Organic carbon in Late Quaternary sediments: Responses to paleoenvironmental changes in the Laptev and Kara seas (Arctic Ocean)

Organisches Material in spätquartären Sedimenten: Rekonstruktion der Paläoumweltbedingungen in der Laptev- und Karasee (Arktischer Ozean)

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# Danksagung

# Abstract

Surface sediments and selected sedimentary records recovered from the Kara and Laptev seas and the adjacent continental margin were studied using organic petrography (maceral analysis) and organic-geochemical analysis. The overall goal of this study was to reconstruct the modern depositional conditions and the development of the paleoenvironment during the last ~15.0 ka, as documented in the organic matter (OM) composition of these sediments. This study shows that the exclusively use of organic-geochemical parameters (bulk parameters, specific biomarkers) in the Eurasian shelf sediments may reveal contradictory information about the composition of OM. The mixture of terrestrial, freshwater and marine organic matter often cannot be distinguished unequivocally without microscopical examinations, like organic petrography or palynology. Additionally, maceral analysis permits estimates of the different particulate organic matter (POM) portions of sediments.

In the studied surface sediments the OM is dominated by terrigenous macerals (Ø 70%). Moreover, the occurrence of freshwater alginite in the sediments off the river mouths is used as indicator for river discharge into the marine systems of the Kara and Laptev seas. Increased marine organic matter (MOM) portions of 20-40 % at the Laptev Sea continental slope and north of the estuaries of the Ob and Yenisei rivers in the Kara Sea reflect primary productivity in the water-column and are explained by temporary open-water conditions and an adequate fluvial nutrient supply.

The temporal and spatial variations in the organic carbon composition of the studied geological records reflect paleoclimatic and paleoceanographic changes during the Last Glacial and the Holocene. At the end of the Last Glacial the north-western part of the Kara Sea was influenced by the Svalbard-Barents-Sea-ice-sheet as documented by diamictons in the St. Anna Trough. The POM in these diamictons is dominated by resistant reworked macerals and coal fragments. In comparison the Laptev Sea shelf is supposed to be fallen dry during the glacial sea-level low stand and it was not ice-sheet covered. Rivers draining the Laptev

Sea and the Siberian hinterland even during the Last Glacial, but in reduced supply compared with Holocene times.

During deglaciation of the St. Anna Trough since ~13.3 ka MOM deposition is related to increased primary productivity triggered by the influence of Atlantic water masses. Furthermore, the occurrence of freshwater alginites indicate active draining rivers. In comparison to the Kara Sea where the inflow of Atlantic water masses is reported prior to deglaciation time, evidence for Atlantic water masses reaching the eastern Laptev Sea continental slope is given at 10.4 ka, as indicated by increased MOM portions and specific dinoflagellate cysts which are adapted to warmer water masses.

In the early Holocene the shelves were affected by drastic environmental changes. The post-glacial sea-level rise resulted in transgression of the shelves. Moreover, increased precipitation, melting of local glaciers in the Siberian hinterland and defrosting of the permafrost soils lead to an enlarged freshwater supply. This is reflected in an increase of freshwater alginites and deposition of immature land plant material. The increased erosion of the shelf sediments caused by the transgression and the increased fluvial sediment supply result in exceptional high sedimentation rates of 1000 cm/ky on the shelf and accumulation rates of organic carbon up to 12,0 gC/cm<sup>2</sup>/ky. With the rising sea-level marine conditions became established at the Laptev Sea continental margin as documented in an increased deposition of MOM since 9.5-8.0 ka. In the studied cores of the St. Anna Trough the fluvial signal in the Holocene is rather low in comparison to the cores from the Laptev Sea.

### Kurzfassung

Ausgewählte Oberflächensedimente und Sedimentkerne aus der Kara- und Laptevsee und dem angrenzenden Kontinentalhang wurden auf ihre organische Kohlenstoffzusammensetzung mittels organischer Petrographie (Mazeralanalyse) und organisch-geochemischer Analysen untersucht. In den Sedimenten sind die rezenten Ablagerungsbedingungen sowie die Entwicklungsgeschichte des Ablagerungsraumes während der letzten 15 000 Jahre dokumentiert. Die Studie zeigt, daß die alleinige Anwendung organisch-geochemischer Verfahren für die Charakterisierung organischen Materials in den Sedimenten der Eurasischen Schelfgebiete häufig erschwert und nicht immer eindeutig ist. Da sich das organische Material aus einer Mischung sowohl von terrestrischen und marinen Komponenten als auch Süßwassermaterial zusammensetzt, müssen mikroskopische Untersuchungen, wie z.B. die Mazeralanalyse oder die Palynologie, zur Unterscheidung herangezogen werden. Darüber hinaus können mit der Mazeralanalyse die verschiedenen Anteile des partikulären organischen Materials in den Sedimenten abgeschätzt werden.

Die Zusammensetzung der organischen Substanz in den Oberflächensedimenten ist durch einen überwiegenden Anteil an terrestrischen Mazeralen gekennzeichnet (Ø 70%). Darüber hinaus können Süßwasseralginite in den Sedimenten im Flußmündungsbereich als Anzeiger für den Flußwassereintrag in das marine System der Kara- und Laptevsee genutzt werden. Die beobachteten erhöhten Anteile an mariner organischer Substanz (20-40%) am Laptevsee-Kontinentalhang und nördlich der Ästuare in der Karasee werden auf eine erhöhte Primärproduktion in der Wassersäule zurückgeführt. Die erhöhte Primärproduktion wird durch die Zufuhr von Nährstoffen über die entwässernden Flüsse und saisonal eisfreie Bedingungen erklärt. Anhand der zeitlichen und räumlichen Variationen in der Zusammensetzung des organischen Materials in den untersuchten Sedimentkernen können Aussagen über die paläoklimatischen und paläoozeanographischen Veränderungen während des Zeitraumes vom letzten Glazial bis ins Holozän getroffen werden. Während des letzten Glazials stand der nordwestliche Teil der Karasee unter Einfluß des Barentssee-Eisschildes, welches

in der Verbreitung von Diamiktablagerungen im St. Anna Trog dokumentiert ist. Das partikuläre organische Material in den Diamikten wird durch resistentes, umgelagertes Material und Kohlebruchstücke charakterisiert. Dagegen wird davon ausgegangen, daß der Laptevsee-Schelf während des letzten Glazial aufgrund des erniedrigten Meeresspiegels trockengefallen und nicht von einem Eisschild überdeckt war. In der Laptevsee gibt es Hinweise für aktive Flußsysteme während des letzten Glazials, wenn auch, im Vergleich zum Holozän, in reduziertem Ausmaß.

Nach dem Rückzug des Barentssee-Eisschildes vor etwa 13 300 Jahren kam es verstärkt zur Ablagerung marinen organischen Materials, welches als Signal für eine erhöhte Primärproduktion interpretiert wird und auf einen verstärkten Einfluß atlantischer Wassermassen zurückgeführt werden kann. Süßwasseralgen in den post-glazialen Sedimenten deuten auf aktive Flußsysteme in der Karasee hin. Im Gegensatz zur Karasee, für die von verschiedenen Autoren während des letzten Glazials ein Einfluß atlantischer Wassermassen angenommen wird, lassen sich am östlichen Laptevsee-Kontinentalhang erst vor 10 400 Jahren Hinweise für einströmendes Atlantikwasser finden. Dies wird durch eine erhöhte Ablagerung von marinem organischem Material und bestimmten, an warme Wassermassen adaptierten, Dinoflagellatenzysten dokumentiert.

Im frühen Holozän unterliegt das Gebiet des Laptevsee-Schelfes drastischen Veränderungen der Umweltbedingungen. Zum einen kommt es zur Transgression des Schelfes aufgrund des postglazialen Meeresspiegelanstieges, zum anderen werden enorme Mengen an Süßwasser freigesetzt. Dies wird durch den erhöhten Eintrag von Süßwasseralginiten und "frischem" Landpflanzenmaterial angezeigt. Als Quellen für das Süßwasser werden erhöhte Niederschlagsmengen im Holozän, das Abschmelzen lokaler Gletscher im sibirischen Hinterland und das Auftauen der Permafrostböden diskutiert. Die Transgression, welche zur großräumigen Erosion der Schelfsedimente führt und ein erhöhter fluviatiler Eintrag terrestrischer Sedimente hat außergewöhnlich hohe Sedimentationsraten (1000 cm/1000 Jahre) und dadurch hohe Akkumulationsraten von organischem Kohlenstoff (12,0 gC/cm²/1000 Jahre) auf dem Schelf zur Folge.

Die Einstellung mariner Bedingungen mit dem Anstieg des Meeresspiegels am Laptevsee-Kontinentalhang vor etwa 9 500 bis 8 000 Jahren ist durch eine höhere Akkumulation mariner Komponenten dokumentiert. Die Untersuchungen an den Kernen aus dem St.Anna Trog zeigen einen weniger starken Einfluß der Flüsse auf das marine System der nördlichen Karasee. Dagegen zeigen relativ hohe Anteile marinen organischen Materials den Einfluß atlantischer Wassermassen an.

V

## 1. Introduction and objectives of this study

The Siberian shelf seas play an important role for the hydrological cycle in the Arctic Ocean. A huge freshwater discharge, sea-ice production and deep-water formation directly influence the thermohaline circulation and, thus, the global climate system (e.g. Aagaard and Carmack 1994; Thiede and Myhre 1996). The Laptev Sea is regarded as the main production area for sea-ice crossing the central Arctic Ocean with the Transpolar drift towards the Fram Strait (Pfirman et al. 1997, and references therein). Variations in sea-ice cover affect the surface albedo, the temperature and salinity structure of the upper water masses and biological processes (e.g., Carmack et al. 1995; Stein et al. 1999, and references therein). The freshwater input by the Siberian rivers is essential for the sustainment of the strong stratification of the near-surface water masses and for sea-ice formation (Aagaard and Carmack 1989). The annually discharge of freshwater to the Arctic Ocean is about 3300 km<sup>3</sup> in total, from this amount 60% are already supplied by the rivers draining into the Laptev and Kara Seas (Gordeev et al. 1996).

During the last years several studies on e.g. sea-ice, water-column and late Quaternary sediments were carried out in the Eastern Arctic Ocean and the Siberian hinterland for a better understanding of the complex environmental conditions and their changes through time (e.g. Kassens et al. 1999, and further references therein). In this study we have focused on surface sediments and sediment records from the Kara and Laptev seas and the adjacent continental margin (Fig.1.1) representing the time interval from the Last Glacial to the Holocene. The primary objective of this study is to understand the controlling mechanisms of organic-carbon accumulation in the Eastern Arctic Ocean, using an organic petrography approach.

The organic-carbon deposition in the complex system of the Eurasian shelf seas is influenced by different factors. A pronounced seasonality of sea-ice coverage, river discharge, primary productivity of marine organic matter, Atlantic-water inflow, and influx of terrigenous, aquatic material are the main factors controlling



Fig.1.1: Study area with core locations and schematically representation of a) the surface water circulation (after Gordienko and Laktionov 1969), b) river discharge, c) the intermediate and bottom circulation pattern (Rudels et al. 1994; Jones et al. 1995), d) submerging Atlantic surface water (after Gordienko and Laktionov 1969) and, e) Arctic bottom water formation (Jones et al. 1995). The dotted line shows the maximum extend of the Late Weichselian Glaciation according to Svendsen et al. (1999), the black line the ice-sheet extend after Kleiber and Niessen (subm.). SZ = Severnaya Zemlya, NZ = Novaya Zemlya, K = Kotelnyy, BS = Barents Sea, KS = Kara Sea, LS = Laptev Sea, ES = East Siberian Sea

d) submerging Atlantic surface water >>

e) Arctic bottom water formation 🔗

a) surface water circulation pattern

b) River discharge 寿

c) intermediate and bottom water circulation pattern

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the supply and sedimentation of organic matter (e.g., Stein et al. 1999). On the shelf the organic material accumulates and/or is further transported by sea-ice and turbidites towards the open central Arctic Ocean (Nürnberg et al. 1994; Lindemann 1998; Stein et al. 1999). The influence of aeolian transport is of minor importance in the study area (e.g. Darby et al. 1989). While the permanent sea-ice cover in the central Arctic Ocean impede higher primary production (Wheeler et al. 1996) increased primary productivity is reported from seasonally ice-free areas, like the Eurasian shelves (Boetius and Damm 1998). The modern environmental conditions are reflected by organic matter and assemblages of microfossils (diatoms, dinoflagellate cysts) preserved in marine surface sediments (Fahl and Stein 1997; Cremer 1999; Djinoridze et al. 1999; Kunz-Pirrung 1999; Polyakova 1999). Therefore, characterization and estimations of the different organic matter types in sediment records allow interpretations of spatial and temporal changes and, moreover, reconstructions of the paleoenvironment.

The exclusively use of organic-geochemical parameters for characterization of the organic carbon composition is hampered in the Eurasian shelf seas (Fahl and Stein 1999). The different organic-matter sources (in terms of freshwater, terrigenous and marine origin) cannot be distinguished unequivocally without a comparison with microscopical data sets derived from organic petrography or palynology. Thus, in this study we concentrate on organic petrography for the following objectives:

- characterization of particulate organic matter in Quaternary marine sediments;
- estimations of the different organic matter portions in terms of terrigenous, marine and freshwater origin;
- interpretations of the maceral distribution in recent sediments for understanding the modern depositional conditions on the Eurasian shelves and the adjacent continental margin;

- reconstruction of the paleoenvironmental conditions at the Eurasian continental margin from Last Glacial to Holocene times; and
- comparison of microscopical data with organic-geochemical parameters and discussion of the problems in identification of organic matter sources.

#### 1.1 Outline of this study

This dissertation comprises recently published or submitted manuscripts dealing with results of studies carried out on late Quaternary sediments from the Laptev and Kara Seas and the adjacent continental margin. In Chapter 2 and 3 results from studies on surface sediments from the Laptev and Kara seas are presented. Chapter 4 and 5 adress to the paleoenvironmental development of the study area during Last Glacial to Holocene times.

In Chapter 2 (Particulate organic matter in surface sediments of the Laptev Sea (Arctic Ocean): Application of maceral analysis as organic-carbon-source indicator. Boucsein and Stein 2000, in: Marine Geology 162, pp. 573-596) the geographical distribution of macerals in surface sediments of the Laptev Sea and the adjacent continental margin is analyzed and discussed. Moreover, the data is compared with organic-geochemical data sets for discussing the problems in characterization of the different organic matter types in marine sediments.

Maceral data give information about the different organic matter sources in terms of terrigenous, freshwater and marine origin and can be related to the different environmental conditions in the Laptev Sea. Although the organic material from the shelf is dominated by terrigenous organic matter increased portions of marine organic matter are recorded at the upper continental slope. This indicates increased surface-water productivity caused by an adequate fluvial nutrient supply and seasonal open-water conditions. The strong fluvial influence is reflected by freshwater alginite occurring north of the river mouths draining into the Laptev Sea.

The interpretation of the modern depositional conditions and the quantitative estimation of the marine and terrigenous proportions of the organic matter in the

surface sediments are the basis for paleoenvironmental reconstructions of sediment records, carried out in the subsequent studies.

