenstoff wurden dort bestimmt, wo erhöhte TOC- und Biomarkerwerte in den Oberflächensedimenten gefunden wurden. Eine Rekonstruktion der Paläoumwelt wurde anhand der zeitlichen und räumlichen Verteilung von TOC in Sedimenten durchgeführt.

Zusätzlich wurde ein Sedimentkern vom westlichen Hang des Yermak Plateaus mit einer ausserordentlich hohen zeitlichen Auflösung bearbeitet. Eine gekoppelte organisch-geochemische und sedimentologische Untersuchung wurde durchgeführt, um sowohl die Bodenwasserströmungen (Sedimentologie) als auch die Oberflächenwasserbedingungen (organische Geochemie) zu rekonstruieren. Kurz andauernde Variationen in der Ablagerung von Biomarkern wurden während des Bølling-Allerøds festgestellt, das die Haupterwärmungsphase und Deglaziation in Europa repräsentiert. In solchen Abschnitten, die auch als TOC Events I-V bezeichnet wurden, konnten erhöhte Konzentrationen von marinen Biomarkern gemessen werden. Die organisch-geochemischen und sedimentologischen Aufzeichnungen sind im Einklang mit

Klimarekonstruktionen, die vom grönländischen Eiskern GISP2 vorliegen. Der Abschnitt der Jüngeren Dryas muss allerdings kontrovers diskutiert werden, da eine Entkopplung des Bodenwassersignals vom Oberflächensignal beschrieben wurde. Eine höhere Produktivität und eine damit zusammenhängende bessere Erhaltung in der Jüngeren Dryas könnten mit regionalen Besonderheiten, wie zum Beispiel veränderten Windverhältnissen, zusammenhängen. Während in den meisten Teilen Europas kalte, fast glaziale Bedingungen beschrieben wurden, gibt es Hinweise von terrestrischen Aufzeichnungen im Westen Svalbards und lakustrinen Sedimenten Südgrönlands, dass zumindest im Sommer warme und trockene Bedingungen vorgeherrscht haben könnten (Björck et al., 2002).

1. Introduction

The climate of the last glacial/deglacial cycle underwent significant changes from periods with large ice sheets on the continents and extensive sea-ice cover to periods comparable with present climate. Climate change is caused by fluctuating orbital parameters that caused variations in solar energy input to the Earth (e. g. Berger et al., 1984; van Geel et al., 1999; Renssen et al., 2000 and references therein). The world ocean and its circulation patterns are very important, since they store and transport heat. They play an important role in balancing Earth temperatures. During the last two decades, a global thermohaline circulation pattern was recognised, which is crucial for the climatic development in the last glacial/deglacial period (Global Ocean Conveyor Belt) (e.g. Broecker, 1991; Rahmstorf, 2002).

The area of investigation, the Fram Strait, is situated at the northernmost end of the global conveyor belt. The 600 km wide and average 2500 m deep Fram Strait builds the only deep-water gateway between the Atlantic and Arctic Ocean. The opening of the Fram Strait and the northwestern Svalbard margin probably began in the late Palaeocene, when Arctic North America broke up from Eurasia (Kristoffersen, 1990; Eiken and Hinz, 1993). The Fram Strait itself is a transform fault system, which is subdivided in several smaller rifting centres (e. g. Crane et al., 1982). The Fram Strait is characterised by a year-round sea-ice cover, while marginal zones north and west of Svalbard (eastern Fram Strait) are ice-free in summer and partially in winter. This fact is enabled by a complex system of interconnected currents and water masses.

The eastern Fram Strait is entered by warm, saline Atlantic water via the West Spitsbergen Current (WSC). The Atlantic water was identified in two distinct water depths, below 500 m west and north of Svalbard and between 1000-1500 m on the western Yermak slope (Schlichtholz and Houssais, 1999 a & b; Rudels et al., 2000). The western Fram Strait is dominated by cold, less saline water masses, flowing to a southern direction alongside the eastern continental margin of Greenland. Between 78° and 79°N, a major part of the Atlantic water is redirected to the East Greenland Current (EGC) via the Return Atlantic Current (RAC) (e. g. Manley, 1995 and references therein). On their way to the Arctic Ocean, Atlantic water masses cool, get denser and start to sink (Rudels et al., 1994). Even small variations in surface temperatures and salinity may have drastic consequences to deep-water formation and, thus, influence the flow of warm water masses and the present-day mild climatic conditions in Europe.

In areas like the Arctic Ocean/Fram Strait, low primary productivity was described in Arctic surface waters due to a perennial sea-ice cover (Subba Rao and Platt, 1984; Wheeler et al., 1996). Sea-ice coverage has a major influence on the development of marine biota, oceanic circulation and surface albedo. At marginal ice-zones and oceanic fronts, however, primary productivity may exceed the low Arctic Ocean productivity values by far (1 g C m^{-2} d^{-1}; Hirche et al., 1991). High productivity has been measured especially at the sea-ice edges north and northwest of Svalbard and east of Svalbard (Andreassen et al., 1996; Wassmann et al., 1999; Owrid et al., 2000; Rat'kova and Wassmann, 2002).

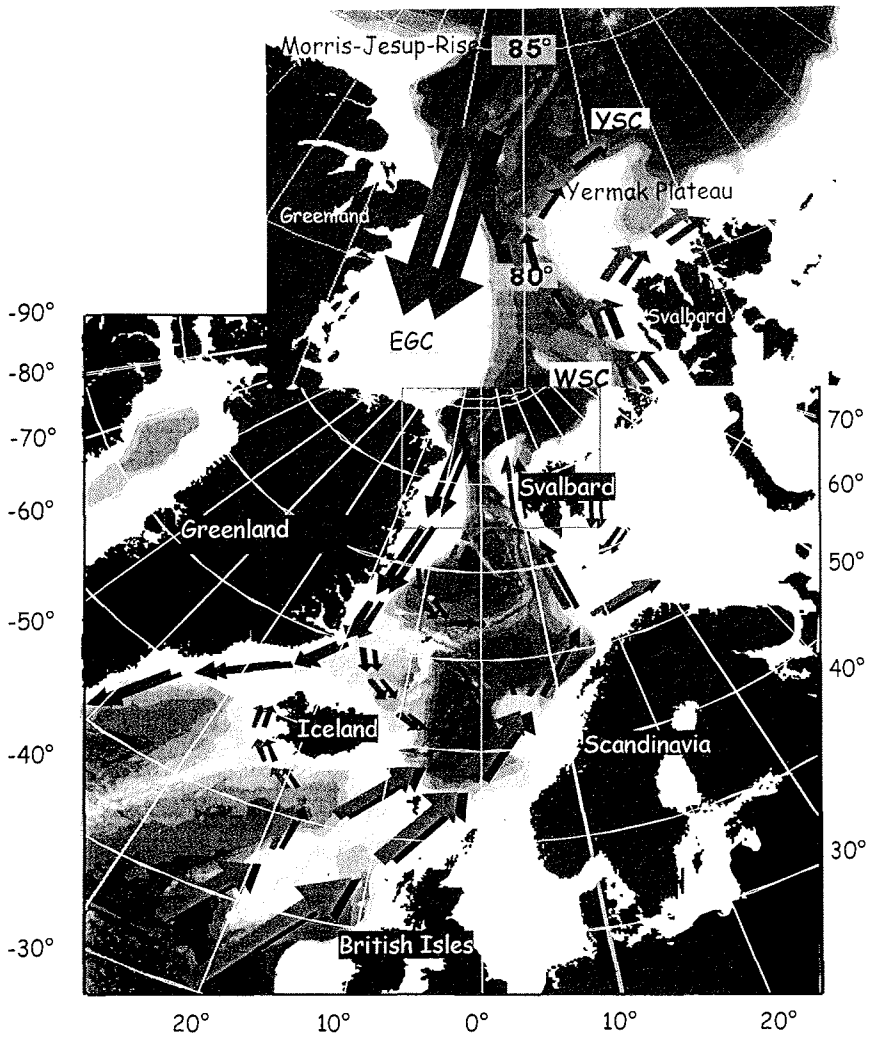

Fig. 1.1. General circulation pattern in the North Atlantic and the adjacent Fram Strait (e.g. Schlichtholz and Houssais, 1999 a & b; Rudels et al., 2000 and references therein): WSC= West Spitsbergen Current, YSC= Yermak Slope Current, NSC= North Spitsbergen Current, EGC= East Greenland Current).

An efficient vertical transport through the water column by formation of aggregates and an increased lateral transport of suspended matter cause high accumulation and preservation of organic carbon in sediments (Ittekkot et al., 1992; Knies and Stein, 1998). A close relationship of oceanic circulation, organic carbon accumulation and preservation was observed and correlated with climate records from Greenland ice cores (GRIP, GISP2; e. g. Grootes et al., 1993; Dansgaard et al., 1993), terrestrial records (e.g. Mangerud and Svendsen, 1992; Svendsen et al., 1996) and sediment cores from the Arctic and North Atlantic Ocean (see Chapter 4).

Palaeoenvironmental reconstructions were difficult due to low productivity rates and rapid degradation of labile organic compounds in the Arctic Ocean environment. Calcareous and siliceous microorganisms (diatoms, foraminifers, coccolithoporoids, radiolarians) are rare in Arctic Ocean sediments. However, biomarkers from marine phyto- and zooplankton organisms could be identified even in remote areas like the Arctic Ocean (e. g. Belyaeva and Eglinton, 1997; Schubert and Stein, 1997; Zegouagh et al., 1998; Fahl and Stein, 1997; 1999; Fernandes and Sicre, 2000; Belicka et al., 2002).

The use of biomarkers as palaeoenvironmental proxies is a well-established geochemical tool, especially in low and mid-latitude realms. The amounts of terrestrial biomarkers, however, are very low in marine areas (e. g. Farrimond et al., 1990; Prahl et al., 1994). In the almost perennial ice-covered Arctic Ocean, the composition of organic carbon and biomarkers in sediments is significantly influenced by sea-ice transported terrestrial material (Schubert and Stein, 1997) and/or by riverine input (Fahl and Stein, 1997; 1999). Additionally, an effective lateral transport of suspended matter is important for accumulating organic carbon in sediments (Rutgers van der Loeff et al., 2002 and references therein). Previous sediment trap studies show, that the vertical flux of terrigenous organic matter from melting sea-ice to the seafloor can be very important or even dominant in the Arctic realm (Hebbeln and Wefer, 1991; Hebbeln, 2000). Nevertheless, the amount of marine organic matter in surface sediments may reach values up to 50% or even higher in Arctic Ocean and Yermak Plateau surface sediments (Schubert and Calvert, 2001).

Investigations on palaeoceanography, flux and accumulation of organic carbon in Fram Strait during the last glacial/interglacial cycle was the topic of numerous studies conducted in the last decade (e. g. Hebbeln 1992, Hebbeln et al., 1994, 1998; Elverhøi et al., 1995; Schubert, 1995; Andersen et al., 1996; Hebbeln and Wefer, 1997; Knies and Stein, 1998; Vogt et al., 2001, Taylor et al., 2002a, 2002b). The low resolution of the majority of sedimentary records, however, prevented the identification of short-term fluctuations, especially in the last deglaciation. In cores from the Fram Strait and Yermak Plateau area, however, we obtained one sediment record from the last deglaciation (see chapter 4), that allowed to study short-time events during the last glacial/deglacial period with a resolution comparable to the Greenland ice-core records (e. g. GISP 2/GRIP; Grootes et al., 1993; Dansgaard et al., 1993).

1.1. Organic-geochemical proxies and their usage as environmental markers

To interpret transport, deposition and preservation processes of organic carbon and their relevance as environmental markers in recent and (palaeo) sediments, information about sources of distinct organic-carbon proxies is required. The information, whether the organic carbon is of a marine or terrigenous source can be obtained by different organic-geochemical proxies (e. g. C_{org}/N-ratios, hydrogen indices, $\delta^{13}C_{org}$ values) and more detailed from extractable organic matter by biomarkers (fatty acids, sterols, *n*-alkanes, *n*-alkanols) and their stable carbon isotope ratios (Meyers, 1997 and references therein). Here, we want to give a brief introduction and summary of various organic-geochemical proxies used in the following chapters.

1.1.1 Organic geochemical bulk proxies

Organic carbon/nitrogen (C_{org}/N) ratios

Organic carbon/nitrogen (C_{org}/N) ratios are measured and used to distinguish between a marine or terrigenous source in marine sediments. Marine phyto- and zooplankton is characterised by low ratios between 5-10, whereas terrigenous organic matter usually shows values > 15 (Borodowskiy, 1965; Scheffer and Schachtschabel, 1984). However, it has to be considered, that C_{org}/N ratios represent C_{org}/N_{org} ratios. Generally, the amount of inorganic nitrogen is negligible in comparison to organic nitrogen in sediments, when considering Total Organic Carbon (TOC) values > 0.5 %. In samples with low TOC concentrations, the inorganic nitrogen values might be increased, especially as bound ammonium in clay minerals, preferably illites (Müller, 1977). In sediments with high illite concentrations, C_{org}/N results should be interpreted carefully or verified by N_{org} analysis as proposed by Schubert and Calvert (2001) to avoid misinterpretation.

Stable carbon isotope composition of the organic matter

Stable carbon isotope investigations are a common tool for estimating marine and terrigenous input of organic matter. To subdivide marine and terrigenous organic matter, a terrestrial and marine end member must be identified. Terrigenous organic matter can be characterised by light isotope values of –26 to –28 ‰ (C_3 land plants). Land plants using the C_4 pathway are characterised by heavy isotopes of about –14 ‰, but are rare in high latitude areas (Teeri and Stowe, 1976). To distinguish the marine end member is more difficult. In low latitudes, heavy values between –20 to –22 ‰ are characteristic for marine phyto- and zooplankton. However, in high latitudes, values between –16.7 and –30.4 ‰ were observed (Rau et al., 1989, 1991; Goericke and Fry, 1994). These variations can be explained by increased dissolved CO_2 concentrations at low surface water temperatures (e. g. Goñi et al., 1997; Rau et al., 1997). Sea-ice algae may produce extremely heavy isotope values (-15 to –8 ‰) (Gibson et al., 1999). Therefore, it is very difficult to determine the marine end member in the Arctic realm by means of total organic carbon isotopes. A combined biomarker and carbon isotope investigation on specific biomarkers was used to get more detailed information of stable carbon isotopes of marine and terrigenous organisms (Goñi et al., 2000; Schubert and Calvert, 2001, see also chapter 2).

Rock-Eval pyrolysis

Rock-eval pyrolysis parameters (S2-peak, hydrogen indices) are useful indicators to give a characterisation of organic carbon in sediments with TOC values > 0.5 % (Tissot and Welte, 1984, Stein, 1991). The hydrogen index (HI) corresponds to the amount of pyrolysable hydrocarbons per gram TOC (mg HC/ g TOC). Terrigenous organic matter is characterised by values < 100 mg HC/ g TOC, whereas marine organic matter values between 300-800 mg HC/ g TOC are typical.

1.1.2. Biomarker composition

Organic bulk parameters are very useful proxies to identify the general composition of organic matter in sediments (Meyers, 1997). Specific biomarkers, however, enable a much more detailed information about the proportions of marine and terrigenous organic matter in sediments (e. g. Brassell et al., 1986; Yunker et al., 1995; Fahl and Stein, 1999, Goñi et al., 2000). Biomarkers are organic compounds, which are synthesised by different organisms. Specific molecular structures are typical for distinct organisms. Although the amount of biomarkers in sediments is low (1-2 % of TOC), they are useful proxies to classify sources and different depositional environments. In remote areas such as the Arctic Ocean and the adjacent Fram Strait/Yermak Plateau, marine microfossil contents (e. g. diatoms, dinoflagellates, coccolithophoroides and foraminifers) in sediments are very low. Therefore, biomarkers are excellent proxies to reconstruct phyto-/zooplankton surface water productivity and/or lateral and vertical transport processes in the water-column. A detailed characterisation and classification of biomarkers (sterols, fatty acids, *n*-alkanes, *n*-alkanols) with literature data and stable carbon isotopes is given in chapter 2 and 4 more detailed.

1.2. Material and Methods

The investigated surface sediment samples and sediment cores from the northern Fram Strait/Yermak Plateau area were cored during "Polarstern" cruises ARK-XIII/2 in 1997, ARK-XV/2 in 1999 and ARK-XVI/1 & 2 in 2000. The complete biomarker sample set was stored at –30°C after being sampled onboard of "Polarstern". Bulk organic carbon samples (e. g. TOC, HI) were freeze-dried and homogenised. Total organic carbon values were determined by a Leco CS analyser. Hydrogen indices were analysed by a Vinci Rock-Eval 6 (Espitalié et al., 1977). For biomarker extraction, approximately 8-12 g freeze-dried sediment per sample was used. The extraction and purification of biomarkers was done by a modified method based on Folch et al. (1957) and Bligh and Dyer (1959). Further details of biomarker sample treatment and analytical work can be found in chapters 2 and 4.

1.3. Main objectives

In order to investigate the potential of organic carbon and especially biomarker proxies in present and past environments, detailed organic carbon bulk parameter and biomarker analysis were conducted on surface sediments and two sediment cores from the Fram Strait/Yermak Plateau area.

For this purpose, a detailed investigation of several surface samples was performed to understand the modern distribution and depositional processes of organic matter (especially biomarkers) under almost perennially sea-ice and a complex oceanographic situation with opposing Atlantic and Arctic water masses. From previous studies we know, that in the eastern Fram Strait, relatively high TOC concentrations were found. Therefore, a detailed investigation of organic-geochemical bulk parameters (hydrogen indices, C_{org}/N-ratios, $\delta^{13}C_{org}$) and especially biomarkers (long-chain *n*-alkanes, *n*-alkanols, sterols, and fatty acids) was conducted.

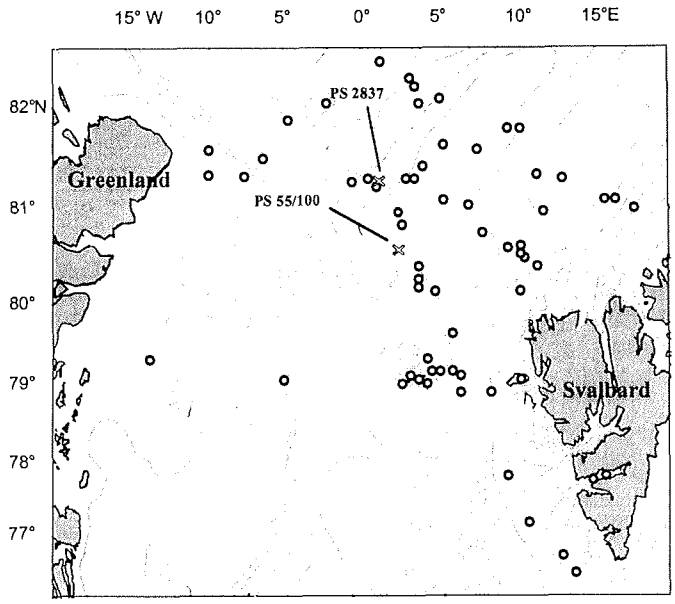

Fig. 1.2. Working area with investigated stations. Circles: Surface sediments; Crosses: Surface sediments and cores.

The surface samples yielded high numbers of biomarkers with a great variety of marine phytoplankton and zooplankton markers as well as terrigenous biomarkers. Biomarker studies have been performed, recently, on several surface sediment samples from the Arctic Ocean in the broadest sense. A main topic was to examine, if specific biomarkers have the potential to trace and differentiate between a marine or terrestrial origin.

Until now, this problem was not solved in a satisfactory manner. Therefore, biomarker studies from several authors on various organisms from marine, aquatic and terrestrial environments were taken into account to distinguish the potential source of specific biomarkers. In a second step, stable carbon isotope measurements on specific biomarkers were conducted to revise and secure the origin of the classified biomarkers. From this new, coupled biomarker-stable carbon isotope approach it is feasible to distinguish undoubtedly between marine biomarkers and terrigenous biomarkers in marine sediments. In addition, little information exists about transport and depositional processes of marine and terrigenous biomarkers in surface sediments of ice-covered regions up to now.

The second focus was laid on the reconstruction of palaeoceanography and the amount of organic carbon being preserved in the last glacial-interglacial-cycle of the Fram Strait. So far, marine micropalaeontology investigations and stable isotopes (oxygen, carbon) are well-established proxies for reconstructing palaeogeographical conditions. We show promising results for the palaeoceanographical use of specific biomarkers and organic geochemical bulk proxies from long sediment cores. In contrast to mid- to low-latitude high productivity areas, less information is available about organic carbon distribution

in the Arctic realm, so far. The use of specific biomarker data is compared with bulk organic-geochemical and sedimentological parameters. From this data set, we reconstructed average organic carbon accumulation rates and erected an organic carbon budget of the Fram Strait for the last 30,000 years in three different time slices.

In addition, the last deglaciation (9,000-17,000 years) period was studied in detail on the basis of a coupled organic-geochemical and sedimentological approach at one sediment core from the Yermak slope. A coupled bottom-current and surface water study should help us to decipher short-term climatic variations in the northernmost part of Europe. A combination of organic geochemistry (representing the surface water signal), and sedimentology (representing the bottom water signal) should be compared with ice-core data and terrestrial records. Due to a high temporal resolution in the studied sediment core in the last deglaciation, a reconstruction and correlation with major climatic changes could be established. Similarities and varieties of surface water and bottom water information as well as global and regional climate variations should be recognised for the last deglaciation in the Fram Strait/Yermak Plateau area.

1.4. Individual studies

Each of the following chapters is representing a paper being submitted to a scientific journal or book. In the following part a short overview of each study is given. The references of each chapter are combined into one list in chapter 6.

Chapter 2:

Aliphatic lipids in recent sediments of the Fram Strait/Yermak Plateau (Arctic Ocean): Composition, sources and transportation processes

Daniel Birgel, Jens Hefter, Ruediger Stein: submitted to Marine Chemistry

Surface sediment samples from three transects in the Fram Strait/Yermak Plateau were investigated by molecular and isotopic organic geochemical methods to determine the origin of extractable lipid compounds. A detailed molecular and isotopic characterisation of the studied compounds allowed us to assign the majority of compounds to three lipid pools. Along the western Yermak slope, high TOC contents up to 1.6 % and highest biomarker concentrations were measured, although this region is permanently ice-covered. This study provides a detailed insight into Arctic Ocean carbon dynamics and the impact of ocean-currents on the deposition and composition of organic carbon.

Chapter 3:

Northern Fram Strait and Yermak Plateau: Late Quaternary variability and burial of organic carbon and palaeoceanographic implications

Daniel Birgel and Ruediger Stein, accepted for publication in: Organic carbon cycle of the Arctic Ocean. Edited by R. Stein and R. Macdonald, Springer Verlag, New York.

A detailed investigation of bulk organic-geochemical parameters was conducted from surface sediments and long-sediment cores from the Northern Fram Strait/Yermak Plateau. The recent distribution and sources of organic carbon in surface sediments on four transects and the last glacial-deglacial distribution in sediment cores using new and literature data was given. From long sediment cores, bulk and organic carbon accumulation rates were presented. For the Holocene (0-11,000 years), the entire Fram Strait was subdivided in seven zones. For each of these zones a budget was calculated, showing a great variety of organic carbon deposition in different zones of the Fram Strait.

Chapter 4:

The last deglaciation in the Fram Strait (Arctic Ocean) with respect to oceanic and atmospheric variations: a coupled high-resolution organic-geochemical and sedimentological study.

Daniel Birgel and H. Christian Hass, submitted to Quaternary Science Reviews

From a sediment core, short-time climatic variations in the northern Fram Strait/Yermak Plateau area were studied. The sediment core is characterised by elevated total accumulation rates (up to 100 g cm^{-2} ky^{-1}). By using a coupled organic-geochemical and sedimentological approach, a reconstruction of near-bottom and surface water conditions was conducted. The marine biomarker and sedimentological records were consistent with climate reconstructions obtained from Greenland ice cores and thermohaline circulation variations. For the Younger Dryas period, however, the signals varied, suggesting a regional characteristic in the Northern Fram Strait/Yermak Plateau region.

Chapter 2

(submitted to Marine Chemistry)

Aliphatic lipids in recent sediments of the Fram Strait/Yermak Plateau (Arctic Ocean): Composition, sources and transportation processes

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Abstract

Surface sediments (*n*=39) from the western Fram Strait and across the Yermak Plateau (Arctic Ocean) were investigated by molecular and isotopic organic geochemical methods to determine the composition, distribution and origin of extractable aliphatic lipids (*n*-alkanes, *n*-alkanols, fatty acids). Supplementary bulk geochemical parameters (TOC-content, $\delta^{13}C_{org}$) were also determined, including additional samples nearby. Recently, it was shown that the western flank of the Yermak Plateau is influenced by a current-driven lateral input of particulate organic matter from the South (Soltwedel et al., 2000). This transportation mechanism includes a near-bottom resuspension-settling loop with an average particle residence time of 1-2 months (Rutgers van der Loeff et al., 2002). The supposed influence of the so-called "Yermak Slope Current" on the lipid composition of the organic matter transported northwards to an area of permanent ice-cover has not been investigated up to now. Enhanced organic carbon contents of up to 1.6% along the western slope of the Yermak Plateau and north off Spitsbergen, corroborated by an average $\delta^{13}C_{org}$ value of –22.3 ‰, indicated most of the organic material to be of a marine origin, despite ice-cover. The extractable aliphatics contributed up to 1% of the sedimentary organic carbon and were dominated by fatty acids (0.7-9.1 mg/g TOC), whereas *n*-alkanes and *n*-alkanols contributed only minor amounts (0.1-0.4 mg/g TOC). The detailed molecular and carbon isotopic characterisation of the studied aliphatic compounds allowed to assign most of them to three lipid pools, representing: (a) primary production (marine phytoplankton, sea-ice algae), (b) secondary inputs (by feeding of zooplankton, benthic organisms and bacteria on the former) and (c) terrestrial-derived contributions. The amounts of the first two compound groups dominated, but varied significantly in relation to the environment and were generally highest at the MIZ, but also along the permanently ice-covered western flank of the Yermak Plateau. There, a general gradual decrease in concentration of the primary and secondary compounds with increasing distance from the ice-edge indicated long-distance (aprox. 200 km) transportation of organic matter (produced at or near the MIZ) within the topographically steered current towards the north. In contrast, compounds attributable to a terrestrial source were of only minor importance in terms of absolute concentrations and less variable, but showed as a consequence of the weakening signal of primary and secondary production increasing relative proportions from an average of 8-14 % at and southwards of the MIZ up to 26-34 % on the Yermak Plateau and towards the central Arctic Ocean. This study shows that organic-geochemical and molecular isotopic studies can provide

further insights into the Arctic Ocean carbon dynamics but also provide an example on the impact of ocean-currents on the deposition and composition of organic matter.

2.1. Introduction

The Arctic Ocean and the surrounding areas are considered to be a low productivity environment due to the presence of an almost perennial sea-ice cover, low availability of light, nutrients and suspended matter (Subba Rao and Platt, 1984). The largely closed sea-ice cover not only has an important influence on the abundance and diversity of marine biota, but also on the oceanic circulation and surface albedo. Despite low annual primary production (1-15 g C m^{-2} $year^{-1}$; English, 1961; Wheeler et al., 1996; Gosselin et al., 1997) for the ice-covered central parts of the Arctic Ocean, increased seasonal phytoplankton and zooplankton productivity at the MIZ and within the Arctic shelf-seas is now continuously recognised, connected with high vertical export and accumulation rates of organic carbon to the surface sediments (Andreassen et al., 1996; Owrid et al., 2000; Birgel and Stein, in press). For the Barents Sea, adjacent to the east of the Yermak Plateau, it was assumed that MIZ-associated production sweeping into the Arctic Ocean results in an annual production of 50-150 g C m^{-2} $year^{-1}$ (Olli et al., 2002 and ref. therein). Such an increased fixation of atmospheric CO_2, in the form of primary photosynthate but also as secondary organic carbon from organisms of higher trophic levels might, upon ultimate burial in sediments, leave a distinct impact on the global climate.

Deep-water exchange between the Arctic and Atlantic Ocean is enabled only in the Fram Strait. It is a major driver of global thermohaline circulation, controlling heat transfer and climate changing processes between the Arctic and the world oceans (ARCSS Workshop Steering Commitee, 1990; NAD Science Committee, 1992). Up to now knowledge of organic matter composition in terms of biomarker distributions and concentrations is still limited for recent sediments of the northern Fram Strait. To improve our precognition of these remote regions, several expeditions were conducted with ice-breaking research vessels to the perennially ice-covered Arctic Ocean (Fütterer, 1992; 1994) and northern Fram Strait/Yermak Plateau (Stein and Fahl, 1997; Jokat, 2000; Krause and Schauer, 2001) in the last decade. Organic carbon contents of surface sediments from the Fram Strait and Arctic Ocean areas were investigated earlier (Hebbeln and Berner, 1993; Stein et al., 1994a), but biomarker studies previously concentrated only on selected compounds, e.g. on short- (*n*-C_{17}, *n*-C_{19}) and long-chain (*n*-C_{27}, *n*-C_{29}, *n*-C_{31}) *n*-alkanes and short-chain fatty acids ($C_{16:0}$, $C_{16:1}$, $C_{18:0}$, and $C_{18:1}$) (Schubert 1995; Schubert and Stein, 1997). However, to get more detailed information on the sources and composition of extractable organic matter (EOM) in surface sediments, it is necessary to investigate a greater variety of potential biomarker compounds, including their stable carbon isotopic composition. For this study, the molecular and carbon isotopic variations of aliphatic lipids (fatty acids, *n*-alkanols and *n*-alkanes) in recent sediments of the Fram Strait and on the Yermak Plateau has been investigated. The use of biomarker data as proxies reflecting recent environmental conditions and for palaeoenvironmental reconstruction is a well-established geochemical tool. For sediments from open ocean and deep-sea

areas of mid- to low-latitude regions, biomarker compositions mainly reflect primary productivity in the water column, whereas the amounts of freshwater and terrestrial-derived compounds generally are low (e.g. Farrimond et al., 1990; Prahl et al., 1994). In contrast, in sediments of the almost perennial ice-covered Arctic Ocean, organic matter composition might be significantly effected by a "terrestrial overprint" related to sea-ice transportation processes (Dethleff et al., 2000). The supply of terrigenous organic matter from melting sea-ice to the seafloor, and by transport within currents is important, as can be seen from previous bulk parameter investigations (e.g. Hebbeln and Berner, 1993; Stein et al., 1994a; Schubert and Stein, 1997, Birgel and Stein, in press). Nonetheless, Wheeler et al. (1996) described a low to moderate primary productivity under permanent sea-ice in the Arctic Ocean, but concluded that it is "less productive than oligotrophic ocean regions not covered by ice". However, from bulk $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ data of ice-covered Arctic marine surface sediments, contributions of marine organic matter up to 50 % were estimated (Schubert and Calvert, 2001) and circumarctic shelf regions and the MIZ are nowadays considered to belong to the most productive environments on earth, particularly during springtime (Wassmann, 2002).

The major goal of this study was to identify and distinguish processes (i.e. primary and secondary production, allochthonous/terrestrial inputs) and the influence of environmental aspects (e.g. ice-cover, current systems) on the deposition of aliphatic lipids in surface sediments of the eastern Fram Strait and on the Yermak Plateau. A first estimation on the composition of the organic matter (e.g. the proportions of marine and terrigenous material) was achieved by bulk data analysis (TOC, $\delta^{13}C_{org}$).

2.2. Materials and methods

2.2.1. Study area

The surface sediment samples studied cover an area from approximately 76°N to 82.5 °N and 5°W to 20°E between Greenland/Spitsbergen and north of Spitsbergen, known as the Fram Strait and Yermak Plateau (Fig. 2.1.). The investigation area is influenced by a number of environmental aspects. These are e.g. permanent or temporary sea-ice cover and a system of oceanic currents, which, amongst other things, leave their impact on the organic matter composition and distribution within seafloor sediments. Two major currents, the warm West Spitsbergen Current (WSC) and the ice-infested East Greenland Current (EGC), balance the exchange of Arctic and Atlantic water masses and subdivide Fram Strait in two domains.

Flowing polewards, the WSC carries warm and saline Atlantic waters along the western coast of Spitsbergen, keeping this region ice-free almost throughout the year (Fig. 2.1.). Here, the WSC is about 100 km wide and is confined over the continental slope. At about 79°N, the WSC divides in subbranches. The Return Atlantic Current (RAC) recirculates Atlantic water southward to the eastern edge of the EGC (Gascard et al., 1988; Manley, 1995, Schlichtholz and Houssais, 1999a & b). About 22 % of the northward flowing Atlantic waters have been estimated to become redirected to the south via the RAC (Manley, 1995). The remaining Atlantic water of the WSC then is subdivided into the North

Spitsbergen Current (NSC, also referred as Svalbard Branch) and the Yermak Branch at about equal water mass volumes (Manley, 1995). Deflected by coriolis-forcing, the NSC (Svalbard Branch) turns east and stays close to the continental shelf north off Spitsbergen, at a depth of approximately 250 m (Manley, 1995). The Yermak Branch follows the western slope of the Yermak Plateau, but part of it also spreads over the Plateau. Most relevant to our study, an intermediate to deep, bottom-intensified subbranch of the Yermak Branch, named Yermak Slope Current (YSC) by Schlichtholz and Houssais (1999a) has been identified. The YSC, consisting mainly of cold, low-salinity Norwegian Sea deep-water, however, has to follow the western and northern slope of the Yermak Plateau at a water depth of about 1000-1500 m, as indicated in Fig. 2.1.

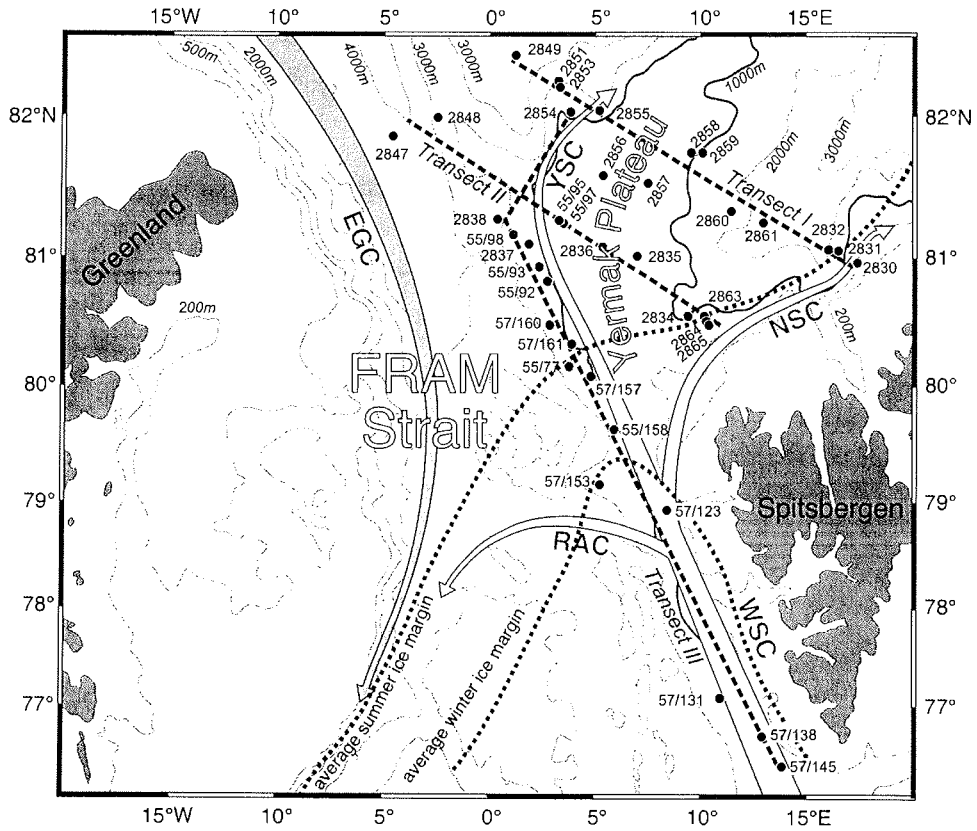

Fig. 2.1. Map of the study area indicating positions of sampling stations (black dots), locations of *Transects* I-III, average winter and summer ice margin and major currents. The area of the Yermak Plateau is marked by the bold 1000 m isobath. The position of the summer ice margin crossing the *Transects* is derived from satellite and shipboard observations during the sampling periods. Light grey arrows track the inflow of warm, saline Atlantic water (WSC = West Spitsbergen Current, RAC = Return Atlantic Current, NSC = North Spitsbergen Current, YSC = Yermak Slope Current), dark grey arrow shows the outflow of cold, fresh Arctic water and sea-ice (EGC = East Greenland Current).

The main outflow of Arctic water masses occurs in the western part of the Fram Strait via the East Greenland Current (EGC). The EGC transports cold, fresh water and sea-ice southwards out of the Arctic (Saloranta and Svendsen, 2001), resulting in a permanent ice-cover throughout the year reaching far to the south. Current velocities of the WSC were measured west of Svalbard with 9-16 cm/s in water depths between 500-1500 m (Fahrbach et al., 2001), whereas YSC velocities are reduced to 1-3 cm/s (Schlichtholz and Houssais, 1999a & b). For the NSC, average velocities are even lower than YSC velocities.

2.2.2. Samples, lipid extraction and analysis

The surface sediment samples (0-1 cm) were recovered during the expeditions ARK XIII/2 (Stein and Fahl, 1997), ARK XV/2 (Jokat, 2000) and ARK XVI/1 & 2 (Krause and Schauer, 2001) on RV *Polarstern*. The sampling was carried out either with a giant box corer or a multicorer.

All samples were stored at –30°C until further treatment. Bulk samples were freeze-dried and homogenised and partitioned into subsamples. TOC was determined by means of a LECO CS analyser. Subsamples analysed for total organic carbon isotopic composition ($\delta^{13}C_{org}$) were acidified with 0.1 N HCl prior to measurement and dried at 60°C for 12h. $\delta^{13}C_{org}$-measurements were performed in duplicate on an ANCA-SL 20-20 mass spectrometer (Europa Scientific). Subsamples for lipid analysis were extracted and purified by a modified method based on Folch et al. (1957) and Bligh and Dyer (1959). Prior to extraction and fractionation, the following internal standards were added for quantification of the respective compound class: squalane, nonadecanoic acid methyl ester and cholest-5-en-3β-ol-d_6. Sediment samples were extracted in three steps using 40 ml each of methanol, methanol:dichloromethane (1:1, by volume) and dichloromethane. The combined total extract was transesterified with 1 ml of 5 % concentrated hydrochloric acid in methanol for 12 hours at 50°C. Silica gel column chromatography was used to separate *n*-alkanes by elution with hexane and a combined FAME (Fatty Acid Methyl Ester) and *n*-alkanol/sterol fraction, eluted with hexane/ethylacetate (80:20), by volume. Sterols/*n*-alkanols were silylated with 500 µl BSTFA (N, O-Bis trimethylsilyltrifluoroacetamide with 1-% trimethyl-chlorosilane) for 2 hours at 60° C.

All biomarkers were analysed with a Hewlett Packard gas chromatograph (HP 6890) on a 30 m DB5-MS capillary column (J & W Scientific, 0.25 mm i.d.; film thickness 0.25 µm), using a temperature program as follows: 60°C (2 min), 150°C (rate: 15°C/ min), 320°C (rate: 3°C/min), 320°C (10 min isothermal). The injection volume was 1 µl (Gerstel Cold Injection System; 60°C (10s), 300°C (60s), rate 12°C/s). Helium was used as carrier gas. Identification of compounds was achieved by GC retention times compared to authentic reference compounds and additionally confirmed by MS fragmentation patterns on a Hewlett Packard 5890 GC/MS using identical conditions as described above for GC analysis.

The compound-specific carbon isotope analysis (irm-GC/MS) of selected samples was carried out with a HP 6890 GC coupled via a Finnigan GCC-II-interface to a Finnigan Delta^{plus}XL gas mass spectrometer. Samples were injected in pulsed-splitless mode and compound separation was achieved on a J & W DB1-MS capillary column (length = 60m, i.d. = 0.32mm, film thickness = 0.25µm, carrier gas = helium). The GC-temperature was programmed from 30°C (5 min) to 150°C (15°/min.) and then to 320°C (20min) at a rate of 3°C/min. Carbon isotope ratios are notated as δ-values ($\delta^{13}C$ [‰]) relative to the PDB-standard and have been corrected for the addition of carbon during derivatisation. Several CO_2-pulses of known ^{13}C value at the beginning of each run were used for calibration. Reported $\delta^{13}C$ values were obtained by two to three replicate analyses of each sample to calculate the average carbon isotopic composition. Instrumental precision was checked regularly with standard mixtures of *n*-alkanes (C_{16}-C_{30}), fatty acid methyl esters (C_{19}, C_{31}) and cholesterol-d_6, all of known carbon isotopic composition and resulted in standard deviations < 0.4.

The isolines presented in the distribution map of TOC are based on the VG Gridding Algorithm supplied by the ODV-software package (Schlitzer, 2002), allowing to construct a variable resolution, rectangular grid, where grid-spacing along X and Y directions varies according to data density.

2.2.3. Data presentation and subgrouping of samples

Based on the organic carbon contents and distribution (see below) and the geographical, hydrographical and environmental settings, the samples originating from the eastern part of the Fram Strait and covering the area and surrounding of the Yermak Plateau have been either arranged onto different *Transects* (*I-III*, indicated in Fig. 2.1.) or into groups characterising different regions of the investigation area.

The approximately longitudinal *Transects I & II* are both located >80°N and directed across the Yermak Plateau. Most stations contained therein derive from permanently ice-covered locations. However, both *Transects* include towards the east stations seasonally influenced by the MIZ and stations with temporary open water conditions. *Transect III* is directed from approximately 76.5°N in the south (open water) across the MIZ towards the north (permanently ice-covered) and follows the inflow of Atlantic water from the WSC along the western flank of the Yermak Plateau within the YSC. Besides our study, oceanographic and biological investigations were performed on similar stations or adjacent *Transects* and stations recently (Andreassen et al., 1996; Owrid et al., 2000; Soltwedel et al., 2000; Rudels et al., 2000; Rutgers van der Loeff et al., 2002; Schewe and Soltwedel, in press). Despite presenting data of individual stations along the above mentioned *Transects*, stations have been arranged also in groups representative of the following subareas: Open Water (OW), Marginal Ice Zone (MIZ), Yermak Plateau (YP; water depth of about 1000m), deep (>2000m) Arctic Ocean (AO) and stations on the western flank of the Yermak Plateau (YSC, Yermak slope current).

2.2.4. Grouping of aliphatic lipids

Among the numerous individual aliphatic lipids detected, some must be considered to be rather unspecific with respect to a distinct source, but others have the potential to trace and differentiate at least between a "marine" and "terrestrial" origin, respectively to indicate autochthonous and allochthonous contributions. Rather than trying to separate distinct organism groups (e.g. diatoms, dinoflagellates, sea-ice algae) probably contributing in varying relations to the organic fraction of the sediments, we decided to define three "lipid pools", representative in a more general meaning for organic carbon amounts derived from:

a.) Primary production (marine phytoplankton, sea-ice algae),

b.) Secondary inputs (either by feeding of zooplankton, benthic organisms, and bacteria on the former and thus "recording" primary production),

c.) Terrestrial-derived contributions.

Based upon their structure and, where possible also by their compound specific carbon isotopic composition, individual compounds of the lipid classes investigated (fatty acids, *n*-alkanes and *n*-alkanols) have been attributed to the above mentioned groups and summed up in concentration. These groups and summed amounts will later be used to illustrate and discuss their distribution in relation to ice-cover, the MIZ, current regime and transportation processes, and the proportion of the "terrestrial" extractable organic carbon fraction occurring within the surface sediments on and around the Yermak Plateau. It is obvious that a reduction to these groups retains all information relevant for an interpretation of the dataset with respect to the sources and deposition of sedimentary lipids for the area of investigation.

With respect to primary production (and per definition), this group should include compounds derived from photoautotrophic carbon fixation. In contrast to the temperate marine environment, however, in polar seas the range of potential primary producers is extended and includes algae living within, on, or under sea-ice, at the MIZ or in open water areas. Fatty acids identified within our sediments representative of primary production include e.g. 16:1*n-7*, 20:5*n-3*, 22:6*n-3* and 14:0, thus compounds commonly attributed to a phytoplankton source (e.g. Volkman, 1986). Ideally, organic carbon derived from primary production will be exported throughout the water column and preserved within the sediments. However, a varying part of it is supplied to and transformed by pelagic and benthic heterotrophic organisms and either re-enters the marine organic carbon cycle as CO_2 or is fixed as secondary organic carbon within the biomass of heterotrophic consumers and up to higher trophic levels. Besides the respiration of primary organic carbon to CO_2, secondary organic carbon will also likely contribute to the sedimentary organic carbon pool, e.g. as biomass and lipids of bacteria, benthic organisms and zooplankton. Bacterial contributions to the sedimentary organic carbon fraction can be deduced e.g. by the occurrence of specific bacterial lipids such as straight chain, iso- and anteiso-C_{15} and-C_{17} fatty acids (Perry et al., 1979, Volkman et al., 1980). Within the water column, zooplankton grazing especially by copepods is a major

control on the amount of primary produced organic matter exported from the euphotic zone to the seafloor. However, zooplankton not only may reduce the flux of primary organic carbon to the sediment, but can also enhance it by producing large, fast-sinking fecal pellets, which channels the otherwise slowly sinking phytoplankton carbon rapidly to great depths (Wexels Riser et al., 2002). A significant part of the primary organic carbon taken up by grazing will be converted to zooplankton lipids as products of *de novo* synthesis or by modifications of the ingested primary lipids. As an adaptation to the cold and to the strong seasonality in food availability, copepods from both polar oceans store large amounts of lipid reserves to maintain their life cycles during winter. Wax esters were identified as the paradigmatic depot lipid (Albers et al., 1996) in polar marine copepods, containing predominantly monounsaturated C_{20} and C_{22} fatty acids usually not encountered in other marine organisms. Therefore, these fatty acids are considered to be markers of calanoid copepods (Sargent and Henderson, 1986; Sargent and Falk-Petersen, 1988, Albers et al., 1996). Other fatty acid constituents of copepods derive directly from the diet and are incorporated unchanged, as known for polyunsaturated, so called essential fatty acids such as 22:6*n-3* and 20:5*n-6* (Albers et al., 1996).

Given the examples outlined above, in the subsequent sections of this paper, aliphatic lipids derived from either of both principle sources will be referred to as "primary products" and "secondary compounds", however, with respect to the environment from which they originate, they also will be termed "marine" in contrast to compounds referred to as "terrestrial".

Long-chain, odd-numbered *n*-alkanes, long-chain, even-numbered *n*-alkanols, and long-chain, even-numbered *n*-fatty acids (all > C_{21}) are commonly attributed to a terrestrial source, as these are the major classes of aliphatic cuticular land-plant wax components (for a recent review see Kunst and Samuels, 2003). Initially we intended to include all of the above-mentioned compounds into the lipid group representing terrestrial contributions, but based on their individual carbon isotopic composition, the long-chain even numbered fatty acids (LCFA) appeared to be of a mixed origin and not of the same source as the long-chain *n*-alkanols and *n*-alkanes. Therefore, only a distinct amount of the LCFA within the sediments have been attributed to a higher land-plant origin, which will be addressed to in more detail in section 2.3.5.

2.3. Results and discussion

2.3.1. Total organic carbon (TOC) content

The distribution of total organic carbon (TOC) contents in the Fram Strait is given in the map shown in Fig. 2.2. To improve data density, additional own data from stations nearby and from previous studies (Hebbeln and Berner, 1993; Stein et al., 1994a; Kierdorf, 2001, Birgel and Stein, in press; see also chapter 3) have been included, despite the samples used for lipid analysis (indicated by white outlines). TOC values ranged from < 0.5 up to > 1.5 %. In general, TOC-contents divide the Fram Strait along 0° into two regions, with lower values (< 0.75 %) to the west and higher (> 0.75 %) TOC-contents toward the east. The lower TOC contents in the western part correspond to the permanently ice-covered area influenced by the cold and less productive Arctic

waters of the EGC. However, a local maximum with TOC-values > 1.25 % is developed east off Greenland in an area between ca. 80/81°N and 10/15°W, corresponding to the region of open water (ice-free) conditions of the NE Greenland polynya. According to Hebbeln and Berner (1993), this is related to enhanced primary productivity caused by the open water conditions of the polynya, providing light and nutrients favouring phytoplankton growth.

Towards the eastern part of the Fram Strait, surface sediments are generally characterised by increased TOC-values (>0.75 %). Towards the shallow western Spitsbergen shelf TOC-values increase up to > 1 %. Higher biological productivity, caused by open water conditions and the "warm" surface waters of the WSC seems to be the most reasonable explanation for enhanced TOC-contents on the slope west off Spitsbergen. In addition, an input of terrigenous organic matter across the slope (mainly via gravity-driven, near-bottom downslope transportation, Hebbeln and Berner; 1993) towards the deeper central Fram Strait is supplied by the fjords of Spitsbergen, where TOC contents amount up to > 1.5 %.

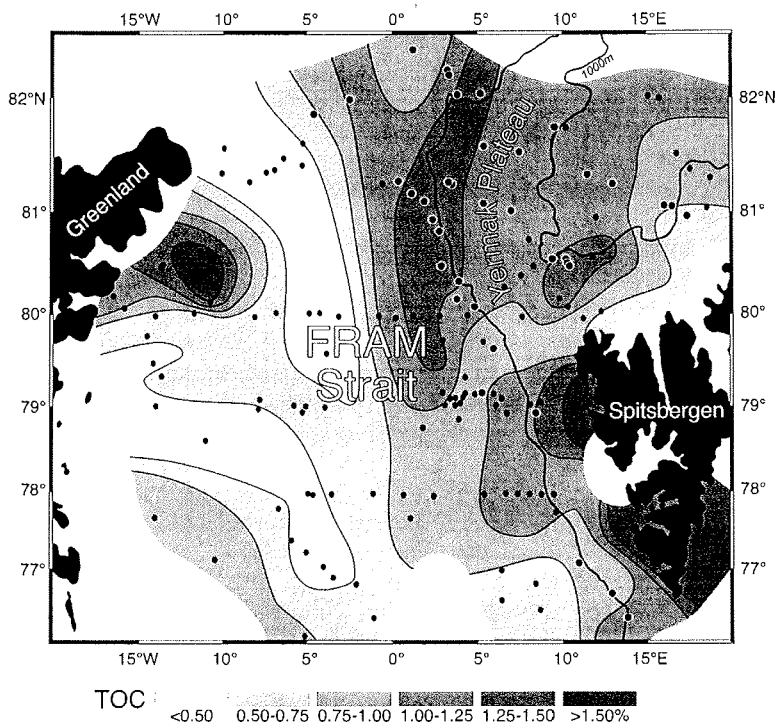

Fig. 2.2. TOC-content (%) of surface sediments in the Fram Strait. Samples used for lipid analysis are indicated by a white outline.

Most interesting, locally enhanced TOC contents (>1.25 %) are further recorded in the surface sediments situated on the western flank of the Yermak Plateau and north off Spitsbergen. For stations located close to 80°N, these elevated C_{org} values are reasonable explained by enhanced seasonal productivity in the

vicinity of the ice-edge, where melting processes locally supply nutrients. North of Spitsbergen, productivity might be additionally triggered by relatively warm Atlantic water transported via the NSC. However, most of the stations on the western flank of the Yermak Plateau up to approximately 82°N, where TOC-contents also reach > 1.25 %, are ice-covered throughout the year. For these stations, it seems not plausible to relate enhanced organic carbon contents to overlying surface water productivity. As described above, this part of the Yermak Plateau is influenced by the Yermak Slope Current (YSC, *cf.* Fig. 2.1.). Therefore, high TOC-values at these stations might result from the northward transportation of organic carbon along the western part of the Yermak Plateau within the YSC. This is in good agreement with contemporary studies describing resuspension and particle transport occurring especially on the western flank of the Yermak Plateau (Rutgers van der Loeff et al., 2002). Based on pigment distributions within the same area, such a transportation mechanism from south to north was also proposed by Soltwedel et al. (2000).

2.3.2. Concentrations and distribution of compound classes and $\delta^{13}C_{org}$

The concentrations of the respective aliphatic compound classes, their sum and the $\delta^{13}C_{org}$ values of the investigated samples are given in Tab. 2.1., indicating also the *Transects* and/or subareas, to which the stations have been assigned to.

Total concentrations of aliphatic lipids varied considerably and approximately by one order of magnitude, from 1147 μg/g TOC (PS2851) in the northernmost part of the Fram Strait up to 9549 μg/g TOC (PS55/77) in the vicinity of the MIZ at 80°N, 5°E. Total fatty acids not only clearly dominated the aliphatic lipids, but also showed a high variability from 742 (PS2851) up to 9077 μg/g TOC (PS55/77). Total *n*-alkanes ranged from 167 (PS2865) to 392 μg/g TOC (PS57/131), and comparable concentrations were found for *n*-alkanols (85–431 μg/g TOC, PS57/138 and PS55/95, respectively). Thus, at all stations the concentrations of fatty acids exceeded those of *n*-alkanes and *n*-alkanols at least by factors of > 5-10.

Despite the large variations observed in the concentrations of the lipid classes, $\delta^{13}C_{org}$ values remained relatively constant (average -22.3 ‰ ±0.4 S.D., *n*=38) and varied from -23.9 ‰ (PS 57/131) to -21.5 ‰ (PS 2849). It should be noted that only two out of the 38 samples showed a relative ^{13}C-depletion corresponding to $\delta^{13}C_{org}$-values < -23 ‰. Both, the carbon isotopic composition and the high abundance of fatty acids (mainly composed of mono- and polyunsaturated compounds, see below) as a first hint point towards a dominating proportion of organic material derived from a marine source. The suggested predominant marine origin for most of the organic matter inferred from the bulk carbon isotope ratios is in accordance with reports from other regions of the Arctic Ocean. The average $\delta^{13}C_{org}$ value of –22.3 ‰ (± 0.4 S.D) obtained within our study can be compared to the value of –21.6 ‰ (± 0.3) representative of Arctic pelagic primary producers determined by Hobson and Welch (1992) and to the range of $\delta^{13}C_{POC}$ from -22.0 to –23.2 ‰ (*n*=3) in surface waters of the North East Water Polynya in the western part of the Fram Strait (Notholt, 1998).

Tab. 2.1. Concentrations of aliphatic lipid classes (μg/g TOC) and $\delta^{13}C_{org}$ of surface sediments in northeastern Fram Strait. Bold numbers indicate minimum and maximum values.

Sample	*Transect*/ subarea[1]	*n*-alkanes	*n*-alkanols	fatty acids	total	$\delta^{13}C_{org}$ [‰]
PS2830	I	331	268	1573	2172	-22.6
PS2831	I/MIZ	266	190	2778	3234	-22.3
PS2832	I	252	187	1578	2017	-21.9
PS2834	II/YP	262	181	1356	1799	-21.9
PS2835	II/YP	223	207	1380	1810	-22.0
PS2836	II/YP	242	201	1261	1704	-22.2
PS2837	III/YSC	258	142	1412	1812	-22.4
PS2838	III	228	151	1407	1786	-22.1
PS2847	II/AO	242	190	1091	1523	-21.9
PS2848	II/AO	265	199	1378	1842	-22.0
PS2849	I/AO	249	226	951	1426	**-21.5**
PS2851	I/AO	235	170	**742**	**1147**	-22.1
PS2853	I/AO	218	184	1159	1561	-22.2
PS2854	I/III/YSC	180	313	2283	2776	-22.3
PS2855	I/YP	257	147	1117	1521	-22.0
PS2856	I/YP	265	173	1256	1694	-21.9
PS2857	I/YP	252	227	1257	1736	-21.8
PS2858	I/YP	235	160	1527	1922	-22.5
PS2859	I/YP	246	193	1247	1686	-22.4
PS2860	I	239	144	1063	1446	-22.0
PS2861	I	251	191	1192	1634	-22.2
PS2863	II/MIZ	267	190	1487	1944	-22.1
PS2864	II/MIZ	242	225	2222	2689	-22.1
PS2865	II	167	122	1262	1551	-22.9
PS55/77	III/MIZ	261	211	**9077**	**9549**	-22.4
PS55/92	III/YSC	278	172	3838	4288	-22.5
PS55/93	III/YSC	289	287	5231	5807	-22.4
PS55/95	II/YSC	273	**431**	3223	3927	-22.3
PS55/97	II/YP	261	191	1579	2031	-22.3
PS55/98	III/YSC	292	182	4053	4527	-22.2
PS55/158	III/OW	245	120	3263	3628	-22.3
PS57/123	III/OW	209	97	2131	2437	-22.6
PS57/131	III/OW	**392**	131	1863	2386	**-23.9**
PS57/138	III/OW	n.d.	**85**	1529	1614	-23.5
PS57/145	III/OW	n.d.	93	1758	1851	n.d.
PS57/153	III/OW	223	107	3324	3654	-22.0
PS57/157	III/MIZ	355	195	4136	4686	-22.5
PS57/160	III/YSC	266	190	6631	7087	-22.4
PS57/161	III/YSC	280	153	3240	3673	-22.4

([1]abbrev. used for subareas: AO = Arctic Ocean (>2000m water depth, >81.5°N); YP = Yermak Plateau (approx. 1000m water depth); OW = Open water (<80°N); MIZ = Marginal Ice Zone; YSC = Yermak Slope Current. n.d. = not determined)

Compilations of $\delta^{13}C_{org}$ values from Arctic Amerasian continental shelf sediments (Naidu et al., 2000) and the Siberian Laptev Sea shelf (Mueller-Lupp et al., 2000) showed a general cross-shelf increase in $\delta^{13}C_{org}$ due to seawards increasing contributions of marine organic carbon. Depending on the shelf area, values of –24 ‰ to –21 ‰ were attributed to represent the marine organic carbon source, whereas the terrestrial proportions of organic carbon showed a rather uniform $\delta^{13}C_{org}$-value of approximately –27 ‰. For comparison, $\delta^{13}C_{org}$-ratios from typical modern Arctic tundra vegetation range from –27.2 to –29.2 ‰ (Pfeiffer and Jansen, 1993; Gundelwein, 1998).

The different characteristics for the subareas defined with respect to the occurrence of aliphatic lipids are most obvious from the averaged concentrations given in Tab. 2.2. It is noteworthy that the averaged total fatty acid concentrations (and consequently also the sum of total aliphatics) showed a marked difference with respect to the environmental regimes, whereas the average total amounts of *n*-alkanes and *n*-alkanols did not show major variations.

On average, lowest amounts of total aliphatics were present in those regions covered permanently by ice, i.e. in surface sediments north of the Yermak Plateau towards the deeper (> 2000 m) Central Arctic Ocean (AO, 1500 μg/g TOC, Tab. 2.2.) and on the shallower (< 1000 m) Yermak Plateau itself (YP, 1767 μg/g TOC, Tab. 2.2.). Total fatty acid concentrations averaged 1064 μg/g TOC for the AO and 1331 μg/g TOC on the YP. As mentioned, both regions are characterised by a permanent ice-cover, increasing in thickness with northerly direction. Thus, the somewhat reduced concentrations of total fatty acids in the AO compared to the YP might reflect an influence of the thickness of the ice-cover on the amounts of fatty acids produced and deposited in the sediments. Maximum average concentrations of total aliphatics (4420 μg/g TOC) and total fatty acids (3940 μg/g TOC) have been obtained for stations situated under or in the vicinity of the MIZ (Tab. 2.2.), supposed to represent the zone of highest seasonal primary productivity. Despite maximum average amounts, surface sediments originating from the area related to the MIZ are also characterised by a high variability, as expressed by the range in total fatty acid concentrations (min. 1944 μg/g TOC, max. 9077 μg/g TOC).

Both, maximum concentration and variation thus might reflect the highly dynamic and productive environmental conditions of the MIZ. In the open water (OW) areas south of the MIZ, total aliphatic lipids averaged 2595 μg/g TOC and total fatty acids 2311 μg/g TOC, which is lower than at the MIZ but higher than compared to the ice-covered AO and YP. For the YSC region, even though situated also under permanent ice-coverage, concentration levels of aliphatic lipids were found to be surprisingly high (total: 4237 μg/g TOC, fatty acids: 3739 μg/g TOC, Tab. 2.2.) and better compare to those at the MIZ rather than to the low amounts observed for the YP and AO. With respect to the different regions, average concentrations of total *n*-alkanes and *n*-alkanols remained fairly constant. As they did not mirror the variations observed for the fatty acid amounts in relation to their point of deposition, (Tab. 2.2.) we suggest that *n*-alkanes and *n*-alkanols mostly originate from other sources than primary or secondary production.

Tab. 2.2. Average, minimum and maximum values of aliphatic lipid classes (μg/gTOC) and $\delta^{13}C_{org}$ for different subregions of northeastern Fram Strait

	n-alkanes	*n*-alkanols	fatty acids	total	$\delta^{13}C_{org}$ [‰]
AO[1]					
average	*242*	*194*	*1064*	*1500*	*-21,9*
min	218	170	742	1147	-22,2
max	265	226	1378	1842	-21,5
YP[1]					
average	*249*	*187*	*1331*	*1767*	*-22,1*
min	223	147	1117	1521	-22,5
max	265	227	1579	2031	-21,8
MIZ[1]					
average	*278*	*202*	*3940*	*4420*	*-22,3*
min	242	190	1487	1944	-22,5
max	355	225	9077	9549	-22,1
YSC[1]					
average	*265*	*234*	*3739*	*4237*	*-22,4*
min	180	142	1412	1812	-22,5
max	292	431	6631	7087	-22,2
OW[1]					
average	*267*	*106*	*2311*	*2595*	*-22,9*
min	209	85	1529	1614	-23,9
max	392	131	3324	3654	-22,0

([1] for abbrev. see Table 2.1. and text)

Regarding the averaged $\delta^{13}C_{org}$ for the different regions given in Tab. 2.2., a slight enrichment in ^{13}C of about 1 ‰ was observed when comparing sediments from open water stations (average –22.9 ‰) and those from permanently ice-covered regions (average AO: -21.9 ‰; YP: -22.1 ‰). Thus, $^{13}C_{org}$-enrichment towards the north either reflects a likely higher contribution of organic carbon produced by ice algae, but could also derive from a dilution of marine and/or ice algae derived organic matter with slightly enhanced proportions of a terrestrial source further to the south. Conversely, as the northern stations display a depletion in ^{13}C of about –4 ‰ compared to the assumed –18 ‰ for ice algae (see above), the overall contribution of ice algae seems to be low even in the permanently ice-covered region, or is diluted by an additional input of an isotopically light organic carbon source. However, we will not follow up this discussion, as all explanations of a given carbon isotopic composition with at least three probable sources will remain highly speculative.

2.3.3. Composition and sources of sedimentary fatty acids

In the following, an overview on the composition of the fatty acids identified in the samples is provided, and their potential sources are discussed paying special emphasis to the uniqueness of the Arctic environment. The highly variable amounts of the individual fatty acids are given in detail in Tab. 2.3., which also indicates (by letters A, B, and C) those compounds attributable to the different lipid pools (*cf.* Section 2.2.4.). To facilitate a comparison of the fatty

acid distribution with respect to the different regional settings (see above), averaged values are additionally presented in Tab. 2.4.

The fatty acids consisted of branched (iso-/anteiso-C_{15} and C_{17}), *n*-saturated, monounsaturated (MUFA) and polyunsaturated (PUFA) compounds. In all samples, even numbered fatty acids (especially those with 14, 16 and 18 carbon atoms) showed a strong predominance. Relative proportions of saturated fatty acids (C_{14}-C_{28}) ranged from 25 % at the MIZ (station PS55/77) up to 56 % in the northern, ice-covered part of the Fram Strait (station PS2851), mostly in covariance with total monounsaturates (MUFA, 29 % to 59 %, Tab. 2.3.). However, the fatty acids also contained significant proportions of polyunsaturates (PUFA, Tab. 2.3.), up to 22 % at station PS55/77.

Tab. 2.3. Fatty acid composition (µg/g TOC) of surface sediments from the eastern Fram Strait and on the Yermak Plateau

		Transect	I	I	I	I+III	I	I	I	I	I	I	I	I	I
		Area	AO	AO	AO	YSC	YP	YP	YP	YP	YP				MIZ
Compound	Lipid pool	Station	2849	2851	2853	2854	2855	2856	2857	2858	2859	2860	2861	2832	2831
n-Saturates															
14	A		40	32	48	98	44	54	46	57	48	43	54	78	113
15	B		13	10	15	28	13	16	13	17	15	13	13	19	24
16			153	119	169	339	161	190	185	230	189	157	183	263	436
17	B		4	6	9	23	10	10	6	9	8	9	5	7	30
18			47	34	41	70	31	37	43	40	37	34	34	41	72
20			28	19	19	33	16	20	29	23	22	20	21	24	22
21			7	5	4	6	7	6	5	6	4	7	6	6	11
22			35	25	26	47	27	30	36	36	32	31	28	37	32
23			11	4	9	19	12	12	14	13	13	10	14	12	11
24	C		54	55	59	115	62	68	70	72	75	65	58	62	71
25			12	12	12	18	11	14	20	15	17	15	17	19	14
26	C		57	56	59	104	55	60	63	68	67	63	60	61	60
27			13	15	13	20	13	13	16	15	14	16	15	12	11
28	C		45	23	43	83	25	45	41	39	38	33	31	34	45
Monounsaturates															
16:1*n*-7	A		119	97	202	470	206	223	231	270	219	174	243	318	625
16:1*n*-5	A		27	24	39	86	36	14	57	56	43	39	60	31	108
18:1*n*-9	B		51	24	52	103	64	62	63	103	64	45	50	71	159
18:1*n*-7	B		43	41	108	226	99	111	89	131	102	89	101	152	266
20:1*n*-9	B		8	3	28	9	27	21	10	20	12	14	5	7	36
20:1*n*-7	B		5	4	3	17	3	4	10	9	3	4	14	10	9
22:1*n*-11, *n*-9	B		38	24	15	40	31	32	31	47	28	25	27	34	33
Polyunsaturates															
18:2			13	5	9	13	11	27	30	38	16	9	25	48	30
18:4*n*-3	A		34	26	36	47	22	18	6	26	29	24	9	24	38
20:2			10	8	8	12	7	9	13	8	7	8	5	14	9
20:4*n*-6	A		4	4	15	20	8	17	15	24	12	12	12	27	112
20:5*n*-3	A		5	3	15	23	14	20	12	29	10	8	14	28	222
20:4*n*-3	A		6	4	6	11	4	7	0	7	5	6			13
22:6*n*-3	A		5	6	4	11	3	5	2	7	8	7	3	5	15
Branched															
i-15	B		23	19	36	70	35	41	40	42	42	31	31	50	53
ai-15	B		29	25	44	95	42	49	46	51	51	38	42	65	64
i-17	B		5	5	7	16	9	10	8	11	8	7	7	9	21
ai-17	B		8	7	9	15	9	10	9	11	9	7	9	13	16
Total (µg/g TOC)			951	742	1159	2283	1117	1256	1257	1527	1247	1063	1192	1578	2778
% saturated			54	56	45	44	44	46	47	42	46	48	45	43	34
% MUFA			31	29	39	42	42	37	39	42	38	37	42	40	44
% PUFA			8	7	8	6	6	8	6	9	7	7	6	9	16
% branched			7	7	8	9	8	9	8	7	9	8	7	9	6
16:1/16:0			1.0	1.0	1.4	1.6	1.5	1.2	1.6	1.4	1.4	1.4	1.7	1.3	1.7
18:1/18:0			2.0	2.0	3.9	4.7	5.2	4.7	3.5	5.9	4.5	3.9	4.4	5.4	5.9

(continued on next page)

Tab. 2.3. (continued)

		Transect	I	II	II	II	II	II	II	II	II	II	II	III	III
		Area		AO	AO	YSC	YP	YP	YP	YP	MIZ	MIZ			YSC
Compound	Lipid pool	Station	2830	2847	2848	55/95	55/97	2836	2835	2834	2863	2864	2865	2838	55/98
n-Saturates															
14	A		78	48	65	99	62	49	55	42	68	110	55	66	200
15	B		20	12	17	19	14	14	17	13	14	22	11	19	29
16			276	171	225	349	250	186	203	177	242	366	186	215	521
17	B		21	8	7	15	7	9	8	5	6	12	6	12	11
18			51	43	47	59	41	38	41	40	40	66	29	45	56
20			27	23	25	21	9	22	20	20	22	30	13	18	25
21			5	7	6	4	6	7	7	6	6	7	3	7	7
22			40	32	35	33	38	30	29	23	28	33	19	26	27
23			12	8	11	20	13	10	13	10	11	10	6	13	12
24	C		82	65	65	69	68	63	58	48	65	62	35	68	60
25			19	17	17	15	22	12	12	18	21	17	8	14	20
26	C		81	64	69	65	72	54	49	54	70	62	32	65	61
27			16	18	16	14	18	11	14	11	26	19	14	13	19
28	C		70	68	46	72	54	27	36	33		39	38	40	38
Monounsaturates															
16:1*n*-7	A		269	175	257	815	309	227	286	332	312	429	261	247	1012
16:1*n*-5	A		28	29	34	408	44	39	52	165	38	40	44	68	947
18:1*n*-9	B		61	44	67	323	89	67	67	55	90	232	64	58	198
18:1*n*-7	B		99	83	125	178	115	128	140	86	99	34	114	143	28
20:1*n*-9	B		23	9	7	19	14	9	15	7	9	16	21	15	24
20:1*n*-7	B		5	6	13	67	15	7	2	14	15	12	9	2	44
22:1*n*-11, *n*-9	B		33	30	19	93	23	38	29	23	33	32	21	28	75
Polyunsaturates															
18:2			20	6	21	36	50	13	13	28	28	125	22	10	145
18:4*n*-3	A		41	36	10	28	25	27	28	7	14	49	18	24	47
20:2			13		11	7		9	5	9	15	26	5	8	13
20:4*n*-6	A		18	4	18	85	53	24	19	16	30	93	65	17	61
20:5*n*-3	A		62	7	16	165	62	18	27	16	74	107	62	26	227
20:4*n*-3	A		6		7	11		7	5	7			7	8	
22:6*n*-3	A		7	3	4	12	5	8	13	3	6	10	12	13	5
Branched															
i-15	B		30	28	41	47	36	42	45	32	39	57	29	43	48
ai-15	B		41	37	59	51	44	47	54	41	49	71	33	55	65
i-17	B		11	7	9	16	11	10	10	7	11	18	11	10	15
ai-17	B		12	7	10	9	11	8	11	8	9	16	10	11	13
Total (µg/g TOC)			1573	1091	1378	3223	1579	1261	1380	1356	1487	2222	1262	1407	4053
% saturated			51	53	47	26	43	42	41	37	42	39	36	44	27
% MUFA			33	34	38	59	39	41	43	50	40	36	42	40	57
% PUFA			11	5	6	11	12	8	8	6	11	18	15	8	12
% branched			6	7	9	4	6	8	9	6	7	7	7	8	3
16:1/16:0			1.1	1.2	1.3	3.5	1.4	1.4	1.7	2.8	1.4	1.3	1.6	1.5	3.8
18:1/18:0			3.1	2.9	4.1	8.5	4.9	5.2	5.1	3.5	4.7	4.0	6.1	4.5	4.1

(continued on next page)

Tab. 2.3. (continued)

		Transect	III	III	III	III	III	III	III	III	III	III	III	III	III
		Area	YSC	YSC	YSC	YSC	YSC	MIZ	MIZ	OW	OW	OW	OW	OW	OW
Compound	Lipid pool	Station	2837	55/93	55/92	57/160	57/161	55/77	57/157	55/158	57/153	57/123	57/131	57/138	57/145
n-Saturates															
14	A		62	262	223	340	177	591	221	164	188	122	95	63	36
15	B		16	35	31	57	28	51	30	26	28	25	23	19	16
16			218	719	572	1194	512	1353	627	485	582	375	291	192	242
17	B		15	30	10	25	8	13	27	12	9	27	17	13	11
18			34	85	53	112	49	72	54	65	49	50	46	30	51
20			15	22	21	48	20	23	31	39	19	12	16	11	22
21			7	5	8	10	6	7	5	3	6	2	4	3	5
22			25	38	28	47	27	27	25	22	24	14	20	10	17
23			10	19	10	19	10	10	9	8	8	5	7	4	6
24	C		64	91	64	95	61	78	54	54	55	36	48	26	40
25			11	10	18	27	14	14	15	10	13	5	6	7	10
26	C		61	70	62	99	58	61	57	52	57	25	45	22	46
27			8	89	29	54	24	12	20	11	26	10	7	12	20
28	C		20		33	88	33		51		46			49	15
Monounsaturates															
16:1*n*-7	A		309	1575	1256	1956	1068	3612	1307	940	1309	640	488	248	318
16:1*n*-5	A		64	81	90	86	61	93	125	58	65	66	72	235	273
18:1*n*-9	B		129	406	150	1047	136	176	246	126	105	73	84	76	159
18:1*n*-7	B		22	380	264	125	227	591	435	399	159	236	184	151	35
20:1*n*-9	B		17	25	16	46	17	31	42	16	13	13	18	14	15
20:1*n*-7	B		6	80	28	39	31	36	51	51	25	13	44	28	41
22:1*n*-11, *n*-9*	B		31	44	33	36	31	92	22	29	27	5	11	6	28
Polyunsaturates															
18:2			58	38	70	123	63	97	67	59	63	15	23	26	93
18:4n-3	A		11	96	36	76	59	231	74	19	72	40	36	27	26
20:2			7	6	24	98	22	63	21	38	23	14	4	16	32
20:4*n*-6	A		31	288	111	208	78	800	87	140	53	59	48	66	47
20:5*n*-3	A		36	500	432	197	256	773	224	282	150	129	94	65	45
20:4*n*-3	A		6	38		28		15	64				7		22
22:6*n*-3	A		6	10	11	11	8	16	9	9	7	8	13	15	5
Branched															
i-15	B		44	71	53	74	57	49	47	43	50	37	41	33	28
ai-15	B		48	79	56	96	67	51	54	55	66	51	47	32	32
i-17	B		13	23	24	101	18	21	20	24	16	14	16	11	17
ai-17	B		11	16	24	68	12	18	16	22	14	13	11	20	8
Total (µg/g TOC)			1412	5231	3838	6631	3240	9077	4136	3263	3324	2131	1863	1529	1758
% saturated			40	28	30	33	32	25	30	29	33	33	33	30	31
% MUFA			41	50	48	50	49	51	54	50	51	49	48	49	49
% PUFA			11	19	18	11	15	22	13	17	11	12	12	14	15
% branched			8	4	4	5	5	2	3	4	4	5	6	6	5
16:1/16:0			1.7	2.3	2.4	1.7	2.2	2.7	2.3	2.1	2.4	1.9	1.9	2.5	2.4
18:1/18:0			4.5	9.3	7.8	10.5	7.4	10.7	12.5	8.1	5.4	6.2	5.9	7.6	3.8

Station locations are given in Fig. 2.1., for area abbreviations (AO, YP, MIZ, OW, YSC) see Tab. 2.1. and section 2.2.4. *: sum of both isomers, MUFA: monounsaturated fatty acids, PUFA: polyunsaturated fatty acids, letters A, B, C indicate assignment of fatty acids to the lipid pools explained in section 2.2.4. Note that the amounts of long chain fatty acids assigned to lipid pool C in this table are not corrected for their observed mixed origin (see text).