Chapter 3 (Quantity and quality of organic carbon in surface sediments of the Ob and Yenisei estuaries and adjacent coastal areas: marine productivity vs. terrigenous input. Boucsein, B., Fahl, K., Siebold, M. and, Stein, R. 1999, in: Reports on Polar Research 300, pp. 116-126) presents results of a combined study of organic petrography and organic-geochemical analyses performed on surface samples taken during the Kara Sea expedition of RV "Akademik Boris Petrov" in 1997. The organic matter in the Kara Sea sediments is mainly of terrigenous origin with increased amounts of marine material in the western part (Ob bay), as indicated by macerals and biomarkers. Furthermore, by means of maceral analysis freshwater alginite was found, indicating the freshwater supply to the Kara Sea by the Ob and Yenisei rivers. Discrepancies between the results from the surface samples and from the surface-water layer gives evidence for the strong seasonality of surface water salinity and influx of terrigenous and freshwater material.

In Chapter 4 (The variability of river discharge and Atlantic-water inflow at the Laptev Sea continental margin during the last ~15,000 years: Implications from maceral and biomarker records. Boucsein, B., Fahl, K. and Stein, R., Int. Journal of Earth Science, in press) organic petrological characteristics of two sediment cores from the eastern Laptev Sea are presented and discussed, considering the paleoenvironmental evolution during Last Glacial to Holocene times. Moreover, the importance of a multi-parameter approach including both, organic-geochemical and microscopical data like e.g., palynology and maceral analysis to describe the composition and source of organic matter, is emphasized. Thus, maceral data, organic-geochemical parameters (total organic carbon content, hydrogen indices, *n*-alkanes, fatty acids, sterols) and palynological data are compared and discussed. The results allow an interpretation of organic matter deposition and, therefore, a reconstruction of the paleoenvironmental conditions of the eastern Laptev Sea continental margin during the last ~15,000 years.

In Chapter 5 (New insights in organic matter deposition along the Kara and Laptev seas continental margin (eastern Arctic Ocean) during the late Quaternary: Evidence from organic-geochemical and petrographical data. Boucsein, B., Knies, J. and Stein, R.) we outline the environmental history of the Kara and Laptev Seas and the adjacent continental margin during the last ~13,500 years. The study is based on interpretations of the organic matter composition by means of organic petrography and organic-geochemical bulk-parameters (total organic carbon contents, hydrogen indices) performed on five sediment records. One main interest was to compare the organic matter accumulation in the sediments of the Kara Sea vs. the Laptev Sea regarding the different environmental conditions since the Last Glacial. While the St. Anna Trough was influenced by the Svalbard-Barents-Sea-ice-sheet as documented by the widespread distribution of diamictons, characterised by reworked organic matter and coal fragments, the Laptev Sea shelf was and not covered by an extended ice-sheet and exposed due to the lowered sea-level. Furthermore, the variations in deposition and origin of organic matter during deglaciation and the Holocene are related to changes in climate, sea level, river discharge, surface-water productivity and Atlantic water inflow along the Eurasian continental margin.

2. Particulate organic matter in surface sediments of the Laptev Sea (Arctic Ocean): Application of maceral analysis as organic-carbon-source indicator Boucsein, B. and Stein, R.

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### 2.1 Abstract

Surface sediments from the Laptev Sea and adjacent continental slope were studied for their composition of particulate organic matter by means of maceral analysis. The composition of macerals in sediments gives information about the environment, terrigenous supply from the hinterland, and marine organic matter. With reference to their biological sources we distinguish between terrigenous and marine macerals. We found that the particulate organic matter in the surface sediments of the Laptev Sea is predominantly of terrigenous origin (Ø 78 %). However, distinct variations exist when looking in detail. In the shelf area, sediments may contain up to 99 % terrigenous organic matter. Freshwater algae occur directly north of the river mouths, reflecting the strong fluvial influence. Relatively high amounts of marine organic matter (20-40 %) are restricted to the upper continental slope, the Vilkitsky Strait and W of the New Siberian Islands, explained by increased surface-water productivity due to increased fluvial nutrient supply, open-water conditions, and phytoplankton blooms at the ice-edge.

### 2.2 Introduction

The Laptev Sea belongs to the Siberian part of the Arctic Ocean and covers about 460,000 km<sup>2</sup> (Fig.2.1). The average water depth is less than 50-60 m and decreases to 15-20 m in the shallow southern part (Holmes and Creager 1974). Several submarine valleys, developed in the Last Glacial during times of lowered sea-level by erosion of the rivers, cross the shelf from the South to the North

(Holmes and Creager 1974; Kleiber and Niessen 1999). Holocene sedimentation mainly takes place in these submarine valleys (e.g., Kuptsov and Lisitzin 1996; Stein and Fahl 2000). In winter the ice regime of the Laptev Sea is characterized by an approximately 1800 km long belt of open water (polynya) (Dethleff et al. 1993) reaching a width of 100 km (Barnett 1991). At the end of May to June thawing starts and in September most of the Laptev Sea is ice free. The location of the ice margin varies annually (Timokhov 1994; Namilov 1995; Eicken et al. 1995, 1997).



Fig.2.1: Location of surface samples and main studied Area A and Transects B - E (cf. Fig.4). (PS = Polarstern; IK = Ivan Kirejev). Numbers indicate supply of suspended matter in 10<sup>6</sup> tons/year (Gordeev et al. 1996). For the rivers Khatanga, Lena, and Yana the supply of particulate organic carbon in 10<sup>6</sup> tons/year is shown in parentheses (Rachold and Hubberten 1999). Kerogen concentrates were made from grey shaded samples.

During the short Arctic summer enormous amounts of freshwater are transported by the large Siberian rivers onto the shelf. About 60 % of the total Arctic continental run-off (3300 km<sup>3</sup>) is supplied by the rivers draining into the Laptev and the Kara seas. The freshwater discharge of the Lena River is already about 520 km<sup>3</sup> per year (Aagaard and Carmack 1989). The resulting brackish surface plume is extending 350 km northward (Martin et al. 1993; Létolle et al. 1993) and forms a halocline above the intermediate and deeper Arctic water masses with salinities of about 34 to 35 psu (Timokhov 1994). Mixing of freshwater with surface and intermediate water masses cause a strong gradient in salinity of the surface water from the river mouths to the shelf break from 6 to 30 psu (Dmitrenko et al. 1995).

The large Siberian rivers also supply huge quantities of suspended matter (17.6\* 10<sup>6</sup> tons/year) and particulate organic matter (OM)(0.8-1.3\* 10<sup>6</sup> tons/year) to the Laptev Sea shelf (Martin et al. 1993; Gordeev et al. 1996; Rachold and Hubberten 1999). On the shelf the material accumulates or is further transported by sea ice into the Central Arctic Ocean (Fig.2.2). By gravitational transport (e.g., turbidity currents, debris flows) the material is carried into the deep basins (Nürnberg et al. 1994; Stein and Korolev 1994). Additionally, marine OM is produced in the water column.



Fig.2.2: Factors controlling accumulation of organic matter in the Laptev Sea and the adjacent continental margin (modified after Stein and Korolev 1994).

Thus, OM in sediments may give information about the environment, terrigenous supply from the hinterland, and surface-water productivity. Previous studies in the Laptev Sea concerning the content and origin of OM in surface sediments exist and are based on organic-geochemical parameters (TOC-content, HI-values, C/N-

ratios, biomarkers; Stein 1996, Fahl and Stein 1997, 1999), plant pigments (Boetius et al. 1996), and micropaleontological studies (Kunz-Pirrung 1998). In shelf environments controlled by huge freshwater input like in the Laptev Sea organic-geochemical parameters are very difficult to interpret in terms of organic carbon origin (see discussion in Fahl and Stein 1999). For this reason a microscopical study like maceral analysis is used in this study to enable a more precise distinction and quantification of marine and terrigenous particulate OM.

This study on surface sediments is regarded as basis for similar studies to be performed on sediment cores for reconstruction of changes in paleoenvironment and terrigenous sediment supply on geological time scales.

# 2.3. Material and methods

34 surface samples (Fig.2.1) recovered during RV "Polarstern" Cruise Arctic '93 (ARK-IX/4; Fütterer 1994) and RV "Ivan Kirejev" Cruise Transdrift I (Kassens and Karpiy 1994) were studied for their maceral composition. The siliciclastic surface sediments are mainly fine-grained (silty clay) with more sandy sediments in the western Laptev Sea and in front of the river mouths (Washner 1995).

Samples were embedded in a cold-setting epoxy-resin and subsequently ground flat and polished. Maceral analysis was performed in oil-immersion with a Zeiss-Axiophot microscope using incident light and, additionally, fluorescent light (wavelength: 395-440 nm, blue-light-filter: Zeiss No. 05). In routine petrographic analysis, relative abundance of macerals is obtained by point-counting of bulk sediment including mineral matrix, and is reported as volume percent (Stach et al. 1982). This method is inapplicable for our studies of marine sediments because of their low TOC-contents (~1 %) (for discussion see: Wagner 1993). On selected samples only about 20-40 macerals were registered in 2000 counted points when applying the point-counting method. For an adequate statistical analysis, however, at least 100-200 macerals should be counted. For this reason, the abundances of the different maceral groups were obtained by counting only macerals without mineral matrix. Counting was performed by 2D-scanning at 1000x magnification.

At least about 200-300 macerals were counted and calculated as "grain%". The grain length of the macerals varies in some samples between <10  $\mu$ m and 80-100  $\mu$ m. Therefore, the grain length of each maceral was measured, too. In the succeeding evaluation the different sizes were normalised to the grain length of 10-20  $\mu$ m.

In general, macerals are distinguished into the three main groups vitrinite/huminite, inertinite and liptinite, and several subgroups, according to the nomenclature described by Stach et al. (1982). The classification is mainly based on organic petrography studies of coals and sedimentary rocks. For our studies of recent marine sediments from high-latitudes a modification of the classic maceral concept was necessary. With reference to the environment and different biological sources we distinguished between terrigenous and marine macerals as shown in Table 2.1.

For the determination of the maturity vitrinite reflectance (Ro%) was measured on kerogen concentrates. Kerogen was concentrated by treating sediments successively with cold HCI (10 %) and HF (40 %) to remove carbonates and silicates, respectively. Vitrinite reflectance (Ro%) was measured in oil-immersion at 546 nm wavelength and calculated as a mean of 50 measurements per sample (where possible). Standards with a reflectance of 1.699 % (Zeiss: GGG) and 0.58 % (Zeiss: Saphir) were used.

### 2.4. Results

Terrigenous macerals e.g., huminite and the subgroups textinite and telinite were observed. Textinite is partly good preserved with non-gelified cell walls, open cell lumens, and a strong fluorescence intensity. Telinite appears dark-brown to grey with cell structures, but no fluorescence occurs. Fusinite, a subgroup of inertinite with typical bogen structures, was only observed in a few samples.

Maceral group	Maceral	Origin
Terrigenous	Huminite Vitrinite Inertinite Detritus	Land plants L fragments <10 µm
Macerals	Coal fragments	Coal
	Liptinite: Sporinite Cutinite Suberinite Freshwater- Alginite	Spores/Pollen Cuticles Bark/Cork Algae e.g. Chlorococcalean algae: <i>Botryococcus</i> or <i>Pediastrum</i>
Marine Macerals	Lamalginite Dinoflagellate cysts Marine Liptodetrinite	Marine Algae L fragments >10µm
Liptodetrinite, terrigenous-marine	Liptinite <10µm	fragments of terrigenous and marine Liptinites

Table 2.1: Modified classification of macerals used in this study.

The terrigenous liptinites consist of the subgroups sporinite, cutinite, suberinite, and freshwater alginite. As freshwater alginite we define chloroccocalean algae e.g. *Botryococcus* or *Pediastrum*. These algae live in freshwater and only a few species tolerate slightly higher salinities (up to 8 psu) (Matthiessen and Brenner 1996). In river-affected shelf areas like the Laptev Sea *Botryococcus* and *Pediastrum* are used as an indicator for freshwater discharge (Kunz-Pirrung 1998). *Botryococcus* shows a blue-green to yellow fluorescence colour. In white light *Botryococcus* is pale-brown to red-brown. The shape is roughly spherical and the colonies show well-defined internal structures. *Pediastrum* also shows strong fluorescence colours from green to yellow. In white light they appear pale brown to translucent. Colonies are flat and plate like. Unfortunately, in the sediments of the Laptev Sea chloroccocalean algae often only remain as fragments and hence are

difficult to identify. For more details about biology and morphology of *Botryococcus* and *Pediastrum* we refer to Batten and Grenfell (1996a, b).

Lamalginite and dinoflagellate cysts have been placed to the group of marine macerals. Lamalginites are alginites described as thin, crenulated, filamentous bodies (Hutton et al. 1980; Hutton 1987; Senftle et al. 1993; Taylor et al. 1998). In the surface sediments of the Laptev Sea lamalginites show a strong fluorescence with blue-green to yellow colours. In white light they appear translucent to pale brown.

Dinoflagellate cysts are organic-walled planktic microfossils and do not belong to the macerals s.str. according to Stach et al. (1982). Some dinoflagellates form organic-walled cysts, as part of their life cycle, which are resistant to degradation and preserved in sediment records (Taylor 1987). The dinoflagellate cysts observed in the Laptev Sea sediments indicate marine conditions (Kunz-Pirrung 1998). Our method (reflected light microscopy) is restricted to dinoflagellate cysts showing fluorescence; non-fluorescing dinoflagellate cysts are transparent in white light and cannot be recognized. Hence palynological methods are necessary in order to examine dinoflagellate cysts more completely. Fragments of dinoflagellate cysts and lamalginites with grain sizes >10  $\mu$ m are considered as an independent group "marine liptodetrinite".

Fragments of vitrinite/huminite and inertinite with grain sizes <10 µm are classified as detritus and, in case of particles showing fluorescence, as "terrigenous-marine liptodetrinite". In contrast to other authors (e.g., Wagner 1993, Hölemann 1994) who place liptodetrinite to the marine macerals, we consider it as an own group because in the Laptev Sea and the adjacent continental margin liptodetrinite can originate from marine as well as from terrigenous macerals. Organic grains consisting of more than one maceral are classified as coal fragments.

#### 2.4.1. Geographical distribution of macerals

Although the particulate OM in the surface sediments from the Laptev Sea and the continental slope is predominantly of terrigenous origin (Ø: 78 grain%) significant differences in composition can be recognized. Figure 2.3 shows the distribution of the three main maceral groups, more detailed information is summarized in Figure 2.4.



Fig.2.3: Distribution of the main maceral groups in the surface sediments.

The shelf area (Area A, Figure 2.4) near the river mouths can be distinguished from the area further offshore and the continental slope as follows:

The shelf area in the vicinity of the river mouths mainly consists of terrigenous OM (Ø: 91 grain%), followed by liptodetrinite (Ø: 8.6 grain%); only in one sample marine OM was observed (IK9316: 4.1 grain%)(Figs. 2.3 and 2.4). Freshwater algae were determined with an average of 2.0 grain% in area A, and up to 8.6 grain% close to the mouth of the river Anabar. Sporinite, mainly bisaccate pollen grains (e.g., *Pinus* spp.), cutinite, and suberinite were observed with amounts ranging from 2-25 grain%. A predominance of coniferous pollen

described by Naidina and Bauch (1999) in the Laptev Sea sediments agrees with our observation. In comparison sediments in the Transects B-E (Fig. 2.4) from the continental slope, west of the New Siberian Islands, and from the Vilkitsky Strait show relatively high amounts of marine macerals. In Transect B marine OM with an average of 22.6 grain% was found. Transect C is characterized by an increase from 4.5 to 9.5 grain% in the marine OM from the upper slope to the basin. At location PS2476 of Transect C the marine OM reaches a maximum value of 17.7 grain%, whereas the amounts of huminites/ vitrinites and inertinites decrease. At locations PS2467 and PS2463 of Transect D huminite/ vitrinite and inertinite form the major portion. Minor amounts of freshwater algae occur at location PS2469 (2.9 grain%) and location PS2468 (3.1 grain%). With the exception of location PS2463 marine OM occurs in all samples of Transect D with an average of 6.3 grain%; a maximum value of 15.4 grain% was reached at location PS2465.