Branched fatty acids showed less variability and were of minor relative and absolute abundance. Overall, they accounted for only 5 to 10 % of the total fatty acids. The short-chain C_{16} and C_{18} fatty acids were of paramount abundance throughout all samples, with (a) a general predominance of the respective monounsaturated compounds (i.e. the ratios 16:1/16:0 and 18:1/18:0 being >1, Tab. 2.3.) and (b) a higher abundance of C_{16} than C_{18} structures. Compared to C_{16} and C_{18} monounsaturated fatty acids, $C_{20:1}$ and $C_{22:1}$ were present at distinct lower levels. Polyunsaturated fatty acids ranged in carbon atom numbers from 18 to 22 and contained a number of 2 to 6 unsaturations. 20:4 and 20:5 not only clearly dominated the PUFA-fraction, but also were often found at higher amounts than 18:1 and the long-chain saturates (> *n*-C_{22}). When comparing

individual fatty acids among all stations, significant differences in the extent of the respective concentration ranges (i.e. the ratio of maximum/minimum concentrations) became obvious, depending on the fatty acid type. As a general rule, this variability increased in magnitude from even LCFA ~ branched < saturates < MUFA < PUFA. Thus, the concentrations of branched and even numbered LCFA varied only by a factor of about 5-10, whereas those of the MUFA and PUFA varied by factors of up to ~60 and ~270, respectively. In terms of absolute amounts, the concentrations of the two major C_{16}-fatty acids varied from 119 to 1353 μg/g TOC (16:0) and 97 to 3612 μg/g TOC (16:1*n-7*), respectively. The highest variability was observed for 20:5*n-3*, ranging over two orders of magnitude from 3 up to 773 μg/g TOC (Tab. 2.3.).

Though averaging smoothes much of this variability, distinct differences in the fatty acid compositions characterising the environmental settings remained still obvious (Tab. 2.4.). On average, stations associated with the position of the MIZ not only contained highest total fatty acid amounts (3940 μg/g TOC) and the highest fraction of PUFA (18.1 %) but also lowest proportions of saturated (30.3 %) and branched (3.5 %) compounds. Compared to the MIZ, this situation is reversed for surface sediments deposited under permanent ice-cover, (with the exception of YSC-stations, see below) were saturates (50.5 and 42.9 %) and branched fatty acids (7.8 and 7.9 %, AO and YP, resp., Tab. 2.4.) are of more relative importance and total fatty acid concentrations are lowest (1064 μg/g TOC, AO and 1331 μg/g TOC, YP). Surface sediments from the area of open water conditions compare in fatty acid composition to those of the MIZ, but the organic carbon fraction of OW-stations contained only about half the amounts (2311 μg/g TOC) of total fatty acids than the average of MIZ (3940 μg/g TOC). Though under permanent ice-cover (comparable to AO and YP), surface sediments on the western Yermak Slope contained fatty acids similar in concentration and distribution as stations at the MIZ (Tab. 2.4., YSC). The reasons for it and implications thereof are addressed in a subsequent section.

The region of the MIZ is known to provide favourable environmental conditions for an enhanced seasonal productivity and indeed, most of the dominating fatty acids described above can reliably be explained to derive from primary production. The most prominent fatty acid within our samples, 16:1*n-7* is a common lipid-constituent in microalgaes of diverse taxa, such as diatoms, dinoflagellates, prymnesiophytes and haptophytes. 16:1*n-7* amounts up > 30 % to the fatty acids of diatoms whilst other algae, e.g. green algae, contain distinct lower down to trace levels (Volkman et al., 1989; Viso and Marty, 1993). Other short-chain fatty acids, such as 14:0, 16:0, 16:1*n-9, n-5*, 18:1*n-9, n-7* are usually encountered from the freshwater to the marine aquatic environment. Being other frequent constituents of the lipid fraction from diverse phytoplankton species (Volkman et al., 1989; Viso and Marty, 1993; Pond et al., 1998; Volkman et al., 1998), their occurrence in water, particulate and sediment samples is therefore usually related to surface water productivity, although not restricted to an exclusive marine origin.

Tab. 2.4. Averaged concentrations (µg/g TOC) of fatty acids in surface sediments for subregions of northeastern Fram Strait

	Area	AO	YP	MIZ	OW	YSC
Compound	lipid pool					
n-Saturates						
14	A	46	51	220	111	183
15	B	13	15	28	23	30
16		167	197	605	361	553
17	B	7	8	18	15	17
18		42	39	61	48	65
20		23	20	26	20	26
21		6	6	7	4	7
22		30	31	29	18	34
23		9	12	10	6	15
24	C	59	65	66	43	77
25		14	16	16	8	17
26	C	61	60	62	41	73
27		15	14	18	14	32
28	C	45	38	27	18	46
Monounsaturates						
16:1*n*-7	A	170	256	1257	657	1058
16:1*n*-5	A	31	56	81	128	228
18:1*n*-9	B	47	70	181	104	311
18:1*n*-7	B	80	111	285	194	181
20:1*n*-9	B	11	15	27	15	22
20:1*n*-7	B	6	7	25	33	39
22:1*n*-11, *n*-9	B	25	31	42	18	48
Polyunsaturates						
18:2		11	25	69	46	68
18:4*n*-3	A	28	21	81	37	50
20:2		7	7	27	21	24
20:4*n*-6	A	9	21	224	69	110
20:5*n*-3	A	9	23	280	127	230
20:4*n*-3	A	5	5	18	5	12
22:6*n*-3	A	4	6	11	9	9
Branched						
i-15	B	29	39	49	39	58
ai-15	B	39	47	58	47	70
i-17	B	7	9	18	16	28
ai-17	B	8	9	15	15	21
Total (µg/g TOC)		1064	1331	3940	2311	3739
% saturated		50.5	42.9	30.3	31.6	31.4
% MUFA		34.8	41.1	48.1	49.7	50.5
% PUFA		6.9	8.1	18.1	13.6	13.4
% branched		7.8	7.9	3.5	5.1	4.7
16:1/16:0		1.2	1.6	2.2	2.2	2.3
18:1/18:0		3.0	4.7	7.6	6.2	7.6

For area abbreviations see Tab. 2.1. and section 2.2.4. For individual fatty acid amounts averaged for the respective areas cf. Tab. 2.3.

It is obvious that in estuaries, shelf regions and marginal seas, thus areas supposed to be influenced by riverine inputs; they may also derive from freshwater/lacustrine species. For the Arctic, this has been shown e.g. for the Siberian Laptev Sea (Fahl and Stein, 1999). Despite an origin from pelagic marine or freshwater/lacustrine phytoplankton, for the polar environment the algal assemblages related to the ice (living in the ice, meltwater-ponds on the ice, in the water column close to the underside of the ice, or close to the ice-edge) provide another attractive and plausible source for the above-mentioned fatty acids. Several studies (e.g. Henderson et al., 1998; Falk-Petersen et al., 1998) have investigated the fatty acid distributions of ice-algal assemblages and phytoplankton from the MIZ in the Barents Sea, adjacent to the east of our investigation area. From these studies it is known that the ice-algal assemblages found under the ice and close to the MIZ are dominated by diatoms such as *Nitzschia frigida* and *Melosira arctica*, congruent with the universal predominance of diatoms in assemblages of sea-ice algae (e.g. Kirst and Wiencke, 1995).

The fatty acid compositions (wt.% of total lipids) of the above mentioned diatoms were found to consist mainly of 14:0, 16:0, 16:1*n-7* and 20:5*n-3*, i.e. of compounds widespread also in diatoms of the temperate environment. High ratios of 16:1/16:0 (>1) have been proposed as an additional proof for the predominant presence of diatoms in marine ecosystems (Parrish et al., 2000). Because of their known ubiquity within sediments but also within organisms of all taxa, the saturated short-chain fatty acids (esp. C_{16} and C_{18}) are considered to be less source-specific than mono- and polyunsaturated fatty acids. Their often-observed predominance in sediments is at least partly explained by their greater long-time resistance to decay either in the water-column or after sedimentary burial. In general, these transformations result in (1) a selective or enhanced preservation of saturates compared to mono- and polyunsaturates and (2) a relative increase of compounds possessing higher carbon atom numbers. With respect to our data, the combination of high ratios of 16:1/16:0, 18:1/18:0, overall low amounts of LCFA and high amounts of PUFA (Tabs. 2.3., 2.4.) indicate that decompositional processes are not a crucial factor controlling the fatty acid composition of the surface sediments. This then decreases also the possibility that 16:0 and 18:0 in our sediments result preferentially from degradational processes, however, we cannot exclude other sources (e.g. zooplankton) contributing significant amounts. In contrast, we likely relate the saturated *n*-fatty acids 14:0 to primary production, consistent e.g. with a high abundance of this compound within diatoms (Volkman et al., 1989; Viso and Marty, 1993), including Arctic ice algae and phytoplankton from the MIZ (Falk-Petersen et al., 1998).

Almost all of the dominant phytoplankton synthesise a variety of polyunsaturated fatty acids at high levels. Diatoms are known to be the primary source of 20:5*n-3*, but can produce also significant amounts of 20:4*n*-3 (Volkman et al., 1989, Zhukova and Aizdaicher, 1995). Our results indicate that both are the principal compounds contributing to the high sedimentary amounts of PUFA in the eastern Fram Strait and on the Yermak Plateau (Tabs. 2.3., 2.4.), adding further evidence towards the predominance of organic matter derived from primary production. Arctic diatoms from the ice assemblage of the

Barents Sea have been shown to contain elevated proportions of 20:5*n-3* up to exceeding the amounts of 16:1*n-7* by a factor of about 2 (Falk-Petersen et al., 1998), however we did not observe this for the sediments.

Arctic and Antarctic zooplankton (copepods) as well as a variety of Arctic benthos organisms have been shown to contain significant levels of 18:1 as well, at comparable or even higher contents than 16:1 (Albers et al., 1996; Graeve et al., 1997). For copepods, 18:1*n-7* is known to result from a subsequent chain elongation following the dietary uptake of a 16:1*n-7* fatty acid (Sargent and Henderson, 1986) and a similar synthetic pathway has been proposed for organisms of the benthos community collected on the shelves off northeast Greenland, Spitsbergen and the western Barents Sea (Graeve et al., 1997). A chain elongation pathway of 18:1*n-9* to 22:1*n-11* via the intermediate 20:1*n-9* is known for copepods of both Polar Oceans (Kattner and Hagen, 1995). As an energetic adaptation to the cold, copepods from high-latitudes are known for their extensive accumulation of storage lipids almost exclusively (> 70 % of total lipid) as wax esters dominated by fatty acids such as the monounsaturates 20:1*n*-9 and 22:1*n-11*, beside 18:1 (Kattner and Hagen, 1995; Albers et al., 1996; Graeve et al., 1997). These specific fatty acid constituents of wax-esters are also known from copepods of the Fram Strait (Kattner et al., 1989), at the MIZ, and in copepods from open waters of Spitsbergen (Scott et al., 2001). PUFA such as 20:5*n-3* and 20:4*n-6* are essential fatty acids for most of the higher marine organisms, including zooplankton. Their variable amounts within Arctic copepods and various benthic organisms are considered to reflect different feeding behaviours (Graeve et al., 1997; Scott et al., 2002).

A variety of organisms other than zooplankton are known to be capable for the biosynthesis of C_{18} monounsaturated fatty acids. 18:1*n-7* has been considered to be a bacteria-specific fatty acid marker (Parker and Taylor, 1983; Gillan and Sandstrom, 1985), but a compilation on the fatty acid composition of some representative marine bacteria (Russel and Nichols, 1999) shows 18:1*n-7* only to account for 1-3.6 wt.% of total fatty acids. The odd-numbered *n*-fatty acids with 15 and 17 carbon atoms as well as their *iso*- and *anteiso*-homologues identified in the samples investigated also point towards a bacterial origin (Leo and Parker, 1966; Cooper and Blumer, 1968; Boon et al., 1979; Perry et al., 1979; Sicre et al., 1988). Compared to the higher relative abundances of *n*-, i- and ai-C_{15} and ai-C_{17} acids (8.4-17.5 %) given for marine bacteria by Russel and Nichols (1999), 18:1*n-7* (1-3.6 %) is of only minor importance. Vice versa, the higher amounts of 18:1*n-7* compared to *n*-, *i*-, and *ai*-C_{15} and ai-C_{17} fatty acids within our samples (*cf.* Tabs. 2.3., 2.4.) then point towards a source of 18:1*n-7* other than bacteria, most likely zooplankton.

Long-chain saturated fatty acids (C_{24}-C_{30}) with a strong predominance of even-numbered carbon chains are typical constituents found in surface waxes of higher land plants (Eglinton et al., 1968; Simoneit, 1978; Naraoka and Ishiwatari, 2000). Therefore, their occurrence in marine sediments is usually attributed to reflect terrestrial inputs via riverine or eolian transport or, more important for the Arctic, by sea-ice-transportation. In earlier works (Volkman et al., 1998 and herein), however, it was remarked, that microalgae and bacteria may also produce small amounts of these fatty acids, but less than 2 % relative to C_{14}-C_{20} fatty acids. The occurrence of long-chain fatty acids, e.g. C_{24}, has

been noted also for Arctic phytoplankton and ice algae (Henderson et al., 1998). Based on stable carbon isotopic evidence (see also section 2.3.5.), significant contributions of long-chain, even-numbered saturated fatty acids to the marine sedimentary organic carbon pool derived from a "non-terrestrial" source are now continuously recognised.

In summary, the fatty acid compositions of the sediments from the Fram Strait and on the Yermak Plateau are dominated by products derived from primary production, most likely of a diatom origin as indicated by high amounts of 16:1*n-7*, 20:5*n-3*, 20:4*n-6* and 14:0. Another suite of fatty acids, attributable most likely to bacteria (branched fatty acids) and zooplankton (mainly copepods, 20:1, 22:1 and 18:1 fatty acids) provided evidence that varying parts of the initially produced organic carbon is shifted towards other trophic levels. Compared to the amounts of fatty acids of primary and secondary origin, long-chain fatty acids of a probable, but not exclusive (see section 2.3.5.) higher land plant origin are of definite minor importance. The overall composition of the fatty acid fractions, dominated by high amounts of MUFA and PUFA indicates a "fresh" status of the organic material and points to a rapid export to the seafloor.

2.3.4. Composition and sources of sedimentary *n*-alkanes and *n*-alkanols

In addition to the fatty acids, the distributions of *n*-alkanes and *n*-alkanols were investigated for their contents of compounds of a supposed higher land plant origin and to answer the question if the long-chain fatty acids detected are a reliable measure for terrestrial contribution. The investigation of the hydrocarbon fraction revealed that this compound class consisted primarily of *n*-alkanes in a carbon atom number range from C_{15} up to C_{32}, with the higher homologues usually prevailing (Tab. 2.5.). The *n*-alkanes from cuticular waxes of higher land plants typically range from C_{23}-C_{35} with a distinct prevalence of odd-carbon chain lengths and a concentration maximum typically at C_{27}, C_{29} or C_{31} (Eglinton et al., 1962; Eglinton and Hamilton, 1967; Rieley et al., 1991; Kunst and Samuels, 2003). As the sedimentary *n*-alkanes also showed a pronounced occurrence of odd-numbered homologues in the carbon atom number range >C_{25}, we attribute the sum of C_{25}-C_{31} odd numbered *n*-alkanes to reflect contributions from higher plant derived material. The concentrations of total *n*-alkanes revealed no major variation amongst stations and were generally low compared to the fatty acid fraction (*cf.* Tabs. 2.1., 2.2.). Long-chain *n*-alkanes of supposed higher land plant origin contributed 20 to 47 % to the total *n*-alkanes (Tab 2.5.).

The *n*-alkanols also present in land plant cuticular waxes have a carbon atom number range from C_{22} up to C_{34} and are exclusively comprised of even numbered compounds (Eglinton and Hamilton, 1967; Kolattukudy, 1970; Rieley et al., 1991; Knust and Samuels, 2003). The *n*-alkanols detected in the surface sediments from the Fram Strait and on the Yermak Plateau (Tab. 2.6.) also consisted of even numbered compounds, ranging from C_{16} to C_{28}. Station locations are given in Fig. 2.1., for area abbreviations (AO, YP, MIZ, OW, YSC) see Tab. 2.1. and section 2.2.4. Compounds attributed to a higher land plant origin are indicated by the letter C.

Table 2.5. *n*-alkane distribution in surface sediments from northeastern Fram Strait

Comp.	Lipid pool	*Transect*	I	I	I	I+III	I	I	I	I	I	I	I	I	I
		Area	AO	AO	AO	YSC	YP	YP	YP	YP	YP				MIZ
		Station	2849	2851	2853	2854	2855	2856	2857	2858	2859	2860	2861	2832	2831
15			0.5	1.1	0.9	1.6	5.0	4.0	-	1.4	1.1	0.7	2.3	1.4	1.6
16			2.5	4.9	4.0	5.4	11.5	9.9	1.3	5.7	4.9	4.1	6.4	4.8	7.2
17			6.7	9.5	8.9	8.0	15.2	15.0	6.6	10.3	10.5	9.0	11.4	10.7	11.9
18			8.6	12.3	10.7	10.6	15.2	15.1	9.9	11.7	12.3	12.1	13.0	11.7	15.9
19			12.2	16.0	13.9	14.6	20.0	20.3	14.6	15.9	16.3	16.3	16.0	14.5	23.2
20			11.6	14.4	13.0	11.4	15.7	16.1	13.6	13.0	14.2	14.8	14.8	14.0	17.2
21			15.1	15.8	14.6	12.5	16.5	17.2	15.9	14.8	15.8	16.6	16.5	15.9	18.4
22			14.3	15.0	13.7	11.6	16.0	16.3	15.0	14.3	15.2	15.3	15.2	15.0	17.8
23			20.8	18.1	17.0	13.2	18.0	18.9	19.7	17.3	18.5	19.0	19.5	19.8	19.6
24			13.4	13.1	12.5	10.0	13.4	13.8	13.9	12.3	13.5	13.6	13.7	14.0	14.8
25	C		22.5	18.1	17.3	12.8	17.6	18.6	21.2	18.0	19.1	18.9	19.6	20.5	19.0
26			11.0	10.9	10.7	8.5	11.6	11.9	11.8	10.6	11.4	11.2	11.2	11.7	12.2
27	C		29.5	21.8	20.5	14.5	20.3	21.9	27.4	22.9	23.5	22.5	24.1	25.4	21.7
28			8.5	9.6	9.1	7.5	10.2	10.4	10.3	9.6	10.2	9.8	9.4	10.3	11.0
29	C		33.1	23.2	22.0	15.4	21.2	23.5	31.0	24.8	25.4	23.9	25.5	26.7	23.1
30			5.0	6.4	5.9	5.1	6.8	7.2	7.1	6.7	7.0	6.4	6.4	7.0	7.6
31	C		31.1	20.9	19.7	14.0	18.3	20.4	28.8	22.0	22.9	21.2	22.6	24.1	19.3
32			2.8	3.7	3.6	3.1	4.3	4.4	4.0	3.9	4.0	3.7	3.6	4.0	4.8
Total (µg/gTOC)			249.2	234.5	218.0	179.7	256.6	264.8	252.0	235.3	245.7	238.9	251.4	251.8	266.1
∑C (µg/gTOC)			116.1	83.9	79.5	56.7	77.4	84.4	108.4	87.7	90.9	86.5	91.8	96.8	83.1
Total % C			47	36	36	32	30	32	43	37	37	36	37	38	31

Comp.	Lipid pool	*Transect*	I	II	II	II	II	II	II	II	II	II	II	III	III
		Area		AO	AO	YSC	YP	YP	YP	YP	MIZ	MIZ			YSC
		Station	2830	2847	2848	55/95	55/97	2836	2835	2834	2863	2864	2865	2838	55/98
15			3.8	1.1	2.7	3.2	2.8	0.2	1.7	2.5	2.8	0.9	2.1	2.4	4.7
16			11.9	4.3	8.1	9.6	7.4	2.9	5.1	7.7	6.8	4.3	6.0	6.7	11.4
17			18.3	7.1	13.0	14.4	9.9	8.2	8.5	10.8	9.8	9.3	7.8	11.3	14.8
18			19.4	10.3	14.4	15.4	14.4	11.4	9.9	12.6	13.6	12.2	8.9	12.4	17.6
19			26.3	14.1	19.9	23.4	18.4	15.4	13.3	17.8	19.0	16.4	13.3	16.1	22.3
20			20.3	13.2	16.0	16.2	16.6	14.1	11.4	13.8	15.2	14.6	9.3	13.8	18.3
21			21.9	15.3	17.6	17.4	17.9	16.0	12.9	15.7	17.1	16.1	10.3	15.0	19.9
22			21.1	14.6	16.4	19.4	16.4	15.0	12.0	15.5	16.1	14.8	11.4	14.0	18.0
23			24.1	19.4	19.4	19.1	19.8	18.7	16.4	19.3	19.9	18.3	11.8	17.1	21.4
24			17.1	13.7	14.2	14.0	14.7	13.6	11.5	13.6	14.2	13.3	8.5	12.5	16.3
25	C		22.8	20.5	19.1	18.5	19.6	19.2	17.9	20.1	20.3	18.7	11.8	16.9	21.1
26			13.8	11.8	12.1	12.4	12.5	11.7	10.0	11.5	12.1	11.6	7.6	10.6	13.7
27	C		27.1	24.8	22.7	21.9	23.2	24.2	23.4	25.6	25.4	23.0	14.5	20.0	23.9
28			12.1	10.0	10.7	10.6	10.8	10.2	8.8	10.1	10.5	9.9	6.3	9.5	11.9
29	C		29.6	27.6	24.5	23.7	24.1	26.6	26.4	28.1	27.4	25.0	15.9	21.1	24.4
30			8.6	7.1	7.4	7.3	7.4	7.2	5.6	7.0	7.3	6.9	4.2	6.5	7.6
31	C		27.3	23.4	22.4	21.3	21.3	23.6	24.5	26.1	25.3	22.1	13.6	18.0	20.4
32			5.2	3.7	4.6	5.7	4.2	4.0	3.3	4.2	4.2	4.2	3.4	3.8	4.7
Total(µg/gTOC)			330.6	241.9	265.3	273.3	261.3	242.4	222.7	262.0	266.9	241.5	166.9	227.6	292.4
∑C (µg/gTOC)			106.8	96.3	88.8	85.3	88.2	93.7	92.2	100.0	98.3	88.7	55.8	75.9	89.8
Total % C			32	40	33	31	34	39	41	38	37	37	33	33	31

Tab. 2.5. (continued)

Comp.	Lipid pool	*Transect*	III	III	III	III	III	III	III	III	III	III	III	III	III
		Area	YSC	YSC	YSC	YSC	YSC	MIZ	MIZ	OW	OW	OW	OW	OW	OW
		Station	2837	55/93	55/92	57/160	57/161	55/77	57/157	55/158	57/153	57/123	57/131	57/138	57/145
15			6.4	5.7	4.7	2.1	4.3	5.9	19.9	1.9	3.4	7.4	1.6	n.d.	n.d.
16			11.8	13.6	9.9	6.5	10.2	12.8	23.5	7.9	8.3	13.4	9.8	n.d.	n.d.
17			17.2	15.3	17.3	11.5	13.7	19.2	23.6	11.9	12.4	15.5	21.4	n.d.	n.d.
18			16.0	18.0	16.7	15.0	17.6	16.7	23.4	15.4	14.3	16.1	28.6	n.d.	n.d.
19			19.0	27.3	22.1	19.5	21.3	24.9	28.1	23.8	19.8	19.2	35.7	n.d.	n.d.
20			16.2	18.0	17.8	17.2	18.8	16.7	22.3	18.0	15.0	15.3	34.2	n.d.	n.d.
21			17.0	19.2	18.9	18.7	19.8	17.5	22.8	18.8	15.7	15.0	33.7	n.d.	n.d.
22			15.4	18.8	17.9	17.2	18.1	15.6	21.2	20.3	15.3	13.8	31.3	n.d.	n.d.
23			18.1	20.0	20.0	20.8	20.9	17.7	23.2	18.4	15.4	13.5	30.3	n.d.	n.d.
24			13.6	14.9	15.0	15.2	15.8	13.8	18.2	14.5	12.2	11.1	25.6	n.d.	n.d.
25	C		17.3	18.9	19.0	20.0	20.0	16.7	21.7	15.7	14.6	11.5	25.4	n.d.	n.d.
26			11.4	12.5	12.6	12.8	13.1	11.5	15.1	11.5	10.4	9.0	20.6	n.d.	n.d.
27	C		19.5	21.6	21.4	22.9	21.9	18.2	23.0	15.8	15.7	11.2	23.2	n.d.	n.d.
28			10.0	11.1	11.0	11.0	11.4	10.3	13.0	9.8	9.1	8.4	17.2	n.d.	n.d.
29	C		20.4	22.5	22.3	23.4	22.2	18.8	23.5	15.8	16.9	11.1	21.1	n.d.	n.d.
30			7.0	7.9	7.6	7.4	8.1	5.9	7.8	6.7	6.5	5.3	11.6	n.d.	n.d.
31	C		17.7	19.2	19.2	20.5	18.3	14.6	19.4	13.1	14.4	8.7	14.8	n.d.	n.d.
32			4.1	4.9	4.4	4.3	4.4	4.0	5.2	5.2	4.0	3.1	6.4	n.d.	n.d.
Total (µg/gTOC)			258.0	289.3	278.0	266.0	280.1	260.6	354.8	244.6	223.3	208.7	392.4	n.d.	n.d.
∑C (µg/gTOC)			74.8	82.2	82.0	86.8	82.4	68.3	87.6	60.5	61.6	42.5	84.5	n.d.	n.d.
Total % C			29	28	30	33	29	26	25	25	28	20	22	n.d.	n.d.

Station locations are given in Fig. 2.1., for area abbreviations (AO, YP, MIZ, OW, YSC) see Tab. 2.1. and section 2.2.4. Compounds attributed to a higher land plant origin are indicated by the letter C. n.d. = not determined.

Total *n*-alkanols were in an equal concentration range than total *n*-alkanes. In most samples, concentrations of the n-alkanols > C_{22} are higher than the corresponding short chain homologues and often maximized in C_{26}. In accordance with their known dominance in plant waxes, we assumed the *n*-C_{22} to n-C_{28} alkanols also to reflect terrestrial contributions.

2.3.5. Carbon isotopic composition of selected compounds

When possible (in terms of concentrations and sufficient chromatographic resolution), compound specific stable carbon isotopic ratios have been determined for fatty acids, *n*-alkanes and *n*-alkanols for 11 samples selected out of the total of 39. Instead of reporting these $\delta^{13}C$ values for each station and compound investigated separately, we show the range and average carbon isotopic ratio for the different compounds in Fig. 2.3.. For comparison, the figure also includes the range and average of $\delta^{13}C_{org}$ as reported in Tab. 2.1.. Although the samples investigated cover a large area, there is only a small (~3 ‰) overall variability with respect to the ^{13}C-content of both, TOC and of distinct compounds. On the other hand, $^{12}C/^{13}C$-ratios for the suite of compounds measured range from -33 ‰ up to -19 ‰, i.e. the difference between

compounds being depleted in ^{13}C and those enriched in ^{13}C is approximately 14 ‰.

Tab. 2.6. Distribution of *n*-alkanols in surface sediments from northeastern Fram Strait

Comp.	Lipid pool	*Transect*	I	I	I	I+III	I	I	I	I	I	I	I	I	I
		Area	AO	AO	AO	YSC	YP	YP	YP	YP	YP				MIZ
		Station	2849	2851	2853	2854	2855	2856	2857	2858	2859	2860	2861	2832	2831
16			12.0	15.3	16.8	28.3	16.1	17.5	15.5	15.1	15.3	11.6	17.2	18.1	17.4
18			38.8	31.3	38.1	52.4	23.5	30.4	27.6	22.7	29.4	24.2	26.7	32.5	39.1
22	C		40.1	32.6	32.4	51.2	29.7	33.3	41.8	32.6	38.1	30.8	36.2	37.2	36.8
24	C		31.2	24.7	26.2	97.9	21.4	27.3	33.0	24.0	30.3	22.7	28.0	26.7	29.2
26	C		66.8	37.5	42.0	50.3	34.3	38.5	67.8	39.9	48.1	33.6	50.7	46.6	36.2
28	C		36.9	28.2	28.8	33.2	21.6	25.6	41.4	25.2	31.8	21.1	32.5	26.2	31.2
Total (µg/gTOC)			225.7	169.6	184.3	313.2	146.6	172.5	227.0	159.6	193.0	143.9	191.2	187.3	189.9
∑C (µg/gTOC)			174.9	123.0	129.3	232.5	107.0	124.6	184.0	121.7	148.3	108.1	147.4	136.7	133.4
Total % C			77	73	70	74	73	72	81	76	77	75	77	73	70

Comp.	Lipid pool	*Transect*	I	II	II	II	II	II	II	II	II	II	II	III	III
		Area		AO	AO	YSC	YP	YP	YP	YP	MIZ	MIZ			YSC
		Station	2830	2847	2848	55/95	55/97	2836	2835	2834	2863	2864	2865	2838	55/98
16			19.6	14.0	22.7	260.5	20.4	18.9	15.2	14.3	15.5	20.1	11.9	17.5	21.3
18			46.0	38.8	31.3	33.9	24.6	35.7	33.2	30.7	18.5	59.5	21.3	24.4	37.0
22	C		44.4	31.8	41.3	35.9	40.1	38.9	40.1	29.0	37.9	41.4	24.9	30.5	35.0
24	C		42.4	26.5	29.0	27.4	29.9	29.2	29.2	24.3	29.5	29.6	17.1	20.9	25.0
26	C		67.2	46.8	45.7	43.4	46.8	48.3	54.3	49.1	54.1	45.1	26.7	34.7	38.3
28	C		48.5	32.2	29.3	29.9	29.5	30.1	35.0	33.3	35.0	29.5	20.0	22.7	25.8
Total (µg/gTOC)			268.1	190.1	199.3	431.0	191.3	201.1	206.9	180.8	190.4	225.2	121.9	150.6	182.4
∑C (µg/gTOC)			202.5	137.3	145.3	136.6	146.2	146.4	158.5	135.8	156.4	145.6	88.7	108.7	124.0
Total % C			76	72	73	32	76	73	77	75	82	65	73	72	68

Comp.	Lipid pool	*Transect*	III	III	III	III	III	III	III	III	III	III	III	III	III
		Area	YSC	YSC	YSC	YSC	YSC	MIZ	MIZ	OW	OW	OW	OW	OW	OW
		Station	2837	55/93	55/92	57/160	57/161	55/77	57/157	55/158	57/153	57/123	57/131	57/138	57/145
16			18.8	136.8	25.9	31.8	22.6	27.1	45.6	17.6	17.7	30.4	39.5	25.1	15.1
18			18.0	26.3	23.3	27.2	26.2	37.3	39.8	31.2	17.9	22.2	34.7	33.3	22.4
22	C		30.9	38.8	37.3	41.6	34.5	45.3	34.4	23.7	24.8	15.0	19.0	9.7	16.9
24	C		23.6	26.6	25.8	29.8	22.7	31.5	24.8	16.7	17.6	11.2	12.2	6.5	12.0
26	C		31.8	36.7	37.2	39.8	25.8	44.9	30.7	18.7	20.0	11.5	16.4	6.2	16.1
28	C		19.0	21.2	22.2	19.5	21.1	24.4	19.8	12.1	8.9	6.3	9.4	4.2	10.9
Total (µg/gTOC)			142.2	286.5	171.6	189.6	152.8	210.5	195.0	120.0	106.9	96.6	131.1	85.1	93.4
∑C (µg/gTOC)			105.4	123.4	122.4	130.6	104.1	146.1	109.7	71.2	71.3	44.1	56.8	26.7	55.9
Total % C			74	43	71	69	68	69	56	59	67	46	43	31	60

Station locations are given in Fig. 2.1., for area abbreviations (AO, YP, MIZ, OW, YSC) see Tab. 2.1. and section 2.2.4. Compounds attributed to a higher land plant origin are indicated by the letter C.

In the discussion that follows we will show that, as indicated in Fig. 2.3., a $\delta^{13}C$-value of about –26 ‰ is a reasonable boundary separating "terrestrial" and "marine" derived aliphatic lipids from the surface sediments in northeastern Fram Strait and on the Yermak Plateau. *n*-alkanes ($C_{25,27,29,31}$) and *n*-alkanols ($C_{22,24,26}$) are most depleted in ^{13}C, ranging from -33 ‰ to -29 ‰ (Fig. 2.3.). Such a carbon isotopic depletion is commonly attributed and in accordance with inputs derived from a terrestrial (higher land plant) source possessing a C_3 biosynthetic pathway. For example, Collister et al. (1994) studied a range of plants of differing CO_2 metabolism and reported weighted mean ($C_{27\text{-}35}$) *n*-alkane values of -31 ‰ to -39 ‰ (average: -32 ‰, *n*=10) for C_3 land-plants. Collister et al. (1994) and others (e.g. Huang et al., 1996; Ficken et al., 1998) also showed that biosynthetically related *n*-alkyl lipids (e.g. *n*-alkanes, *n*-alkanols, *n*-fatty acids) in epicuticular waxes of the same plant have similar carbon isotopic compositions. Therefore, the similarity in the carbon isotopic composition of the long-chain *n*-alkanols and of the long-chain *n*-alkanes in our samples (Fig. 2.3.) most likely points to a common C_3 land plant source.