West of the New Siberian Islands in samples IK9373A, PS2450 and PS2453 (Transect E) freshwater algae occur, however, only in minor amounts (0.8-3.3 grain%). Compared to the other transects the highest amount of marine OM with a value up to 43.8 grain% was determined in Transect E at location PS2461.

#### 2.4.2. Preservation of macerals

The grain size of terrigenous organic particles can be used as indicator for the proximity of the source (Rullkötter et al. 1992, and references therein). In the surface sediment samples a decrease in grain size of huminte/vitrinite and inertinite from the shelf to the continental slope is observed while the amount of detritus (<10  $\mu$ m) increases, as shown especially in Transect C and D. This can be explained by a stronger fragmentation due to long-distance transport. Inertinite and vitrinite are often subrounded or rounded and, therefore, also suggest long-distant or high-energy transport.



Fig.2.4: Maceral composition in surface sediments from Area A and Transects B-E.



Fig.2.4 (continued)

Vitrinites and huminites often show weathering as documented by microfractures. Nevertheless, well-preserved textinites with distinct cell structures and partly resinite fillings were observed. Submicroscopic fluorescing OM or bituminite were not found in the surface sediment samples.

## 2.4.3. Maturity of organic matter

For determination of the maturity of the organic matter random vitrinite reflectance (Ro%) was measured on kerogen concentrates. The polymodal distribution of the reflectance (Fig.2.5) indicates different maceral groups and coalification stages. In all cases the first maximum peak (<0.6 Ro%) belongs to the huminite/vitrinite of sub-bituminous rank (after North American/ ASTM classification, see: Stach et al. 1982).



Fig.2.5: Vitrinite reflectance determined in kerogen concentrates.

#### 2.5. Discussion

The different factors controlling the flux and accumulation of OM in the Laptev Sea, i.e., marine primary production and terrigenous supply, are summarized in Figure 2.2. Primary production depends on abiotic factors like temperature, light and dissolved nutrients (e.g., Harrison and Cota 1991). The permanent ice cover in the central part of the Arctic Ocean impede primary production (Subba Rao and Platt 1984; Wheeler et al. 1996). In comparison in the ice-free area of the Laptev Sea during summer relatively high production rates of around 200 mgCm<sup>-2</sup>d<sup>-1</sup> are reported by Boetius and Damm (1998). Due to remineralization in the water column only low contents of labile marine organic compounds are preserved in the surface sediments (Boetius and Damm 1998). On the other hand, the huge river discharge is of major importance for the deposition of terrigenous OM in the Laptev Sea.

By determination and quantification of the OM from different sources, information about the recent organic carbon cycle can be obtained. Several organicgeochemical and palynological studies dealing with the content and origin of OM already exist for the Laptev Sea area (e.g., Boetius et al. 1996; Stein 1996; Fahl and Stein 1997, 1999; Kunz-Pirrung 1998). It has to be considered, however, that organic-geochemical analysis and palynological methods only examine portions of the organic matter, either extracts or sieved kerogen concentrates (>6 µm). Furthermore, in coastal environments influenced by huge freshwater input like in the Laptev Sea organic-geochemical parameters are very difficult to interpret (Fahl and Stein 1999). Thus, accurate quantification of marine and terrigenous proportions of the total OM is not possible. Studying bulk sediments containing all particulate OM by means of maceral analysis, on the other hands, may allow to calculate percentage values of the marine and terrigenous OM fractions, but with some restrictions. As described before we cannot recognise non-fluorescing dinoflagellate cysts. Additionally, the method depends on the resolution of light microscopes. Therefore, we are only able to quantify particles approximately  $>2 \mu m$  and, the quantification of finely disseminated OM is not possible. However, background-fluorescence as an indicator for fluorescing submicroscopic OM was not observed in the Laptev Sea surface sediments. Another limitation is that

liptodetrinite (fragments of liptinite) can originate from marine as well as from terrigenous macerals. Therefore, a clear classification of this particles is not feasible.

Organic-geochemical bulk parameters (TOC-content, C/N-ratios and hydrogen indices (HI)) give a first indication about the content and composition of OM in the surface sediments of the Laptev Sea (Stein 1996, Stein and Fahl 2000). Total organic carbon values vary between 0.3 and 2.3 %. Maxima occur in the vicinity of the eastern Lena Delta, off the Olenek river mouth, southwest of the New Siberian Islands, and in the central part of the lower Laptev Sea continental slope. As shown in Figure 2.6 most of the HI-values plot into the field of kerogen type III indicating a dominantly terrigenous origin. Samples with  $T_{max}$  values >435 °C suggest the presence of more mature reworked organic matter.



Fig.2.6: Diagram of hydrogen index vs. T<sub>max</sub> values (Stein and Nürnberg 1995).

In general, high abundances of terrigenous macerals support low HI-values i.e., also suggesting a dominance of terrigenous OM. A correlation between HI-values and the amounts of marine and terrigenous/ freshwater liptinites does not exist as shown in Figure 2.7a, b.

Samples with HI-values about 100 mg/gC may contain very low proportions of marine OM, but also proportions as high as 40 %. This has also been recorded in other ocean areas where the OM is characterized by low HI-values (e.g. Stein et al. 1986; Stein 1991). Thus, the HI-values cannot be used for a quantitative

Laptev Sea. determination of marine or freshwater/ terrigenous material in the sediments of the



Fig.2.7: Hydrogen index (mgHC/gC) vs. maceral groups (grain%) (a: marine liptinite; b: terrigenous liptinite and freshwater algae).

data and are related to the sedimentation of a phytoplankton bloom. thus, supply of marine OM. Measurements of chlorophyll a and phaeopigments edge (up to 100 mg/m<sup>2</sup>) by Boetius et al. (1996) near the ice-edge correlate with these fatty acids were interpreted as indicators for increased primary productivity and, from marine phyto- and zooplankton (Fahl and Stein 1999) increase near the icefatty acids 16:1(n-7) and 20:5(n-3) which derive from freshwater algae as well as esters in the vicinity of the eastern Lena Delta, indicating terrigenous input. The information about the sources of OM, however, with some restrictions. Fahl and Stein (1997) report high amounts of long-chain n-alkanes and long-chain wax Specific marine biomarkers such as n-alkanes and fatty acids can give more exact and to the west and north of the Lena Delta (Fahl and Stein 1997). These

Although our results also show higher amounts of marine macerals near the iceedge, they do not show marine particulate OM north-west of the Lena Delta as documented by the concentration of fatty acids. Instead, minor amounts of freshwater algae were determined. As shown in Figure 2.8 a possible explanation for this discrepancy is that these short-chain fatty acids can also be synthezised by freshwater phytoplankton (Léveillé et al. 1997; Fahl and Stein 1999). For this reason, using biomarkers as a single tracer to distinguish between marine and freshwater sources in river-influenced shelf areas is not sufficient.



Fig.2.8: Macerals (grain%) vs. short-chain fatty acids (µg/g TOC)(fatty acid data from: Fahl and Stein 1997). Letters indicate samples from Area A and Transects B-E.

Based on these results an unequivocal interpretation in terms of organic-carbon source is only possible by a combination of organic geochemical analysis and microscopic studies like maceral analysis and palynological methods. The distribution of the palynomorphs (Kunz-Pirrung 1998) agrees well with our results from maceral analysis. The aquatic palynomorph assemblages reflect the strong salinity gradient in the surface water and the adjacent Arctic Ocean. Close to the river mouths and within the submarine valleys mainly chlorococcalean algae were observed showing the strong influence of freshwater input and, therefore, decreasing towards the shelf break. Furthermore, the sediments from the continental slope are characterized by dinoflagellate cysts indicating a marine environment (Kunz-Pirrung 1998) which is also shown in the increase of marine macerals (Figs. 2.3 and 2.4).

Maceral data enable to quantify the marine and terrigenous proportions of the particulate OM with the restrictions mentioned above. Marine OM occurs mainly in the area of the upper continental slope, the Vilkitsky Strait and W of the New Siberian Islands with an average of 14 % (Figure 2.4; range from 6 to 23 %). Increased marine productivity in these areas can be explained by an adequate nutrient supply by the Siberian rivers, sea-water salinities, partly ice-free conditions and melting which induce phytoplankton growth. Highest values of marine OM (up to 44 %) were observed near the ice-edge position, explained by increased marine OM production (cf. Strömberg 1989; Legendre 1992). The shelf area is dominated by terrigenous OM reaching up to 99 % (Fig.2.3 and 2.4). Near the river mouths minor but significant amounts of freshwater algae were observed directly reflecting the influence of the rivers. Our quantitative estimates of the marine and terrigenous proportions of the OM in surface sediments are the basis for further studies on organic carbon budgets (cf. Stein and Fahl 1999) as well as the paleoenvironmental interpretation of organic-carbon records determined in sediment cores.

#### 2.6. Conclusions

- Shelf seas of high latitudes like the Laptev Sea, are characterized by a strong freshwater supply, high seasonality of sea ice-cover, and primary productivity. For the determination and interpretation of organic-carbon fluxes in coastal environments it is necessary to distinguish between freshwater/terrigenous OM and marine OM. This is relevant particularly with regard to further studies on sediment cores for the reconstruction of changes in the paleoenvironment.
- The interpretation of organic-geochemical parameters in shelf areas is difficult Hydrogen index values and even biomarkers can not be interpreted unequivocal in terms of freshwater/terrigenous vs. marine origin. Thus, we propose a combined approach of organic-geochemical and microscopical studies for a detailed and precise identification of organic-carbon sources. The advantage of microscopical studies, in particular maceral analysis is the

feasibility to distinguish particulate OM of different sources definitely. Additionally, maceral analysis provide quantitative estimates of the particulate OM.

 Our data indicate that at the Laptev Sea continental slope 20 % to almost 40 % of the particulate OM preserved in surface sediments is of marine origin, with the maximum values determined at the ice-edge. In the inner Laptev Sea, on the other hand, up to 99 % of the particulate OM is of terrigenous origin, including freshwater alginites.

# 3. Quantity and quality of organic carbon in surface sediments of the Ob and Yenisei estuaries and adjacent coastal areas: marine productivity vs. terrigenous input

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### 3.1 Introduction

Two main mechanisms are controlling the accumulation of organic matter in the sediments of the Kara Sea. The large rivers Ob and Yenisei supply significant quantities of freshwater onto the shelf (Lisitsyn and Vinogradov 1995; Bobrovitskaya et al. 1996; Johnson et al. 1997) and deliver terrigenous organic matter and aquatic algae. Additionally, marine organic matter is produced in the water column.

In order to distinguish between the different sources of the organic material maceral analysis, organic-geochemical bulk parameters and biomarkers (shortand long-chain <u>n</u>-alkanes, fatty acids and pigments) were used to determine the quality (marine vs. terrigenous) and quantity of the organic carbon fraction in the surface sediments taken during the 28<sup>th</sup> cruise of RV "Akademik Boris Petrov" (Matthiessen and Stepanets 1998) (Fig. 3.1). Previous organic-geochemical investigations (i.e., total organic-carbon content (TOC), hydrogen indices (HI), C/N-ratios) indicate the importance of terrigenous input of organic matter (Galimov et al. 1996; Stein 1996). Studies of lipid biomarkers in surface sediments in the Ob estuary show also a predominance of terrestrial constituents and an increase in planktonogenic and bacterial lipids further offshore (Belyaeva and Eglinton 1997).

In complex systems such as the Eurasian continental margin characterized by high input of terrestrial/aquatic organic matter and strong seasonal variation in sea-ice cover and primary productivity, the interpretation of the organic geochemical data is much more complicated and restricted in comparison to similar data sets from low-latitude open-ocean environments (Fahl and Stein 1999). Microscopical studies (maceral analysis/ palynology), however, allow a direct visual inspection of the particulate organic matter and allow to differentiate particles of different biological sources. Thus, a combination of both methods as shown in this study, yields a more precise identification of organic-carbon sources.



Fig. 3.1: Locations of stations

#### 3.2 Methods

Analysis of Bulk Parameter and Biomarkers

Total nitrogen and organic-carbon contents were determined by means of a Heraeus CHN-analyzer (for details concerning the method see Stein 1991). The
hydrogen index (HI in mgHC/gTOC) was determined as described by Espitalié et al. (1977). The results are listed in Appendix 3.1.

For lipid analyses the surface sediment samples were stored at -80°C or in dichloromethane : methanol (2:1, by vol.) at -23 °C until further treatment. The sediment (2g/ parameter) was homogenised, extracted and purified as recommended by Folch et al. (1957) and Bligh and Dyer (1959). An aliquot of the total extract was used for analyzing <u>n</u>-alkanes and fatty acids.

#### <u>n-Alkanes</u>

The alkanes were separated from the other fractions by column chromatography with hexane. The composition was analyzed with a Hewlett Packard gaschromatograph (HP 5890, column 50 m x 0.25 mm; film thickness 0.25  $\mu$ m; liquid phase: HP 1) using a temperature program as follows: 60 °C (1 min), 150 C (rate: 10 °C/min), 300 °C (rate: 4 °C/min), 300 °C (45 min isothermal). The injection volume is 1  $\mu$ l (Cold Injection System: 60 °C (5 s), 300 °C (60 s, rate: 10° C/s). Helium was used as carrier gas. The composition was qualified by a standard mixture; for the quantification squalane was added before any analytical step.

#### Fatty acids

An aliquot of the total extract was used for preparing fatty acid methyl esters and free alcohols by transesterification with 3 % concentrated sulfuric acid in methanol for 4 hours at 80 °C. After extraction with hexane the composition was analyzed with a Hewlett Packard gaschromatograph (HP 5890, column 30 m x 0.25 mm; film thickness 0.25 µm; liquid phase: DB-FFAP) using a temperature program as follows: 160 °C, 240 °C (rate: 4 °C/min), 240 °C (15 min isothermal) (modified according to Kattner and Fricke, 1986). The injection volume is 1 µl. The fatty acids and alcohols were identified by a standard mixture (Marinol standard was kindly made avaibable by J.R. Sargent, Scotland). For quantification an internal standard (19:0 fatty acid methyl ester) was added.

### **Pigments**

The tetrapyrrolic pigments were determined by measuring the absorbance of their solvent extract (90% acetone) at a wavelength of 410 nm (Rosell-Melé, 1994; Rosell-Melé and Koç, 1997). Additionally the measurement was carried out at 645 and 663 nm to determine chlorophyll abundances. The turbidity factor (absorbance at 750 nm) was substracted.

#### Maceral Analysis

The source of particulate organic matter can be characterized by determination of the different maceral groups. The classic maceral concept is based on coal petrography studies. In general, macerals are divided into the three main groups vitrinite/ huminite, inertinite and liptinite, and several subgroups, according to the nomenclature described by Stach et al. (1982). For our investigations of marine sediments of high-latitudes a modification of the classic maceral concept was necessary. We distinguish between terrigenous and marine macerals. Terrigenous macerals include the main groups vitrinite/ huminite, inertinite and liptinite and different subgroups (e.g., textinite, sporinite, cutinite etc.). Fragments (<10 µm) of vitrinite/huminite and inertinite are classified as detritus and, in case of particles showing fluorescence, as liptodetrinite. Liptodetrinite can be originated from marine as well as from terrigenous macerals and must be considered as an own group. Chlorophycean algae such as Botryococcus or Pediastrum are classified as limnic-brackish alginite and belong to the terrigenous macerals. Marine macerals include finely lamellar alginite (lamalginite) (e.g., Senftle et al. 1993; Hutton et al. 1980) and dinoflagellate cysts. Fragments of dinocysts and lamalginite with a grain size >10 µm are considered as an own group and are classified as "marine liptinites".

Maceral analysis was performed on bulk sediments embedded in a cold-setting epoxy-resin which was subsequently grounded and polished. The amount of the different maceral groups were obtained by counting at 1000x magnification using incident light and blue-light exication. At least 200-300 macerals were counted as grain% under consideration of their grain size. In the subsequent evaluation the

different sizes were converted to the grain size of 10-20  $\mu$ m in diameter. Sampling of the surface sediments is described in Matthiessen et al. (1998).

# 3.3 Results and discussion

Microscopical and organic-geochemical analysis revealed that the composition of organic matter in surface sediments from the western part of the investigation area (Ob Bay, Gydanskii Bay) differ from the eastern part (Yenisei Bay). Total organic carbon (TOC) maxima of >2 % occur in both river mouths (Fig. 3.2).



Fig. 3.2: Distribution of total organic carbon in surface sediments.

The high TOC contents in the Ob Bay, however, correlate well with hydrogen index (HI) values >100 mgHC/gTOC (Fig. 3.3) indicating a significant influence of marine organic matter whereas the high TOC contents in the Yenisei Bay commonly correspond to low HI values (<100 mgHC/gC) indicating the predominance of terrigenous organic carbon.



Fig. 3.3: Hydrogen index in surface sediments.

This is also supported by the biomarker results (Figs. 3.4, 3.5). High amounts of long-chain <u>n</u>-alkanes indicate dominently terrigenous organic matter (Fig. 3.6). Only in the western part (and north of Taymyr Peninsula) the highest amounts of short-chain fatty acids (Fig. 3.4) and chlorophyll <u>a</u> (Fig. 3.5) suggest increased marine organic matter being preserved in the surface sediments. The high accumulation of inorganic as well as organic (mostly terrestrial, but partly also marine) material in the river and seawater mixing zone of the river mouths is

probably due to "mariginal filter effect". This effect was described by Lisitsyn (1995) suggesting that 93-95 % of the suspended matter was accumulated in this zone.



Fig. 3.4: Distribution of short-chain fatty acids in surface sediments.

In general, the microscopical investigations support the bulk parameters and the biomarker data and show that the POM of the Kara Sea sediments is dominated by terrigenous macerals ( $\emptyset$  73 %; Fig. 3.7). The results show relatively high amounts of marine organic matter occuring in the western part of the investigation area (up to 35 %), in the Ob Bay (up to 36 %) and Gydanskii Bay (up to 27 %). In the eastern part and Yenisei Bay the abundance of marine macerals is insignificant (<8 %), and the sediments are mainly dominated by terrigenous macerals.



Fig. 3.5: Distribution of chlorophyll <u>a</u> in surface sediments.

Limnic-brackish alginite *Pediastrum* and *Botryococcus*, partially good preserved, occur in the Ob and Gydanskii bays (up to 7 %) and in small amounts further north in samples of the 74°-Profile. These algae groups are usually adapted to freshwater conditions and indicate river inflow (e.g. Kunz-Pirrung 1999). In contrast only small amounts of these algae occur in the Yenisei Bay.

Relatively well preserved terrigenous macerals, e.g. textinite, a subgroup of huminite, was observed in the south of the river mouths. In comparison the area further offshore (74°-Profile) is characterized by an increase of terrigenous detritus of huminte/ vitrinite (grain sizes <10  $\mu$ m) because of a stronger fragmentation due to a further lateral transport (Fig.3.8).



🖉 300-350 µg/gTOC 🕕 200-300 µg/gTOC 0<200 µg/gTOC

Fig. 3.6: Distribution of n-alkanes in surface sediments.

Fast environmental changes, e.g. strong seasonality of salinity of the surface water layer (Churun and Ivanov 1998), sea-ice cover and river inflow in the Kara Sea, make comparisons of data derived from organic matter in the surface water layer with data from organic matter preserved in surface sediments difficult.

For example the nutrients in the surface water of the eastern part are already depleted (0-0.5  $\mu$ m nitrate) and due to this the chlorophyll <u>a</u> concentration is rather high (Nöthig et al. 1999). This "productivity" signal is not reflected in the surface sediments. In the western part it is just the opposite. Due to the distribution of biomarkers and macerals indicating increased marine organic matter preserved in the surface sediments, we would expect high concentrations of chlorophyll <u>a</u> and

as well as in the eastern part depleted nutrients. The nitrate concentration, however, is still (or already) high, and the pigment contents are rather low.



Fig. 3.7: Distribution of maceral groups in surface sediments.

The distribution of palynomorphs in the surface water layer also shows discrepancies in the composition of organic matter of the suspension load and in the surface sediments (Matthiessen and Boucsein 1999). For that reason further studies considering the seasonal variability are needed (e.g., sediment traps).



Fig. 3.8: Distribution of maceral groups along the transects.

Station	Ntot	N'tot	C/N	CaCO <sub>3</sub>	TOC	Н	01	Tmax
(MUC)	(%)			(%)	(%)	mg CO <sub>2</sub> /	mg CO <sub>2</sub> /	(°C)
						g TOC	g TOC	
BP97-01	0.236	0.194	5.65	2.2	1.33	59	309	386
BP97-10	0.235	0.251	8.65	0	2.04	148	319	461
BP97-12	0.279	0.289	7.98	0	2.23	146	314	480
BP97-17	0.176	0.176	7.67	0.7	1.35	163	319	479
BP97-19	0.275	0.303	7.55	0	2.08	123	241	390
BP97-21	0.216	0.238	7.88	0	1.70	62	229	382
BP97-27	0.231	0.273	9.95	0	2.30	62	269	398
BP97-32	0.270	0.318	11.77	0	3.18	71	202	417
BP97-35	0.208	0.229	10.99	0	2.29	63	238	405
BP97-39	0.169	0.158	6.9	1.4	1.16	76	290	392
BP97-42	0.097	0.091	7.33	1.0	0.71	62	271	388
BP97-43	0.239	0.264	8.19	0	1.96	63	311	383
BP97-46	0.263	0.294	7.83	0	2.06	83	243	397
BP97-47	0.159	0.161	7.94	2.8	1.27	74	338	401
BP97-48	0.142	0.143	7.66	0.9	1.09	71	331	398
BP97-49	0.172	0.176	7.42	1.4	1.28	72	349	389
BP97-50	0.203	0.204	7.05	0.7	1.43	82	272	393
BP97-52	0.130	0.122	6.72	1.1	0.87	92	265	395
BP97-55	0.197	0.184	7.09	2.6	1.40	66	372	392
BP97-56	0.146	0.134	6.92	3.2	1.01	65	357	393
BP97-58	0.120	0.09	5.62	2.6	0.68	70	366	338

Appendix 3.1: Organic geochemical parameter of surface sediments.

4. The variability of river discharge and Atlantic-water inflow at the Laptev Sea continental margin during the last 15,000 years: Implications from maceral and biomarker records

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# 4.1 Abstract

In order to reconstruct the depositional environment from the Laptev Sea continental slope and shelf during the last ~15,000 yrs.BP maceral analysis was carried out on two sediment cores (PS2458-4, PS2725-5) and compared with organic-geochemical parameters. During the transition from the Last Glacial to the Holocene the environment of the Laptev Sea shelf was controlled by the postglacial sea level rise, variations in river discharge, surface-water productivity, and Atlantic water inflow along the Eurasian continental margin. Based on our results we identify the following significant changes of the environment: 1) at about 13,500 yrs.BP the first step of deglaciation (Termination 1a) is documented by the deposition of marine and freshwater organic matter, 2) at about 10,400 yrs.BP the first post-glacial influence of Atlantic water inflow along the Eastern Laptev Sea continental margin is indicated by an increase in marine organic matter 3) at the beginning of the Holocene an increased fluvial supply is documented by an increase in freshwater alginite and, 4) since ~9,500 -8,000 yrs.BP modern marine conditions are established at the Laptev Sea continental margin as documented in increased amounts of marine macerals, biomarkers (dinosterol, brassicasterol, short-chain fatty acids) and dinoflagellate cysts.

### 4.2 Introduction

The organic matter (OM) in the sediments of the Eurasian shelf seas and the adjacent continental margin has a complex composition because different

processes influence its supply, dispersal and deposition. The environment of the Laptev Sea is strongly influenced by a large volume of freshwater delivered by the Siberian rivers. For example the freshwater discharge of the Lena River is about 520 km<sup>3</sup> per year (Aargard and Carmarck 1989). The supply of suspended matter and particulate OM onto the Laptev Sea shelf by the Lena River is estimated to be 17.6\*10<sup>6</sup> tons/year and 0.8-1.2\*10<sup>6</sup> tons/year, respectively (Martin et al. 1993; Gordeev et al. 1996; Rachold and Hubberten 1999). The suspended OM transported by the Lena River is mainly of terrigenous origin (Lara et al. 1998). Rachold and Hubberten (1999) discussed terrestrial and additionally, autochthonous riverine phytoplankton as sources for the particulate OM delivered by the rivers. The major portion of the OM accumulates on the inner shelf (Kuptsov and Lisitzin 1996). Nevertheless, significant amounts are further transported by sea-ice and turbidity currents or debris flows into the Central Arctic Ocean (Lindemann 1998, Stein et al. 1999).

As described from organic-geochemical studies (Fahl and Stein 1997) and organic petrography (Boucsein and Stein 2000) the OM in the surface sediments of the Laptev Sea shelf is predominantly of terrigenous origin. Moreover, palynomorph and diatom assemblages in the surface sediments document the large freshwater supply (Kunz-Pirrung 1999; Cremer 1999).

During the short Arctic summers the Laptev Sea is mostly ice-free. Relatively high productivity rates of about 200 mgCm<sup>-2</sup>d<sup>-1</sup> were observed in the ice-free areas of the Laptev Sea near the ice edge (Boetius and Damm 1998). Most of the organic compounds are remineralized in the water column and only small amounts are preserved in the surface sediments. Nevertheless, marine OM is preserved in the surface sediments of the upper continental slope and near the ice edge as documented by assemblages of dinoflagellate cysts (Kunz-Pirrung 1999), chlorophyll <u>a</u> and phaeopigment contents (Boetius et al. 1996; Heiskanen and Keck 1996), biomarkers (Fahl and Stein 1997) as well as by marine macerals (Boucsein and Stein 2000).

In this case study we will show the importance of characterization of the different OM sources (in terms of freshwater, terrigenous and marine origin) for interpretations of organic carbon flux, especially in shelf environments. The interpretation of organic-geochemical data as organic-carbon-source indicators is less definitive in marine systems like the Laptev Sea, which are affected by freshwater supply. For example short-chain fatty acids, pigments, and short-chain *n*-alkanes can be derived from freshwater as well as from marine phyto- and zooplankton. Thus, these biomarkers cannot be used as single tracer for distinguishing between freshwater and marine sources (c.f. discussion in: Fahl and Stein 1999). Similar problems exist by using Hydrogen indices (HI) to identify marine OM. Higher HI-values, often used as indicator for marine OM in marine records, can be resulted from alginite of marine and/or lacustrine origin (Tissot and Welte 1984). For that reason, HI-values must be interpreted cautiously in river-influenced systems.

Microscopical studies like palynology or organic petrography are helpful tools for a more precise distinction and quantification of the particulate OM. The distribution of particulate OM preserved in marine sediments document the different environmental conditions. As shown in petrological studies on Quaternary marine sediments from the North Atlantic and North Sea, for example, maceral analysis can be used for paleoceanographic and paleoclimatic interpretations (Wiesner et al.1990; Hölemann and Henrich 1994; Wagner and Henrich 1994).

In a first step we have studied the composition and geographical distribution of the particulate OM in the Laptev Sea surface sediments (Boucsein and Stein 2000) as a basis for paleoenvironmental reconstructions of sediment records presented in this study. The major goals of this study are 1) to identify organic-carbon sources by using maceral analysis and compare these data with organic-geochemical parameters, 2) to use a modified organic facies concept for the interpretation of temporal and spatial changes in composition of organic carbon, and 3) to reconstruct the paleoenvironmental changes during the last ~15,000 yrs.BP in relationship to sea-level rise, climatic changes, variability of river discharge, and Atlantic water inflow.

# 4.3 Material and Stratigraphy



Fig.4.1: Study area and location of cores PS2458-4 (983 m water depth) and PS2725-5 (77 m water depth) from the Laptev Sea shelf and the continental margin. Black arrows marks Lena River discharge.



coast line 10,000 yrs.BP (after global sea-level curve of Fairbanks 1989)

coast line 13,000 yrs.BP (after global sea-level curve of Fairbanks 1989) During RV "Polarstern" Expeditions ARK-IX/4 in 1993 (Fütterer 1994) and ARK-XI/1 in 1995 (Rachor 1997) sediment cores from the Laptev Sea were recovered. In this study data from sediment core PS2458-4 (eastern Laptev Sea continental slope: 78.17°N, 133.40°E) and sediment core PS2725-5 (eastern Laptev Sea shelf; 78.66°N, 144.16°E) are presented (Fig.4.1).

### PS2458-4

Core PS2458-4 taken from the upper continental slope of the eastern Laptev Sea at a water depth of 983 m, consists of a 8 m long sedimentary sequence of very dark olive-gray silty clay (Fütterer 1994) of dominantly terrigenous origin as based on clay mineralogy (Müller 1999). The uppermost 25 cmbsf taken from the undisturbed box core PS2458-3 recovered from the same position as core PS2458-4, are of dark brown to very dark brown color. Bivalves were used for AMS-<sup>14</sup>C dating (Table 4.1) (Spielhagen et al. 1996; subm.). Until now no dating exists in the lowermost part (625-800 cmbsf). Using constant linear sedimentation rate the core may represent the last ~15,000 yrs.BP. At a depth of 100 cmbsf, there is evidence of a hiatus lasting 6-8000 yrs. (Spielhagen et al. 1996; subm.). The uppermost 100 cmbsf are probably not older that 100-200 yrs.BP.

#### PS2725-5

Core PS2725-5 was taken on the eastern Laptev Sea shelf at a water depth of 77 m and consists of a 4.8 m long sedimentary sequence. The sediments are dominated by very dark gray, dark olive, and black silty clay with common to abundant spots/layers between 30 and 178 cmbsf (Rachor 1997). The lowermost 40 cmbsf contain significant amounts of sand (Müller 1999). Based on AMS-<sup>14</sup>C dating of bivalves, the sediments represent the last ~9,000 yrs.BP (Stein and Fahl, 2000; Table 4.1).

Core	Depth (cm)	Age <sup>14</sup> C BP	Age <sup>14</sup> C BP (440yrs. reservoir corrected)	cal. years BP	LSR (cm/ 1000yrs)	References
PS2458	201	7980	7980 ±110	8862	124	Spielhagen et al. (subm.)
PS2458	252	8830	8390 ±55	9250	210	Spielhagen et al. (subm.)
PS2458	294	9030	8590 ±100	9705	132	Spielhagen et al. (subm.)
PS2458	335	9340	8900 ±120	9986	50	Spielhagen et al. (subm.)
PS2458	369	10020	9580 ±70	10955	180	Spielhagen et al. (subm.)
PS2458	467	10600	10160 ±75	11683	65	Spielhagen et al. (subm.)
PS2458	530	11560	11120 ±100	13080	68	Spielhagen et al. (subm.)
PS2458	578	12270	11830 ±65	13817	100	Spielhagen et al. (subm.)
PS2458	625	12750	12310 ±150	14208		Spielhagen et al. (subm.)
PS2725	0	-710	recent	recent	13	Stein and Fahl (2000)
P\$2725	115	8340	7900 ±60	8643	91	Stein and Fahl (2000)
PS2725	207	9170	8730 ±90	9654	822	Stein and Fahl (2000)
PS2725	392	9280	8840 ±60	9879	1152	Stein and Fahl (2000)
PS2725	430	9340	8900 ±60	9912		Stein and Fahl (2000)

Table 4.1: AMS-<sup>14</sup>C datings used in this study taken from Spielhagen et al. (subm.) and Stein and Fahl (2000).