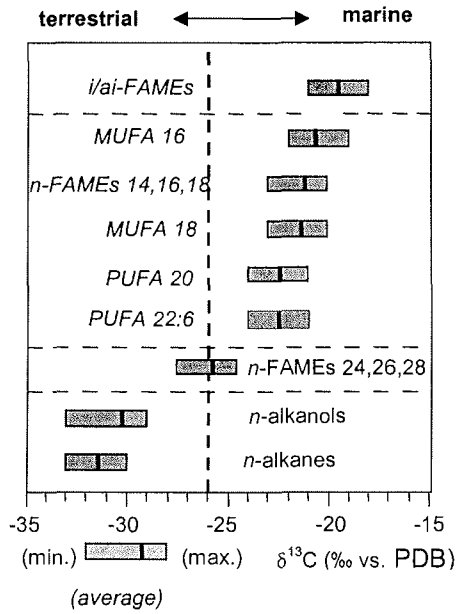

Fig. 2.3. $\delta^{13}C$-values (range and average) of C_{org} and aliphatic lipids in surface sediments of the Fram Strait and on the Yermak Plateau. i/ai-fatty acids: iso- and anteiso-C_{15} fatty acids; MUFA 16: 16:1*n-7* and *n-9* fatty acids; MUFA 18: 18:1*n-9* and *n-7* fatty acids; PUFA 20: 20:4*n-6* and 20:5*n-3* fatty acids; PUFA 22:6: 22:6*n-3* fatty acid; *n*-alkanols: long-chain (C_{22}-C_{26}) even carbon numbers; *n*-alkanes: long-chain (C_{25}-C_{31}) odd carbon numbers. Given values cover 38 samples for $\delta^{13}C_{org}$ and 11 samples for compound-specific $\delta^{13}C$-values, distributed over the entire investigation area. The light grey line indicates the assumed boundary separating marine and terrestrial-derived lipids.

Long-chain fatty acids (LCFA) with even carbon atom numbers, also of a probable plant wax origin, are significantly enriched in ^{13}C compared to *n*-alkanes and *n*-alkanols, by an average of 5 ‰ (Fig. 2.3.). Their average carbon isotopic composition (-26 ‰), intermediate to the range observed for *n*-alkanes and *n*-alkanols (-33 ‰ to -26 ‰, see above) and compounds of a "marine" origin (-26 ‰ up to -19 ‰, see below) rather points towards a mixed origin of the LCFA in our samples. Naraoka and Ishiwatary (2000) observed a gradual increase in ^{13}C of up to +6 ‰ for LCFA in a section from riverine to estuarine to open ocean surface sediments and attributed this to seawards increasing contributions of LCFA derived from marine primary productivity. The same was concluded upon the stable carbon isotopic composition of LCFA in a recent study of the Altamaha river mouth (Shi et al., 2001).

Compared to the ^{13}C-depleted terrestrial *n*-alkanes and *n*-alkanols and the intermediate $\delta^{13}C$ values for the LCFA of a mixed origin, the fatty acids contributing the highest proportions to the sedimentary organic carbon contents (i.e. saturated, monounsaturated and polyunsaturated fatty acids up to C_{22}) are relatively enriched in ^{13}C (Fig. 2.3.). Within this suite of fatty acids, the PUFA structures ranged from about -24 ‰ to -21 ‰, saturated C_{14}-C_{18} compounds and C_{18} monounsaturates from -23 ‰ to -20 ‰, and C_{16} monounsaturates from

about -22 ‰ to -19 ‰. Branched fatty acids (i/ai-C_{15}) were the most ^{13}C-enriched aliphatic lipids, ranging from approximately -21 ‰ up to -18 ‰ (Fig. 2.3.). The carbon isotopic compositions of all of these lipids, i.e. of all the C_{14}-C_{22} fatty acids, are consistent with a marine source and are typical for lipids derived from marine organisms (e.g. Freeman et al., 1995; Pancost et al., 1997; van Dongen et al., 2002). It is known that the carbon isotopic composition of a consumer closely reflects its diet and this basic principle has been used to trace organic carbon flows through food webs (e.g. Peterson, 1999; Boschker and Middelburg, 2002). Following this concept, the carbon isotopic composition of fatty acids presumed to derive from zooplankton and bacterial sources (e.g. MUFA 18, i/ai-C_{15}, *cf.* preceding section and Fig. 2.3.) imply that organic carbon derived from primary production is their principle organic carbon source.

2.4. Processes controlling extractable organic matter composition

In the following discussion, we will focus on the summed amounts of aliphatic lipids representing primary production, secondary contributions and terrestrial-derived compounds. Notice that upon their carbon isotopic composition (see above), the amounts of LCFA (Tab. 2.4.) had to be corrected to account for their mixed origin. For this purpose we applied a simple two-endmember carbon isotopic mixing calculation, assuming that the $\delta^{13}C$ value for the higher land plant derived proportions of LCFA is represented by the measured carbon isotopic composition of the C_{26} *n*-alkanol. The second ("marine") endmember was then defined by the respective $\delta^{13}C$-value of the 16:1*n*-7 fatty acid from the same sample. For the available number of samples (n=11), the so obtained terrestrial proportions of LCFA ranged from 45 to 57 % (average 51.5 %, 4.8 S.D). Given this low variability and to include those samples where compound specific carbon isotopic ratios were not measured, we took a constant proportion of 50 % of the LCFA to be derived from a higher land plant origin.

To discuss the respective lipid pools with respect to environmental processes, Figs. 2.4. & 2.5. have been arranged according to the *Transects* shown in Fig. 2.1. Major features such as ice-cover, currents, seafloor topography and the occurrence of high-suspended matter loads in the water column are schematically included in Figs. 2.4. & 2.5. to provide an overview of these external forces in relation to the distribution of the sedimentary lipid pool inventory. Details on the total amounts of lipids as partitioned to the respective pools are provided in Tab. 2.7.

Transects I & II (Fig. 2.4.) are both located across the Yermak Plateau in an approximate NW-SE direction, whereas *Transect I* is situated further to the northeast. Both *Transects* extend from the Spitsbergen shelf (water depth < 500 m) over the Yermak Plateau (average water depth. 1000 m) towards the deeper Central Arctic Ocean (> 2000 m). *Transect III* follows the inflow of the WSC from the south of Spitsbergen up to 82°N and surface sediments were sampled from approximately comparable water depths (1000-2000 m).

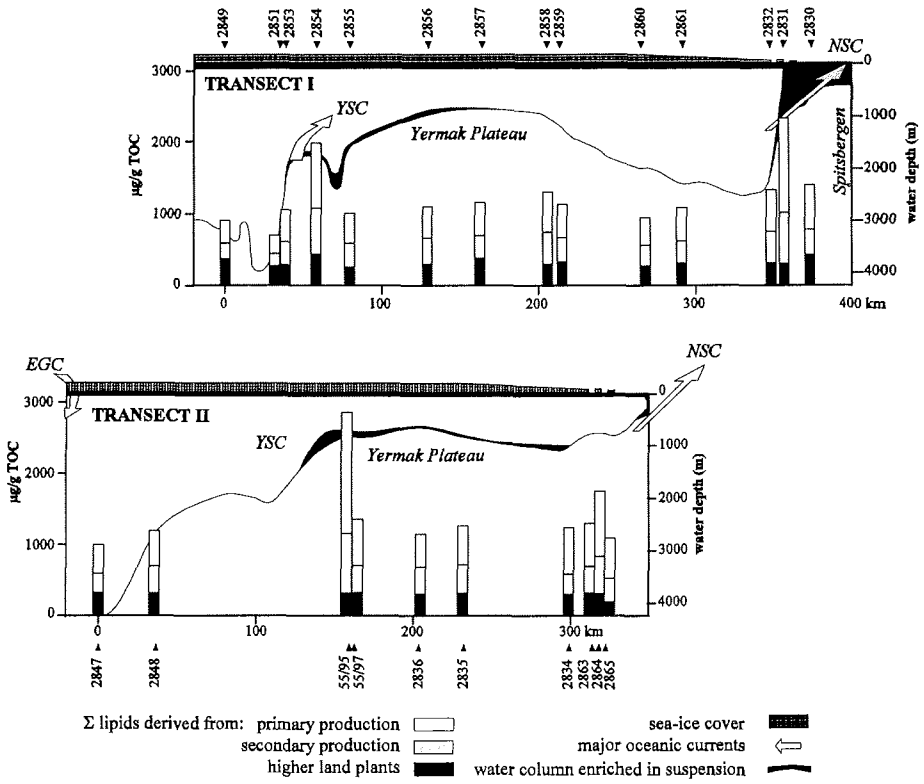

Fig. 2.4. Totalised lipids of different sources in surface sediments across the Yermak Plateau. For locations of *Transect I & II* see Fig. 2.1. The thickness of ice-cover and water column parts enriched in suspension (adapted from Rutgers van der Loeff et al., 2002) is schematically and not scaled in vertical extension. For individual amounts of lipid pools at the respective stations see Tab. 2.7..

2.4.1. Distribution of lipid pools in perennially ice-covered areas (Transects I and II)

Most of the stations in *Transect I & II* derive from an area with a permanent sea-ice cover, providing a permanent shade of the upper water column also in those times of the year, where light is available in the high Arctic. While in general primary productivity is supposed to be low under such conditions (Wheeler et al., 1996), adapted algal communities growing in the bottom of the ice, at the ice-water interface, as well as phytoplankton, accounts for average primary production rates of 275 mg C m^{-2} day^{-1} in the Nansen Basin (Gosselin et al., 1997), north of the Yermak Plateau. At least double the amounts of carbon are produced at the MIZ of Fram Strait according to the range of values published (426 mg C m^{-2} day^{-1}, Smith et al., 1987; 7-720 mg C m^{-2} day^{-1}, Hirche et al., 1991).

With respect to our data, lowest total lipid amounts of primary production were contained in surface sediments from the northernmost deep-sea stations of *Transects I & II* (258-493 µg/g TOC; PS2849-PS2953, PS2847, PS2848, Fig. 2.4., Tab. 2.7.). In contrast, the amounts of primary produced lipids no less than

doubled (919-1320 µg/g TOC) in surface sediments close to the MIZ (Stations. PS2864 *Transect II*; PS2831, *Transect I*; respectively, Fig. 2.4. Tab. 2.7.). As this mirrors the differences in primary production rates when comparing deep-sea and MIZ (see above), we thus can conclude that the sedimentary contents of lipids attributed to primary productivity are mainly controlled and closely related to the surface water productivity. On the Yermak Plateau, the sum of lipids representing primary production ranged from 405-557 µg/g TOC (Stns. 2854-2832) in *Transect I* and 465-657 µg/g TOC (Stns. PS55/97-PS2863) in *Transect II*. This compares to the amounts detected for stations under seasonally open water conditions on the shallow Spitsbergen shelf (Stns. PS2830, PS2865, 616 and 569 µg/g TOC, resp., Fig. 2.4., Tab. 2.7.). On the Yermak Plateau, the concentrations of lipids recording primary production varied not systematically, i.e. no distinct trend with increasing northwards distance from the ice-edge was observed. Except to this observation, Stns. PS2854 (*Transect I*) and PS55/95 (*Transect II*), both situated on the western flank of the Yermak Plateau at comparable water depth, showed distinctively enhanced contents (906 and 1716 µg/g TOC) of lipids expressing primary production, in case of Stn. PS55/95 even exceeding the amounts at the MIZ. Obviously, both stations received these elevated amounts by an additional source, other than surface water productivity and we will follow this aspect later. Independent to our study, the above described characteristics of water and sea-ice related primary productivity recorded in surface sediments, including the anomaly on the western flank of the Yermak Plateau, have been described by means of chloroplastic pigments determined at identical stations (Soltwedel et al., 2000).

Water column and sediment trap investigations on the shelf off northern Spitsbergen (Andreassen et al., 1996), along the MIZ in the Barents Sea (Wassmann et al., 1999) and in the northern North Atlantic (Ramseier et al., 1999, 2001) were conducted to study productivity and particle flux at the MIZ in great detail. Ramseier et al. (1999, 2001) proposed a high productivity strip close to the mean annual MIZ, termed the BMIZ (Biological Marginal Ice Zone). Maximum concentrations of nutrients, chlorophyll *a*, high production of phytoplankton in surface waters, as well as maximum fluxes of POC and opal were obtained from sediment traps at various depths (Andreassen et al., 1996; Ramseier et al., 1999; Hebbeln, 2000; Owrid et al., 2000). Total sedimentation rates of particulate matter were 10 to 100 times higher at the MIZ compared to stations under permanent sea-ice. Nonetheless, the contributions of phytoplankton cells accounted for only about 5.6 % to the vertical flux of POC in the MIZ off northern Spitsbergen (comparable to the positioning of the MIZ in Fig. 2.4.), albeit higher than the average 1 % in areas covered by multi-year ice (Andreassen, 1996). It is obvious that the export of organic carbon from the upper water column to the seafloor is not only a function of sinking phytoplankton cells. Other factors such as the formation of dense aggregates and fecal pellet production by zooplankton give supplementary support to the downward flux of organic matter from surface waters.

Lithogenic particles, originating from fluvial supply of rivers draining into the Laptev Sea and incorporated into sea-ice, are transported via the transpolar drift across the Arctic Ocean towards the northeastern Fram Strait (e. g. Dethleff et al., 2000).

Tab. 2.7. Distribution of totalised aliphatic lipids attributed to different lipid pools in surface sediments of northeastern Fram Strait

	Transect	I	I	I	I+III	I	I	I	I	I	I	I	I	I
	Area	AO	AO	AO	YSC	YP	YP	YP	YP	YP				MIZ
Lipid pool	Station	2849	2851	2853	2854	2855	2856	2857	2858	2859	2860	2861	2832	2831
Primary (µg/gTOC)		311	258	439	906	405	439	455	557	458	388	468	588	1320
Secondary (µg/gTOC)		228	169	325	640	341	366	324	450	342	283	303	438	710
Terrestrial (µg/gTOC)		368	274	289	440	255	296	379	299	329	275	313	312	304
% Primary		34	37	42	46	40	40	39	43	41	41	43	44	57
% Secondary		25	24	31	32	34	33	28	34	30	30	28	33	30
% Terrestrial		41	39	27	22	26	27	33	23	29	29	29	23	13

	Transect	I	II	II	II	II	II	II	II	II	II	II	III	III
	Area		AO	AO	YSC	YP	YP	YP	YP	MIZ	MIZ			YSC
Lipid pool	Station	2830	2847	2848	55/95	55/97	2836	2835	2834	2863	2864	2865	2838	55/98
Primary (µg/gTOC)		619	399	493	1716	657	465	551	648	608	919	569	548	2580
Secondary (µg/gTOC)		354	270	374	837	378	378	398	290	372	521	329	396	549
Terrestrial (µg/gTOC)		426	332	324	325	332	312	322	304	322	316	197	271	294
% Primary		44	40	41	60	48	40	43	52	47	52	52	45	75
% Secondary		25	27	31	29	28	33	31	23	29	30	30	33	16
% Terrestrial		30	33	27	11	24	27	25	24	25	18	18	22	9

	Transect	III	III	III	III	III	III	III	III	III	III	III	III	III
	Area	YSC	YSC	YSC	YSC	YSC	MIZ	MIZ	OW	OW	OW	OW	OW	OW
Lipid pool	Station	2837	55/93	55/92	57/160	57/161	55/77	57/157	55/158	57/153	57/123	57/131	57/138	57/145
Primary (µg/gTOC)		591	2892	2238	3016	1783	6186	2128	1666	1922	1093	890	767	799
Secondary (µg/gTOC)		351	1189	689	1714	633	1129	989	804	512	506	496	403	389
Terrestrial (µg/gTOC)		252	286	284	358	263	284	278	185	211	117	188	75	106
% Primary		49	66	70	59	67	81	63	63	73	64	57	62	62
% Secondary		29	27	21	34	24	15	29	30	19	30	31	32	30
% Terrestrial		21	7	9	7	10	4	8	7	8	7	12	6	8

Station locations are given in Fig. 2.1., for area abbreviations (AO, YP, MIZ, OW, YSC) see Tab. 2.1. and section 2.2.4.. For definition of lipid pools see text (section 2.2.4.). To account for their mixed source, amounts of LCFA from Tab. 2.3. have been partitioned into lipids of primary and terrestrial origin upon their carbon isotopic composition as explained in the text.

Consequently, an average percentage of 70-80 % of lithogenic matter was found in sediment traps from the Fram Strait under permanent ice-cover, with a predominant accumulation when sea-ice is melting (Hebbeln and Wefer, 1991; Andreassen et al., 1996; Ramseier et al., 1999; Hebbeln, 2000). Sea-ice entrained lithogenic matter mainly consists of fine fraction (70-90 % < 63 µm, Dethleff et al., 2000), which can act due to their sorption capacity as a further transportation medium for organic matter upon sinking. The idea of such a "mineral ballast effect" as an aid for the transfer of organic matter from the water column to the sediment has been introduced by Ittekkot et al. (1992) and was adapted for the Barents Sea by Knies and Stein (1998).

The second lipid pool contained in surface sediments on the Yermak Plateau comprises compounds derived of secondary production, mainly from zooplankton and bacterial activity. Based upon traditional views on food web structures, the organic carbon source of these organisms originates from primary production, and this was well reflected by the similarity in the compound specific carbon isotopic composition of the fatty acids from bacteria and zooplankton compared to the fatty acids derived from primary production (see Fig. 2.3.). However, comparing the amounts of primary lipids and those of secondary origin (Fig. 2.4., Tab. 2.7.) revealed an overall positive correlation, and indeed, this can be expressed e.g. by a simple linear relationship in the form of $\sum$secondary lipids = 0.599 * $\sum$lipids primary production (R^2=0.73). Thus,

at all stations of *Transect I & II* the amounts of zooplankton and bacterial derived lipids are at about 60 % of the lipids attributed to primary production. This positive correlation is surprising, as normally one would await an inverse relationship between primary and secondary producers, i.e. a higher consumption should lower the amounts of primary produced organic carbon. As this it not observed in our case, we could hypothesise that most of the amounts of primary produced lipids contained in the surface sediments must have rapidly escaped the water column without being significantly reduced by microbial degradation and zooplankton grazing in terms of lipid quantities. This was already mentioned with respect to the quality of the fatty acid compositions at all stations (e.g. high ratios of 16:1/16:0, high relative proportions of PUFA, see section 2.3.3.). Accordingly, the amounts of primary and secondary products in the surface sediments then would rather be decoupled than correlated, as rapidly sinking organic matter is no more (or only for a short time) available as food for at least the zooplankton community. The expressed relationship of primary and secondary lipids in the surface sediments might thus be regarded as a result of effective export of a distinctive part of primary produced organic matter (aggregated phytodetritus, faster sinking and larger species, e.g. diatoms, ballasted by lithogenic matter; see above), whereas another part of primary producers remains sustained in the upper water column and might be utilised in the bacterial and zooplankton food loop and reach the seafloor as secondary lipids thereof. Additionally, fecal pellets might provide another ballast effect leading to the rapid export of primary produced organic matter. It is known that the abundance of distinct phytoplankton species blooming at the ice-edge changes seasonally in species composition and is usually dominated by diatoms in spring (e.g. Andreassen et al., 1996). In summer and early autumn (September) phytoplankton is composed primarily of flagellates (Rat'kova and Wassmann, 2002). The grazing pressure of calanoid copepods in summer and autumn is much higher than in spring, because they have to accumulate large lipid reserves for overwintering. Therefore zooplankton feeding and the vertical export via zooplankton fecal pellets might be more important towards the end of the phytoplankton bloom. Diatoms can be rapidly exported from the upper water column and reach great depths, with aggregation playing a prominent role in this process (Alldredge and Jackson, 1995), whilst most flagellates remain sustained. As we determined lipids from surface sediments integrating longer time spans, this seasonality should be obviously smoothed out. Thus, the observed positive correlation of primary and secondary lipids indeed can be regarded as a result of the above-described processes.

Although we observe distinctively lower amounts of both primary and secondary lipids over the shallower Yermak Plateau than compared to the ice-edge of both *Transect*s (Fig. 2.4.), this is not associated with a gradual decrease as supposed with increasing distance from the ice-edge in northwards direction. Rather, concentration levels remain relatively uniform up to a distance of ca. 200 km north of the MIZ and also compare to the levels in seasonally open waters south of the MIZ. Schlichtholz and Houssais (1999a) identified a weak influence of Atlantic water from a southern direction over the Yermak Plateau, called the Yermak Plateau Current (YPC). This Atlantic water, however was found to be denser, colder and fresher, i.e. more admixed, than the Atlantic water on the western side of the Plateau (Rudels et al., 2000), likely as a result of upwelling colder waters caused by cyclonic surface circulation (Muench et al.,

1992) and an intensified tidal mixing (Hunkins, 1986) over the Yermak Plateau. Though weak, this inflow leads to an advection of phyto- and zooplankton (or organic matter thereof) from the more productive open waters and/or from the MIZ over the Plateau, as indicated by the presence of Atlantic diatom species and copepods (e. g. *Calanus finmarchicus*) from sediment traps under sea-ice (Falk-Petersen et al., 2000). In summary with admixing of the water-column by upwelling and tidal motion (see above), the overall comparable amounts of primary and secondary lipids in surface sediments on the Yermak Plateau are likewise explained.

Compared to marine primary and secondary lipids, the amounts contributed by higher land plants are overall low in *Transect I & II* (Fig. 2.4.), ranging from 255 -440 μg/g TOC and 197-332 μg/g TOC, respectively (Tab. 2.7.). High concentrations in *Transect I* found at the southernmost station PS2830 on the shallow Spitsbergen shelf are probably derived from coastal inputs, as suggested by enhanced amounts of suspension load in this part of the *Transect* (see Fig. 2.4., Rutgers van der Loeff et al., 2002). However, compared to the amounts of terrestrial-derived compounds in sediments nearby, this supply seems to be only of minor local importance. In the southern part and shallow shelf region of *Transect II*, no signs of such a local supply of terrestrial-derived lipids were observed, in fact, concentrations of higher land plant compounds were lowest at station PS2865. Therefore, the nearby landmass seems not to be a significant source explaining the amounts of higher land plant lipids on the Yermak Plateau. Rather we suggest that they most probably derive from sea-ice transportation via the Transpolar Drift (see above).

In both *Transects*, distinctive stations on the western flank of the Yermak Plateau were outstanding from the general trends of lipid distribution and from stations nearby. At station PS2854 (Tr. *I*), the amounts of lipids derived from primary and secondary production were distinctively enhanced (906 and 640μg/gTOC, resp.) and better compared to the amounts found at the MIZ (albeit in a distance of 250 km) than to stations in the surrounding. This was even more obvious for station PS55/95 of *Transect II* (Fig. 2.4.), as there the concentrations of primary and secondary lipids even exceeded those of the MIZ (stations PS2863, PS2864). As these locally enhanced abundances of marine lipids could with regard to the surrounding stations and the ice-conditions obviously not be explained by a supply from the upper water column, they have to be sourced elsewhere.

2.4.2. Distribution of lipid pools tracking the WSC/YSC inflow (Transect III)

Based upon the above findings, samples included in *Transect III* were choosen at about a constant water depth (1000-2000 m) to follow the Atlantic water inflow from the WSC at the southern tip of Spitsbergen (77°N) and the YSC up to 82°N at the northwestern flank of the Yermak Plateau. In the following discussion, we will emphasize especially on the inflow of Atlantic waters occurring at intermediate and close to bottom depths (see also section "study area"). Fig. 2.5. shows the distribution of the respective lipid pools along this *Transect* in conjunction with these intermediate to deep currents. At first sight, but also when compared to *Transects I & II* (Fig. 2.4.), it is obvious that when tracking the inflow of Atlantic water, the distribution of lipid classes, except

terrestrial proportions, behaves much different, i.e. the overall variability is greater, but also lipids of especially primary production reach distinctively higher amounts. Station PS2854, which was found outstanding in *Transect I* is also included in *Transect III* and can be used for direct comparison, has relative to most other stations in *Transect III* lower amounts of primary and secondary lipids. Notice however, that the northernmost station PS2854 nonetheless contains primary and secondary lipids in contents equal or even slightly higher than open water stations in the south on the western Spitsbergen shelf (PS57/131; PS57/138, PS57/145, Fig. 2.5.). Permanently open water conditions exist in the southeastern Fram Strait and on the western continental slope of Spitsbergen due to the inflow of warm, nutrient-rich Atlantic water of the West Spitsbergen Current (WSC). These conditions increase primary productivity in open surface waters as measured e.g. by Hirche et al. (1991). From sediment traps deployed north and west of Spitsbergen (Andreassen et al., 1996; Owrid et al., 2000) it was found, that vertical export of marine phytoplankton and fecal pellet aggregations are (a) higher in open water areas than under sea-ice, (b) lower than at the MIZ and (c) that the highest variability occurs at the MIZ. This can be seen as a basic conceptual model with respect to the distribution of primary productivity and associated vertical fluxes in sections from permanent ice-cover to the MIZ to open water conditions, as e.g. also proposed for the Greenland Sea by Peinert et al. (2001). In line with this model, highest total lipid concentrations of primary production at station PS55/77 argue for a direct benthic-pelagic coupling, i.e. the surface sedimentary lipid record at this stations seems to reflect enhanced primary production and export from the MIZ. This seems also to be true for the southern, open water part of *Transect III*. The increase in surface sedimentary lipid contents of primary production, when comparing the southern open water stations PS57/145 – PS57/123 (~800-1000 µg/g TOC) to open water stations PS57/157-PS57/153 (~2000 µg/g TOC) adjacent to the MIZ might thus indicate a higher productivity at northern open water stations, explainable by a general higher availability of nutrients closer to the MIZ due to upwelling and ice-melt. However, when looking at the contents of marine lipids as recorded in surface sediments starting from the MIZ in northwards direction under the ice, the whole region on the western flank of the Yermak Plateau behaves, for at least a distance of about 200 km, different than expected. Starting from the ice-edge at station PS55/77, the surface sedimentary amounts of primary lipids are (a) comparable and even higher than at the open water stations, (b) highly variable and (c) show a distinct decrease in concentration with increasing distance from the MIZ. Thus, in contrast to the MIZ and the open water stations, but also in contrast to most stations of *Transect I & II*, it is obvious that the distribution of primary lipids is not relatable to upper water column productivity. Rather, their distribution on the western slope of the Yermak Plateau seems to be primarily coupled to the Yermak Slope Current. Recently it was described that this current causes a distinct benthic nepheloid layer (BNL) along the western flank of the Yermak Plateau (Rutgers van der Loeff et al., 2002, see also Fig. 2.4.). By measuring ^{234}Th depletion in the bottom water mass of the Yermak slope, these authors also provided evidence for the existing of a settling-resuspension loop in the order of 80-120 mg suspension m^{-2} day^{-1} and with an average particle residence time of 1-2 months within the BNL. In the surface sediments ^{234}Th is enriched, indicating removal of particulate matter from the BNL. Elevated numbers of suspension feeders in the Yermak slope and high amounts of fresh organic

matter (chlorophyll α) in the surface sediments are additionally indicating a major lateral advection of primary produced matter (Soltwedel et al., 2000; Rutgers van der Loeff et al., 2002). At stations north of the sea-ice cover, primary produced material concentrations (2000 – 4000 µg/g TOC) were exceeding those from the neighbouring Yermak Plateau stations, decidedly. The influence of the YSC, however is monotonically decreasing with growing distance from the MIZ, suggesting a gradually weakening velocity of the YSC. Nevertheless the lateral advection of allochthonous particulate organic matter via the WSC/YSC is the major depositional controlling process of primary and secondary produced organic matter in surface sediments of this distinct permanently ice-covered and low productive zone of the northern Fram Strait (Figs. 2.4. & 2.5.).

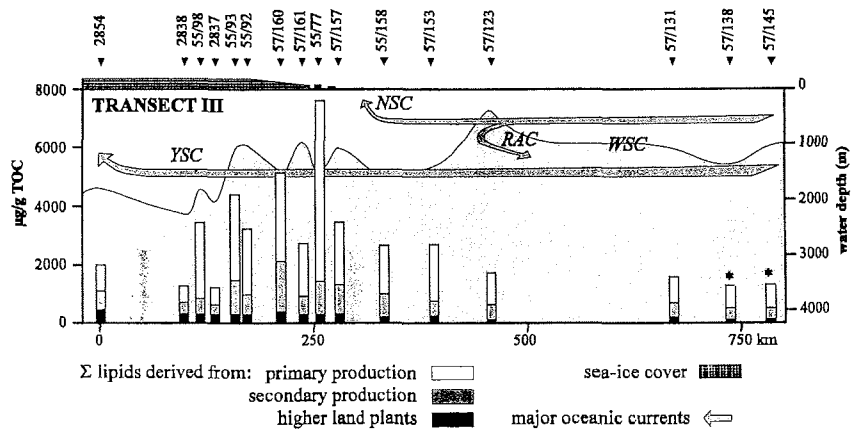

Fig. 2.5. Totalised lipids of different sources in surface sediments following the inflow of Atlantic water in eastern Fram Strait from 76°N – 82°N to the western flank of the Yermak Plateau. For locations of stations see Fig. 2.1. The thickness of the ice-cover is schematically and not scaled in vertical extension. For individual amounts of lipid pools at the respective stations see Tab. 2.7. *: Amounts of higher land plant lipids slightly underrepresented, as *n*-alkanes were not determined.

2.4.3." Marine" vs. "terrigenous" organic matter

For the Arctic shelves, adjacent continental slopes and also for most central Arctic basins, the proportions of marine vs. terrestrial organic carbon were estimated upon a variety of organic-geochemical methods. Nonetheless, an overall consistency was achieved describing most of these parts as dominated (i.e. in general > 50 %) by allochthonous, river-supplied terrestrial organic carbon (Schubert and Stein, 1997; MacDonald et al., 1998; Stein and Fahl, 2000; Mueller-Lupp et al., 2000, Goñi et al., 2000; Belicka et al., 2002, amongst others). Based upon bulk stable carbon isotopic evidence, however, Schubert and Calvert (2001) calculated that the terrestrial fraction in eastern central Arctic surface sediments and on the Yermak Plateau could be as low as 30 % (but the same authors mentioned also a probable contribution of as high as 48% derived from C_{org}/N_{org} ratios).

In Fig. 2.6., the average proportions for the three distinctive lipid pools are summarised for the different regions of the investigation area. Overall, primary and secondary marine lipids are dominating relative to terrestrial-derived lipids in the surface sediments. In the northernmost, permanently ice-covered areas (AO, Arctic Ocean > 2000m water depth; YP, Yermak Plateau < 1000 m water depth), highest contributions of terrestrial-derived compounds (26-33 %) in surface sediments were found (Fig. 2.6.). Apart of this, the region influenced by the Yermak Slope Current (YSC), comparable in ice-cover and positioning to the YP, on average contained only 10 % terrestrial lipids. In equivalence, areas located further south, (MIZ, OW, Fig. 2.6.) also contained only about 8-9 % terrestrial-derived compounds, despite their situation close to or even on the Spitsbergen shelf.

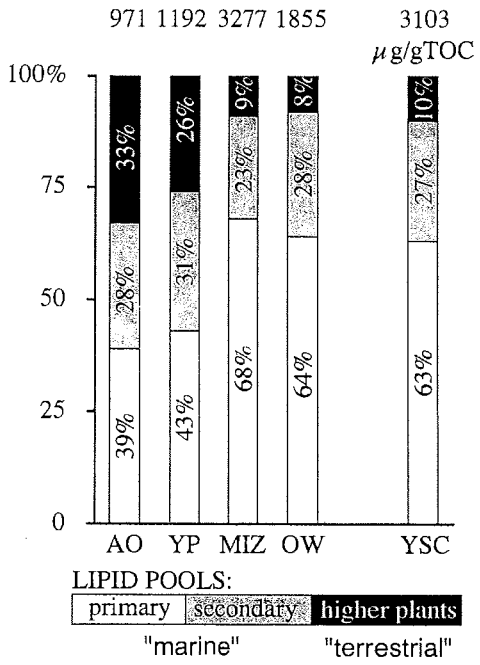

Fig. 2.6. Relative mean proportions of lipid pools for different areas in northeastern Fram Strait. Numbers on top represent mean total amount of the summed fractions. AO: Arctic Ocean (> 2000m), YP: Yermak Plateau (1000-1500m), MIZ: marginal ice zone, OW: open water, YSC: Yermak slope current. Individual percentages for all stations are given in Tab. 2.7..

The subdivision of marine-derived compounds in compounds of primary and secondary origin revealed a relative constant percentage (27-31%) of secondary lipids for all areas, except the MIZ, where their proportion is reduced to 23%. Simultaneously, highest absolute amounts of total lipids but also out of primary production (see numbers on top of Fig. 6) are associated with this region. This might indicate that the zooplankton and bacterial community is not able to handle the locally enhanced primary productivity at the MIZ at about the same rate than in areas of lower productivity.

It is interesting to note that when assigning both, primary and secondary lipids as marine-derived compounds, the resulting terrestrial proportions for the northernmost part of the investigation area (26-33 %) is equal to the 30 %-fraction obtained from bulk organic carbon isotopic compositions in the adjacent part of the central arctic ocean. Additionally, we also observed a gradual increase in the terrestrial proportions towards the Central Arctic Ocean (also expressed in the 26 vs. 33 % difference between YP and AO, Fig. 2.6.). However, notice also that not accounting for the fraction of secondary lipids would enhance the terrestrial proportions for distinct samples of up to > 50 % (cf. Tab. 2.7.). For the deeper parts of the investigation area and also for most parts of the northeastern Yermak Plateau, our data thus fit well into previous estimates. However, enhanced marine contributions (mean 64–68 %, max. 81%, Fig. 2.6., Tab. 2.7.) at the MIZs and open waters northwest and north off Spitsbergen clearly differentiates this Arctic Ocean shelf region when compared e.g. to the Siberian shelves.

2.5. Conclusions

Determining the molecular and carbon isotopic composition of the aliphatic lipid fraction and discussing their surface sedimentary distribution in consideration of oceanographic and biological aspects, besides ice-cover, provided important information about organic carbon depositional processes in surface sediments of the northeastern Fram Strait and on the Yermak Plateau. According to their nature in terms of structure and carbon isotopic composition, about 80 % of the identified lipids were partitioned into three lipid pools, characteristic of (a) primary production, (b) secondary origin (zooplankton, bacteria) and (c) terrestrial-derived compounds. Most of the suggested origins of distinct lipids found support in their carbon isotopic composition, however LCFA of supposed higher land plant origin appeared to be a mixture of marine and terrestrial origin. The northeastern Fram Strait and the Yermak Plateau is dominated by considerable amounts of autochthonous marine carbon of both, primary (mainly diatoms) and secondary (zooplankton, bacteria) producers. The fraction of lipids derived from primary production successfully escapes degradation in the water column and dominates over secondary lipids, suggesting an important surface water-benthic coupling. Maximum marine biomarker concentrations in surface sediments close to, or at the ice-edge northwest and north off Spitsbergen reflected the development of large phytoplankton blooms associated with the MIZ. Sediments from an average water depth of 1000-2000 m on the western Yermak Slope are outstanding from this sedimentary organic matter record of surface water productivity related to the MIZ, as they not only contain equal or even higher amounts of marine lipids compared to the MIZ, but also in contrast to stations nearby on the shallower Yermak Plateau of equivalent ice-conditions and low productivity. This specific area on the western flank of the Yermak Slope is influenced by a current-driven lateral advection of particulate organic matter in northwards direction. Particulate matter with a lipid signature characteristic of the MIZ in terms of quality and quantity can be transported in a suspension-resuspension settling-loop over distances more than 200 km. With growing distance from the MIZ, however, the transportation and deposition of marine organic matter decreases towards north, indicating a gradually weakening of the current velocity.

Terrestrial lipids are also supplied to this area, but provide only a minor fraction because of the overall strong imprint of primary and secondary lipids. The presence of these terrestrial compounds expresses the export from plant wax derived material to the Yermak Plateau and eastern Fram Strait. As the absolute concentration levels of terrestrial lipids are at about equal throughout the region, the terrestrial contribution represents a diffuse background signal, most probably as a result of long range sea-ice transportation from the north, without remarkable contributions of the nearby Spitsbergen landmass. The imposed signal of primary and secondary production is notable lower downslope the northern Yermak Plateau towards the deeper (> 2000m) central Arctic Ocean. As a consequence terrestrial lipid proportions increase up to about 40% towards values previously recognised in the deep central Arctic basins.

The dataset obtained for this study is to the best of our knowledge the most comprehensive survey of extractable organic matter composition and distribution for a defined high latitude area of the Arctic Ocean in terms of sample density and numbers. This study shows, that organic-geochemical molecular and isotopic measurements can provide an enhanced insight in organic carbon dynamics, but also pinpoint the influence of ocean-currents for the preservation and long-range redistribution of marine organic matter in sediments.

Chapter 3

(in "The Organic Carbon Cycle of the Arctic Ocean", edited by R. Stein and R. Macdonald, Springer Verlag, New York.)

Northern Fram Strait and Yermak Plateau: Late Quaternary variability and burial of organic carbon and palaeoceanographic implications

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3.1. Introduction

The environment of the Fram Strait, the only deep-water connection of the Arctic Ocean to the world oceans via the North Atlantic (Fig. 3.1.), is influenced by the distribution of sea-ice and two opposing current systems. The northward flowing West Spitsbergen Current (WSC) transports warm, near-surface water (Manley, 1995; Rudels et al., 2000) to the northern Fram Strait. About 22% of the northward flowing Atlantic waters are re-circulated within the RAC (Return Atlantic Current) between 78 and 80°N, west of Svalbard. At 80°N the WSC splits into the Svalbard branch (ca. 33 % of the WSC waters) and the Yermak branch (ca. 45 % of the WSC waters). On the western side of the Fram Strait, the East Greenland Current (EGC) transports cold and low-salinity water southwards along the eastern continental margin of Greenland. (Fig. 3.1.).

Primary production in ice-covered areas of western Fram Strait is limited by sea-ice cover, and influenced by the predominant water mass. Productivity in the interior Arctic Ocean is generally low (0.09 g C m^{-2} d^{-1}) (Wheeler et al., 1996). At marginal ice zones and oceanic fronts in the Fram Strait, however, primary productivity exhibits strong fluctuations and may exceed 1 g C m^{-2} d^{-1} (Hirche et al., 1991). The accumulation of organic carbon in sediments depends not only on the supply from primary productivity, but also on selective degradation in sediments. Efficient vertical transport through the water column by formation of aggregations ("ballast effect") (Ittekkot et al., 1992; Knies and Stein, 1998) and increased lateral transport by strong currents enable a higher preservation of organic carbon in the sediments. In this region, the WSC is capable of transporting large amounts of suspended organic matter to the ice-covered regions in northern Fram Strait (Rutgers van der Loeff et al., 2002).

Numerous studies have dealt with palaeoceanography and the associated organic carbon accumulation in the sediments of Fram Strait and adjacent regions during the last glacial/ interglacial cycle (e.g., Hebbeln, 1992; Hebbeln et al., 1994; Elverhøi et al., 1995; Andersen et al., 1996; Hebbeln and Wefer, 1997; Hebbeln et al., 1998; Notholt, 1998; Vogt et al., 2001, Taylor et al., 2002a). However, in most of the sedimentary records a low temporal resolution prevents the identification of short-term climatic fluctuations, like those reconstructed from high-resolution terrestrial ice-core records, (e.g. GISP2 /

GRIP; Grootes et al., 1993). Occasionally, short-term events recorded as enhanced organic matter accumulation have been found in cores from the northern Fram Strait / Yermak Plateau region (Knies and Stein, 1998; Vogt et al., 2001). These events are caused by a rapid incorporation of organic matter in fine-grained material followed by rapid transfer to the seafloor.

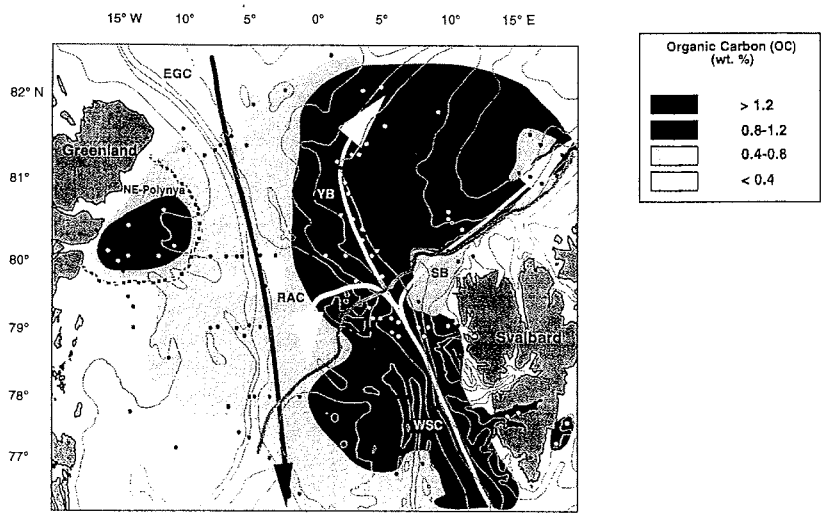

Fig. 3.1. Distribution map of total organic carbon in surface sediments from the Fram Strait. Black/ White dots indicate OC surface sample points (Hebbeln and Berner, 1993; Stein et al., 1994a; Kierdorf, 2001, this paper). White arrows: West Spitsbergen Current (WSC) and its extensions: the Yermak Branch (YB), the Svalbard Branch (SB), and the Return Atlantic Current (RAC). Black arrow: East Greenland Current (EGC). Light grey line: average summer sea-ice distribution. Black dotted line: NE-Greenland polynya.

Rapidly changing climatic and oceanographic conditions can be recorded exceptionally well by undisturbed deep-sea sediments, particularly in the distribution and variability of organic carbon in sediments. Yet, there exists little information about the regional response during the last deglaciation and the potential influence of terrigenous material on marine sedimentation of organic carbon in northern Fram Strait. To address this problem, we studied two high-resolution cores spanning the time intervals of the last glacial, the last deglaciation and the Holocene. Here, we present data on the distribution and sources of organic carbon in surface sediments and in long sediment cores. Accumulation rates of total sediment and organic carbon for three different time intervals are calculated and an organic carbon budget for Fram Strait/Yermak Plateau is presented for the Holocene.

3.2. Data Base, Material and Methods

The surface sediment samples (0-1 cm) and long sediment cores were recovered during the RV *Polarstern* expeditions ARK XIII/2 (Stein and Fahl, 1997), ARK XV/2 (Jokat , 2000) and ARK XVI/1 and 2 (Krause and Schauer, 2000). Sampling was carried out with a giant box corer and a multicorer, and

long sediment cores were recovered with a gravity corer and a Kastenlot. All samples were stored at -30°C until further treatment. Total organic carbon (OC), hydrogen indices (HI) and stable carbon isotopes ($\delta^{13}C_{org}$) were determined on homogenised bulk samples. Unhomogenised subsamples were extracted and purified for biomarker determination according to a method modified from Folch et al. (1957) and Bligh and Dyer (1959), for details see also chapter 2.2. Here, we produce a synthesis from previously published data (Hebbeln, 1992; Hebbeln and Berner, 1993; Hebbeln et al., 1994; Stein et al., 1994a; Hebbeln and Wefer, 1997; Notholt, 1998; Vogt et al., 2001) augmented with new results.

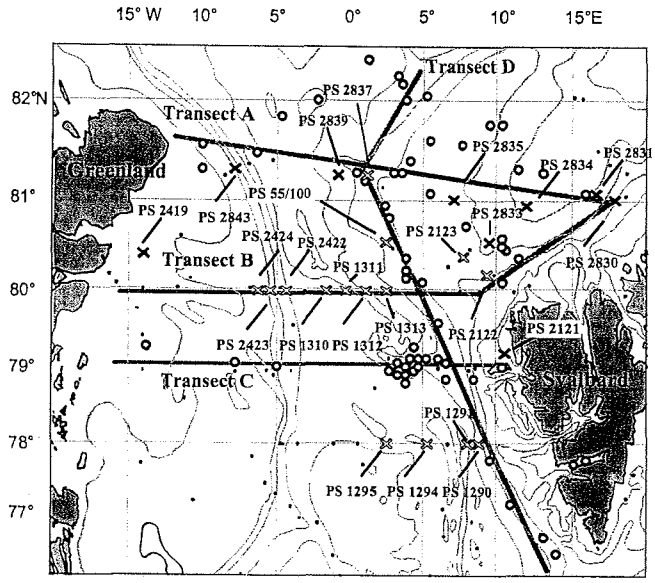

Fig. 3.2. Map of the study area. White crosses: Locations of cores for which accumulation rates were calculated for all three intervals (see Table 3.1.) (Hebbeln, 1992; Notholt, 1998; Vogt et al., 2001, this paper). Black crosses: Core locations for which only Holocene accumulation rates were calculated (Stein and Fahl, 1997). White large dots: Surface samples in which hydrogen indices and $\delta^{13}C_{org}$ values were determined (this paper). Black small dots: Surface samples with hydrogen indices or $\delta^{13}C_{org}$ values (Hebbeln and Berner, 1993; Stein et al., 1994a; Kierdorf, 2001). Dotted lines: Transects A-D with surface sediment data (see Fig. 3.3.).

OC was determined using a LECO CS analyser. The determination of hydrogen indices (HI) is a useful proxy to estimate the proportions of terrigenous and marine organic matter in sediments (Tissot and Welte, 1984). Analysis was performed by a Rock-Eval 6 (Espitalié et al., 1977). To examine the composition of the organic matter more detailed, we determined $\delta^{13}C_{org}$ values as well as specific biomarkers, i. e., long-chain *n*-alkanes (C_{27}, C_{29}, C_{31}) as a proxy for land-derived vascular plant material (e. g. Prahl and Muelhausen, 1989; Yunker et al., 1995), and brassicasterol (24-Methyl-cholesta-5, 22-dien-3β-ol) as a typical marker of diatoms and coccolithophores (e. g. Nichols et al., 1984; Meyers, 1997). For further organic-geochemical parameters as proxies for the identification of organic carbon sources we refer to Chapter 1.1. The stable carbon isotopes were measured using a mass spectrometer (ANCA-SL 20-20

Europa Scientific). Biomarkers were determined by gas chromatography on a Hewlett-Packard 6890 and gas chromatography/mass spectrometry on a Hewlett-Packard GC/MS 5890 (details of the analytical procedure are given in chapter 2.2.2.).

To interpret the organic-carbon records and to calculate accumulation rates and an organic carbon budget it is necessary to obtain a precise stratigraphical framework using AMS ^{14}C dates and stable oxygen isotopes of the planktonic foraminifera *Neogloboquadrina pachyderma sin.*. Age models for the investigated cores have been established (Hebbeln 1992; Hebbeln et al. 1994; Elverhøi et al. 1995; Notholt 1998; Vogt et al. 2001; Nørgaard-Pedersen et al., in press) and radiocarbon ages have been transformed to calibrated ages according to Bard (1998) and Stuiver et al. (1998). Additional age information was obtained by correlating OC-curves of selected cores.

3.3. Distribution and Sources of Organic Carbon in Surface Sediments

The OC surface map (Fig. 3.1.) implies two obvious domains. The first domain, western Fram Strait, shows OC values of 0.2 to 0.8 %, suggesting low organic carbon input and/or diminished preservation in surface sediments. The surface sediments of the Arctic Ocean/ Fram Strait peripheral zone have a predominantly terrigenous source (Stein et al., 1994a; Hebbeln and Berner, 1993) and are mainly composed of inorganic material transported by glaciers. In the three Transects A, B, and C (Fig. 3.2.), the lowest OC values were found in sediments of the Greenland shelf and slope.

Low hydrogen indices imply a dominantly terrigenous source for organic carbon (Fig. 3.3.). The $\delta^{13}C_{org}$ values are equivocal on first sight. In Transect B light values toward the Greenland margin indicate a dominantly terrigenous source (Fig. 3.3.). In contrast, slightly heavier values are observed in Transects A and, especially under the NE-polynya (Transect A), where values up to -20 ‰ were observed. These heavier isotopic compositions might be produced by the incorporation into sediments of higher proportions of ice algae, which are reported to be isotopically heavy. Gibson et al. (1999) found a carbon isotopic composition of sea-ice algae up to -8 ‰.

For Transects A and D, we obtained additional information from long-chain *n*-alkane and brassicasterol data (Fig. 3.4.). In Transect A, long-chain *n*-alkane concentrations > 70 μg/g OC are typical whereas brassicasterol values are low (40 μg/g OC), with two exceptions at stations PS2837 and PS2836 at the western Yermak Plateau slope and at stations PS2830 and PS2831 in the Svalbard branch of the WSC. There, a stronger contribution of marine phytoplankton (brassicasterol: 40-110 μg/g OC) and a minor contribution of terrigenous organic matter (long-chain *n*-alkanes < 70 μg/g OC) were observed. In Transect D, we found a lower terrigenous organic matter flux to the surface sediment, indicated by lower long-chain *n*-alkane values (< 70 μg/g OC). On the other hand a stronger contribution of marine organic matter is indicated by significantly increased brassicasterol values (> 50 μg/g OC) in large parts of the Yermak branch of the West Spitsbergen Current (Fig. 3.4.). Detailed investigations were performed on similar samples by Birgel et al. (submitted) on

fatty acids, *n*-alkanes, and *n*-alkanols (see chapter 2.2.2.). These compounds represent more than 70 % of the analysed biomarkers and enable an improved insight in organic carbon distribution in the northern Fram Strait.

Enhanced vertical transport, especially in the autumn, has been observed in the NE-polynya (Bauerfeind et al., 1997; Ramseier, et al., 1997). This transport is possibly supported by the formation of new sea-ice and the associated formation of superdense water. Such a mechanism would lead to accelerated transport to the seafloor of aggregates of sea-ice algae mixed with terrigenous detritus (Bauerfeind et al., 1997). Most of the marine organic matter is degraded, 40 to 70 % of the organic matter is re-circulated in the euphotic zone (Deming et al., 1995), and less than 7 % of the particulate organic matter reaches the seafloor. Pesant et al. (2002) showed that storms accelerate the vertical transport of primary produced organic matter. They noted that 21 to 60 % of the primary produced material, especially diatoms, could be exported very quickly in this way from the upper water column to the seafloor, especially in summer months. It is possible, that our stations in the NE polynya were affected by such storm events, which would promote enhanced preservation of marine organic matter in the surface sediments. The East Greenland slope and the central part of the Fram Strait (Fig. 3.3.) are dominated by OC values of 0.4 to 0.8 %. Hydrogen indices increase slightly from west to east, remain below 100 mg HC/g OC, typical of predominantly terrigenous organic matter. The $\delta^{13}C_{org}$ distribution with values of -22 to -22.5 ‰ suggests a different composition of organic matter in the investigated sediments than from hydrogen indices. Normally, stable carbon isotopes of planktonic organic matter show $\delta^{13}C_{org}$ values of -19 to -20 ‰. In sediments of high latitudes, however, a depletion of ^{13}C has formerly been observed (Rau et al. 1982 1991; Schubert and Calvert, 2001). Terrestrial organic matter shows values between -26 to -28 ‰, normally. Therefore, $\delta^{13}C_{org}$ values, which lie between -22 and -22.5 ‰, indicate a mixture of marine and terrigenous organic matter in our investigated areas. From biomarker records, we record a significant deposition of long-chain *n*-alkanes, indicating a distinct terrigenous organic matter component in the organic flux to the surface sediments (Fig. 3.4.).

The second domain, eastern Fram Strait, is characterised by OC values > 0.8 %, indicating a higher flux and/or better preservation of organic matter in the sediments (Fig. 3.1.). In the deeper parts of the western Svalbard and Yermak slope (Svalbard Branch/Yermak Branch) higher OC values were measured (Fig. 3.1.). The hydrogen indices suggest a stronger contribution of marine organic matter in the surface sediments. Although the northernmost Transect A remains dominated by terrigenous organic matter, Transects B and C show values >100 mg HC/g OC (Fig. 3.3.), indicating a stronger influence of the WSC and partial open water conditions. The $\delta\ ^{13}C_{org}$ values obtained for eastern Fram Strait are similar to those for central Fram Strait, varying between -22 to -22.5 ‰, which are slightly heavier than the (-23 to -23.5 ‰) range determined for similar samples collected from the Yermak Plateau by Schubert and Calvert (2001).

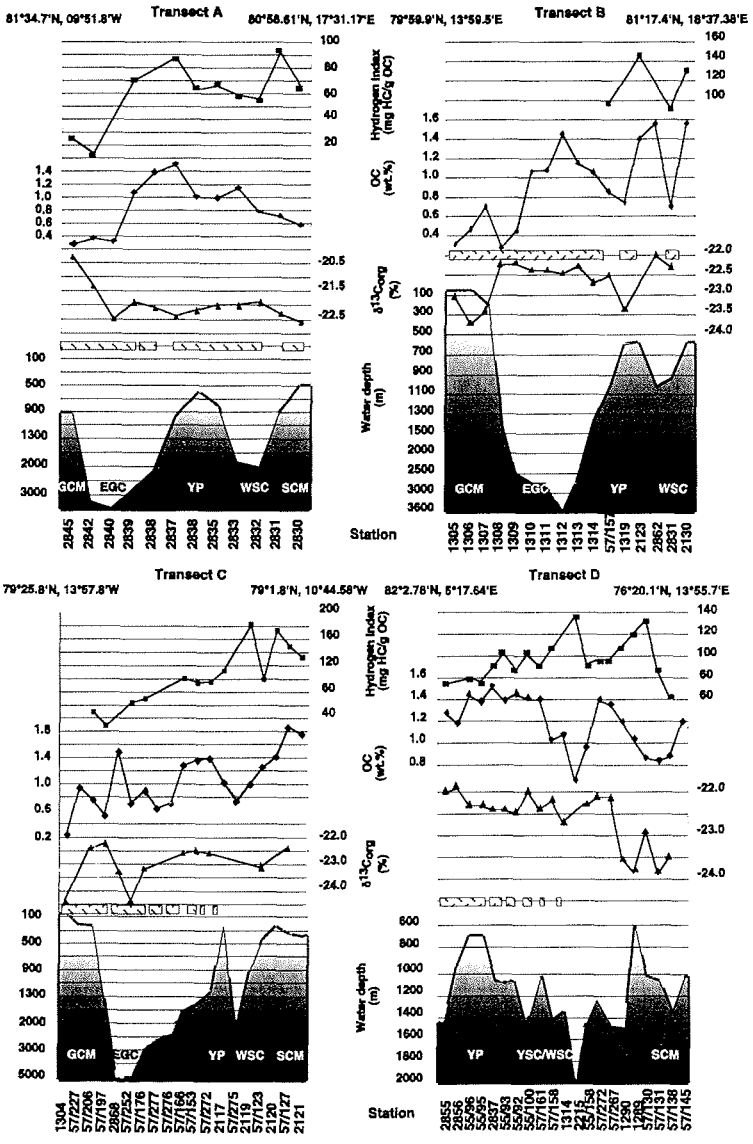

Fig. 3.3. Transects A-D in the northern Fram Strait. For locations see Fig. 3.2. OC-values (see Fig. 3.1.), hydrogen indices and $\delta^{13}C_{org}$ values (Hebbeln and Berner, 1993; Stein et al., 1994a, this paper) on the x-axis, water depth on the y-axis. Transects A-C are West-East Transects from the cold-water dominated western part of the Fram Strait to the warm-water dominated eastern part. Transect D is a north-south profile following the WSC and the Yermak Branch extensions (YB/SB). GCM= Greenland Continental Margin; EGC= East Greenland Current; YP= Yermak Plateau; WSC= West Svalbard Current; SCM= Svalbard Continental Margin; YSC= Yermak Slope Current.

The OC/N_{tot} ratios in marine organic matter typically vary between 8 and 10 (Redfield et al. 1963), whereas terrestrial organic matter has ratios of > 20 (Scheffer and Schachtschabel, 1984). Schubert and Calvert (2001) measured OC/N_{tot} ratios on the Yermak Plateau between 7 and 10, thus suggesting a predominant marine composition of organic matter. However, the plot of OC versus total nitrogen intersects the nitrogen axis at 0.022 % (Fig. 3.5.; Schubert and Calvert, 2001), implying a significant amount of inorganic nitrogen (N_{bou}) in these sediments. Correcting the nitrogen data for inorganic nitrogen, accordingly, yields OC/N_{org} ratios between 9 and 16, indicating a more mixed marine/terrigenous source, comparable with our hydrogen indices and carbon isotope values.

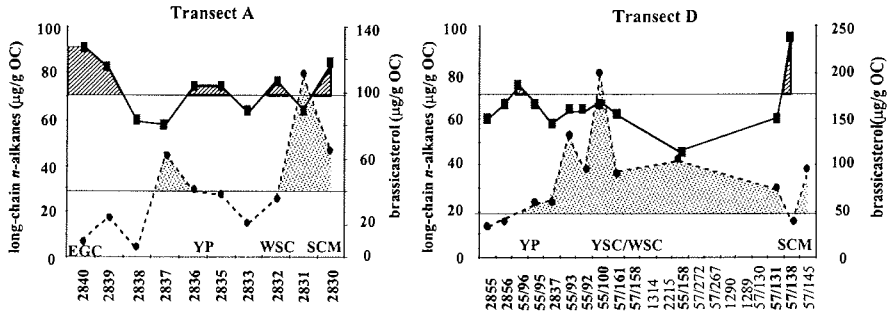

Fig. 3.4 Long-chain *n*-alkane and brassicasterol distributions of Transects A and D in the northern Fram Strait. Bold numbers on the x-axis are indicating stations, for which biomarker samples are available. Y-axis: black squares are representing long-chain *n*-alkane (terrigenous organic matter) concentrations (µg/g OC); black dots are representing brassicasterol (marine organic matter) concentrations (µg/g OC). Hatched areas: predominant terrigenous organic material deposition, indicated by high long-chain *n*-alkane concentrations. Dotted areas: predominant marine organic matter deposition, indicated by high brassicasterol concentrations. For abbreviations see figure 3.3..

Maximum OC values were obtained in the easternmost area of the northern Fram Strait (0.8-1.9 %) (Fig. 3.3.). In the northernmost section of Transect D, $\delta^{13}C_{org}$ values are heavy to intermediate, and hydrogen indices vary between 80-140 mg HC/g OC, indicating a distinct increase of marine organic matter in this part of Transect D (Fig. 3.3.). The supply of terrigenous material, which is transported from the Arctic Ocean by sea-ice (Dethleff et al., 2000) and released during melting when ice meets warm Atlantic water, is suggested from increased long-chain *n*-alkane values (60-90 µg/g OC) in this domain (Fig. 3.4.). The two branches of the WSC, the Yermak Branch flowing to the north and the Svalbard Branch flowing in a north-east direction to the north of Svalbard (Fig. 3.1.), transport WSC water to the perennially ice-covered Yermak Plateau (Manley, 1995).

Suspended particulate organic matter is supplied by the WSC from the southern Svalbard slope areas and the Svalbard shelf and fjord zones to the northernmost Fram Strait (Fig. 3.3.). Soltwedel et al. (2000) detected higher bottom water temperatures reaching an average 0.8° C in 1000 m water depth (Yermak Branch) and 2.0 °C in 500 m water depth (Svalbard Branch) in areas

influenced by the Yermak Branch/Svalbard Branch. High concentrations of chlorophyll α in the sediments from this region indicate fresh marine organic matter transported laterally by Atlantic water. This suggestion is supported by increased values of marine-derived brassicasterol (50-200 µg/g OC) in Transects A and D (Fig. 3.4.). The strong influx of nutrient-rich, warm Atlantic water supports exportable production at the marginal ice zones northwest of Svalbard and at the frontal zones of the southern Fram Strait (Heimdal, 1983; Andersen, 1989; Andreassen et al., 1996; Ramseier et al., 2001). Aggregation of the dominantly terrigenous organic matter from the Svalbard archipelago and the Barents Sea (Berner and Wefer, 1990), with minor amounts of primary produced marine organic matter in the Fram Strait, enables a quick vertical transport to the seafloor ("ballast effect"; see above). Primary production in the northern Fram Strait is supported additionally by the release of nutrients from melting sea-ice (see above). The organic matter incorporated in the sea-ice may originate from as far away as Siberia (Dethleff et al., 2000).

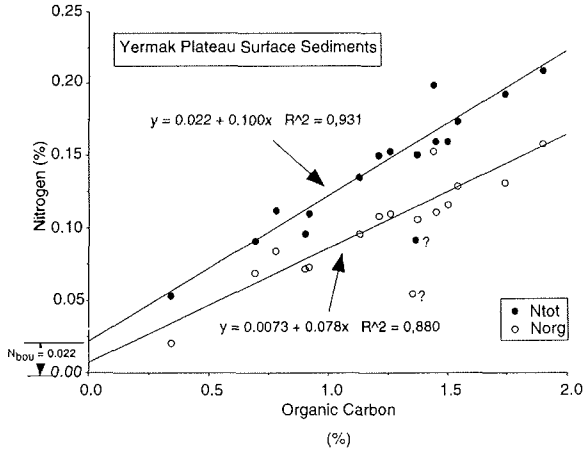

Fig. 3.5. Correlation between total nitrogen (N_{tot}) and total organic carbon (OC (wt. %)) and between organic nitrogen (N_{org}) and total organic carbon for the Yermak Plateau (ARK XIII/2) surface samples (Schubert and Calvert, 2001).

In the northern part of Transect D, HI-values (80-100 mg HC/g OC) and $\delta^{13}C_{org}$ values (-22 to -22.5 ‰) in the Yermak Branch area (Fig. 3.3.) indicate mixed sources of organic matter. The HI-values, however, suggest predominantly terrigenous organic matter (see above) whereas the $\delta^{13}C_{org}$ values indicate a mixed terrigenous/marine organic matter source, transported via the WSC to the northernmost positions. Increased concentrations of long-chain *n*-alkanes and a decreased flux of brassicasterol to the seafloor suggest a relative increase in terrigenous organic carbon (Fig. 3.4.). In Transect B, the HI and $\delta^{13}C_{org}$ values are comparable to those measured along Transect D. Only for the Yermak Plateau Transects B/D were high long-chain *n*-alkanes, low HI and light $\delta^{13}C_{org}$ values observed. It seems likely that terrigenous organic matter is better preserved here than marine organic matter, similar to the shelf deposits off East Greenland (brassicasterol < 50 µg/g OC, long-chain *n*-alkanes > 70 µg/g OC). In the Kongsfjorden outlet (Transect C), a higher marine organic content is

implied (HI >100 mg HC/g OC), and intermediate $\delta^{13}C_{org}$ values (-22.5 to -23 ‰) were obtained. We propose that comparable processes operate in the vicinity of the Svalbard fjords as those observed over the shelf and upper slope regions of the Laptev Sea where primary production is increased by riverine nutrient input (Boetius and Damm, 1998). Nutrient-rich suspensions are released from melting glaciers in the proximal fjords supplying nutrients to these regions and to the adjacent shelf where primary production is already well-supported by the warm, Atlantic waters flowing in from south. The consequent increased sedimentation rates and the lateral and vertical influx of organic matter lead to enhanced preservation in surface sediments.

3.4. Late Quaternary Organic Carbon Records and Palaeoenvironment

Five cores from eastern Fram Strait (Fig. 3.2.; PS2837, PS55/100, PS2122, PS1294, PS1290) were examined in detail for OC, $\delta^{13}C_{org}$-values, and hydrogen indices (our data together with data from Hebbeln et al., 1994; Knies, 1994; Elverhøi et al., 1995; Vogt et al., 2001). Based on AMS ^{14}C-ages and the OC records three time slices were chosen to show the development during the last 30,000 calendar years BP, the last glacial (Oxygen Isotope Stage - OIS - 2), the deglaciation, and the Holocene interglacial.

The last Glacial (30-18 cal. kyr BP) (OIS 2)

In the eastern Fram Strait, the Last Glacial Maximum (LGM) is characterised by heavy $\delta^{18}O$-values (Hebbeln et al., 1994; Elverhøi et al., 1995), and a maximum extent of the Svalbard Barents Sea Ice Sheet (SBIS) (Mangerud et al., 1992; Mangerud and Svendsen, 1992; Mangerud et al., 1998; Mangerud et al., 2002) which was supported by increased moisture supply. This latter was a result of two Atlantic water advances, reaching the Fram Strait (Nordway Events = NE) between 34 and 28 (NE 2) and 24 and 18 (NE-1) cal. kyr (Hebbeln et al., 1994; Dokken and Hald, 1996; Hald et al., 2001). In our sediment cores, the NE-2 and NE-1 events are characterised by low OC values, mixed $\delta^{13}C_{org}$-values (-23 to -24 ‰) and terrigenous HI- values (10-30 mg HC/g OC) (Figs. 3.6. and 3.7.) in eastern Fram Strait. During the NE-1 and NE-2 events, the entire Svalbard archipelago was covered by the SBIS with the result that no terrigenous or freshwater material could be exported from the fjords. In the NE-1/2 horizons of core PS2837, at least 8% of the benthic foraminifers came from the Atlantic (Wollenburg et al., submitted). Palaeoproductivity values calculated from benthic foraminifers, however, remained low due to a decreased supply of nutrients in the surface waters. In addition, low organic carbon values might derive from slightly increased numbers of benthic foraminifers (Wollenburg et al., submitted), which would have fed on organic matter in sediments. Except for ice-rafted detritus with low OC values, only small amounts of organic matter were transported to the seafloor.

From 26.9 to 23.8 cal. kyr, an enormous OC peak was detected in all cores from the eastern Fram Strait (Fig. 3.6.). This organic carbon event (Event I) (Knies and Stein, 1998) can be assigned to the maximum ice-advance of the SBIS, an advance that started ca. 28 cal. kyr ago and reached its maximum extension 23.6 cal. kyr ago (Andersen et al., 1996; Knies et al., 2000). During

this period, the Svalbard glaciers reached the shelf edge (Mangerud and Svendsen, 1992; Mangerud et al., 2002), and fine-grained organic material was eroded from the shelves and exported over the shelf edge by the prograding ice (Fig. 3.6.).

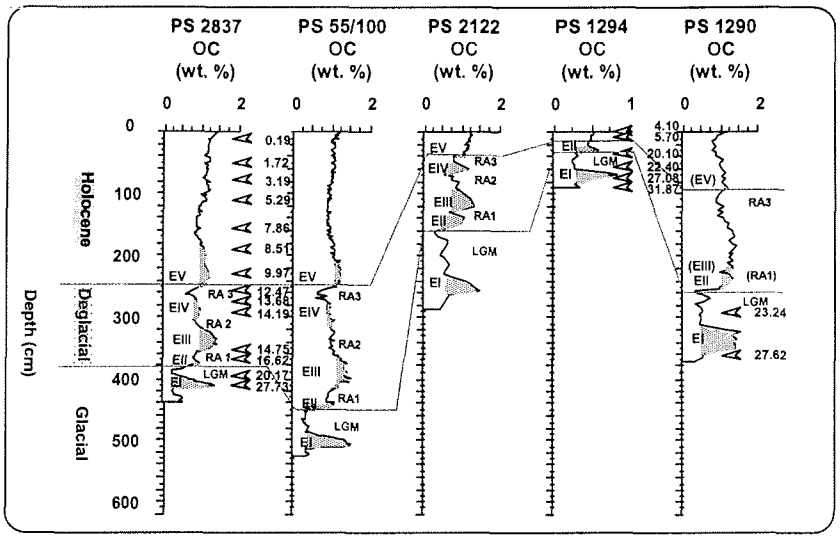

Fig. 3.6. OC records of 5 sediment cores from different locations in the Fram Strait (see Table 3.1., Fig. 3.1.) used for core correlation (Hebbeln et al., 1994; Notholt, 1998; Vogt et al., 2001). Arrows mark calibrated ages BP, calculated from ^{14}C ages using the equations of Bard (1998) and Stuiver et al. (1998). Original ^{14}C ages and age models for this paper are from Hebbeln (1992); Hebbeln et al. (1994); Notholt (1998); Vogt et al. (2001); and Nørgaard-Pedersen et al., 2003). E I-V: high preservation events with an increased influx of organic carbon (Knies and Stein, 1998; this paper). RA 1-3: re-advances of the SBIS (Mangerud et al., 1998; Svendsen et al., 1996) with decreased preservation and influx of organic carbon to investigated core positions.

In contrast, Dokken and Hald (1996) postulated a short-term melting of the SBIS during the time of Event I. A quick retreat of glaciers and a massive outflow of suspended, fine-grained, organic-rich material to the areas of the northern seas was described (cited below). An additional source of OC-rich sediments (with a dominantly terrigenous origin as indicated by light $\delta^{13}C_{org}$ values) may have been the Spitsbergenbanken and the Barents Sea shelves (Bjørlykke et al., 1978; Elverhøi et al., 1995). The terrigenous organic matter accumulating in sediments at this time, however, was accompanied by a significant amount of marine organic matter, indicated by an increased hydrogen index and a maximum in brassicasterol (50 µg/g OC) (Fig. 3.7.). Primary production probably did not increase during this period (Wollenburg et al., submitted) and the inflow of Atlantic water may even have decreased or temporarily stopped. The increased supply of suspended, fine-grained material led to aggregation of terrigenous debris with marine organic matter and, consequently accelerated transport through the water column (Knies and Stein, 1998). Diminished feeding on organic matter by benthic foraminifers brought on by a deterioration in their living conditions due to short-term high accumulation rates probably also improved preservation of organic carbon in the sediment.

Unfortunately, there are too few dated intervals to assess with confidence how long Event I lasted but it may have lasted only a few hundred years, comparable to the following events II to IV during the deglacial phase (see below). Event I was detected in all investigated cores of the eastern Fram Strait (Figs. 3.6. and 3.7.).

Event I was identified in several cores from the eastern Greenland margin (Nam et al., 1995), the Vøring Plateau, northern Iceland Plateau (Wagner and Henrich, 1994), as well as in the southern Fram Strait (Hebbeln et al., 1994; Elverhøi et al., 1995), the northern Barents Sea (PS 2138; Knies and Stein, 1998), and the northern Yermak Plateau (PS 2212; Vogt et al., 2001). The widespread effect of this event may indicate an intense and short-term retreat of large ice-shields all over the North Atlantic and the Northern Seas linked to an enormous outflow of suspended material. After the influx of fine-grained OC had ceased, the sedimentation of coarse-grained material and ice-rafted detritus (IRD) increased from 24 cal. kyrs on (Hebbeln et al., 1994; Elverhøi et al., 1995; Andersen et al., 1996, Birgel, 1999). A renewed influx of Atlantic water in southern Fram Strait (NE-1; Hebbeln et al., 1994; Dokken and Hald, 1996) triggered the final build-up of the SBIS to the shelf edge. At the LGM the glaciers around Spitsbergenbanken and Svalbard reached the shelves and produced conditions comparable with the NE-2-Event (Andersen et al., 1996). Erosion of organic-carbon-rich siltstones from the Svalbard shelf regions and lateral transport in the WSC to the northern Yermak Branch and Svalbard Branch areas immediately ceased.

The deglaciation (18-11 cal. kyr BP)

With the onset of the deglaciation (Termination I) a rapid shift to lighter oxygen isotope values was recorded in the Arctic Ocean and the southern Fram Strait (Jones and Keigwin, 1988; Hebbeln et al., 1994; Stein et al., 1994b; Knies and Stein, 1998). These values were interpreted as a meltwater anomaly reflecting the onset of the SBIS decay (Elverhøi et al., 1995). A shift to lighter $\delta^{18}O$-values at the beginning of the deglaciation can be correlated with increasing OC values and HI indices in all investigated cores (Figs. 3.6. and 3.7.). Due to insufficient age points, the entire deglaciation of the SBIS (15.7-11.9 cal. kyr) was described by Knies and Stein (1998) as one single OC-event (Event II). However, there is evidence for a short-term OC-Event II (16.0 to 15.4 cal. kyr) in our cores and three following additional short-term OC-Events (see below). These deglacial pulses mirror the successive decay of the SBIS with three re-advances toward glacial-like conditions in the Yermak (PS2837, PS55/100) and Svalbard branches (PS2122) of the WSC (Figs. 3.6. and 3.7.).