# 4.4 Methods

#### Maceral analysis

In general, macerals are distinguished into the three main groups vitrinite/huminite, inertinite and liptinite, and several subgroups, according to the nomenclature described by Taylor et al. (1998). This classification is based on organic petrography studies on coals and sedimentary rocks. For our purpose of studying recent marine sediments a modification of the classic maceral concept was necessary. With reference to the environment and different biological sources we

have distinguished between terrigenous and marine macerals as shown in Table 4.2.

Maceral group	Maceral	Origin		
Terrigenous	Huminite Vitrinite Inertinite Detritus	Land plants fragments <10 µm		
Macerals	Coal fragments	Coal		
	Liptinite: Sporinite Cutinite Suberinite Freshwater- Alginite	Spores/Pollen Cuticles Bark/Cork Algae e.g. Chlorococcalean algae: <i>Botryococcus</i> or <i>Pediastrum</i>		
Marine Macerals	Lamalginite Dinoflagellate cysts Marine Liptodetrinite	Marine Algae fragments >10µm		
Liptodetrinite, terrigenous-marine Liptinite <10µm		fragments of terrigenous and marine Liptinites		

Table 4.2: Modified classification of macerals (Boucsein and Stein 2000).

Bulk-sediment samples were embedded in a cold-setting epoxy-resin and polished. Maceral analysis was performed in oil-immersion with a Zeiss-Axiophot microscope using incident light and, additionally, fluorescent light (wavelength: 395-440 nm, blue-light-filter: Zeiss No.05). The abundances of the different maceral groups were obtained by counting only macerals without mineral matrix. Counting was performed by 2D-scanning at 1000x magnification. At least about 200-300 macerals were counted and calculated as "grain %". The grain length of the macerals varies in some samples between <10  $\mu$ m and 80-100  $\mu$ m. For that reason, the grain length of each maceral was estimated in order to prevent that small particles become over-estimated. In the succeeding evaluation the different sizes were normalized to the grain length of 20  $\mu$ m. Nevertheless, quantification of

macerals by counting has to be considered as "semi-quantitative", because the method depends on the resolution of light microscopes. We are only able to quantify particles > 2  $\mu$ m and quantification of finely disseminated OM is not possible. For more details concerning the method and its applicability see Boucsein and Stein (2000).

#### Organic-geochemical analyses

Organic-geochemical parameters carried out on sediment records and discussed in this study include the bulk parameters hydrogen index values (HI in mgHC/gTOC) and TOC contents (%) and specific biomarkes (long-chain *n*alkanes, short-chain fatty-acids, sterols). The results are shown in Figures 4.2 and 4.3. For a detailed description concerning the methods of organic-geochemical analyses we refer to Fahl and Stein (1999).

# Calculation of linear sedimentation rates (LSR) and accumulation rates

The linear sedimentation rates (LSR; cm/ky) of Core PS2458-4 were calculated using calendar years from Spielhagen et al. (subm.) (Table 4.1). Mass accumulation rates (MAR; g/cm<sup>2</sup>/ky) of the bulk sediment were calculated from LSR and dry bulk density following van Andel et al. (1975). The accumulation rates of TOC (%) were calculated from mass accumulation rates using:

#### TOC-AccR = MAR \* (TOC/100).

The linear sedimentation and accumulation rates of Core PS2725-5 are taken from Stein and Fahl (2000).

#### 4.5 Results

### Organic-geochemical analyses

### PS2458-4

The TOC-values are relatively high throughout the core ranging from 1-1.5 % and, as documented in the distribution of organic geochemical parameters, the OM is



predominantly of terrigenous origin (Fig.4.2). Based on the results from organicgeochemical analyses the core can be divided into two sections.

The lower core section (790 to 370 cmbsf) is characterized by low HI-values (<100 mgHC/g TOC) and relatively high concentrations of long-chain *n*-alkanes

(200  $\mu$ g/g TOC) indicating terrigenous OM. In comparison the upper core section (370 cmbsf to the surface) shows a more marine character. This is documented by a remarkable increase in concentrations of short-chain fatty acids (up to 40  $\mu$ g/g TOC), dinosterol (up to 110  $\mu$ g/g TOC), brassicasterol (up to 80  $\mu$ g/g TOC), and an increase of HI-values (up to 200 mgHC/g TOC) (Fig.4.2).

### PS2725-5



Fig.4.3: Organic-geochemical bulk-parameters (TOC, Hydrogen index), biomarker ( $\mu$ g/g TOC) distribution (Fahl and Stein 1999) and, main maceral groups (marine organic matter (MOM), terrigenous organic matter (TOM), liptodetrinite) in the sediment sequence of core PS2725-5. Stratigraphy is based on AMS-<sup>14</sup>C datings from Stein and Fahl (2000) (see table 4.1).

In this core organic-geochemical parameters show less variations than in core PS2458-4 (Fig.4.3). At the basis of the core (470 to 450 cmbsf) TOC values are

very low with an average of 0.4 %, increasing to values between 0.8 and 1.3 % in the sedimentary sequence above (i.e., 450 cmbsf to surface). The HI-values are low throughout the entire core (<100 mgHC/g TOC) while the concentration of long-chain *n*-alkanes is high (300-400  $\mu$ g/g TOC). In comparison to core PS2458-4 the concentration of the short-chain fatty acids are ten times higher (300  $\mu$ g/g TOC).

#### Macerals and organic facies

The origin of the organic facies concept traces back to coal petrographers (Stach et al. 1982). A definition is given by Jones (1987) who distinguishes four different organic facies types A-D in dependence of their hydrocarbon contents, documented in microscopical characteristics and Hydrogen- and Oxygen index values (HI and OI values).

Based on this classification the sediments from core PS2458-4 and PS2725-5 belong to facies types C and D because of their high amounts of terrigenous OM, HI-values predominantly of 50-150 mgHC/g TOC and relative low TOC-contents (0.5-1.5 %). Generally, organic-geochemical parameters do not show significant variations throughout the studied cores. Only in the upper part of Core PS2458-4 a distinct increase in marine biomarkers is recorded. Maceral data, however, show more variations which allow to distinguishing sub-facies types. Thus, we suggest a modified organic facies. According to the maceral composition in the sediments of cores PS2458-4 and PS2725-5 we define 5 different types of organic sub-facies as shown in Figure 4.4, 4.5 and Table 4.3. Wagner and Henrich (1994) used an organic facies model for Quaternary sediments of the Norwegian-Greenland Sea based on organic-geochemical and maceral data combined with sedimentological parameters. In contrast, in our studied cores the definition of sub-facies types is only based on maceral distribution because sedimentological and organic-geochemical parameters show less to no variations.

### PS2458-4

For the definition of organic sub-facies types we used specific sub-macerals (Fig.4.4). In the lower core section (790 to 370 cmbsf) the OM is characterized by

terrigenous macerals with an average of 78 %. From the core basis to the depth of 690 cmbsf and from 470 to 550 cmbsf the sediments even contains terrigenous OM with amounts > 80 %. At the depth of 760 cmbsf and from 470 to 390 cmbsf there is a distinct increase in the amount of immature material from land plants (textinite and huminite) and freshwater alginite (*Botryococcus and Pediastrum*) which we define as sub-facies b. Freshwater algae are used as an indicator for freshwater input into the Laptev Sea (Kunz-Pirrung 1998, 1999; Boucsein and Stein 2000). The portions of huminite and textinite at the depth of 760 cmbsf reach 40 %, and 2.8 % of freshwater alginite was observed. At the depth of 470 to 390 cmbsf the amount of huminites and textinites is relatively high with an average of 21 % and a maximum of 34 % at 450 cmbsf. In this core section the portion of freshwater algae reaches an average value of 1.8 % with a maximum value of 3.5 % at 390 cmbsf.

organi	c subfacies types
а	>10% MOM
aa	>10% MOM + Dinoflagellate cysts
b	Freshwater algae (>2,5%) Huminite/Textinite (>30%)
С	Background fluorescence
d	>20%Vitrinite >5% Inertinite >1,5% Coal

Table 4.3: Classification of organic sub-facies used in this study.

At the depth of 690 to 570 cmbsf the sediments show a high portion of liptodetrinite (fragments of liptinite <10  $\mu$ m) causing background fluorescence (BGF) which we define as sub-facies c. Here, a quantification of macerals by counting is not possible because major portions of the liptinitic particles are too small. The OM mainly consists of liptodetrinite. Additionally, well preserved textinite, reworked alginite (marine and freshwater origin) and pollen grains, inertinite and vitrinite are found.



Marine OM with an amount of >10 % including dinoflagellate cysts (0.9 %) only occurs at the depth of 490 cmbsf and is defined as sub-facies aa. At 740 cmbsf marine OM reaches an amount of >10 % but without dinoflagellate cysts and is defined as sub-facies a.

The enhanced marine character of the OM in the upper core section (370 cmbsf to surface) indicated by the organic-geochemical parameters, is supported by the maceral data. At the depth of 370 cmbsf the amount of marine macerals increases from 3.5 % to 11.5 %. At the depth of 350 cmbsf a maximum of 21 % was observed including 2 % dinoflagellate cysts. The average of marine macerals in the core section from 370 to 180 cmbsf is 12.5 % including 0.9 % dinoflagellate cysts. In the uppermost core section (180 to 12.5 cmbsf) the portion of marine OM decreases while the amount of terrigenous OM increases. Only at the depths of 140 and 80 cmbsf marine OM values of >10 % occur.

Some higher amounts of coal fragments, vitrinite and inertinite were observed at the depths of 120, 100 and 40 cmbsf (Fig.4.4). These macerals are originated from terrigenous reworked and/or inert OM and are resistant to oxidation and degradation. We define this type of OM as sub-facies d.

At the surface marine OM increases again to a value of 20 % with a dinoflagellate cyst content of 1. 45% (sub-facies aa).

#### PS2725-5

In general, the maceral data support the organic-geochemical parameters, indicating the dominance of terrigenous OM throughout the core. Differences, however, are obvious when looking into detail. The results of maceral analysis (Fig.4.5) reveal high contents of mature and inert OM (>10 % inertinite, >30 % vitrinite; sub-facies d) in the sediments of the lowermost core section (470 to 430 cmbsf). At a depth of 430 cmbsf background fluorescence (subfacies c) was observed similar to that found in Core PS2458-4. In the upper core section (418 cmbsf to the surface) the OM is dominated by terrigenous macerals (Ø 65 %), however, relatively high amounts of marine macerals with an average value of

17 % and a maximum value of 27 % at 40 cmbsf were determined (subfacies a, aa). Dinoflagellate cysts are common (Ø 0.8 %) with a maximum value of 2.7 % at 40 cmbsf (sub-facies aa). The relatively high amounts of marine macerals in the upper core section correlate with high concentrations of short- chain fatty acids, indicating that a significant portion of marine OM is preserved in the shelf sediments.



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#### 4.6 Discussion

#### 4.6.1 Preservation of organic matter

The preservation of marine OM in sediments is mainly controlled by surface water productivity and sedimentation rates (e.g. Müller and Suess 1979; Stein 1990). Additionally, water depth, settling flux of OM to the sea-floor and presence of oxidants are important factors affecting organic carbon accumulation (c.f. Emerson et al. 1985; Berger et al. 1989; Pedersen and Calvert 1990).

In the sediments of Core PS2458-4 from the continental slope (water depth: 983 m) relatively high TOC-values of 1-1.5 % and partly well preserved macerals were observed. In comparison sediments from the central Arctic Ocean contain significantly lower TOC-values with an average of 0.5 % (Stein et. al 1999). This is explained by the fact that the permanent sea-ice cover in the Arctic Ocean reduces productivity of marine OM. Terrigenous OM accumulates mainly on the shelf and at the adjacent continental slope, reaching the deeper open-ocean basins only in minor portions.

In the Holocene sediments at the continental slope (Core PS2458-4) relatively high amounts of marine OM were observed. At a core depth of 350 cmbsf the marine portion of macerals increases to values up to 20 %. Additionally, increased concentrations of short-chain fatty acids, dinosterol, and brassicasterol are recorded. In general, these biomarkers are used as marine organic-carbon source indicators, however, with some restrictions (c.f. discussion in: Fahl and Stein 1999). For example, short-chain fatty acids cannot be used as a single tracer for distinguishing between marine and freshwater sources because they can also be synthesized by freshwater phytoplankton (Léveillé et al. 1997). As previously reported from maceral analysis on Laptev Sea surface sediments (Boucsein and Stein 2000) higher concentrations of short-chain fatty acids are measured in samples containing marine and freshwater alginite. For that reason, a comparison of the organic-geochemical parameters with the results from microscopy is essential for paleoenvironmental reconstructions in order to characterize and interpret the different OM sources. In the sediments of Core PS2458-4 the maceral

composition shows that higher concentrations of short-chain fatty acids correlate with higher amounts of marine macerals (Fig.4.6a). Moreover, the concentrations of brassicasterol and dinosterol in the sediments of Core PS2458-4 also correlate with the amounts of marine macerals (Fig.4.6b, c), indicating marine OM sources. The marine origin is also confirmed by palynological data showing a distinct increase in the amounts of dinoflagellate cysts (Fig.4.2, Matthiessen et al. subm.).



Fig.4.6a, b, c: a) Marine macerals (grain %) vs. short-chain fatty acids ( $\mu$ g/g TOC) in sediments of Core PS2458-4; b) Marine macerals (grain %) vs. dinosterol ( $\mu$ g/g TOC) in sediments of Core PS2458-4; c) Marine macerals (grain %) vs. brassicasterol ( $\mu$ g/g TOC) in sediments of Core PS2458-4.

Even if the amounts of dinoflagellate cysts in the sediments of Core PS2458-4 determined by means of macerals analysis are relatively low they can be used as a tracer for marine OM. From palynological studies on the same samples (Matthiessen et al. subm.) performed on kerogen concentrates (>6  $\mu$ m) we know that values of >10,000 specime/g sediment correlate with values of about 1.5 % for dinoflagellate cysts obtained by means of maceral analysis. Additionally, the occurrence of specific dinoflagellate cysts can be used as indicators for the

environmental conditions. For example, the dinoflagellate cyst *Operculodinium centrocarpum* (*Deflandre and Cookson* 1955) is advected to warmer water masses (cf. Kunz-Pirrung 1998) and its occurrence in the Holocene sediments at the continental slope of the Laptev Sea gives evidence for the influence of Atlantic water masses (Matthiessen et al. subm.). Since well-oxygenated bottom waters on the Laptev Sea shelf should impede accumulation of labile marine OM in the sediments (Boetius and Damm 1998) one explanation for the preservation of marine OM in Core PS2458-4 could be the high sedimentation rate (100cm/ky) during Holocene times (Fig.4.7a) raising the burial rate of organic carbon



Fig.4.7a: Total organic carbon contents (%), accumulation rates of total organic carbon (gC/cm<sup>2</sup>/cal-ky), linear sedimentation rates (cm/cal-ky), and distribution of the main maceral groups (grain %) in Core PS2458-4. AMS-<sup>14</sup>C datings are taken from Spielhagen et al. (subm.), dry bulk density from Nørgaard-Petersen (unpubl. data).

and reducing its residence time in an oxidative environment. Additionally, the higher portions of marine OM may be the result of an increased productivity in the surface water layer.

In the Holocene sediments of the shelf (core PS2725-5; water depth: 77 m) also relatively high portions of marine OM are preserved as documented in the maceral composition (marine macerals:  $\emptyset$  17%) and increased concentrations of fatty acids (Fig.4.3). This can be explained by a higher productivity due to an ample fluvial nutrient supply near the coast and by a shorter settling time for particulate OM due to the shallow water depth. Furthermore, the exceptional high sedimentation rates (1,000 cm/ky) resulting in accumulation rates of organic carbon up to 12.0 gC/cm<sup>2</sup>/ky in the early Holocene (Fig.4.7b), are supposed to be a major factor causing the good preservation of marine OM.



Fig.4.7b: Total organic carbon contents (%), accumulation rates of total organic carbon (gC/cm<sup>2</sup>/cal-ky), linear sedimentation rates (cm/cal-ky) and distribution of the main maceral groups (grain %) in Core PS2725-5.

### 4.6.2 Reconstruction of the paleoenvironment during the last ~15,000 years

During the Last Glacial the Laptev Sea shelf was exposed due to the lowered sealevel (about 120 m, Fairbanks 1989), and several studies revealed that during the Last Glacial Maximum (LGM) there was no large ice sheet in this area (e.g. Dunayev and Pavlidis 1988; Hahne and Melles 1997; Kleiber and Niessen 1999). For the Weichselian sea-level low stand evidence for active rivers on the exposed shelf draining freshwater and sediment into the Arctic Ocean, are given by high resolution seismic profiling data (Kleiber and Niessen 1999). Data on the vegetation and climatic history of the last 17,000 years based on palynological studies in a core from the Lama Lake (Taymyr Peninsula, Western Siberia) also suggest that there was no glaciation during this time (Hahne and Melles 1997). Due to the lack of a major LGM ice sheet, the post-glacial sea-level rise can be considered as eustatic and the global sea-level curve of Fairbanks (1989) can be applied for the Laptev Sea area. We interpret the deposition of the different organic sub-facies types in core PS2458-4 in relationship to the global sea-level curve of Fairbanks (1989).

The environmental and climatic history of Siberia during Holocene times and the Last Glacial are well described by Khotinsky and Klimanov (1997), Velichko et al. (1997), Hahne and Melles (1997) and Monserud et al. (1998). According to these studies the Weichselian/ Holocene boundary is determined at 10,300 yrs.BP, and an attenuated Younger Dryas event occurs from 11,000-10,300 yrs.BP. A Mid-Holocene warming is recognized throughout northern Eurasia (Monserud et al. 1998).

The marine environment of the Laptev Sea shelf and the adjacent continental slope during the early and Mid-Holocene is described by Bauch et al. (1999), Behrends et al. (1999), Cremer (1999), Kunz-Pirrung (1999), Müller and Stein (subm.), Peregovich et al. (1999) and Stein and Fahl (2000). In comparison only little is known, however, about the marine environment during the transition time from the Last Glacial to the Holocene. Based on the information from the organic carbon composition in surface sediments together with the results from sediment cores we are able to reveal new results about the depositional environment, origin of terrigenous OM from the hinterland, and surface-water productivity for this time period.

The changes in organic carbon composition are related (1) to sea-level rise since the LGM, (2) variations in river discharge, (3) surface-water productivity, and (4) Atlantic water inflow along the Eurasian continental margin.

#### Late Weichselian

Until now datings are absent in the lowermost core section of core PS2458-4 making an interpretation difficult. The extrapolated age at the basis of the core is

about 15,000 yrs.BP. The deposition of sub-facies a and b in this lowermost core section (760 to 740 cmbsf; ~13,500 yrs.BP) may display the first step of deglaciation (Termination 1a). A first warming of the Siberian hinterland initiated by the increasing insolation at the end of marine isotope stage 2 (MIS2) (Berger 1978) probably causes melting of snow fields and small glaciers. As reported from studies on surface sediments most of the terrigenous and freshwater OM accumulates near the coast and the river mouths (Kuptsov and Lisitzin 1996). Mean Holocene accumulation rates of organic carbon in the inner Laptev Sea vary between 0.14 and 2.7 gC/cm<sup>2</sup>/ky while towards the lower slope the values decrease to around 0.02 gC/cm<sup>2</sup>/ky (Fig.4.7a,b). During Termination 1a, however, freshwater OM accumulates at the position of Core PS2458-4 far in the north whereas the amount of freshwater supply is supposed to be low during that time. According to Holmes and Creager (1974) the mouth of the Lena River is supposed to be much further north than today because of the lowered sea-level, i.e., about 300 km north-west of the present delta near to the slope. The farther north position of the Lena River mouth could be an explanation for the deposition of organic subfacies type b at the continental slope. Furthermore, the deposition of organic subfacies type a during that time may result from a reduction of sea-ice cover caused by the first warming and triggering primary production of marine OM in the surface water layer.

#### ~13,500 - 12,000 yrs.BP:

During that time a significant change in OM composition is recorded. The OM is dominated by immature liptinitic (fluorescing) material, in this case, of textinites, liptinites and liptodetrinite (detritus <10  $\mu$ m) causing background-fluorescence (BGF). The occurrence of well preserved textinite indicates short distance transport of the OM. We further observed reworked pollen grains and reworked alginites of freshwater and marine origin characterized by yellow to orange fluorescence colours, inertinite and vitrinite, all indicating resuspension of OM. Additionally, recent freshwater alginite (showing green fluorescence colours) are found indicating the fluvial influence. We define this type of OM as organic sub-facies type c. As possible sources for this mixture of immature liptinitic material with reworked mainly liptinitic material, we assume plants of the tundra vegetation of the shelf and terrestrial shelf sediments. As supported by founds of bones from

e.g., mammoth, reindeer, horse and bison in deposits of the "ice-complex" (Kuzima et al. 1999) the Laptev Sea shelf was inhabited by this mammals during the late Pleistocene and display that this area was an open grassland-tundrabiotop (pers.comm C.Siegert, AWI Potsdam, 1999). The release of this OM due to defrosting of the permafrost soils and freshwater discharge by melting of small glaciers and snow fields in the Siberian hinterland, may have caused transport and sedimentation of OM of sub-facies type c.

During the time from 12,000 - 10,400 yrs.BP the OM composition is dominated by terrigenous macerals (>80 %) and liptodetrinite. Marine OM is not preserved in the sediments indicating that primary productivity was not significantly increased during that time. Probably this deposition document the cooling event of the Younger Dryas (Y.D.) as reported by pollen data from Hahne and Melles (1997) for the time slice of 11,000-10,300 yrs.BP on Taymyr Peninsula.

We found the dinoflagellate cyst *Operculodinium centrocarpum* at a depth of 490 cmbsf in Core PS2458-4 corresponding to an interpolated age of around 10,400 yrs.BP. This dinoflagellate cyst is advected to warmer water masses and its occurrence together with an increase in marine OM gives evidence for the first Atlantic water masses reaching the eastern continental slope of the Laptev Sea after the Last Glacial (Matthiessen et al. subm.).

#### Holocene (~10,300 yrs.BP to Present):

In the early Holocene at ~9,800 yrs.BP an enlarged freshwater discharge to the Laptev Sea continental margin is documented by a remarkable increase in the amounts of freshwater alginite and immature land plant material, defined as sub-facies type b (Fig.4.4). An increased freshwater supply at this time is also reported by studies on clay mineralogy and heavy minerals performed on the same sediment record (Müller 1999; Behrends 1999).

As possible freshwater sources we assume an increased precipitation in Holocene times (Monserud et al. 1998) together with the post-glacial warming causing melting of small glaciers and snow fields in the hinterland. Additionally, the shallow

Laptev Sea shelf (average water depth: 50-60 m) became flooded for the first time after the Last Glacial. The sea-level rose rapidly from 60 m to 20 m below today and may have triggered defrosting of the permafrost soils on the shelf, leading to a release of large freshwater quantities. Moreover, the transgression caused large-scale coastal / sea floor erosion and resuspension of terrigenous OM. This is documented in enhanced amounts of reworked mature and inert OM at the basis of Core PS2725-5 (sub-facies d; Fig.4.5).

Both processes, increased erosion and increased fluvial supply, may explain the high accumulation rates of mainly terrigenous organic carbon reaching values of up to 12.0 gC/cm<sup>2</sup>/ky on the outer shelf as described for Core PS2725-5 (Fig.4.7b). The accumulation rates of organic carbon near the upper slope at the position of Core PS2458-4 also reaches maximum values up to 2.0 gC/cm<sup>2</sup>/ky during the early Holocene (Fig.4.7a).

Since ~9,500 - 8,000 yrs.BP modern environmental conditions were established as documented in increased amounts of marine macerals in both cores (sub-facies type a), marine biomarkers (dinosterol, brassicasterol, short-chain fatty acids) and dinoflagellate cysts (Fig.4.2). The occurrence of specific dinoflagellate cysts shown in Figure 4.2 indicates the influence of warmer Atlantic water masses at the continental margin. Marine primary productivity can be explained by an adequate nutrient supply by the Siberian rivers, partly ice-free conditions and melting processes which induce phytoplankton growth. Increased marine OM production near ice edges are reported by Strömberg (1989) and Legendre et al. (1992) and explained by positive conditions for phytoplankton blooms such as light, ample nutrient supply, and vertical stability of the water column. Additionally, the high sedimentation rates support the preservation of marine OM (c.f. Stein 1991).

We suppose that the increase in primary productivity along the Laptev Sea continental margin at 9,500 yrs.BP is triggered by both increased fluvial nutrient supply and increased inflow of Atlantic water masses. As described by Hald et al. (1999) an enlarged influence of warm Atlantic water masses occurred around 9,500 yrs.BP further west in the St.Anna Trough (Kara Sea) which is documented in increased production of foraminifera and bivalves. The increase of specific

dinoflagellate cysts in Core PS2458-4 (Fig.4.2) supports the idea of increased influence of warmer Atlantic water masses at the Laptev Sea continental slope.

The uppermost unit of Core PS2458-4 probably spanning the last 200 yrs.BP displays increased portions of marine OM. This presumably reflects modern environmental conditions with open-water conditions, fluvial nutrient supply and phytoplankton blooms near the ice edge.

### 4.7 Summary and conclusions

Our interpretation of the environmental conditions in the Laptev Sea during the transition time from the Last Glacial to the Holocene can be summarized as follows:

- Termination 1a: The first step of deglaciation at ~13,500 yrs.BP is documented in the deposition of marine and freshwater OM (sub-facies a and b).
- Until ~12,000 yrs.BP the change in OM composition (sub-facies c) is interpreted as the subsequently defrosting of permafrost soils.
- Termination 1b: First influence of Atlantic Water masses at around 10,400 yrs.BP is indicated by an increase in marine OM and the occurrence of the dinoflagellate cyst *Operculodinium centrocarpum* which is advected to warmer water masses.
- At the beginning of the Holocene a significant change in OM composition which is characterized by the sedimentation of freshwater alginite and immature plant material, is interpreted as an increased influence of the Lena River discharge.
- We assume modern marine conditions since ~9,500 8,000 yrs.BP. This is documented in the deposition of marine macerals (sub-facies a), biomarkers and dinoflagellate cysts indicating increased primary productivity, and is explained by an increased inflow of Atlantic water masses and fluvial nutrient supply.

5. New insights in organic matter deposition along the Kara and Laptev seas continental margin (eastern Arctic Ocean) during the Late Quaternary: Evidence from organic-geochemical and petrographical data.

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### 5.1 Abstract

Organic petrologic studies (maceral analysis, organic-geochemical bulkparameters) were performed on five sediment records along the Eurasian continental margin for a reconstruction of the environmental changes during the last ~15.0 ka. The stratigraphy of the cores is based on a chronological framework combining AMS-<sup>14</sup>C datings, magnetic susceptibility and lithostratigraphic characteristics. Variations in terrigenous, freshwater and marine organic matter deposition indicating paleoceanographic and paleoclimatic changes have been determined during the transition from the Last Glacial to the Holocene.

During the Last Glacial diamictons characterized by reworked terrigenous organic matter (TOM) were deposited in the St. Anna Trough (northern Kara Sea), indicating the advance of the Svalbard-Barents-Sea-ice-sheet to the shelf edge. In contrast, the Laptev Sea shelf further was not covered by an ice-sheet, but fallen dry because of the lowered sea level. During deglaciation, deposition of marine organic matter (MOM) increased due to enhanced surface-water productivity caused by the influence of Atlantic water masses. The occurrence of freshwater alginite gives evidence for river discharge after the Late Weichselian Glaciation. At the eastern Laptev Sea continental slope first influence of Atlantic water masses has been recorded at ~10.4 <sup>14</sup>C ka indicated by an increase of MOM and the occurrence of the dinoflagellate cyst *Operculodinium centrocarpum*.

At the beginning of the Holocene an increased freshwater and sediment discharge by the Siberian rivers lead to high sedimentation rates on the Kara Sea shelf and the Laptev Sea with the adjacent continental margin. Evidence for an intensification of the freshwater discharge to the Laptev Sea in the Holocene are given at ~9.8-9.1 ka, ~5.0 ka and ~2.5 ka. In the Kara Sea an increased freshwater signal is found at ~8.5 ka and ~5.0 ka.

Moreover, higher portions of MOM were accumulated in the St. Anna Trough area and at the Eurasian continental margin at ~9.5-7.3 ka, ~4.4-3.8 ka and ~2.7-2.5 ka and are explained by temporally ice-free conditions and surface-water productivity triggered by an increased inflow of Atlantic water masses.

#### 5.2 Introduction

The hydrographic system of the eastern Arctic Ocean is affected by the inflow of Atlantic water masses and the huge freshwater supply from the Laptev and Kara seas (e.g. Meincke et al. 1997; Aagaard and Carmack 1989) (Fig.5.1).

The Atlantic water flow system splits into two branches, one part crosses the Barents and Kara Sea shelves and enters the Nansen Basin via the St. Anna Trough. The other part continues as the West Spitsbergen Current towards the Fram Strait, and flows eastward along the continental slope (Rudels et al. 1994; Schauer et al. 1997; cf. Fig.5.1). As a counterpart low-saline polar water masses are transported via the Transpolar Drift and the East Greenland Current towards the Atlantic Ocean.

About 60 % of the total Arctic continental runoff is supplied by the rivers draining into the Laptev and Kara seas. This supply of freshwater is essential for the sustainment of the strong stratification of the near-surface water masses of the Arctic Ocean and for sea-ice formation (Aagaard and Carmack 1989). The melting and freezing of sea ice affects the surface albedo, the energy balance, the moisture supply and thus, the ocean-ice-atmosphere interaction (Hibler 1989; Carmack et al. 1995). Additionally, brine formation by salt enrichment during the freezing of sea water leads to water of high density, sinking as plumes into the deeper oceanic layers (Midttun 1985; Jones et al. 1995) the area of the St. Anna Trough and the region around Severnaya Zemlya are possible source areas for such deep water formation.