From a comparison of all cores in the investigated area (Fig. 3.6., Tab. 3.1.), we infer the SBIS to have commenced disintegration from ca. 18 cal. kyr on (Fig. 3.6). The first signal was accompanied by an increased input of IRD and coarse-grained inorganic material (c.f., Elverhøi et al., 1995; Knies and Stein, 1998). Accumulation rates remained low at first (Tab. 3.1.; Fig. 3.8.), plausibly because the ice-sheet of the Svalbard shelf was marine-based incorporating only minor amounts of sediment into the sea-ice (Andersen et al., 1996). Beginning from 16 cal. kyr on, more organic matter was deposited in eastern Fram Strait (Event II, 16 to 15.4 cal. kyr) (Figs. 3.6. and 3.7.). The deglacial

material was probably composed of a mixture of terrigenous organic matter from a Svalbard source (HI: ca. 50 mg HC/g OC, $\delta^{13}C_{org}$ values: -23 to -24 ‰), re-suspended organic matter from a southern source (Hebbeln et al., 1994), and primary produced marine organic matter (brassicasterol) (Fig. 3.7.). An increased preservation of marine organic matter was caused by the "ballast effect" (Ittekkot et al., 1992; Knies and Stein, 1998).

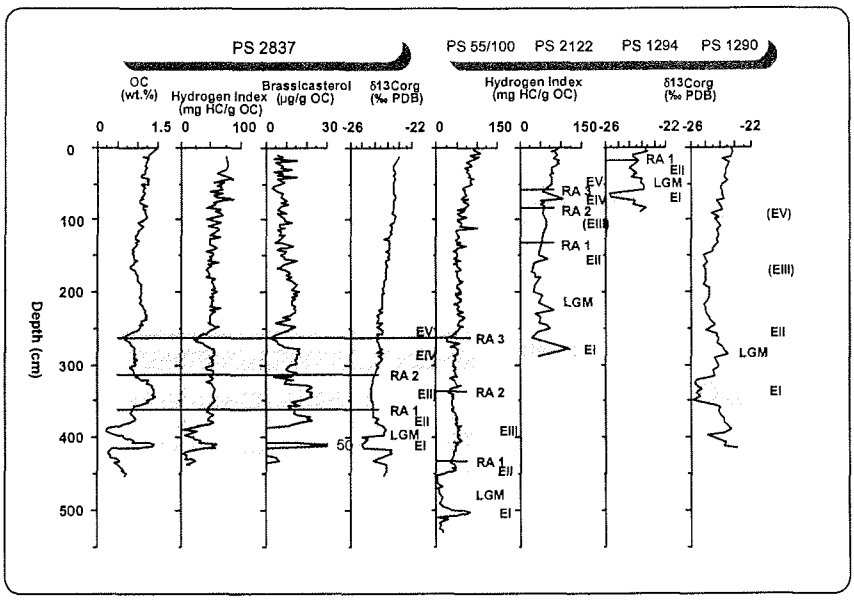

Fig. 3.7 Bulk organic-geochemical parameters □$^{13}C_{org}$ for cores PS1290, PS1294 and PS2837 and hydrogen indices for cores PS2122, PS2837 and PS55/100. For core PS2837 OC-values and brassicasterol vs. depth are also shown. Data from cores PS1294 and PS1290 are from Hebbeln (1992) and Hebbeln and Wefer (1997), data from core PS2122 are taken from Vogt et al. (2001). E I-V: high preservation events with an increased influx of organic carbon to the sediments. RA 1-3: re-advances of the SBIS (after Mangerud et al., 1998; Svendsen et al., 1996).

Mangerud et al. (1992) presented evidence that the Svalbard glaciers did not disappear from the shelf areas until 15.1 cal. kyr and therefore Svalbard cannot be the main and only source area of the OC peaks of Event II detected in our cores. After Event II, a short-term re-advance (RA-1; Figs. 3.5. and 3.6.) of the Svalbard glaciers is suggested (Svendsen et al., 1996), accompanied by low OC values and low accumulation rates (Figs. 3.6. and 3.8.). The following OC-event (Event III, Figs. 3.5. and 3.6.) appears in the Yermak Branch cores (PS2837, PS55/100 and PS2122), with major changes in the flux of organic matter. Event III is another temporary OC-event (14.7 to 14.4 cal. kyr), accompanied by the rapid Bølling short-term warm event. Linear sedimentation rates increased from values of 10 cm ky^{-1} up to 120 cm ky^{-1} in the Yermak Branch (Fig. 3.8.). A massive deposition of clay at the position of PS2837 accompanied by a major decrease of IRD to almost zero was detected in the Yermak Branch area (Hass, pers. comm.; Birgel, 1999). OC values >1.1 % were recorded in all cores from the eastern Fram Strait with light $\delta^{13}C_{org}$ and low

HI, indicating a dominantly terrigenous source (Figs. 3.6. and 3.7.), but a distinct portion of marine organic matter (brassicasterol) was preserved as well (see Event II).

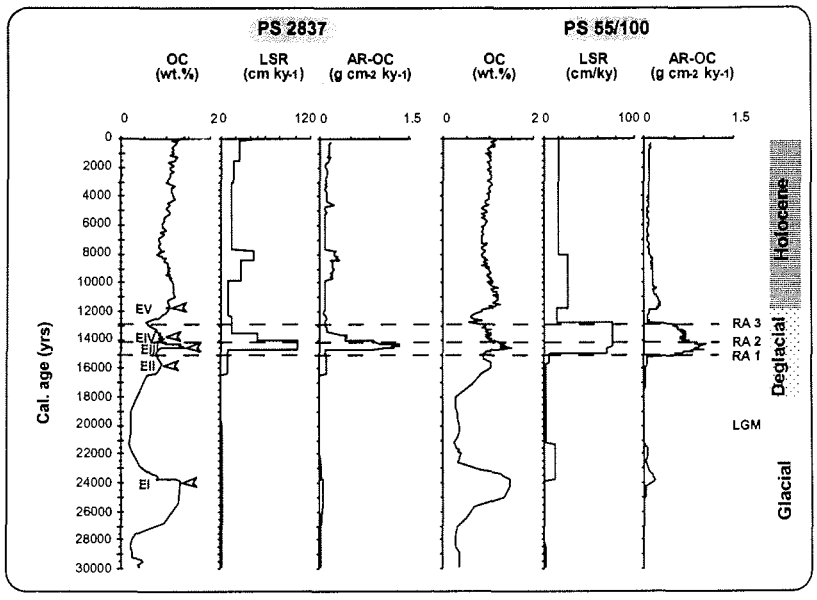

Fig. 3.8 Total organic carbon contents, linear sedimentation rates and accumulation rates of organic carbon of the cores PS2837 and PS55/100 versus calendar years. E I-V: high preservation events with an increased influx of organic carbon. RA 1-3: re-advances of the SBIS.

This second, short-term breakdown, described as major melting of the glaciers on Svalbard, was paralleled by an enormous input of suspended material (Elverhøi et al., 1995; Andersen et al., 1996). Coarse particles were sedimented only on the shelf and the nearby slope areas of Svalbard. Enormous amounts of suspended organic material (Fig. 3.8.) were transported laterally from the fjords, northwards by the WSC and downslope by turbidity currents. A smaller re-advance of glacial conditions (RA-2) was evident in cores PS2837, PS55/100 and PS2122, with a further decreased input of organic matter. This second cooling during the deglacial phase was immediately followed by a third, short-term melting event (Event IV, 14.2 to 13.7 cal. kyr), comparable with the major deglacial Event III, but less pronounced (Figs. 3.5. and 3.6.). Accumulation rates of organic matter were less during Event IV than during Event III (Fig. 3.8.). The major melting of the SBIS and the maximum input and preservation, however, appeared during Event III. The last re-advance of the Svalbard glaciers (RA-3) occurred from 13.7 to 11.9 cal. kyr (Fig. 3.6.), related to the Younger Dryas cold period (Hebbeln et al., 1998). Conditions during this phase were probably comparable with the LGM (Fig. 3.6.). All organic parameters show minimum values and low accumulation rates of organic matter (Fig. 3.8.) because of rapid prograding glaciers and the re-establishing of "LGM-like" conditions (Figs. 3.6. and 3.7.) with ice-covered fjords (Mangerud et al., 2002)

and a reduced influx of fine-grained organic material from the shelves. Cold conditions lasted for ca. 1500 years (Fig. 3.8.). Near 12 cal. kyr the last deglaciation event (Event V) with a comparable input of organic matter as Events II-IV (Figs. 3.6. and 3.7.) introduced stable climatic conditions. The stable inflow of Atlantic water established at this time increased the northward advection of heat leading to increased surface water temperatures indicated by low $\delta^{18}O$ values of planktonic foraminifera (Duplessy et al., 2001). The advected heat might also have initiated an earlier retreat of the glaciers and the sea-ice to modern distributions (Mangerud et al., 1992). OC values were comparable to late Holocene values and remained stable (0.9-1.1 wt. %) until 8 cal. kyr.

The Holocene (11 – 0 cal. kyr)

The Holocene is characterised by stable and warmer conditions in eastern Fram Strait (Hald et al., 1996) until ca. 9 cal. kyr (PS2837; Figs. 3.6. and 3.8.). The glaciers retreated to their modern positions with only minor re-advances. The cessation of the supply of suspended material from glacial melting material produced a relatively low flux of organic matter to the seafloor (Figs. 3.6. to 3.8.). Only between 8.40 to 8.13 cal. kyr (Fig. 3.8., PS2837) is a short-term build-up of the Svalbard glaciers evident as indicated by low OC values. This short-term cooling event, observed synchronously in several locations on the northern hemisphere (e.g., Alley et al., 1997), may have been due to the collapse of the Laurentide ice-sheet releasing large amounts of meltwater. The main reason for this short-time cooling event, however, remains unclear. After this last cooling event, warmer conditions were established again and the modern marine and terrestrial environment remained stable until the present.

3.5. Accumulation rates and budget of organic carbon

To quantify the organic carbon burial and its spatial and temporal variability in the study area, accumulation rates of organic carbon have been calculated for the three time intervals discussed above. A total sediment (TS) and total organic carbon (OC) budget has been estimated for the Holocene. During this time interval relatively stable environmental conditions can be assumed and there is a better database available than for the glacial and deglacial periods.

The last Glacial and Deglaciation

During the glacial period the environmental conditions in the eastern Fram Strait changed drastically (Fig. 3.9.a). The accumulation rates of organic carbon were influenced by massive ice-sheets on the continents and by sea-ice, which covered almost the entire Fram Strait. Only a narrow gateway in eastern Fram Strait enabled Atlantic water to flow to the northern areas (Fig. 3.9.a). Particulate organic and inorganic glacial debris were released from melting icebergs and sea-ice and transported laterally to northern areas (Fig. 3.9.a).

At that time, TS and OC accumulation rates of 10.1 to 12.7 g cm^{-2} ky^{-1} and 0.07 to 0.1 g cm^{-2} ky^{-1}, respectively, were reached in the Svalbard Branch (Tab. 3.1.; Fig. 3.9.a).

Tab. 3.1. Average linear sedimentation rates (LSR), bulk and organic carbon accumulation rates (AR-TS, AR-OC) for the glacial, deglacial and Holocene time periods. The calculation of accumulation rates is based on mean values of total organic carbon (OC), LSR and dry density (DD). WD= water depth. See Figure 3.2. for core positions.

	Core location	WD	LSR	OC	DD	AR-TS	AR-OC
		m	cm ky^{-1}	wt.%	g cm^{-3}	g Sed. cm^{-2} ky^{-1}	g C cm^{-2} ky^{-1}
East Greenland Shelf (Area I)							
PS 2419a	80°27'N, 13°40'W	412					
Holocene			6	0.15	1.44*	8.64	0.01
PS 2424a	80°02'N, 05°44'W	445					
Holocene			2.9	0.21	1.44*	4.15	0.009
Deglacial			26.9	0.42	1.32*	35.53	0.15
Glacial			41.2	0.38	1.5*	61.8	0.24
East Greenland Slope (Area II)							
PS 2843b	81°34'N, 07°17'W	2527					
Holocene			4.2	0.23'	1.45	6.09	0.01
PS 2423a	80°02'N, 05°26'W	829					
Holocene			0.8	0.31	0.6*	0.45	0.001
Deglacial			1.1	0.2	0.86*	0.94	0.002
Glacial			7.2	0.3	1.02*	7.31	0.02
PS 2422a	80°01'N, 04°13'W	1938					
Holocene			0.3	0.21	0.6*	0.2	0.0004
Deglacial			0.3	0.24	0.86*	0.28	0.0006
Northern Central Fram Strait (Area III)							
PS 2839b	81°24,3'N,	2933					
Holocene			3.3	0.81	0.8	2.64	0.02
PS 1310c	80°00'N, 00°82'W	2628					
Holocene			2.4	0.74	0.94	2.22	0.02
Deglacial			2.4	0.45	1.21	2.85	0.01
Glacial			3.4	0.38	1.09	3.71	0.01
PS 1311d	79°97'N, 00°20'E	2628					
Holocene			2.5	0.66	0.79	1.98	0.01
Deglacial			6.9	0.78	0.97	6.71	0.05
Glacial			7.8	0.43	1.02	7.93	0.03
PS 1312d	79°99'N, 01°17'E	3593					
Holocene			2.5	0.56	0.86	2.15	0.01
Deglacial			3.1	1.12	1.44	4.42	0.05
Glacial			4.8	0.59	1.15	5.53	0.03
Southern Central Fram Strait (Area IV)							
PS 1295e	77°99'N, 02°46'E	3112					
Holocene			1.4	0.53	0.74	1.06	0.006
Deglacial			1.4	0.42	0.84	1.18	0.005
Glacial			2.3	0.39	0.92	2.15	0.008
PS 1294e	78°00'N, 05°34'E	2677					
Holocene			1.8	0.5	0.84	1.47	0.007
Deglacial			2.8	0.45	0.91	2.5	0.01
Glacial			3.9	0.4	0.93	3.61	0.03
PS 1291d	78°00'N, 08°07'E	2408					
Holocene			3.2	0.71	1.3	4.16	0.03
Deglacial			8.4	1.12	0.76	6.43	0.07
Glacial			3.9	0.81	1.56	6.13	0.05

(continued on next page)

Tab. 3.1. (continued)

	Core location	WD	LSR	OC	DD	AR-TS	AR-OC
		m	cm ky^{-1}	wt.%	g cm^{-3}	g Sed. cm^{-2} ky^{-1}	g C cm^{-2} ky^{-1}
Yermak Plateau							
(Area V)							
PS 2835b	81°06,1'N, 07°04'E	855					
Holocene			2.5	0.75#	0.84	2.1	0.02
PS 2834b	80°54,8'N, 09°49'E	1024					
Holocene			2.5	0.78#	0.71	1.78	0.01
PS 2833b	80°58,4'N, 11°49'E	1969					
Holocene			3.8	0.86#	0.78	2.96	0.03
PS 2831b	81°06'N, 16°52'E	1024					
Holocene			2.1	0.53#	1.19	2.5	0.01
PS 2830b	80°58,4'N, 17°28'E	513					
Holocene			2.5	0.44#	1.57	3.92	0.02
(Yermak/Svalbard Branch)							
(Area VI)							
PS 2837	81°13'N, 02°22'E	1042					
Holocene			22.6	1.09	0.58	13.08	0.14
Deglacial			24	1.04	0.86	20.64	0.22
Glacial			4.1	0.61	1.12	4.56	0.03
PS 55/100	80°29'N, 02°56'E	1538					
Holocene			20	1.01	0.53	10.59	0.11
Deglacial			38	1.1	0.82	31.13	0.34
Glacial			6.2	0.62	0.98	6.03	0.04
PS 2123f	80°16'N, 09°85'E	574					
Holocene			11.4	1.38	1.44	16.46	0.23
Deglacial			10.9	1.15	1.36	14.85	0.17
Glacial			7	0.77	1.83	12.74	0.1
PS 2122f	80°39'N, 07°54'E	702					
Holocene			9.3	1.08	1.22	11.35	0.12
Deglacial			9	1.06	1.33	11.98	0.13
Glacial			7.8	0.67	1.3	10.11	0.07
West Svalbard Slope							
(Area VII)							
PS 1313d	79°98'N, 02°81'E	2623					
Holocene			11.5	0.9	0.79	9.09	0.08
Deglacial			12.3	1.01	0.92	11.33	0.11
Glacial			7.8	0.58	1.29	10.02	0.06
PS 1290g	78°00'N, 08°72'E	1522					
Holocene			12.8	1.01	0.59	7.54	0.08
Deglacial			12.9	1.24	1.56	20.12	0.25
Glacial			15.7	0.86	1.15	18	0.16
West Svalbard Shelf	79°01'N, 10°43'E	337					
PS 2121h							
Holocene			97.9	2.16	2.62	256.4	5.54

a Notholt (1998),
b Stein and Fahl (1997), preliminary age model and LSR
c Hebbeln (1991)
d Hebbeln (1992)
e Hebbeln and Wefer (1997)
f Vogt et al. (2001)
g Elverhoi et al. (1995)
h Müller (1995)
*=estimated AR, no DD was measured for this cores.
'= estimated OC from nearby surface samples (this paper)
#= averaged OC values from surface samples (this paper)
YB/SB= Yermak Branch/Svalbard Branch of the WSC (see Figs 3.8. & 3.9.)

Compared with deglacial and Holocene accumulation rates, these values are significantly lower. At the Yermak Branch core positions, 4.6 to 6.0 g cm^{-2} ky^{-1} of TS and 0.03 to 0.04 g cm^{-2} ky^{-1} of OC were accumulated. These values are five times less (TS), and ten times less (OC) than sedimentation rates during the deglacial phase. In this phase, an increased deposition of TS and OC occurred (Fig. 3.9.b), especially under the Yermak Branch area (on average 25.9 and 0.28 g cm^{-2} ky^{-1}, respectively) and on the West Svalbard slope (on average 15.7 and 0.18 g cm^{-2} ky^{-1}, respectively).

These increased TS and OC accumulation rates are responses to the decay of the SBIS (see above). Taylor et al. (2002a) calculated average linear sedimentation rates for the North Atlantic up to the southern tip of the West Svalbard slope.

They subdivided the last 27,000 years in two time slices, the Late Weichselian (27-12 ^{14}C ka) and the Holocene (12-0 ^{14}C ka). Sedimentation rates of 10-15 cm ky^{-1} and OC accumulation rates of 0.08-0.12 g cm^{-2} ky^{-1} were calculated for the Late Weichselian in the West Svalbard slope zone. Our linear sedimentation rates are comparable with their values for both time slices.

The OC accumulation rates of the West Svalbard slope zone from Taylor et al. (2002a) are between 0.08-0.12 g cm^{-2} ky^{-1} for the Late Weichselian. We found comparable glacial values of 0.06-0.16 g cm^{-2} ky^{-1}, but values of 0.11 to 0.25 g cm^{-2} ky^{-1} in the deglacial. Accumulation rates in our investigation areas change significantly from the glacial to the deglacial. The disintegration history of the SBIS must be taken into account more precisely, and therefore the glacial and deglacial time slices should be discussed separately.

The western part of the northern Fram Strait remained under a heavy sea-ice sheet in the deglacial period and Greenland and the adjacent shelf areas were covered by massive ice-sheets (Fig. 3.9.b). However, the average accumulation rates (34.6 for TS and 0.13 g cm^{-2} ky^{-1} for OC) are twice as high as during the deglacial phase. The increased supply of glacial material from Greenland is obvious. The deep-sea environment of western Fram Strait was not affected by environmental changes and OC accumulation rates, therefore, did not change noticeably in this area over the last 30,000 years (Tab. 3.1).

The Holocene

Mean Holocene OC accumulation rates in the northern Fram Strait / Yermak-Plateau vary between 0.0004 g cm^{-2} ky^{-1} (OC) on the eastern Greenland slope and 0.227 g cm^{-2} ky^{-1} in the Svalbard branch of the WSC (Fig. 3.9.c). The corresponding values for TS accumulation are 0.2 and 16.6 g cm^{-2} ky^{-1}. The maximum accumulation rates, however, were obtained on the western Svalbard shelf where 256 (TS) and 5.5 g cm^{-2} ky^{-1} (OC) were attained (Tab. 3.1.). For the western part of the Fram Strait, i.e., in the EGC-dominated areas I and II (Fig. 3.9.c), only 0.2 to 6.1 g cm^{-2} ky^{-1} (TS) and 0.0004 to 0.01 g cm^{-2} ky^{-1} (OC) were estimated. Even in the highly productive open water zone of the NE polynya (Fig. 3.1.) the accumulation rates of organic matter were low for the last 11 cal. kyr (Fig. 3.9.c, Tab. 3.1.).

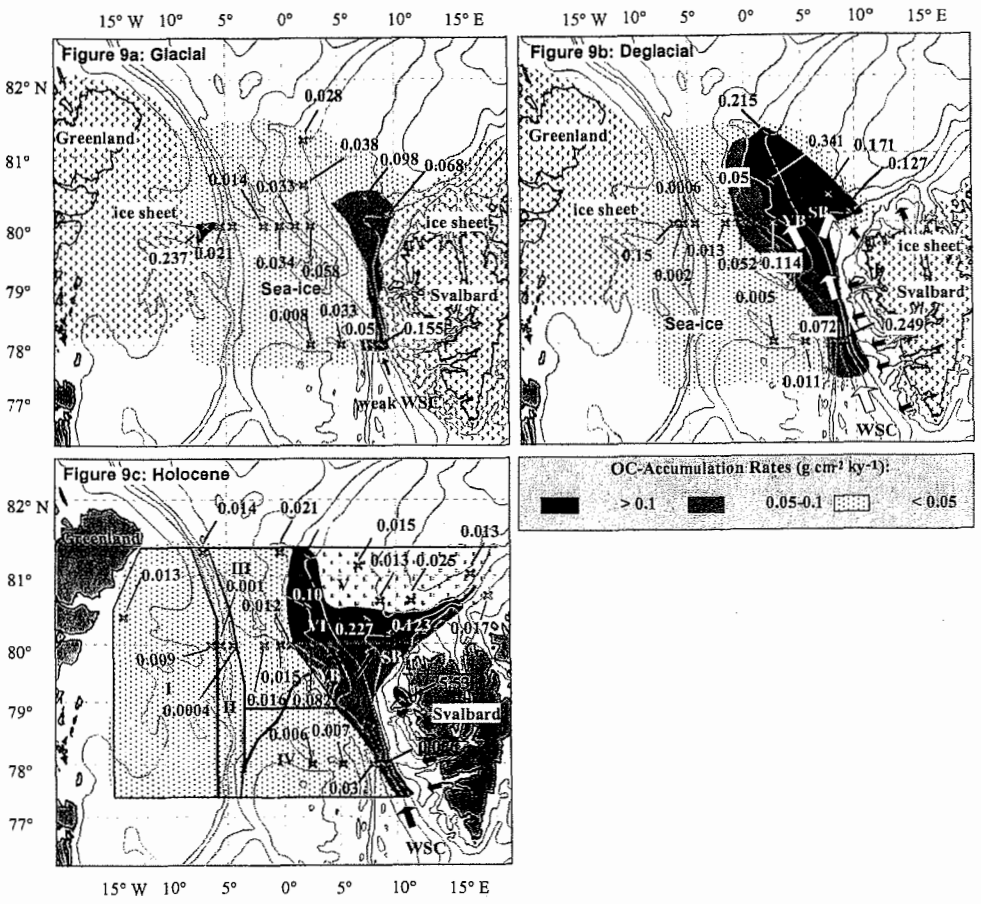

Fig. 3.9 The last Glacial (30-18 cal. kyr), the Deglaciation (18-11 cal. kyr) and the Holocene (11-0 cal. kyr).

(a-c) phases: OC accumulation rates (g cm^{-2} ky^{-1}; Tab. 3.1.) and average ice distribution for the different time slices (after Andersen et al., 1996; Svendsen et al., 1996; Mangerud et al., 2002). White crosses mark positions, for which linear sedimentation rates and accumulation rates were calculated (see Tab. 3.1.).

9a): Black arrows: Inflow of Atlantic water and open-water conditions (NE 1/2) (after Hebbeln et al., 1994).

9b): White arrows: increased inflow of warm, Atlantic water masses (WSC), in the northern Fram Strait (divided into the YB= Yermak Branch, and SB= Svalbard Branch) asynchronous with events I-V. Black arrows: Influx of organic matter from the collapsing Svalbard-Barents Sea Ice Sheet (SBIS) synchronous with events I-V.

9c): Black arrows: increased inflow of warm, Atlantic water masses (WSC), in the northern Fram Strait divided into the YB= Yermak Branch, and SB= Svalbard Branch). Grey arrows: Influx of organic matter from the collapsing Svalbard-Barents Sea Ice Sheet (SBIS). Roman numbers I-VII: Areas, for which an organic carbon budget was calculated (see Tabs. 3.1. and 3.2.). Grey, thick line: Average summer sea-ice edge in the investigated area.

In central Fram Strait (areas III and IV; Fig. 3.9.c), slightly increased values compared with the NE-Greenland areas I and II were obtained with 1.1 to 4.2 g cm^{-2} ky^{-1} (TS) and 0.006 to 0.03 g cm^{-2} ky^{-1} (OC) (Tab. 3.1.).

The northernmost Area (V) is characterised by low accumulation rates of TS (1.78 to 3.9 g cm^{-2} ky^{-1}) and OC (0.01 to 0.03 g cm^{-2} ky^{-1}; Tab. 3.1.; Fig. 3.9.c). A perennial sea-ice cover, low primary productivity, less light and nutrients result in decreased production of organic carbon on the Yermak Plateau.

Furthermore, the Yermak Plateau is not influenced strongly by Atlantic water masses and lateral and vertical transport of nutrients and suspended organic matter by the WSC are weakened or interrupted.

Tab. 3.2. Flux, budget and total accumulation of total sediment (TS) and organic carbon (OC) for the last 11,000 cal. kyrs. BP (Holocene).

Deposition of organic carbon	**Approx. area (km^2)**	**Flux (g cm^{-2} ky^{-1})**		**Budget 10^6 t C/year**		**Total Accumulation (10^9 t)**	
		TS	OC	TS	OC	TS	OC
East Greenland Shelf (Area I)	101,000	6.40	0.01	6.46	0.01	71.10	0.11
East Greenland Slope (Area II)	17,000	2.25	0.005	0.38	0.0009	4.21	0.01
Northern Central Fram Strait (Area III)	35,000	2.25	0.02	0.79	0.007	8.66	0.08
Southern Central Fram Strait (Area IV)	41,000	2.23	0.01	0.91	0.004	10.06	0.05
Yermak Plateau (Area V)	31,000	3.32	0.02	1.03	0.006	11.31	0.07
SB/YB (Area VI)	19,000	12.87	0.15	2.45	0.03	26.90	0.31
West Svalbard Slope (Area VII)	36,000	8.32	0.08	3.00	0.03	32.95	0.32
(West Svalbard Shelf)				not	not	not	not
	no cores	256.42	5.54	calculated	calculated	calculated	calculated
Total Holocene	**280,000**			**15**	**0.09**	**165.2**	**0.95**

Unlike the low accumulation rates of Area I-V, areas VI and VII showed the highest Holocene accumulation rates of organic material (7.5 to 16.5 g cm^{-2} ky^{-1} for TS and 0.08 to 0.23 g cm^{-2} ky^{-1} for OC) in the Fram Strait. The maximum values in Area VI are comparable with those documented in other continental margins of the world oceans (see Stein, 1991). The accumulation rates of organic matter increase monotonically from the southernmost tip of Area VII following the WSC up to the Svalbard and Yermak branches at average water depths between 600 and 1600 m (Fig. 3.9.c).

Holocene total sediment and organic carbon budgets

The investigated region with a total size of 280,000 km^2 was subdivided into eight areas. Budgets of total sediment (TS) and total organic carbon (OC) were calculated from the accumulation rates in Table 3.1. (see also Tab. 3.2., Fig. 3.9.c). During the entire Holocene (0-11 cal. kyrs. BP), 165 x 10^9 t of TS and 0.95 x 10^9 t of OC were deposited in the northern Fram Strait / Southern Yermak Plateau area (Tab. 3.2.). Based on the organic carbon source indicators (hydrogen indices; $\delta^{13}C_{org}$-values) determined in a selected set of sediment cores (see above), about 45 % of the organic carbon (i. e., 0.43 x 10^9 t) is estimated to be of marine origin and 55% (i.e., 0.52 x 10^9 t) of terrigenous origin. The main depotcenter was determined to be in the vicinity of the WSC (areas VI and VII), where 65 % (or 0.63 x 10^9 t) of the OC and 36 % of the TS (or 59.9 x 10^9 t C) were buried in 20% of the total area. The deep-sea environments and the Yermak Plateau (areas II-V) together received 21 % of the TS and 23 % of the OC of the total budget. On the East Greenland shelf (Area I) 71 x 10^9 t of TS (43 % of total budget) and only 0.11 x 10^9 t of OC (11 % of total budget) were accumulated.

3.6. Summary and conclusions

The amount and composition of organic carbon, its spatial and temporal variability, and its palaeoenvironmental significance have been discussed for the Fram Strait/Yermak Plateau area. In addition, a calculation of an organic carbon budget was performed for the Holocene time interval.

In general, preservation and burial of organic matter is controlled by:

- strong lateral transport of suspended matter by Atlantic water during the Holocene and by meltwater plumes during the deglacial phase and probably during the glacial phase;
- enhanced vertical transport facilitated by water masses containing increased amounts of suspended organic matter and therefore better capturing and preserving marine organic carbon through aggregation with terrigenous organic matter;
- increased primary production due to upwelling of nutrients near the sea-ice edges, on the shelves and in the fjords; and
- preferential deposition and preservation of organic carbon due to high bulk accumulation rates.

During approximately the last 30,000 cal. yrs., increased primary production has not been the major reason for increased preservation of organic carbon in the sediments. Rather, it is the lateral input of suspended terrigenous organic matter from the continents and the vertical "ballast effect" which has resulted in a quick vertical transport and increased preservation of marine organic matter in the sediments. High accumulation rates of inorganic material, however, are needed to support aggregation and deposition of the organic carbon. Furthermore, allochthonous organic matter (both marine and terrigenous) is transported to the northernmost Fram Strait by strong currents.

In total, 0.95 x 10^9 t C of total organic carbon have been deposited in the northern Fram Strait / Southern Yermak Plateau area during the Holocene, i.e., the last 11 cal. kyr. Of this, about half is terrigenous, half marine. Most of the organic carbon (65 %) has been buried in sediments under Yermak/Svalbard branch, which accounts for only 20 % of the total area.

Chapter 4

(submitted to Quaternary Science Reviews)

The last deglaciation in the Fram Strait (Arctic Ocean) with respect to oceanic and atmospheric variations: a coupled high-resolution organic-geochemical and sedimentological study

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Abstract. From a high sedimentation rate core, obtained from the Yermak slope (Arctic Ocean), we deduced short-term climatic fluctuations of the last deglaciation episode lasting from 17,000 to 9,000 years BP. By using a coupled organic-geochemical and sedimentological approach, we reconstructed near-bottom current conditions and assessed their significance in relation with comparable global thermohaline circulation patterns and surface water conditions. Highest concentrations and fluctuations of specific marine phytoplankton biomarkers were obtained in the Bølling-Allerød, when the major deglaciation of the Svalbard-Barents-Sea-Ice-Sheet (SBIS) occurred. The marine biomarker record (brassicasterol, $C_{16:1(n-7)}$-fatty acid) and the sedimentological record are consistent with climate reconstructions obtained from Greenland ice cores and thermohaline circulation variations. However, beginning with the Younger Dryas (YD) episode, biomarker data reflecting the surface water conditions diverged from both the bottom current speed record and ice-core data. The atmospheric conditions of the western Fram Strait (reconstructed from biomarker data) and thermohaline circulation signals (reconstructed from sedimentological data) were decoupled in the YD, suggesting a regional characteristic as reported from lake sediments in southern Greenland (Björck et al., 2002)

4.1. Introduction

The climate shift from the Last Glacial Maximum (LGM) to Holocene interglacial climate conditions is principally understood (e. g. Hebbeln et al., 1998; Knies et al., 1999; Hald et al., 2001). A number of rapid climate oscillations occurred in the course of the reorganising climate system. Most of the climate phases during the deglacial were linked to fluctuations in the thermohaline circulation system in the Nordic Seas and the North Atlantic as a result of meltwater influences released from the decaying ice sheets (e. g. Clark et al., 1996; Peltier, 2002; Schmittner and Clement, 2002). However, there are also inconsistencies in climate development that can only be understood if atmospheric parameters are taken into account (Walker, 1995). The obvious lack of moraines and glacier growth on western Svalbard marks the YD cold spell, as a result of changes in moisture supply rather than in air temperatures (Svendsen and Mangerud, 1992; Svendsen et al., 1996). It is thus an important

issue to gain information on the atmospheric conditions that prevailed in the study area during warmer and colder phases of the deglacial.

The climate of the Nordic Seas and the Arctic Ocean is primarily controlled by northward advection of warm and temperate Atlantic waters. Atlantic water masses enter the Arctic Ocean through the Fram Strait, a narrow gateway that forms the only deep connection between the Arctic and the remaining part of the World Ocean (Manley, 1995; Schlichtholz and Houssais, 1999 a and b; Rudels et al., 2000). The Arctic Ocean is a low productivity environment due to its perennial sea-ice cover (Wheeler et al., 1996). Generally, sediments from the northern Fram Strait/Arctic Ocean reveal that organic carbon is predominantly of terrigenous origin (Stein et al., 1994a; Schubert and Stein, 1996; Knies and Stein, 1998). This material is transported via the Transpolar Drift to the Fram Strait from sources as far away as Siberia (Dethleff et al., 2000). Stein et al. (1994a) and Schubert and Stein (1997) postulated that only a minor but significant amount of marine organic matter could be preserved in the vicinity of the Atlantic water inflow. At the marginal ice zone (MIZ) north and east of Svalbard an increased availability of nutrients promoted high primary productivity rates (Andreassen et al., 1996; Owrid et al., 2000; Rat'kova and Wassmann, 2002). These values are exceeding the low productivity rates in the central Arctic Ocean (Hirche et al., 1991). From sediment trap data north of Svalbard, an increased preservation of marine phytoplankton was observed (Andreassen et al., 1996; Ramseier et al., 1999; 2001), indicating an effective vertical transport of aggregates composed of marine phytoplankton under high-productivity conditions. The elevated amounts of organic compounds were accompanied by an increased flux of lithogenic particles near the MIZ (Hebbeln and Wefer, 1991; Hebbeln, 2000). Strong deposition rates of primary produced material (e. g. chlorophyll α) and marine phytoplankton biomarkers (e. g. fatty acids) have been described in Yermak slope surface sediments (Soltwedel et al., 2000; Schewe and Soltwedel, in press; Birgel et al., submitted; see also chapter 2). An effective northward lateral transport of waters carrying marine organic matter from open water regions via the West Spitsbergen Current/Yermak Slope Current was suggested from increased suspension load concentrations and ^{234}Th-depletion in the benthic nepheloid layer of the Yermak slope (Rutgers van der Loeff et al., 2002). An additional theory enabling a quick transport of marine organic matter was described as "mineral ballast effect" in the Arabian Sea (Ittekkot et al., 1992) and applied to sea-ice covered regions (Knies and Stein, 1998). Labile marine organic compounds are attached to terrigenous matter and can be effectively transported to the sea floor.