Fig.5.1: Study area with core locations and schematically representation of a) the surface water circulation (after Gordienko and Laktionov 1969), b) river discharge, c) the intermediate and bottom circulation pattern (Rudels et al. 1994; Jones et al. 1995), d) submerging Atlantic surface water (after Gordienko and Laktionov 1969) and, e) Arctic bottom water formation (Jones et al. 1995). The dotted line shows the maximum extend of the Late Weichselian Glaciation according to Svendsen et al. (1999), the black line the ice-sheet extend after Kleiber and Niessen (subm.). SZ = Severnaya Zemlya, NZ = Novaya Zemlya, K = Kotelnyy, BS = Barents Sea, KS = Kara Sea, LS = Laptev Sea, ES = East Siberian Sea

a) surface water circulation pattern

d) submerging Atlantic surface water >>e) Arctic bottom water formation

b) River discharge

c) intermediate and bottom water circulation pattern

The Siberian rivers transport huge quantities of suspended and particulate organic matter (POM) into the Laptev and Kara seas (Martin et al. 1993; Gordeev et al. 1996; Rachold and Hubberten 1999) where it is deposited and/or further transported by sea ice and turbidites towards the open ocean (Nürnberg et al. 1994; Lindemann 1998; Stein et al. 1999).

Organic matter (OM), preserved in marine sediment records, reveal information about the environmental conditions, e.g. terrigenous supply and surface-water productivity. Studies on, for example, Quaternary marine sediments from the Norwegian-Greenland Sea have shown that organic petrography is a useful tool for characterization of the organic matter fraction in order to interpret paleoceanographic and paleoclimatic changes through time (Hölemann and Henrich 1994; Wagner and Henrich 1994). Moreover, organic-geochemical analysis and organic petrography carried out on surface sediments from the Kara and Laptev Seas and sediment cores from the eastern Laptev Sea continental margin have shown that the exclusively use of organic-geochemical parameters in these shelf sediments may reveal contradictory information about the organic-matter sources. Thus, microscopical examinations are needed to get more precise information about the organic matter composition.

The OM in the Kara and Laptev Sea surface sediments and sediment records is mainly of terrigenous origin but, nevertheless, significant amounts of MOM are preserved indicating primary productivity in the water column (Fahl and Stein 1997, 1999; Boucsein et al. 1999; Boucsein and Stein 2000). Furthermore, the occurrence of chloroccocalean algae, transported by the rivers onto the shelf, can be used as an indicator for freshwater supply (Kunz-Pirrung 1999) and additionally, as tracer for river-runoff in paleoenvironmental reconstructions (Matthiessen et al., subm. to Int. Journal of Earth Science).

Several studies on marine sediment records considering late Quaternary paleoenvironmental changes in the northern Barents Sea and the St. Anna Trough were performed during the last years (e.g. Lubinski et al. 1996; Polyak et al. 1997; Knies and Stein 1998: Knies et al. 1999; Hald et al. 1999; Kleiber et al., subm.). The main objective of this study is to compare the environmental changes of the northern Kara Sea vs. the Laptev Sea (St. Anna Trough area) during the last ~13.0 ka. New data from organic petrography (maceral analysis) and organicgeochemical bulk parameters (TOC, HI-values) are presented, carried out on sediment cores located in the area of the St. Anna Trough and along the northern Kara and Laptev seas continental margin (Fig.5.1). Furthermore, we show that the application of maceral analysis gives detailed information about the OM composition (marine/freshwater/terrigenous) and enable interpretations in terms of paleoriver discharge, changes in the Atlantic water inflow, surface-water productivity and, the supply of terrigenous OM.

#### 5.3 Material / Methods

Our study was performed on sediment cores PL9408 and PL9460 taken during RV "Professor Logachev" Expedition in 1994 (Ivanov et al. 1999) and sediment cores PS2476-3, PS2458-4 and PS2742-5 recovered during RV "Polarstern" Expeditions ARK-IX/4 in 1993 (Fütterer 1994) and ARK-XI/1 in 1995 (Rachor 1997) (Table 5.1). For detailed core descriptions we refer to AWI web page "www.pangaea.de".

Station	Latitude	Longitude	Depth(m)
PL9408 SL	81°77.1´N	67°45.6´E	617
PL9460 SL	76°99.4´N	70°06.2´E	572
PS2742-5 SL	80°78.8´N	103°82.6′E	1890
PS2476-3 SL	77°38.9´N	118°19.4´E	521
PS2458-4 KAL	78°16.6′N	133°39.8´E	983

Table 5.1: Site locations and water depths of the studied cores.

### 5.3.1 Maceral analysis

Maceral analysis was performed on bulk-sediment samples in oil-immersion with a Zeiss-Axiophot microscope using incident light and, additionally, fluorescent light (wavelength: 395-440 nm, blue-light-filter: Zeiss No.05).

According to the nomenclature described by Taylor et al. (1998) macerals are distinguished into the three main groups vitrinite/huminite, inertinite and liptinite, and several sub-groups. For studying recent marine sediments a modification of the maceral concept has been done by e.g. Wagner (1993), Wagner and Henrich

(1994) and, Boucsein and Stein (2000) because the classic maceral nomenclature was developed for coals and organic-rich sediments rather than for the studied sediments. With reference to the environment and different biological sources we distinguished between terrigenous, freshwater and marine macerals (Boucsein and Stein 2000).

Counting was performed by 2D-scanning at 1000x magnification. At least about 200-300 macerals were counted and calculated as "grain %". The grain length of each maceral was estimated in order to prevent that small particles are over-estimated. In the succeeding evaluation the different sizes were normalized to the grain length of 20  $\mu$ m. Nevertheless, quantification of macerals by counting has to be considered as "semi-quantitative" because the method depends on the resolution of light microscopes. We are only able to quantify particles > 2  $\mu$ m and, quantification of finely disseminated OM is not possible. For a detailed discussion of this method we refer to Boucsein and Stein (2000).

### 5.3.2 Organic-geochemical bulk parameters

Total organic carbon (TOC) is determined on both ground bulk samples and HCItreated carbonate-free sediment samples by means of a Heraeus CHN-O-RAPID element analyser. For more details concerning this method see e.g. Stein (1991, and references therein). The Hydrogen index (HI) was determined using Rock-Eval Pyrolysis as described by Espitalié et al. (1977). The HI-value corresponds to the quantity of pyrolyzable hydrocarbons per gram TOC (mgHC/gTOC). In immature carbon-rich (TOC > 0.5 %) sediments, HI values <100 mgHC/gTOC are typical for terrigenous OM (TOM) (kerogen type III), whereas HI values of 300 to 800 mgHC/gTOC (kerogen type II and I) result from alginites of marine and/or lacustrine origin mixed with terrestrial macerals (Tissot and Welte 1984; Taylor et al. 1998).

### 5.4 Lithostratigraphy and Chronology

Until now, high-resolution stratigraphic frameworks for Quaternary deposits in the eastern Arctic Ocean are still rare because of limited occurrence of microfossils.



Fig.5.2: Age model used for the studies cores based on lithological characteristics, magnetic susceptibility and AMS-<sup>14</sup>C datings (see table 5.2).

Thus, stable isotope records and radiocarbon datings are sparse (Knies et al. 2000). However, in order to interpret OM accumulation for paleoenvironmental reconstructions a stratigraphy as precise as possible is necessary. Thus, in this study we use a combined chronological framework based on AMS-<sup>14</sup>C datings, magnetic susceptibility records and lithological characteristics (Fig.5.2). Magnetic susceptibility is a useful tool for core correlation (e.g. Fütterer 1994, Rachor 1997). While the values of magnetic susceptibility are relatively high in sediments of the Last Glacial/ post glacial a distinct decrease at the beginning of the Holocene is

typical for sediment cores from the Laptev Sea continental margin (e.g. Stein et al. 1999). Moreover, we use the chronology and lithological characteristics of sediment records from the Kara Sea described in earlier publications (Polyak et al. 1997, Hald et al. 1999) for a correlation with the studied cores.

Based on x-ray radiographs we distinguish three lithological units in Core PL9408 and Core PL9460 (Stein and Knies 1999). In Core PL9408 (Fig.5.2, 5.3a) Unit III (bottom of core to about 120 cmbsf) consists of a massive diamicton with high amounts of coarse-grained material. Unit II (120-32 cmbsf) is characterized by minor amounts of ice-rafted detritus and an alternation of homogenous mud and laminated intervals. The sediments of Unit I (32 cmbsf to the surface) are bioturbated. In Core PL9460 (Fig.5.2, 5.3b) Unit III (bottom of core to 341 cmbsf) is characterized by a massive diamicton with high amounts of coarse-grained material, Unit II (341-318 cmbsf) consists of laminated mud with ice-rafted detritus, and Unit I (318 cmbsf to the surface) is composed of bioturbated mud. The sediment colours of Core PL9408 and Core PL9460 vary between brownish and dark grey and between dark grey with black dots and black, respectively.

The cores can be correlated with nearby sediment cores studied and dated by Polyak et al. (1997) and Hald et al. (1999). According to these authors the diamictons in the St. Anna Trough reflect the late Weichselian glaciation. Deglaciation is supposed to start prior to 13.3 ka and is documented in the deposition of the intermediate laminated sediment layers (Unit II). Thus, they infer a minimum age of 13.3 ka for the Unit III/II boundary. Unit I is assumed to be deposited after the complete retreat of the ice-sheet at ~10.0 ka.

The chronological framework of Core PS2742-5 and Core PS2476-3 was established by Stein and Fahl (2000) using magnetic susceptibility records (Fig.5.2) (Fütterer 1994; Rachor 1997) and AMS-<sup>14</sup>C datings (see Table 5.2). Notably, the decrease in magnetic susceptibility in Core PS2778 occurred at an AMS-<sup>14</sup>C age of 10.070 ka and marks the Holocene boundary (Fig.5.2). Thus, the decrease in magnetic susceptibility in the lower part of cores PS2742-5 and PS2476-3 (Fig.5.2) is correlated with the Holocene boundary. One single AMS-<sup>14</sup>C

age of 12.5  $^{14}$ C ka rather reflects the boundary between the marine isotope stage (MIS) 1 and 2 in PS2742-5.

According to lithological characteristics and magnetic susceptibility Core PS2742-5 is divided into three units (Fig.5.3): Unit III consisting of silty clay and a diamicton layer (bottom to 343 cmbsf), characterized by large dropstones, reflects the last glaciation. Unit II (343-295 cmbsf) represents the transition time from the Last Glacial to the Holocene, and Unit I (295 cmbsf to surface) represents the Holocene.

Core	Depth	Age <sup>14</sup> C BP	Age <sup>14</sup> C BP	References
	( <b>cm</b> )		(440 yrs.reservoir	
			corrected)	
PS2458	201	7980	7980 ±110	Spielhagen et al. (subm.)
PS2458	252	8830	8390 ±55	Spielhagen et al. (subm.)
PS2458	294	9030	8590 ±100	Spielhagen et al. (subm.)
PS2458	335	9340	8900 ±120	Spielhagen et al. (subm.)
PS2458	369	10020	9580 ±70	Spielhagen et al. (subm.)
PS2458	467	10600	10160 ±75	Spielhagen et al. (subm.)
PS2458	530	11560	11120 ±100	Spielhagen et al. (subm.)
PS2458	578	12270	11830 ±65	Spielhagen et al. (subm.)
PS2458	625	12750	12310 ±150	Spielhagen et al. (subm.)
PS2742	324	12910	12470 ±80	Stein and Fahl (2000)

Table 5.2: AMS-<sup>14</sup>C datings of Core PS2458-4 from Spielhagen et al. (subm.) and of Core PS2742-5 from Stein and Fahl (2000).

Core PS2476-3 (Fig.5.4a) consists of dark brown to dark gray silty clay and is bioturbated throughout the entire core. Based on magnetic susceptibility the sedimentary record is divided into two units (Unit I: bottom to 550 cmbsf; Unit II: 550 cmbsf to surface) and represents the time interval from the last deglaciation until the Holocene.

Core PS2458-4 (Fig.5.4b) consists of a 8 m long sedimentary sequence of very dark olive-gray silty clay of dominantly terrigenous origin (Fütterer 1994; Müller 1999). The uppermost 25 cmbsf taken from the undisturbed box core PS2458-3 recovered from the same position as core PS2458-4, are of dark brown to very dark brown colour. Bivalves were used for AMS-14C dating (Spielhagen et al.,

subm.; table 5.2). At a depth of 100 cmbsf there is evidence of a hiatus lasting 6-8,000 yrs. due to non-deposition or erosion (Spielhagen et al., subm.).

# 5.5 Results

We used organic-geochemical bulk parameters (TOC-values and Hydrogen Index (HI)) to get first information about the content and composition of OM in the sediments. More detailed information about the different sources of the particulate OM (POM) can be obtained by means of maceral analysis.

In general, POM identified in incident light, mainly consist of terrigenous macerals such as vitrinites/huminites, inertinites and detritus of these macerals (grain size <10 µm). Also, liptinites of terrigenous origin, e.g., pollen grains, cutinites and freshwater alginite, are recorded. As freshwater alginite we define chloroccocalean algae, such as Pediastrum and Botryococcus (cf. Batten and Grenfell 1996a,b). In river-influenced shelf areas like the Eurasian shelf seas, these freshwater adapted algae are useful tracers for river-runoff (Matthiessen et al., subm. to Int. Journal of Earth Science; Kunz-Pirrung 1998). The marine macerals consist of lamalginite, dinoflagellate cysts and their fragments (marine liptodetrinite, >10 µm). These macerals can be used as indicators for marine primary production (Boucsein and Stein 2000). As described in palynological studies of surface sediments from the Laptev Sea (Kunz-Pirrung 1999) and of sediment records from the Norwegian-Greenland-Sea (Matthiessen 1995) the occurrence of specific dinoflagellate cysts can be used as indicators for environmental conditions. For example the dinoflagellate cysts Operculodinium centrocarpum (Deflandre and Cookson 1955) is advected to warmer water masses (cf. Kunz-Pirrung 1998) and thus, its occurrence in Holocene sediments at the continental slope of the Laptev Sea gives evidence for the influence of Atlantic water masses (Matthiessen et al. subm.; Boucsein et al. in press).



Fig.5.3a: Maceral composition in grain %, bulk parameters (TOC (%), HI-values (mgHC/gTOC))of core PL9408 from the St. Anna Trough.

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### St. Anna Trough area (northern Kara Sea)

#### PL9408 and PL9460

According to the organic-geochemical bulk parameters the sedimentary sequence of Core PL9408 consists of two intervals (Fig.5.3a). Below 120 cmbsf (Unit III), the TOC content is relatively high with values ranging from 1.1 to 1.7 %, whereas the HI values are very low (< 60 mgHC/gTOC). In the upper part (Units II-I) TOC values vary between 0.4 and 0.9 %, increasing to 1.3 % at the surface. Furthermore, the HI values are increased in the upper section, reaching a maximum of 233 mgHC/gTOC at 85 cmbsf.

In the sediments of Core PL9460, TOC values are lowest in Unit III (<0.6 %), increasing up to 0.9 % in Unit II, and reaching maximum values of 1.3 to 2.3 % in Unit I (Fig.5.3b). The HI values are low in the two lower units (< 80 mgHC/gTOC) and increase to values between 100 and 150 mgHC/gTOC in Unit I. A maximum value of 282 mgHC/gTOC occurs at the surface.

Maceral analysis shows that the POM in the sediments of cores PL9460 and PL9408 from the St. Anna Trough area is mainly of terrigenous origin (Ø: 80-85%) (Fig.5.3a,b). Variations exist, however, when looking at the distribution of specific maceral groups. The POM in the diamicton at the basis of cores PL9460 and PL9408 (Unit III) is characterized by relatively high amounts of coal fragments (PL9460: 5 %/ PL9408: 3 %) and inertinite (5.9 %/ 2.8 %). Additionally, freshwater alginite occur (2.7 %/ 2 %). Relatively high amounts of liptodetrinite (16 %) were observed in Core PL9460. MOM is absent in Unit III of both cores. Marine macerals including lamalginite, marine liptinite and partially dinoflagellate cysts occur first in the sediments of Unit II (transition time), with values up to 12 % in Core PL9408.