Former studies dealt already with palaeoceanographical conditions, flux and accumulation of organic carbon in the Fram Strait during the last glacial/deglacial cycle (e. g. Hebbeln et al., 1994; 1998; Elverhøi et al., 1995; Andersen et al., 1996; Knies and Stein, 1998; Vogt et al., 2001, Taylor et al., 2002a). However, the low temporal resolution of those sedimentary records prevented the identification of short-term fluctuations. Here, we present data of a sediment core from the Yermak slope (northern Fram Strait) that allowed us to study short-time events during the last deglacial period (17,000-9,000 years BP).

The aim of this study was to reconstruct past climatic and oceanographic conditions at high temporal resolution to assess the role of the Arctic Ocean (Fram Strait) in short-term climate change in a combined geochemical and sedimentological study. The sedimentology provides information on palaeo bottom-current dynamics in the northern Fram Strait. In the low-productivity and well ventilated environment where microfossils are rare in sediments, specific biomarkers such as brassicasterol (diatoms), the fatty acid $C_{16:1(n-7)}$ (diatoms) and dinosterol (dinoflagellates) are powerful tools to reconstruct past climatic conditions in the Fram Strait area, suggested from other works in the Arctic Ocean (e. g. Fahl and Stein, 1997; 1999; Knies, 1999; Stein et al., 1999). The sedimentological and geochemical data provide information on different climate aspects that are mixed up in the bulk sediment. In the following, broad-scale and regional effects of the climate development will be discriminated and interpreted.

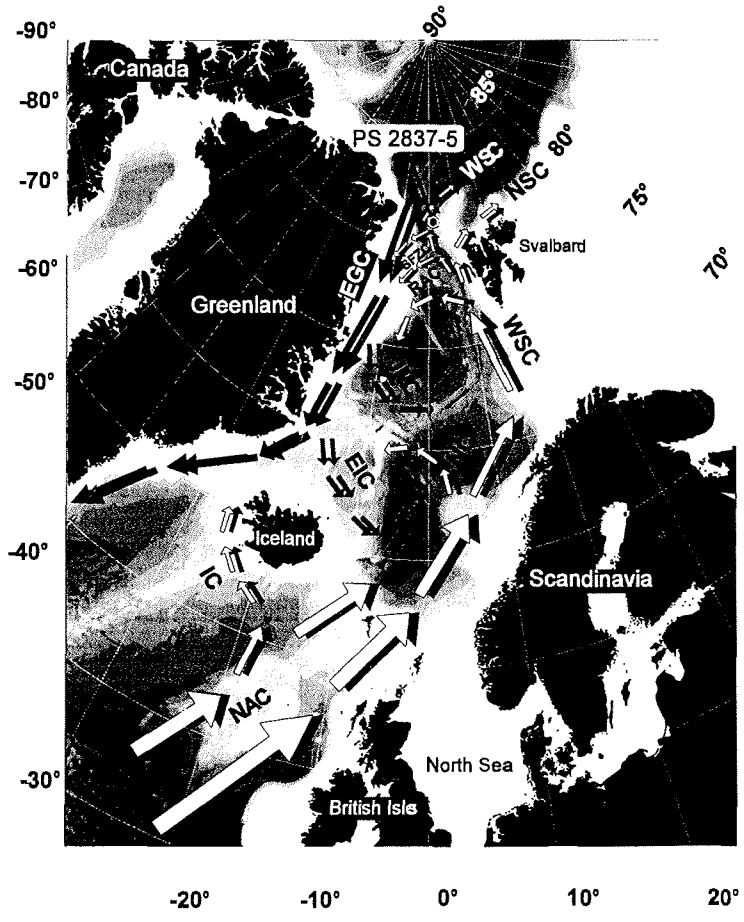

Fig. 4.1. Core location and general circulation pattern in the North Atlantic and the adjacent Fram Strait (Schlichtholz and Houssais, 1999 a and b; Rudels et al., 2000 and references therein): WSC= West Spitsbergen Current, YSC= Yermak Slope Current, NSC= North Spitsbergen Current, EGC= East Greenland Current, JMC= Jan-Mayen Current, EIC= East Iceland Current, NC= Norwegian Current, IC= Iceland Current, NAC= North Atlantic Current.

4.2. Oceanography

The Fram Strait is characterised by two contrasting water masses at the surface: Along the eastern Greenland continental margin the East Greenland Current (EGC) carries cold Polar water masses to the south. In the eastern Fram Strait Atlantic surface water masses flow north forming the West Spitsbergen Current (WSC), which is deflected to the east north of Svalbard (Fig. 4.1.).

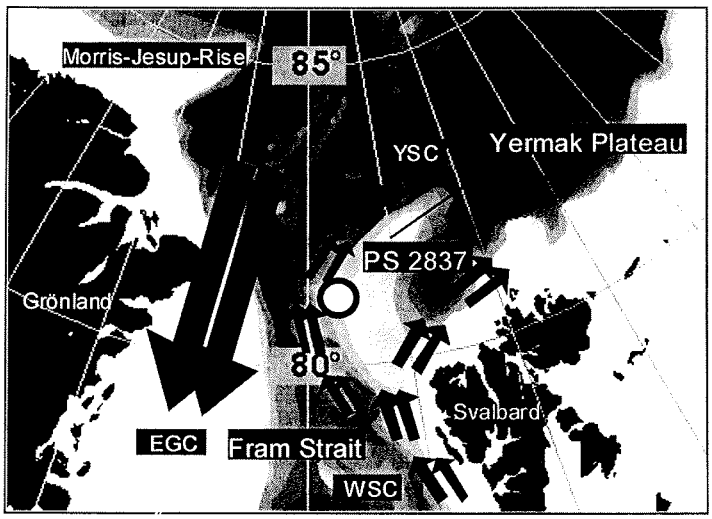

Fig. 4.2. Core position of sediment core PS2837. YSC= Yermak Slope Current, WSC= West Spitsbergen Current, EGC= East Greenland Current.

North-heading waters underlie the WSC, in particular Norwegian Sea Deep Water (NSDW) that originates from thermohaline processes in the Greenland Sea (Swift and Koltermann, 1988; Schlichtholz and Houssais, 1999a). Due to the sill between Svalbard and the Yermak Plateau only waters from less than 500 m water depth are deflected to the east following the north Svalbard shelf. Water masses below the sill depth are forced to flow north along the Yermak Plateau. Numerous currents can be distinguished in the eastern Fram Strait/western Yermak Plateau area. Among these, the Yermak Slope Current (YSC), a contour current at an average water depth of 1,000-1,500 m, directly affects sedimentation at the location of the core presented here (Schlichtholz and Houssais, 1999 a and b; Rudels et al., 2000). Although there are recirculation cells in the Fram Strait between 78°N and 79°N (Return Atlantic Current=RAC) and 79.5°N and 80°N (Spitsbergen Fracture Zone Current=SFZC), the YSC does not appear to be primarily affected by zonal water-mass transport.

4.3. Material and Methods

During RV *Polarstern* cruise ARK-XIII/2, Kastenlot core PS2837-5 (81°13.99'N, 02°22.85'E; 1042 m water depth) was recovered on the western slope of the Yermak Plateau (Fig. 4.2.; Stein and Fahl, 1997). The core position was selected by using the shipboard Parasound echosounding system (Niessen and Kleiber, 1999).

4.3.1. Organic geochemistry

The core was sampled in slices (one centimetre thick) every centimetre for sedimentology and at 2-5 cm intervals for lipid biomarker investigations. All organic-geochemical samples were stored at –30°C.

Total carbon, nitrogen, and organic carbon contents were determined by means of a Leco CS analyser. The carbonate content was calculated as $CaCO_3$ = [Total Carbon (TC)-Total Organic Carbon (TOC)] x 8.333. The hydrogen indices (HI) were analysed by Rock-Eval pyrolysis following Espitalié et al. (1977).

Lipid analysis

For the lipid extraction, 8 g of sediment was freeze-dried, extracted and purified after the method by Folch et al. (1957) and Bligh and Dyer (1959). Internal standards were added before any analytical step. Squalane was added for quantification of *n*-alkanes, $C_{19:0}$ for fatty acid methyl esters and cholest-5-en-3β-ol-d_6 for sterols. The sediment was extracted in three steps with 40 ml methanol, methanol:dichloromethane (1:1), and dichloromethane. Then, the extract was transesterified for 12 hours at 50°C with 1 ml 5 % concentrated hydrochloric acid in methanol. Afterwards, it was extracted three times with 2 ml of hexane. Then, the *n*-alkanes were separated from the sterols and fatty acid fractions by column chromatography with 4 ml of hexane (*n*-alkanes), 4 ml of dichloromethane (fatty acids), and 4 ml of hexane/ethylacetate (80:20) (sterols). After the column chromatography, an aliquot of the extract was silylated for 2 hours at 60°C with 500 µl BSTFA (bis-trimethylsilyl-trifluoroacetamide). The composite of biomarkers was analysed with a Hewlett Packard gas chromatograph (HP 5890, column 30 m x 0.25 mm; film thickness 0.25 µm; liquid phase: DB-5 MS). We used the following temperature program: 60°C (2 min), 150°C (rate: 15°C/ min), 320°C (rate: 3°C/ min), 320°C (10 min isothermal). The injection volume was 1 µl (Gerstel Cold Injection System (CIS): 60°C (10s), 300°C (60s), rate 12°C/s). Helium was used as carrier gas. Identification of the biomarkers based on GC retention times and MS fragmentation patterns.

4.3.2. Sedimentology

Samples for sedimentological analyses were freeze-dried and treated with hydrogen peroxide to remove organic matter. Grain-size analyses were carried out using a sonic sifter (63 - > 1000 µm in PHI steps) and a Sedigraph 1500 (< 2 - 63 µm in 0.1 PHI steps) (see Hass, 2002, for further details on sample treatment). It was refrained from destroying carbonate from the samples for special reasons: Carbonate contents turned out to be low (see chapter 4.5.). In

addition, the average number of carbonate tests (both, planktic and benthic foraminifers) was at 84 individuals per gram sand fraction (Spielhagen, pers. comm.). Acid treatment of the samples yielded negative effects on the adhesive behaviour of the clay and fine-silt fractions that affected the Sedigraph measurements even after multiple cleaning procedures. Further, with removing carbonate as a possible signal of production rather than current sorting, important information on detrital carbonatic IRD would have also been removed. More adverse than beneficial effects would result from acid treatment of the samples, hence, it was chosen to not remove carbonate from those samples selected for sedimentologic investigations.

Current speed at the core location is suggested to be too low for the transport of terrigenous sand-sized materials (Fahrbach et al., 2001, based on data from an array of current-meters located on a transect at 79°N across Fram Strait). Thus, the bulk terrigenous sand fraction and also part of the silt fraction are assumed to be ice-rafted. In order to significantly reduce the influence of ice-rafted silt on the silt fraction (i.e. the fraction used for palaeocurrent-speed analysis), the predominantly ice-rafted sand fraction was related to the predominantly current-sorted silt fraction. Here we use the sortable silt (10 - 63 µm) MEAN diameter ($\overline{SS}$) to assess relative current-speed variations (cf. Bianchi and McCave, 1999). Using the regression equation calculated from the two variables a steady-state condition was calculated. Deviations from the steady state ($\Delta\overline{SS}$) in the coarse direction were interpreted as higher current speed whereas deviations in the fine direction suggest current speed lower than average (see Hass, 2002 for a thorough description of this method). The method applied sharpens existing trends but usually does not produce trends where there are none visible in the original data.

4.3.3. Stratigraphy

The stratigraphy is published elsewhere and was carried out by radiocarbon age determinations on ten samples of approximately 2000 tests each of the planktic foraminifer *Neogloboquadrina pachyderma sin.* by Nørgaard-Pedersen et al. (2003). The reservoir-corrected data were converted to calendar years BP (Present = AD 1950) using CALIB 4.1.2 (Stuiver et al., 1998). Core sections in between the age-dated samples were interpolated. In the following text all age data are given in calendar years BP. Mass accumulation rates (MAR) (g cm^{-2} ky^{-1}) of bulk sediments were calculated from linear sedimentation rates (LSR) (cm kyr^{-1}) and dry bulk density data (g cm^{-3}) after van Andel et al. (1975).

4.4. Organic geochemistry: environmental implications and results

All profiles were discussed versus calibrated ages. Biomarkers were normalised to gram TOC to diminish dilution effects caused by variations in sedimentation rates. The TOC content of core PS2837-5 varies between 0.5 to 1.5 % (Fig. 4.3.). Maximum values were found between 14,700-14,400 years BP. (1.3-1.5 %). Minimum values with 0.6-0.8 % occurred from 13,200-12,800 years BP.

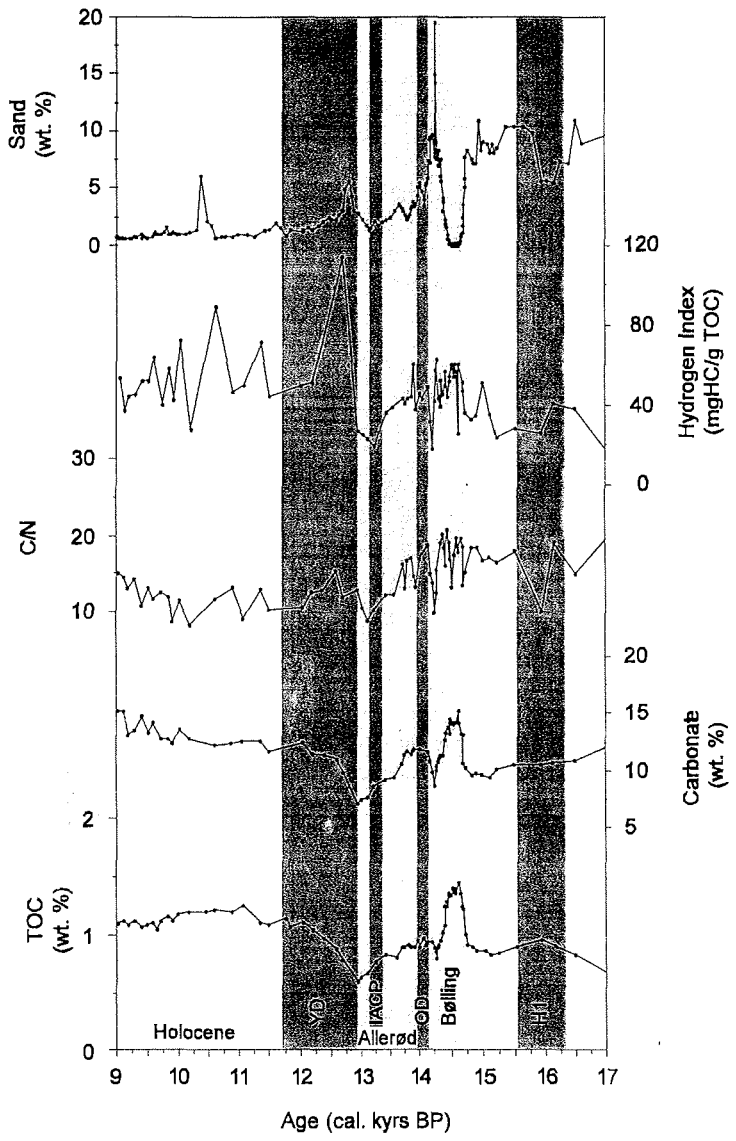

Fig. 4.3. Total organic carbon, carbonate (wt. %), C_{org}/N-ratios, hydrogen index (HI), >63 µm fraction (wt. %) data versus calendar years. YD= Younger Dryas, IACP= Intra Allerød Cold Period, OD= Older Dryas, H1= phase equivalent to Heinrich 1 peak phase.

The C_{org}/N_{tot} -ratios and hydrogen indices provide primary information on the composition and origin of organic matter (terrigenous vs. marine). Generally, terrigenous organic matter is characterised by C_{org}/N_{tot}-ratios > 15 (Scheffer and Schachtschabel, 1984), whereas marine organic matter showed values of 5 to 7 (Borodowskiy, 1965; Scheffer and Schachtschabel, 1984). C_{org}/N_{tot}-ratios vary between 7 and 20, without specific separation of N_{org} and N_{anorg} (see Schubert and Calvert, 2001). Therefore, values of the marine fraction might be too high in

our samples. From 17,000-13,800 years BP, ratios were between 10 and 22, whereas in the younger section (13,800-9,000 years BP) ratios between 8-12 were found (Fig. 4.3.). Hydrogen indices < 100 mg HC/g TOC are typical for terrigenous organic matter in organic-rich immature sediments (TOC > 0.5 wt.%). HI values between 200 to 400 mg HC/g TOC indicate a dominant marine source of the organic matter (Tissot and Welte, 1984; Stein, 1991). Hydrogen indices are < 100 mg HC/g TOC in the entire core section presented here with lowest values from 17,000-13,500 years BP (20-60 mg HC/g TOC) and slightly increased values in the younger section from 13,500-9,000 years BP (40-120 mg HC/g TOC). Increased carbonate values occurred between 14,700-14,500, 14,200-13,700 and from 12,600-9000 years BP. Carbonate is positively correlated with the amounts of planktic and benthic foraminifers in the northern Fram Strait and in core PS 2837-5 (Hebbeln and Wefer, 1997; Nørgaard-Pedersen et al., 2003; Wollenburg et al., submitted).

Three different classes of biomarkers were used to assess sources and compositions of organic matter in the northern Fram Strait:

- Odd-numbered long-chain *n*-alkanes are known to reflect terrestrial organic matter supply to sediments. These compounds are mainly related to a contribution of higher plant waxes (Eglinton et al., 1962). Consequently, long-chain *n*-alkanes *n*-C_{27}, *n*-C_{29}, *n*-C_{31} (e. g. Prahl et al., 1994; Yunker et al., 1995) were used as indicators for terrigenous organic matter.

- The fatty acid $C_{16:1\ (n-7)}$ is synthesised mainly by marine phytoplankton (e. g. Kates and Volcani, 1966; Sicre et al., 1988; Volkman et al., 1989, Volkman et al., 1998). Especially marine diatoms are known as producers of $C_{16:1(n-7)}$. Short-chain saturated and unsaturated fatty acids ($C_{16:0}$, $C_{18:0}$, $C_{18:1}$) were used as marine phytoplankton markers in earlier investigations of Arctic Ocean sediments (e. g. Schubert and Stein, 1997). However, these compounds are ubiquitous in marine environments and therefore not suitable as biomarkers for specific organisms (Shaw and Johns, 1986). $C_{18:1(n-7)}$ is predominantly synthesised by marine zooplankton (e. g. copepods) as well as by benthic micro- and macro-organisms (e. g. polychaeta, brittle stars, decapods; Wakeham, 1995; Albers et al., 1996; Graeve et al., 1997). The fatty acid $C_{18:1\ (n-7)}$ originates from chain elongation and desaturation of an original dietary $C_{16:1\ (n-7)}$ fatty acid (e. g. Kattner and Hagen, 1995; Albers et al., 1996; Graeve et al., 1997). Here we use $C_{16:1\ (n-7)}$ as marker for marine organic phytoplankton, whereas $C_{18:1\ (n-7)}$ is used as marine zooplankton marker.

- Sterols are synthesised by various eukaryotic organisms, including phytoplankton (e.g. diatoms, dinoflagellates, coccolithophoroids), zooplankton and vascular plants (e.g. Huang and Meinschein, 1976; 1979; Volkman, 1986; Volkman et al., 1998). Some sterols are restricted to specific organisms, whereas others are widely distributed among different taxa. Among those, brassicasterol is used as a diatom marker. Dinoflagellates are known to synthesise dinosterol being the most prominent of these organisms (Boon et al., 1979, de Leeuw et al., 1983).

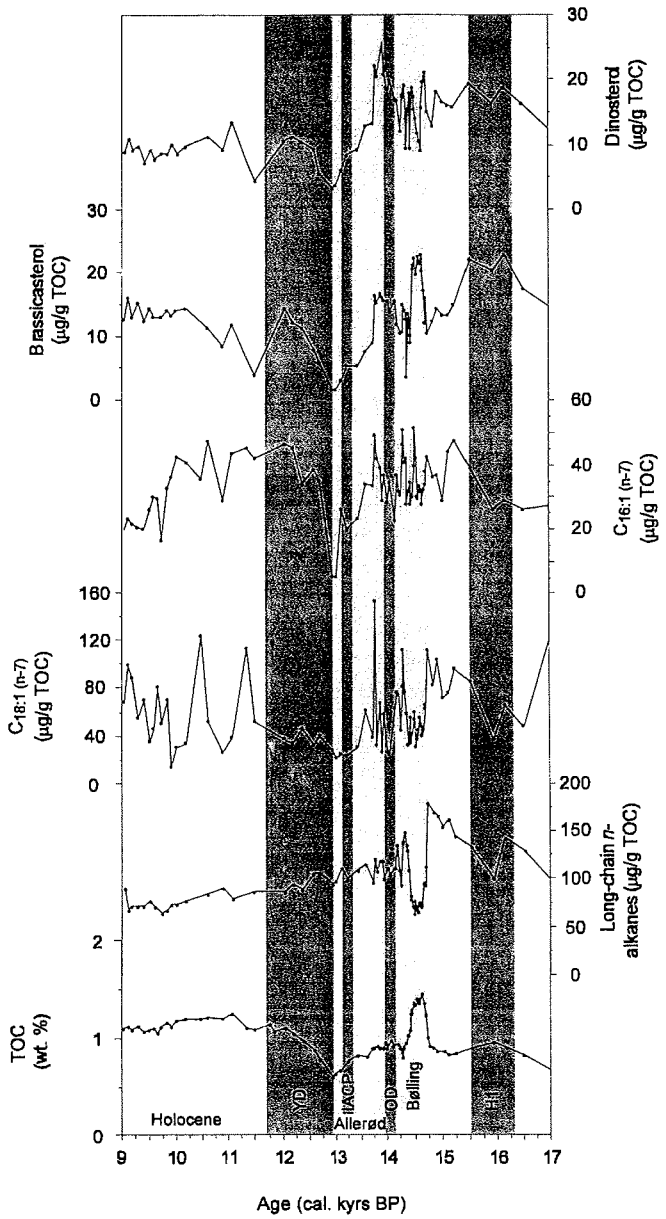

Fig. 4.4. Total organic carbon concentrations (wt.%) and total abundances of long-chain *n*-alkanes (terrigenous-derived), fatty acids $C_{18:1(n-7)}$ (marine zooplankton-derived), fatty acid $C_{16:1(n-7)}$ (marine phytoplankton-derived), brassicasterol (marine phytoplankton-derived; diatoms), dinosterol (marine phytoplankton-derived; dinoflagellates) versus calendar years. YD= Younger Dryas, IACP= Intra Allerød Cold Period, OD= Older Dryas, H1= phase equivalent to Heinrich 1 peak phase.

The contents of long-chain *n*-alkanes ranged from 50 to 200 µg/g TOC with highest values in the early deglaciation from 17,000-14,700 years BP and slowly decreasing values in the younger core section from 14,700-9,000 years BP (Fig. 4.4.). In the Bølling period (14,700-14,300 years BP), where warmer climatic conditions prevailed in Europe (Renssen and Isarin, 2001), minimum concentrations of long-chain *n*-alkanes were measured. Fatty acid $C_{16:1\ (n-7)}$ concentrations varied between 10-55 µg/g TOC with maximum concentrations from 12,500-9,000 years BP and highest variations between 14,700-13,500 years BP (Bølling-Allerød). Lowest values occurred around 13,000 years BP (Fig. 4.4.). Values of $C_{18:1\ (n-7)}$ were in the range of 20 to 120 µg/g TOC. Maximum variations occurred between 14,700-13,500 years BP. Sterols varied between 5 and 30 µg/g TOC. Maximum values were found in the older core section from 17,000-13,600 years BP (10-30 µg/g TOC), where highest fluctuations occurred. In the younger core section (13,600-9,000 years BP) decreased values (10-15 µg/g TOC) were measured. Minimum values were found around 13,000 years BP (Fig. 4.4.).

4.5. Sedimentology: palaeocurrent speed fluctuations

The sortable silt mean and in particular the IRD-corrected value $\Delta\overline{SS}$ provides information on palaeo-bottom-current dynamics. Fig. 4.5. shows that colder periods as visible in the GISP 2 ice-core generally correspond with periods of lower bottom-current strength. Between 16,300 and 15,500 years BP a minor minimum occurred that marks peak Heinrich 1 (H1) conditions (Bond et al., 1993; McCabe and Clarke, 1998). At that time strong ice-rafting events occurred in the North Atlantic that may have had influence on the thermohaline circulation in the Nordic Seas. Apparently, the process that controlled the inflow of intermediate-depth waters into the Arctic Ocean, and that also fed the YSC, was weakened at that period. This was resulting in a fining of the sortable silt fraction at the core location. During the following 800 years bottom currents remained relatively stable. At 14,700 years BP bottom currents dramatically increased for a short period of time before they collapsed to the lowest values in the record. The initial warming at the beginning of the Bølling interstadial most likely controlled this process. It can be assumed that the initial warming was paralleled by intense thermohaline overturn that also accelerated northbound intermediate-depth currents that transported newly formed NSDW into the Arctic Ocean. The rapid warming at the onset of the Bølling interstadial triggered intense melting processes that may have caused deep-water production to temporary shut down, or to move to places that prevented the production of northbound deep water. As a consequence the water mass that fed the YSC became reduced and thus caused the YSC to significantly decelerate as mirrored by a clear shift to the sedimentation of finer grains at the core location. The absence of IRD at that time might have been caused by a temporary closed ice-cover due to large amounts of meltwater entering the Fram Strait, or, alternatively, a plume of fine material affected sedimentation at the core location for a short episode.

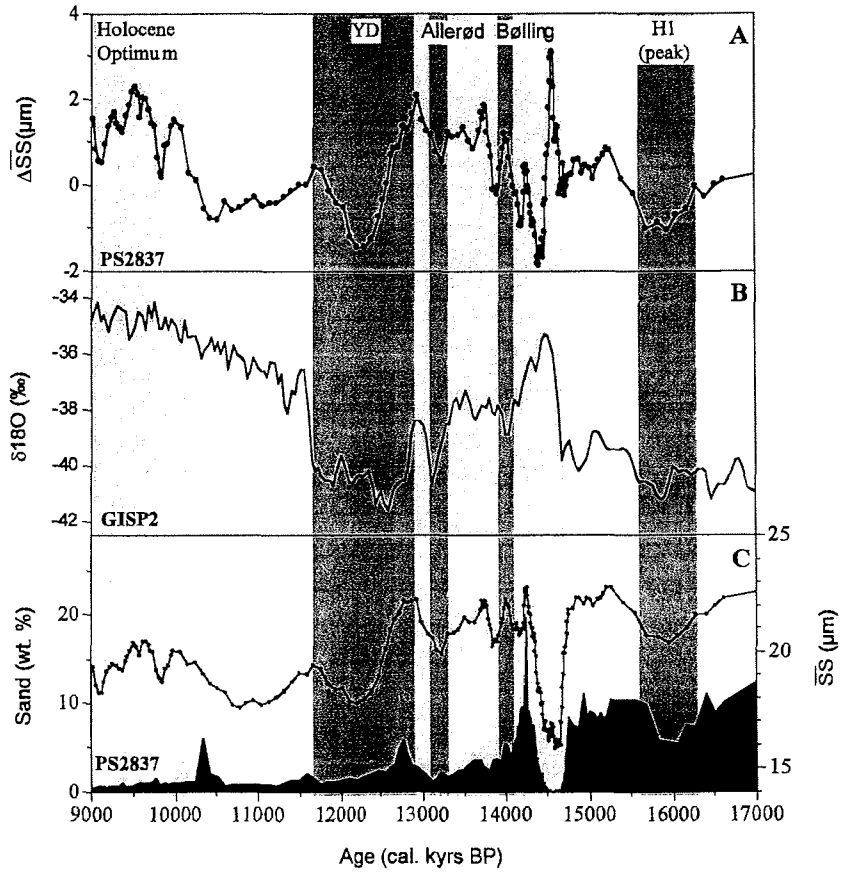

Fig. 4.5. A) IRD-corrected sortable silt mean $\Delta\overline{SS}$ of core PS2837 (unweighed 5 pt. running mean). Negative values indicate lower, positive values indicate higher current speed events (Hass, 2002). B) $\delta^{18}O$ of Greenland ice core GISP 2 (Grootes et al., 1993). C) Sand fraction (=IRD, black area plot); grey curve: sortable silt mean grain size SS as measured (unweighed 5 pt. running mean). YD= Younger Dryas, IACP= Intra Allerød Cold Period, OD= Older Dryas, H1= phase equivalent to Heinrich 1 peak phase.

Yet, conditions quickly changed again and bottom-current speed increased to high levels until 12,700 years BP most likely as a response to the recovering thermohaline circulation. Distinct short-term periods of reduced bottom current activity are centred at 14,200, 13,900, and 13,250 years BP that may be linked to cooler climate episodes such as the Older Dryas and the Intra Allerød Cold Period (IACP). The general trend to increasing current strength was rapidly disrupted around 12,700 years BP when currents collapsed in a way similar to the period of H1. Again meltwater extended over the North Atlantic and the Nordic Seas and reduced thermohaline overturn at the time of the YD cold event (Broecker and Denton, 1989; Keigwin and Lehman, 1994). YD conditions ended at 11,900 years BP with a sudden increase in current strength followed by a decrease to intermediate values at 11,600 years BP. This level remained relatively stable during that time equivalent to Termination I_B until 10,200 years BP suggesting average low inflow of mid-depth waters into the Arctic Ocean.

Thus, bottom currents at the core location were consistent with the major thermohaline reorganisation that took place in the Nordic Seas but current strength remained relatively low until a rapid increase of current speed occurred at 10,300 years BP. It is suggested that due to large amounts of meltwater in the surface ocean thermohaline circulation was either weaker or shallower after the YD, which caused reduced inflow of NSDW into the Arctic Ocean. Between 10,300 and 10,000 years BP the speed of the YSC accelerated to the high values that characterise early Holocene interglacial conditions. It can be inferred that full interglacial thermohaline processes in the Greenland Sea regarding depth and location of deep-water renewal established at that time interval.

4.6. Discussion

The surface and the bottom of the eastern Fram Strait: Two different systems

The studied sediment core PS2837-5 obviously carries information of two systems that reveal different controlling mechanisms. The non-organic record is the result of bottom currents that appear to be closely linked to the North Atlantic thermohaline circulation system. Climate phases triggered by changes in the intensity of deep-water production or vice versa are mirrored by the deep-flow intensities at the western flank of the Yermak Plateau. The biomarker record, however, seems to reflect the actual climate that prevailed in the neighbourhood of the core location. Thus, the combination of both records allows us to discriminate between the broader climate trends that involved fluctuations of the thermohaline circulation in the Nordic Seas and the reaction of the Arctic climate system to thermohaline climate forcing.

4.6.1. The early deglaciation (17,000-14,700 years BP)

The first signals of the beginning deglaciation in the Arctic environment are mirrored by a significant depletion in $\delta^{18}O$ records between 18,000 and 17,700 years BP (Jones and Keigwin, 1988; Hebbeln et al., 1994; Stein et al., 1994b; Knies and Stein, 1998).

Various data (sedimentology, organic carbon) from the area directly influenced by the SBIS suggested that the early retreat of the ice-sheets from the shelf-breaks in these regions started at ca. 17,000 years BP (Elverhøi et al., 1995; Andersen et al., 1996; Svendsen et al., 1996; Knies et al., 1999).

This first deglacial period lasting from 17,000-14,700 years BP (GS-2a; Björck et al., 1998) is characterised by deposition of IRD at the core location (sand contents around 10 % of total sediment, Fig. 4.6.). At that period of time, high concentrations of marine and terrigenous biomarkers (sterols and fatty acids) in a predominating terrigenous organic matrix were accumulated (high C_{org}/N-ratios, low hydrogen indices; maximum long-chain *n*-alkanes; Fig. 4.6.). From 16,300-15,500 years BP, sand contents and current speed decreased, whereas terrigenous long-chain *n*-alkane and fatty acid concentrations (marine phyto-/zooplankton), as well as marine phytoplankton sterols increased simultaneously.

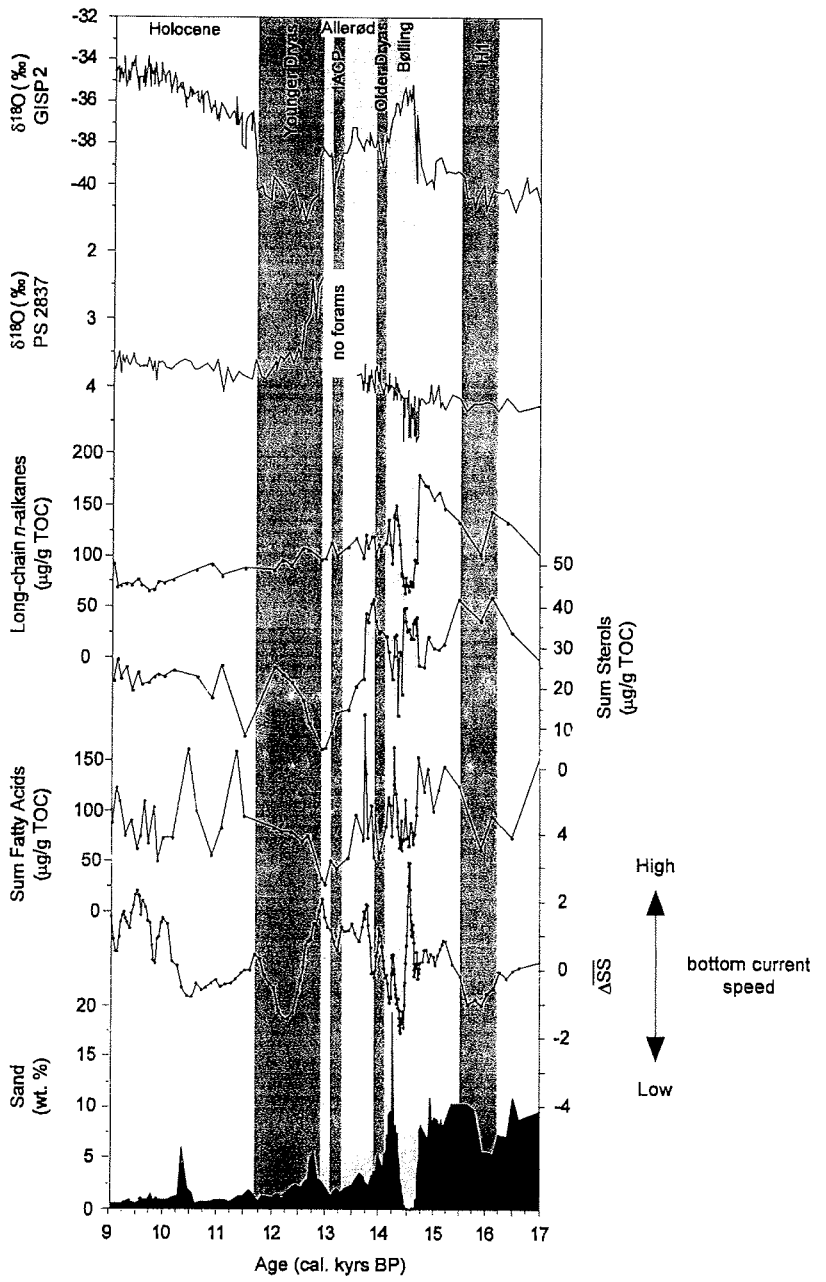

Fig. 4.6. Sedimentological (>63µm, $\Delta\overline{SS}$) and organic-geochemical parameters: fatty acids (sum of $C_{16:1(n-7)}$ and $C_{18:1(n-7)}$), sterols (sum of brassicasterol and dinosterol) and long-chain *n*-alkanes. Oxygen isotopes of sediment core PS2837-5 (*Neogloboquadrina pachyderma sin.*) (Nørgaard-Pedersen et al., 2003) and data of GISP 2 ice-core from Greenland (Grootes et al., 1993) versus calendar years. YD= Younger Dryas, IACP= Intra Allerød Cold Period, OD= Older Dryas, H1= phase equivalent to Heinrich 1 peak phase.

High productivity in open waters in eastern Fram Strait was suggested due to better living conditions in the water column (Fig. 4.6.). The suggested better living conditions in open water zones and at the MIZ were associated with aggregation of marine and terrigenous compounds in the water column, as indicated by high concentrations of marine as well as terrigenous biomarkers in sediments.

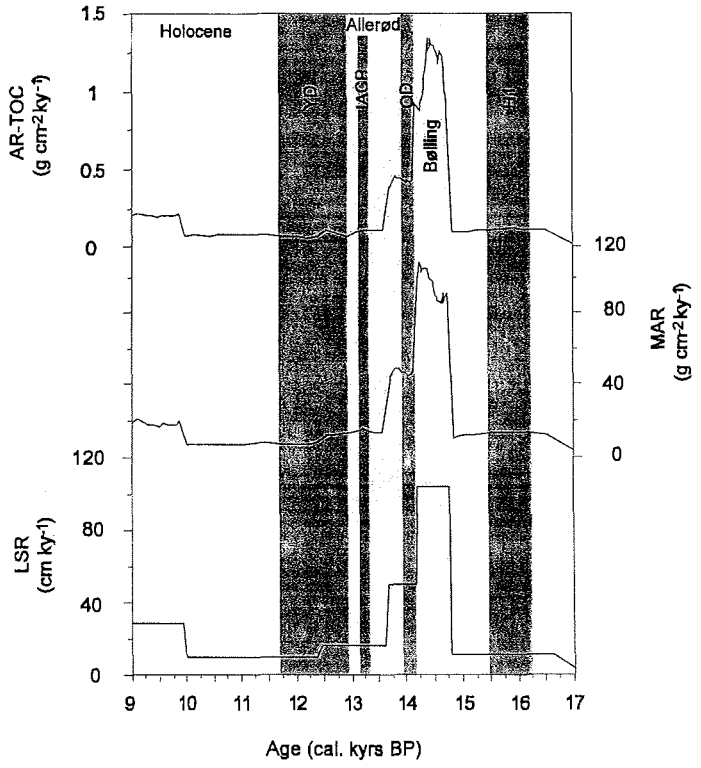

Fig. 4.7. Linear sedimentation rate (cm kyr^{-1}), bulk mass accumulation rate (MAR) (g cm^{-2} kyr^{-1}) and accumulation rates of organic carbon (AR-TOC) (g cm^{-2} kyr^{-1}) versus calendar years. YD= Younger Dryas, IACP= Intra Allerød Cold Period, OD= Older Dryas, H1= phase equivalent to Heinrich 1 peak phase.

These large aggregates were supposed to be protected from degradation and feeding of zooplankton organisms and were exported via current transport as far as to the Yermak slope area (Rutgers van der Loeff et al., 2002 and references therein). When comparing organic carbon accumulation rates of this period with those from the subsequent Bølling (see below), only minor amounts of organic matter were preserved in the Heinrich 1/Oldest Dryas phases in the Nordic Seas (e. g. Bond et al., 1993; Dokken and Hald, 1996; McCabe and Clark, 1998). In the North Atlantic this period is marked by high amounts of IRD, transported with icebergs from the collapsing Laurentide ice sheet (Bond et al., 1992).

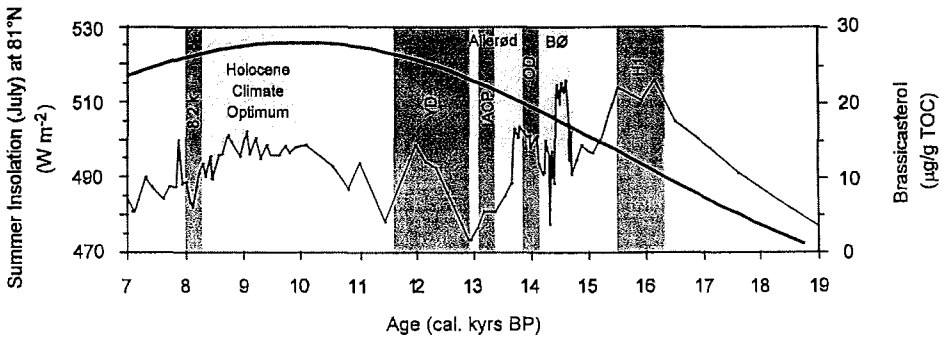

Fig. 4.8. Compilation of brassicasterol (marine phytoplankton marker, especially diatoms) and the summer insolation curve (July) at 81°N (after Laskar, 1990). Maximum insolation occurred from ca. 12,000 to 8,500 years BP. YD= Younger Dryas, IACP= Intra Allerød Cold Period, OD= Older Dryas, BØ= Bølling, H1= phase equivalent to Heinrich 1 peak phase.

Around 15,500 years BP, bottom-currents accelerated again to intermediate values that remained relatively constant until 14,700 years BP, terrigenous long-chain *n*-alkane concentrations were slightly increased at the same time. The deglaciation of the SBIS was in progress since 18,000 years BP as indicated by meltwater peaks and deposition of coarse-grained ice-rafted material (e. g. Elverhøi et al., 1995; Hebbeln et al., 1998). In the Yermak slope area, however, neither a significant increase in bulk accumulation rates nor large meltwater peaks were detected until the onset of the Bølling (Figs. 4.6. and 4.7.).

It is suggested that during peak Heinrich I production of NSDW was either diminished or displaced (or both) resulting in low current speed at the western Yermak slope. However, the accumulation of organic carbon including brassica- and dinosterols was slightly increased and terrigenous organic matter flux was reduced (Fig. 4.6.). Apparently, bioproduction became decoupled from the general climate development, by reacting more to increasing insolation rather than to oceanic and atmospheric climate parameters (Fig. 4.8.).

The first deglacial stage (17,000-14,700 years BP) in northern Europe/Arctic Ocean was triggered by global transgression (Elverhøi et al., 1995; Andersen et al., 1996). The surface temperatures, however, were supposed to be lower than in the succeeding Bølling period (Svendsen et al., 1996). This led to a quick disintegration of the marine-based glaciers from the Barents Sea and Svalbard continental shelf zones (Elverhøi et al., 1995; Andersen et al., 1996). Glaciers were lifted from the shelves by global transgression. Only minor melting and thus no significant IRD deposition occurred close to the Svalbard archipelago (Svendsen et al., 1996). The sea-ice and icebergs were transported northward via strong slope currents and carried away the IRD-bearing icebergs, instantly (Andersen et al., 1996; Dowdeswell and Elverhøi, 2002). On their way north, sea-ice and icebergs released their coarse-grained load by subsurface melting in relatively warm Atlantic waters. A complex situation of current systems from various directions and additionally heavy ice-drift from northern and southern

directions was suggested. Icebergs may have drifted for longer periods alongside the western fringe of Svalbard. As a summary, figure 4.9. shows the depositional processes in this period, schematically.

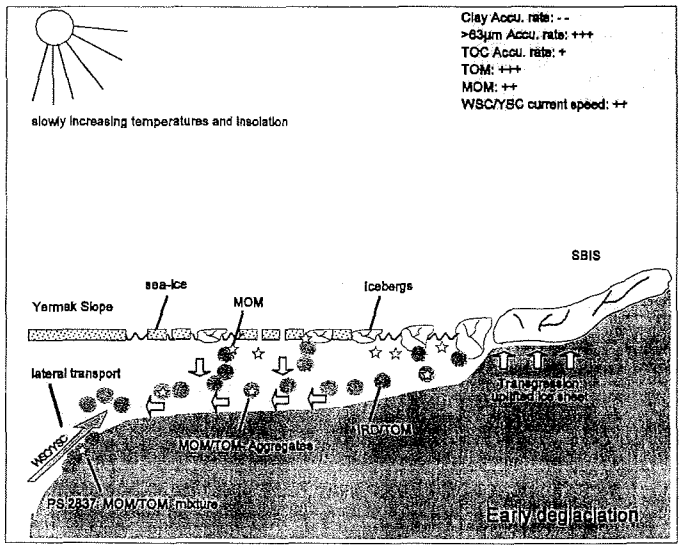

Fig. 4.9. Model showing the environment along the western Svalbard slope and the western Yermak slope during the early deglaciation. Due to slowly increasing temperatures and insolation, productivity of marine organic matter is increasing. Reworked terrigenous organic matter (TOM) was transported as ice-rafted detritus (IRD) with icebergs from Svalbard. Aggregates of marine organic matter (MOM) and TOM were transported downslope and northwards via the WSC/YSC

4.6.2. The Bølling-Allerød interstadial (14,700-12,650 years BP)

The Bølling-Allerød interstadial at high latitudes is characterised by large-scale disintegration of the SBIS. Björck et al. (1998) proposed the subdivision of the Bølling-Allerød (GI-1) into several episodes from the oldest Bølling at 14,700 years BP (GI-1e) to the youngest episode, the final Allerød warm period (GI-1a) ending at ca. 12,650 years BP. Within the Bølling-Allerød, at least two colder periods were identified, the Older Dryas (GI-1d) and the Intra Allerød Cold Period (IACP) or GI-1b.

After the first, marine-based disintegration of shelf glaciers and initial warming in the Pre-Bølling (GS-2a) (Austin and Kroon, 2001; Hendy et al., 2002), significant warming of surface air temperatures in middle and northern Europe occurred from 14,700 years BP (Renssen and Isarin, 2001). The major deglaciation of Svalbard ice-sheets in fjords and on the archipelago started synchronously (Svendsen et al., 1996; Landvik et al., 1998). The continental shelves of Svalbard were ice-free from ca. 15,000 years BP (Mangerud et al., 1998). In marine sediment cores from the northern Fram Strait, maximum TOC concentrations were found in the Bølling-Allerød interstadial of the Fram Strait (Events III/IV; Birgel and Stein, in press, see also chapter 3). At the western

Yermak slope, high marine phytoplankton biomarker concentrations (brassica- and dinosterols, $C_{16:1(n-7)}$, Fig. 4.4.) accompanied increased bulk accumulation rates (90-110 g cm^{-2} ky^{-1} during the Bølling; 50 g cm^{-2} ky^{-1} during the Allerød; Fig. 4.7.). The amount of coarse-grained particles was close to zero in the warmer Bølling and about 5% in the Allerød. It is suggested that meltwater plumes carried large amounts of fine-grained terrigenous anorganic detritus as well as terrigenous organic matter (high C_{org}/N ratios, low hydrogen indices; Fig. 4.3.; Elverhøi et al., 1995; Svendsen et al., 1996; Dowdeswell and Elverhøi, 2002). The material released from decaying glaciers was transported by the WSC to northern Fram Strait (Andersen et al., 1996). Maximum bulk and organic matter accumulation rates were obtained on the Yermak Slope from deglacial meltwater plumes. High amounts of marine biomarkers were deposited in the form of large aggregates of marine and terrigenous organic matter (see above). Apparently, this occurred coeval to drastic changes in the circulation of intermediate waters that most likely mirrored thermohaline processes in the Nordic Seas. When compared to the GISP 2 ice core (e. g. Grootes et al., 1993, Fig. 4.6.) it becomes evident, that the YSC dramatically accelerated exactly at the beginning of the initial Bølling warming. This can be explained with the likewise rapid onset of thermohaline activity in the Nordic Seas (Rahmstorf, 1995). Strong meltwater discharge into the convection areas may then have caused a very short-term flickering between the on and off modes of deep-water production resulting in a collapse of the bottom currents at the core location (see Marchitto et al., 1998; Austin and Kroon, 2001). This collapse led to the deposition of large amounts of fine-grained material out of the above mentioned suspension-laden plumes that were released from the decaying ice shields and newly opened fjords in western Svalbard. However, after a short period of time, probably shorter than 50 years, bottom currents recovered again reflecting the reorganisation of the thermohaline circulation system further south.

The availability of light may have been slightly reduced at times of increased suspension load in the upper water column. Nevertheless, an effective export of biomarkers from the water column via fine-grained aggregates of primary produced organic matter (especially diatoms) enabled an increased deposition of marine phytoplankton biomarkers in the sediments (see Ittekkot et al., 1992; Andreassen et al., 1996). In the Bølling, the marine biomarker flux (especially brassicasterol) was clearly enhanced whereas terrigenous biomarkers (long-chain *n*-alkanes) and marine zooplankton ($C_{18:1\ (n-7)}$ fatty acids) show decreasing values (Fig. 4.4.). The increasing accumulation of fine material is suggesting a relation between the granulometric composition of the sediments and certain biomarkers. Probably, terrigenous biomarkers are preferably attached to coarser particles transported via sea-ice and icebergs, whereas marine biomarkers are preferably connected to fine grain-sizes. The export of fine grained sediment particles and marine organic matter from the high productive marginal ice zones to locations under permanently sea-ice via strong currents was described from surface sediments in the Yermak slope (Soltwedel et al., 2000; Rutgers van der Loeff et al., 2002). Marine organic compounds can be protected by building aggregates of terrigenous and/or lithogenic fine sediments (Rutgers van der Loeff et al, 2002 and references therein). A resuspension-loop of suspended matter in the modern YSC-area was identified (Rutgers van der Loeff et al., 2002). Transport distances of more than 200 kilometres were

proposed, verified by ^{234}Th-measurements in the bottom water layer and in surface sediments. Maximum accumulation rates in the Bølling-Allerød time-slice were indicating an effective transport of suspended material via the WSC/YSC (Fig. 4.7.).

After the sudden breakdown of the YSC at the beginning of the Bølling (most likely linked to fluctuations in deep-water formation in the Greenland Sea), conditions recovered again and current speed increased asymptotically until 12,700 years BP. This likely mirrors the waning influence of meltwater on the thermohaline circulation system. After a short-term period Atlantic surface waters were transporting heat into Fram Strait again. Within this interstadial period, short-term climate deterioration occurred. Accompanied by sea-ice formation, glaciers on Svalbard re-advanced to the western shelf regions during the Older Dryas episode (Svendsen et al., 1996; Landvik et al., 1998). The Older Dryas cold period was marked by strong fluctuations of biomarker concentrations in sediments, suggesting unsuitable conditions in eastern Fram Strait at this time (Fig. 4.4.). Surface temperatures were supposed to be lower than in the Bølling, but obviously remained warm enough to provide enough moisture for glacier growth. At the core position bulk accumulation rates were reduced by more than half (45 g cm^{-2} ky^{-1}) when compared to the Bølling episode. This short-time re-appearance of colder conditions lasted no longer than 200-300 years. During this period, the sand fraction reached values as high as 20 % at ca. 14,300 years BP, marking a period of increased shelf erosion, calving and ice-rafting. In contrast, earlier deglaciation phases were characterised by glaciers that were lifted from the ground due to the rising sea level and thus had less erosive impact on the shelves. The input of long-chain *n*-alkanes reached values as high as in the early deglaciation indicating a stronger sea-ice distribution in the Fram Strait. However, marine biomarkers showed slightly decreased values in this section indicating lower productivity in combination with reduced aggregation processes and preservation of marine organic matter in the sediments.

After the short-time climate amelioration that followed the Older Dryas, a new deterioration phase occurred with slightly lower accumulation rates than in the Older Dryas (Fig. 4.7.). Ice-core data suggest, that the Allerød was more consistent than the Bølling (Fig. 4.6.) but with colder climatic conditions (Renssen and Isarin, 2001). Svalbard fjords were supposed to be ice-free from ca. 13,900 years BP (Svendsen and Mangerud, 1992; Elverhøi et al., 1995), accordingly bulk accumulation rates at the core location dropped to 10-15 g cm^{-2} ky^{-1}. This indicates a reduced flux of deglacial debris and suspension load from the adjacent continents and shelves. At ca. 13,700 years BP, the deposition of marine biomarkers (sterols and marine phytoplankton fatty acids) in sediments abruptly decreased (Fig. 4.6.). Bottom currents suggest continuous climate amelioration until a minor maximum in current speed around 13,700 years BP. At that time the trend reversed and bottom currents slowed down again until minimum at 13,200 years BP suggesting a reduction in thermohaline overturn in the NSDW source areas during the IACP. The GISP 2 record suggests warmer temperatures until 13,500 years BP followed by decreasing temperatures until 13,200 years BP marking the IACP (Fig. 4.5.). Whether oceanic processes preceded atmospheric processes by a century or more or whether this is due to dating uncertainties has yet to be investigated.

The IACP is a short-time, but very drastic cooling event that was described from various places on the northern hemisphere (e. g. Broecker et al., 1988; Lehman and Keigwin, 1992; Levesque et al., 1993; Hendy et al., 2002) as a precursor of the YD cold period. It started 13,200 years BP and lasted for about 200 years. The decrease of organic carbon concentrations was significantly stronger than in the previous cold episode (Older Dryas). It is suggested that conditions for marine phytoplankton at that time were far more unsuitable than earlier in the deglacial and also later during the YD cold phase (Fig. 4.6.). There is no other period of time between 18,000 and 10,000 years BP, in which the TOC record was more or less parallel with the insolation curve, that would have caused a more significant punctuation in the marine planktic life than the IACP (Fig. 4.8.). Between 13,500 and 12,800 years BP the planktic foraminifer record is barren (Nørgaard-Pedersen et al., in press) and TOC and biomarkers dropped significantly whereas the sortable silt record suggests only a minor (but prominent) fluctuation in bottom current speed.

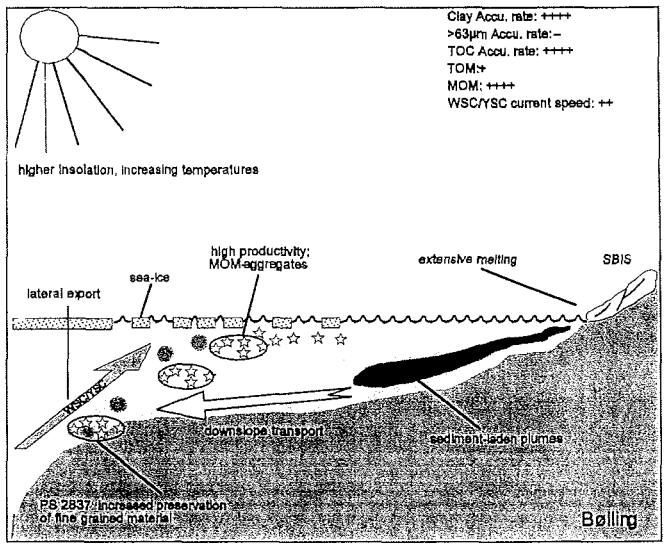

Fig. 4.10. Model showing the environment along the western Svalbard slope and the western Yermak slope during the Bølling. Enormous amounts of suspended organic and inorganic matter were released from the disintegrating SBIS. Due to enhanced living conditions in the euphotic zone, large aggregates were supposed to be transported quickly through the water column. An effective lateral export via the WSC/YSC enabled a transport of organic matter aggregates from high productivity zones to the Yermak slope zone.

Presumably, climatic/surface-ocean conditions were unstable at a level that became a serious ecological problem for the marine phytoplankton that itself was in an unstable state, while coping with rapidly changing conditions ever since the deglaciation began a couple of millennia before (Lehman and Keigwin, 1992; Klitgaard-Kristensen et al., 1998). Since then, no significantly increased

IRD signals were obtained in our core. Therefore, it is likely that the short cold snap of the IACP adversely altered the frame conditions that finally caused an ecological collapse. This assumption is supported by minimum marine biomarker concentrations as well as by minimum benthic foraminifer numbers and the absence of planktic foraminifers in the sediments (Nørgaard-Pedersen et al., in press; Wollenburg et al., submitted). In addition, carbonate contents were at a minimum in the IACP, suggesting strong dissolution in this period as well (Fig. 4.3.). In how far a meltwater peak that occurred at the end of this period (Nørgaard-Pedersen et al., in press), interacted with the described processes has yet to be investigated. As a summary, the following figure shows the depositional processes in this period, schematically (Fig. 4.10.).

4.6.3. The Younger Dryas stadial: a different cold phase in the Fram Strait

From the GRIP and GISP 2 ice-cores and sediment cores, the onset of the YD stadial (GS 1) was at ca. 12,600 years BP (Dansgaard et al., 1993; Grootes et al., 1993; Meese et al., 1997; Björck et al., 1998; Cacho et al., 2001). The YD was the main topic of many investigations in the last decade (e. g. Mayewski et al., 1993; Goslar et al., 1999; Renssen et al., 2001). It was characterised as an event with very cold temperatures and a strong re-advance of glaciers in Europe and North America. Yet, warmer conditions have been recorded in the central tropical Atlantic Ocean (Rühlemann et al., 1999). In the southern hemisphere, the Antarctic Cold Reversal (ACR) reveals a short-term warming during the YD (Jouzel et al., 1995).

In the core from the Yermak Plateau it is obvious, that during the YD the bottom-current record (mirrors thermohaline processes in the Nordic Seas) and the biomarker record (mirrors surface ocean conditions) were decoupled (Fig. 4.6.). As described in the section above, the bottom-currents reacted as expected with significantly reduced current speed most likely as a result of a rapid and strong reduction of deep-water renewal in the Greenland Sea. The TOC record and marine phytoplankton markers (sterols and fatty acids), however, recovered from the minimum values of the IACP without any reaction to the YD cold period. The long-chain *n*-alkanes were slowly decreasing from ca. 14,000 years BP. TOC and especially marine biomarkers increased steadily across the YD section to reach a first maximum at the end of the YD and a second maximum during the early Holocene insolation maximum (Fig. 4.8.). It can be inferred that harsh climate conditions had a tremendous impact on the northern hemisphere with the "central heating" in the North Atlantic and the Nordic Seas being virtually in or close to the off-position (e.g. Manabe and Stouffer, 1995; 1997; Stocker and Wright, 1996; Stocker, 1999), however, living conditions for marine phytoplankton in the Fram Strait/Yermak Plateau area were suitable enough to promote primary productivity in the Fram Strait. At least biomarker data showed comparable concentrations in the following warm Pre-Boreal time-period beginning at ca. 11,000 years. There must have been open water periods during the summer seasons that allowed marine phytoplankton (e.g. diatoms, dinoflagellates) to grow and take advantage of the intense insolation during the YD (Fig. 4.8.).

At the beginning of the YD the IRD record showed a small maximum indicating that either IRD carrying icebergs and sea-ice floes were at today's frequency

(likely), were stuck or blocked further north (those that came with the Transpolar Drift), or took other pathways (unlikely). If there were sources that released more IRD-laden ice than today along Svalbard's west coast during the YD it must have been routed to the east between the Yermak Plateau and northern Svalbard which would require a surface circulation like today.

At least in the northern hemisphere (northern Norway) a drastic decrease of surface air temperatures and a re-advance of glaciers or stagnation of deglaciation were found during the YD (e. g. Renssen and Isarin, 2001; Bondevik and Mangerud, 2002). In the eastern Fram Strait and on western Svalbard, however, glaciers disappeared from the shelves since the end of the Allerød at the latest and did not re-advance during the YD period (Mangerud and Svendsen, 1990; Svendsen and Mangerud, 1992; Svendsen et al., 1996). End moraines from the Little Ice Age cold period were found inside Svalbard fjords, but no re-advance and end moraines from the YD period could be detected (Mangerud and Svendsen, 1990; Svendsen and Mangerud, 1992). Thus, at least from Svalbard no exceptional export of IRD-laden ice during the YD would be expected which at least partly explains the lack of significant IRD accumulation at the western Yermak Plateau. Instead, high TOC and marine biomarker concentrations occur during the YD, although cold and glacial-like conditions were to prevail on the northern hemisphere. We suggest, that climatic conditions in the YD differed decidedly from LGM as well as from Holocene conditions. Summer insolation in the YD was at maximum values (10-11 % higher than today), whereas modern insolation is only about 2 % higher than during the LGM (Mangerud and Svendsen, 1990 and references therein). Mangerud & Svendsen (1990) postulated clear summer days and maximum evaporation in times of maximum insolation of the YD period (Fig. 4.8.). At least in western Svalbard evaporation must have been stronger than precipitation; otherwise glaciers would have re-advanced. Based on terrestrial evidence, Svendsen and Mangerud (1992) suggest that western Svalbard glaciers were already at their modern positions during the YD. It is thus suggested that the prevailing wind direction must have been East, leaving western Svalbard in lee-position of the Polar easterlies as a result of the YD south-shift of the climate zones and related wind belts. Colder sea surface temperatures (SSTs) in the Nordic Seas due to reduced inflow of temperate Atlantic waters (e.g. Mangerud, 1987) would have amplified this process that also lead to the south displacement of the northern hemisphere storm tracks (cf. Hass, 1997). The prevailing easterlies in the Svalbard area would have lead to ascending relatively humid air masses causing increased precipitation and thus glacier growth on eastern Svalbard (Landvik et al., 1998). "Föhn"-like dryer and warmer air masses eventually descended down the west side of Svalbard and inhibited significant glacier growth there. A further effect of Svalbard and the Fram Strait/Yermak Plateau area under the prevailing influence of easterlies would have been that the western Fram Strait and adjacent areas provided open surface waters and newly formed ice would have been transported west.

Along the norwegian coastline, open water conditions were suggested based on phytoplankton data (diatoms) (Koç et al., 1993). Hence a very weak but constant Atlantic water influx may have also been present in the Fram Strait area throughout the YD, which would explain the relative stability of ecological conditions of those organisms that are responsible for the various marine

phytoplankton biomarkers and TOC records in our core. Increased primary production at sea-ice margins during the summer months, coupled with effective aggregation and export of marine phytoplankton without terrigenous compounds was described from investigations of recent sediment trap data (Andreassen et al., 1996; Hebbeln, 2000; Owrid et al., 2000). Additionally, this suggestion was validated from biomarker data of surface sediments in the northern Fram Strait (Birgel et al., submitted, see chapter 2). In periods of higher insolation, reduced cloudiness might have been an additional factor controlling humidity, precipitation and evaporation (Svensmark and Friis-Christensen, 1997).

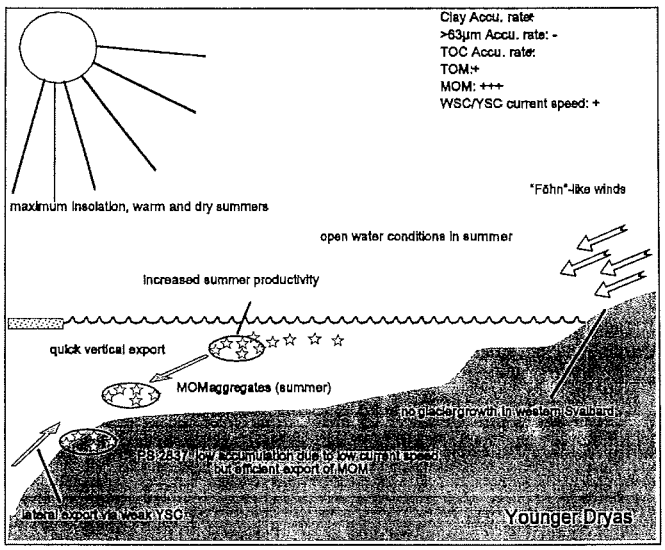

Fig. 4.11. Model showing the environment along the western Svalbard slope and the western Yermak slope during the Younger Dryas. The western Fram Strait was supposed to be ice-free at least during summer. Föhn-like winds from east opened the western Fram Strait and enabled a short, but high productivity and an increased export to the seafloor.

Glaciers were likely not able to accumulate snow under dry and warm summer conditions. Thus, cold but dry conditions in the YD period with extreme winter temperatures were suggested for Europe (Renssen and Isarin, 2001). Warm summer temperatures and slightly increased productivity triggered by maximum insolation has been postulated for the YD along the norwegian coastline (Koç et al., 1993). Large temperature anomalies exceeding a drop of temperatures up to 20°C were modelled for the YD (Schiller et al., 1997; Fawcett, et al., 1997; Renssen and Isarin, 2001), whereas in summer only minor anomalies occurred. These warm conditions were amplified by local weather conditions, such as dry lee conditions with "Föhn"-like effects as suggested from southern Greenland lake sediments (Björck et al., 2002). As a summary, figure 4.11. shows the depositional processes in this period, schematically

4.7. Summary and Conclusion

- In the early deglaciation (17,000-13,000 years BP), marine and terrigenous biomarker fluctuations were reacting coeval with thermohaline and atmospheric changes and can be correlated with other sediment and ice-core records from the North Atlantic/Arctic Ocean.
- Highest concentrations of marine phytoplankton biomarkers in sediments were described in warming periods (Bølling, Allerød). Improved living conditions in open water areas in the eastern Fram Strait were suggested in such episodes. Additionally, an effective lateral and vertical transport via aggregations from highly suspended meltwater plumes from the disintegrating SBIS to the seafloor and to permanently ice-covered positions was observed. Elevated accumulation rates of marine organic matter were found coeval to the major warming and disintegration periods.
- The Intra Allerød Cold Period was marked by a short-term but drastic deterioration of living conditions in the upper water column. Minimum concentrations of marine phytoplankton biomarkers were described under severe living conditions.
- In the YD period, a decoupling of thermohaline circulation and atmospheric/surface water signals occurred. Due to maximum insolation values, living conditions and primary productivity of marine phytoplankton were improved, although a weakened thermohaline circulation was suggested in this period. Dryer and warmer summer conditions comparable with Holocene conditions with "Föhn"-like winds enabled at least in summer open water conditions and higher productivity than reported from other regions in northern Europe.
- Bottom-currents along the Yermak Plateau are closely linked to thermohaline processes in the Nordic Seas providing a highly sensitive recorder of climate change.

It turns out that the deep-currents mirror processes that are supra-regionally linked to large-scale processes relevant to climate development. Despite the core location is only at 1042 m water depth, the bottom-currents do not appear to be affected by local processes. In contrast, processes in the atmosphere and in surface waters reflecting the local palaeoenvironmental conditions primarily affect the biomarker record. These conditions obviously differ from large-scale climate developments during particular phases of the last deglaciation, especially in the YD. The organic-geochemical and sedimentological records from the Yermak Plateau provide new insights in palaeoenvironmental processes including characteristic regional variations.

5. Summary and Outlook

Surface sediments (representing the modern distribution) as well as long sediment cores (representing the last glacial/deglacial cycle) were investigated for composition and flux of organic carbon in the northern Fram Strait/Yermak Plateau. First of all the concentrations of total organic carbon (TOC) have been examined. With organic-geochemical bulk parameters such as C_{org}/N-ratios, hydrogen indices and stable carbon isotopes a preliminary classification of organic carbon was presented in several transects over Fram Strait. The western part of the Fram Strait is characterised by a predominant input and preservation of terrigenous organic matter, whereas the eastern part of the Fram Strait shows higher TOC amounts as well as higher contributions of marine-derived organic matter in sediments. The subdivision is explained by varying sea-ice conditions and primary production rates by opposing currents: the cold, low-productive EGC in the western Fram Strait and the warm, high-productive WSC/YSC in the eastern Fram Strait, strongly influencing the production and preservation of organic carbon in sediments. In the permanently ice-covered western Yermak slope (80°N-82°N) in 1000-1500 m water depth we found increased TOC values (1.2-1.6 wt. %) in surface sediments. A major contribution of terrigenous organic matter was supposed to be found in these sediments, proposed from previous studies in this area. However, based on bulk organic carbon proxies and stable carbon isotopes it was found that 50 % of the organic matter was of marine origin. The distribution of marine/terrigenous organic matter was not only calculated from sediments close to the marginal ice zone (MIZ), but also in the western Yermak slope area under permanently sea-ice. To reassure the high amounts of marine organic matter in surface sediments, a subsequent examination of extractable organic matter was conducted. Highest concentrations of biomarkers were found in the vicinity of the MIZ and in Yermak slope sediments with a predominant contribution of fatty acids (> 75 % of total biomarker lipids). The concentrations of terrestrial-derived material were relatively constant in the investigated area compared with marine-derived material. Maximum concentrations of terrestrial-derived organic matter were determined in permanently ice-covered regions, whereas in open water zones and the MIZ marine-derived compounds were superimposing the terrestrial-derived input. Following the YSC towards north (up to 250 km) we obtained monotonically decreasing marine-derived biomarker concentrations, but even in the northernmost station of the YSC area values were exceeding those from neighbouring stations on the Yermak Plateau, although a permanently ice-coverage was observed in this region. An increased productivity can be excluded under severe sea-ice conditions. Normally, at the MIZ vertical export of organic compounds is provided via large aggregates of fresh marine organic matter, fecal pellets and/or aggregates of lithogenic and organic material from the euphotic zone to the bottom. In the western Yermak slope, however, a strong suspension-resuspension-loop and lateral transport of particulate matter via Atlantic waters is proposed in intermediate water depths, suggesting an effective lateral advection of particulate matter over hundreds of kilometres.

When comparing TOC and biomarker distributions in surface sediments with TOC records and accumulation rates from the last 11,000 years, we found similar TOC distributions for recent and Holocene sediments. The majority of

organic carbon deposited in the Fram Strait (65%) was accumulated in the Yermak slope area, representing only 20 % of the total area of investigation. Although permanently ice-covered conditions were suggested in the Yermak slope area for the last 11,000 years, oceanographic and depositional conditions were supposed to be stable throughout the Holocene from bulk and TOC accumulation rates. On the Yermak Plateau, lateral advection seemed to be irrelevant for organic carbon accumulation today as well as in the last 11,000 years, indicated by low accumulation rates throughout the Holocene. In the deglacial period, accumulation rates were even exceeding Holocene values, caused by additional supply of particulate matter from the disintegrating Svalbard-Barents-Sea Ice Sheet (SBIS). The maximum input of particulate and organic matter was observed in the Bølling episode, when major TOC-events with suspended particulate matter transport and TOC preservation were found in several sediment cores of the Fram Strait. In the glacial, however, lowest accumulation rates were supposed, because large parts of the ocean and continents were ice-covered. Productivity values and accumulation rates of organic matter decreased in this period.

In addition to the investigation of organic carbon budgets and accumulation rates, TOC-records in the eastern Fram Strait were correlated. At least in the glacial and deglacial, definite correlations of peak TOC values were found for five different time periods (Events I-V), coinciding with warmer climate periods (e. g. Bølling warming) and/or deglacial periods. It is noticeable, that all these events are characterised additionally by increased contributions of marine organic matter (dinosterol, brassicasterol, $C_{16:1n-7}$), indicating improved living conditions and preservation in these periods.

The terrestrial record from the Svalbard archipelago is in good agreement with the TOC and biomarker record from marine sediment cores. On the basis of TOC values. palaeoenvironmental studies can be accomplished very well, provided by a sufficient temporal resolution of the chosen sediment cores. However, it is necessary to add organic-geochemical lipids to identify whether the organic matter is of a terrigenous or marine origin. To reassure the significance of organic-geochemical parameters, a coupled sedimentological and organic-geochemical study was conducted, secured by stable oxygen isotopes from a Greenland ice-core. Investigations in two zones of the water column (bottom water: sedimentology, surface water: organic geochemistry) were addressed to the deglacial and warming history of the northern Fram Strait and the Svalbard archipelago. The results of this coupled study could be correlated with results from the thermohaline circulation as well as from the record of the GISP2 Ice Core. However, with the beginning of the Younger Dryas period the organic-geochemical parameters are decoupled from the thermohaline circulation and ice-core records. A regionally steered variation of surface water productivity in the vicinity of Svalbard, paralleled by postulated ice-free conditions in the eastern Fram Strait and minimum extension of western Svalbard glaciers suggests, that warm and dry summers and cold and dry winters appeared. The eastern Fram Strait was opened through "Föhn"-like winds blowing from an eastern direction over Svalbard. Probably, this might have been a regional characteristic of the Svalbard archipelago.

The results clearly reveal the impact of climate-induced environmental changes on the biomarker record. Yet, little information exists about the origin of biomarkers in other regions of the Arctic Ocean and its surrounding seas. In this study, a classification of biomarker groups was proposed by means of literature data and stable carbon isotope measurements of specific biomarkers. This must be proofed for other regions of the Arctic Ocean to reassure if the classification presented here is applicable for other areas of the Arctic Ocean or not. In addition, measurements of stable carbon isotopes should be expanded to sediment cores to verify if the origin of specific biomarkers is constant over a longer time period or if the source of distinct compounds might have changed. Another important topic for future research should be the investigation of degradation processes of specific biomarkers in sediments in combination with investigations of nutrients, benthic activity, grain-size analysis, microfossil degradation, oxygen degradation etc.. It is crucial to conduct further detailed studies of degradation processes in sediments to qualify or disqualify the use of specific biomarkers as palaeoenvironmental markers. Nevertheless, the potential of organic-geochemical parameters as palaeoceanographical proxies even in low productivity ice-covered areas was stressed by the first detailed classification of biomarkers in the Arctic Ocean conducted in this study.

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