In both cores the amounts of freshwater alginite in Unit II are relatively small (<1 %). Textinites and huminites which are originated from immature landplant material occur throughout the sedimentary sequences, showing a remarkable increase in the sediments of Unit II of Core PL9408 (up to 39 %).

In the Holocene sediments of Core PL9408 the amounts of MOM are relatively small (8 %) further decreasing towards the surface. On the other hand, the



Fig.5.3b: Maceral composition in grain %, bulk parameters (TOC (%), HI-values (mgHC/gTOC)) of core PL9460 from the St. Anna Trough Area.

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portions of freshwater alginite increase up to a value of 2.7 % at the surface. The dinoflagellate cyst *Operculodinium centrocarpum* was observed at the depth of 25 cmbsf. In comparison, the amounts of MOM are about 10 % in the Holocene sediments of Core PL9460, increasing towards the surface to a value of 15 %. Additionally, we observed the dinoflagellate cyst *Operculodinium centrocarpum* at the depth of 240 and 120 cmbsf.

## Continental slope NE Severnaya Zemlya (NESZ)

### PS2742-5

Unit III of Core PS2742-5 (Fig.5.4) is characterized by very low TOC contents (<0.3 %) which increase in Unit II to values between 0.4 to 1.0 %. The highest TOC values were found in Unit I (1-1.3 %). The HI values are relatively high in Units II-I, reaching maxima of > 250 mgHC/gTOC at 300, 111, 102, 78 and, 21 cmbsf.

The amounts of terrigenous macerals in the sediment record (Fig.5.4) range from 76 to 94 %. In the diamicton (Unit III) higher amounts of resistant OM (inertinite: 4-5%) are found but coal fragments were absent. In the lowest section of Unit III and Unit II MOM only occurs in minor portions (<3%).

At the boundary between Unit II and the Holocene sediments of Unit I a remarkable increase in freshwater alginite (up to 2.6 %) and MOM (up to 9 %) was observed, correlating with a decrease of magnetic susceptibility (Fig.5.4).

Additionally, the amounts of textinite and huminite increase in Unit I at 182 cmbsf (22 %). Higher portions of coal fragments (1.7 %) are recorded at 221 cmbsf and at the surface. The dinoflagellate cyst *Operculodinium centrocarpum* was observed in the Holocene sediments at 182, 121 and 40 cmbsf.

## Laptev Sea continental margin

## PS2476-4

The sediments of Core PS2476-4 from the western Laptev Sea continental slope represent the transition time from the Last Glacial to the Holocene (bottom to 550 cmbsf) and the Holocene (550 cmbsf to the surface) (Fig.5.5a).



Fig.5.4: Maceral composition in grain % of core PS2742-5 from NEZS continental margin. Bulk parameters (TOC (%), HI-values (mgHC/gTOC)).

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In the lowest core section (bottom to 600 cmbsf) TOC values are very low (<0.5 %) increasing at 580 cmbsf to values about 1 %. Furthermore, the HI values are relatively high with values up to 300 mgHC/gTOC.

Maceral analysis shows that the POM in the lowest core section is dominated by terrigenous macerals (up to 95%) including relatively high amounts of vitrinite (max.: 13%) and inertinite (max.: 7%). MOM occur only in minor amounts (2-6%). At 591 cmbsf background-fluorescence caused by a dominance of liptodetrinite was observed. Here, a quantification of macerals by counting is not possible because major portions of the liptinitic particles are too small.

At the boundary to the Holocene (550 cmbsf) a distinct increase in MOM up to values of about 10 % and in freshwater alginite (up to 2.6 %) can be recognized correlating with a decrease of magnetic susceptibility similar to the results from Core PS2742-5. Throughout the Holocene sediments MOM is recorded with values about 10 %, but decreasing towards the surface. At the depths of 499, 301 and 149 cmbsf the portions of freshwater alginite show distinct peaks.

### PS2458-4

The results from organic-geochemical analysis (bulk parameters, biomarker) and organic petrography of the sediments of core PS2458-4 from the eastern Laptev Sea continental margin are described in detail by Fahl and Stein (1999) and Boucsein et al. (in press). In this study we concentrate on the distribution of specific macerals and bulk parameters as shown in Figure 5.5b for a comparison with the sediment cores described before. The TOC-values in this core are relatively high, ranging from 1-1,5 %. In the lower core section the HI-values are low (<100 mg/HC/g TOC), but with increased values in the upper part. Maceral composition show more variations. In the lower core sections at a depth of 760 cmbsf increased amounts of freshwater alginite, textinite/ huminite and MOM is determined. At the depth of 690 to 570 cmbsf the OM is dominated by fluorescing liptinitic particles, causing background-fluorescence. The portions of freshwater alginite and textinite/ huminite increase at the depth of 470 to 390 cmbsf. The upper core section (370 cmbsf to surface) is characterised by increased portions of MOM and dinoflagellate cysts.



Fig.5.5b: Maceral composition in grain % and bulk parameters (TOC (%), HI-values (mgHC/gTOC)) of core PS2458-4 from the eastern Laptev Sea continental margin. AMS-<sup>14</sup>C datings are taken from Spielhagen et al. (subm., table 5.2).

## 5.6 Discussion

## 5.6.1 Late Weichselian glacial history of the Eurasian shelves

The actual state of reconstructions concerning the extent of the Late Weichselian ice sheets is given by the summary paper of Svendsen et al. (1999, and references therein). According to the authors the extent of the Svalbard-Barents-Sea-ice-sheet (SBIS) was restricted to the western part of the Kara Sea and the Barents Sea while the Russian mainland was not covered by a large ice sheet (Fig.5.1). The St. Anna Trough (northwestern Kara Sea) is supposed to be filled

with grounded glacier ice (Polyak et al. 1997; Hald et al. 1999 and references therein) while it is still under discussion whether the southern part of the Kara Sea was covered by an ice-sheet or not (e.g. Siegert et al. 1999, Velichko et al. 1997). Recent field studies from the Yamal Peninsula (southwestern Kara Sea), however, give evidence that this area was not affected by an ice sheet during the late Weichselian glaciation (Forman et al. 1999). Severnaya Zemlya (SZ) was covered only by local ice caps as postulated from IRD records from the northern Severnaya Zemlya continental margin (Knies et al. 2000) and radiocarbon datings on mammoth tusks from Severnaya Zemlya (Svendsen et al. 1999).

For the Laptev Sea area the post-glacial sea-level rise can be considered as eustatic due to the lack of a major ice sheet (e.g. Dunayev and Pavlidis 1988; Hahne and Melles 1997; Kleiber and Niessen 1999). Thus, the global sea-level curve of Fairbanks (1989) is applicable, showing that the shallow Laptev Sea shelf (average water depth: 50-60m) was exposed during the Last Glacial because of the lowered sea level of about 120m. The Vilkitzky Strait (Fig.5.1), the channel between the Kara and Laptev seas, is also assumed to be fallen dry, based on minor and major element data from marine sediment records (Schoster et al. 1999).

Although the discharge of the Siberian rivers Olenek, Lena and Yana was reduced during the Last Glaciation it is supposed that they were active and delivered freshwater and sediment to the Laptev Sea and into the Arctic Ocean (Nørgaard-Petersen et al. 1998; Kleiber and Niessen 1999, subm.).

### 5.6.2 Paleoenvironmental conditions during the Last Glacial

For the St. Anna Trough area, the distribution of a glacigenic diamicton provides evidence for grounded glacier ice which may have reached the shelf edge during the Last Glacial Maximum (Polyak et al. 1997). The diamictons of cores PL9408 and PL9460 can be correlated with these diamictons. Based on AMS-<sup>14</sup>C datings, the minimum age for the retreat of the grounded ice from the central deep St. Anna Trough is about 13.3 ka (Polyak et al. 1997).

The base of the studied diamictons of cores PL9408 and PL9460 are characterized by reworked terrigenous OM, including high matured coal fragments and inertinite, and framboid pyrite. This OM composition can be compared with organofacies types described by Wagner and Henrich (1994) for diamictons in sediment records from the Norwegian-Greenland Sea. Reworked OM is also common in diamictons of the Barents Sea and can be related to redeposition of Mesozoic bedrocks (Elverhoi et al. 1989; Polyak and Solheim 1994; Polyak et al. 1997).

Additionally, we found freshwater alginite (Fig.5.3a,b). These macerals are originated from chlorococalean algae living in freshwater to brackish waters (e.g. Batten and Grenfell 1996) and indicate freshwater discharge into marine systems (Kunz-Pirrung 1999). Moreover, they can be well preserved in geological records and are used for environmental reconstructions (Matthiessen et al. subm.). We have arguments to assume that in our case the observed freshwater alginite in the diamictons at the basis of cores PL9408 and PL9460 does not indicate freshwater supply to the Kara Sea during the Last Glacial. The accumulation within a diamicton facies and the absence of laminated sediments in this core section do not support a fluvial deposition. Additionally, the area of the St. Anna Trough was covered by a grounded ice sheet (Polyak et al. 1997) excluding the possibility of fluvial discharge below the glaciers. Therefore, we suppose that the recorded freshwater algae are rather originated from meltwater pools occurring during summer periods on top of the glaciers than from river discharge.

The environmental conditions during the Last Glacial at the continental slope further east at cores PS2742-5, PS2476-3 and PS2458-4 (Fig.5.1) are different because this region was probably not affected by a large ice-sheet. While we found a diamicton layer with large dropstones at the basis of Core PS2742-5 recovered from the NESZ continental margin, IRD is almost absent in the Upper Weichselian sediment records from the Laptev Sea continental margin (Müller 1999). Therefore, we assume that the diamicton in Core PS2742-5 rather reflect retreat of local ice caps on Severnaya Zemlya during the Last Glacial.

The OM in the diamicton is characterized by very low TOC-contents, and microscopically studies show a dominance of resistant terrigenous OM like inertinites, vitrinites and fragments of terrigenous liptinites (cutinites, resinites, reworked alginites). This is comparable with the POM composition in the diamictons of cores PL9408 and PL9460.

# 5.6.3 Deglaciation

After Hald et al. (1999) and Polyak et al. (1997) deglaciation of the St. Anna Trough started prior to ~13.3 ka BP and was completed by ~10.0 ka BP. During deglaciation MOM has been started to accumulate as documented in the occurrences of lamalginite, marine liptodetrinite and dinoflagellate cysts in Unit II of cores PL9408 and PL9460 (Fig.5.7). This correlates with an increase in the HIvalues (Fig.5.3a,b) which indicate significantly higher portions of MOM. The accumulation of MOM can be interpreted as a signal for marine primary productivity and was probably triggered by the influence of Atlantic water masses. As reported by Knies and Stein (1998) and Knies et al. (1999) a continuous influence of Atlantic waters along the northern Barents Sea existed already during the Last Glacial Maximum. This is supported by foraminiferal fauna recorded in nearby sediment records of the St. Anna Trough, implying episodically presence of biota during deglaciation (Polyak et al. 1997). Moreover, specific foraminiferal assemblages occurring at 13.3 ka are related to subsurface Atlantic water masses and an increased surface-water productivity (Polyak et al. 1997). Additionally, we found a significant increase in immature landplant material (huminite/textinite) together with freshwater alginite in the sediments of Unit II in Core PL9408 (Fig.5.3a, Fig.5.6). Even if the portions of freshwater alginite are relatively small this may be the first signal for fluvial discharge by the Ob and Yenisei rivers to the northern Kara Sea after the Last Glacial.

During deglaciation the OM in the sediments of Core PS2742-5 at the NESZ continental slope is still dominated by terrigenous OM with high portions of inertinites (Fig.5.4) while the TOC contents are low. Evidence for open water conditions or freshwater discharge is not found because during that time no MOM or freshwater alginite is accumulated.

In contrast more variations in OM composition were found in the sediments of Core PS2458-4 taken from the eastern Laptev Sea continental margin (Fig.5.5b).

The sediment record represents the time interval from ~13.5 ka (extrapolated age) until the Holocene. Due to relatively high sedimentation rates (~60 cm/ka) more detailed insights into the environmental changes during that time can be obtained.



Fig.5.6: Distribution of freshwater alginite (grain %) in the studied cores. Smectite data of core PS2458-4 is taken from Müller (1999). Ages are interpolated based on stratigraphic framework (cf. Fig.5.2).

At ~13.5 ka a first indication for deglaciation of the Laptev Sea shelf is given by the deposition of MOM and an increase in the amounts of freshwater alginite (Fig.5.6, 5.7), indicating primary productivity and freshwater supply. Primary productivity of



Fig.5.7: Distribution of MOM and dinoflagellate cysts (grain %) in the studied cores. Ages are interpolated based on stratigraphic framework (cf. Fig.2).

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MOM at this time is related to a reduction of sea-ice cover possibly caused by a first warming event initiated by the increasing insolation at the end of marine isotope stage 2 (MIS2) (Berger 1978). Additionally, the Lena River Delta is supposed to be about 300 km north-west of the present delta near the continental slope during that time because of the lowered sea-level (Holmes and Craeger 1974). The position near to the slope (and near to the position of Core PS2458-4) explains the deposition of fluvial material far in the north although the river activity is supposed to be low during glacial times.

Between ~13 ka and ~12.0 ka the OM sources must have changed. The macerals are dominated by immature liptinitic (fluorescing) material, in this case, textinites, liptinites and liptodetrinite (detritus <10 µm), causing background-fluorescence (BGF) (Fig.5.5b). A quantification of the macerals was not possible because most of the liptinitic particles are too small (<2 µm). Nevertheless, reworked alginites of freshwater and marine origin, reworked pollen grains, inertinite and vitrinite were found, indicating resuspension of OM. Well-preserved textinite indicates short distance transport of the OM. The occurrence of recent freshwater alginite (showing green fluorescence colors) verify a fluvial influence. As possible sources for this OM we assume plants of the tundra vegetation of the shelf and terrestrial shelf sediments (Boucsein et al. in press). The release of OM due to defrosting of the permafrost soils and freshwater discharge by melting of small glaciers and snow fields in the Siberian hinterland may have caused transport and sedimentation of this admixture of immature liptinitic and reworked material. After this first warming the environmental conditions at the eastern continental slope presumably changed to cooler climatic conditions during the time from ~ 12.0 -11.0 ka with low primary productivity and river-runoff. This is documented by a dominance of terrigenous macerals (>80 %) in the OM composition and the absence of MOM and freshwater material. At about 10.4 ka the dinoflagellate cyst Operculodinium centrocarpum is found indicating the first influence of warmer Atlantic water masses at the eastern continental slope (Fig.5.7).

We found small portions of freshwater alginite and also background-fluorescence in the sediments of Core PS2476-3 from the western continental slope during deglaciation time (Fig.5.5a). Comparable with our results from the eastern Laptev Sea continental margin this OM distribution indicates active draining rivers delivering OM towards the western Laptev Sea continental slope.

### 5.6.4 Holocene (~10.0 ka)

### a) Freshwater signal

At the beginning of the Holocene a huge freshwater discharge to the Eurasian continental margin is documented by the occurrence of freshwater alginite in the studied cores PS2742, PS2476 and PS2458 (Fig.5.6). As reported from maceral analysis of surface samples from the inner Laptev Sea shelf the average amounts of freshwater alginite are about 2 % and only reaches maximum values of 8 % close to the mouth of the river Anabar (Boucsein and Stein 2000). Thus, we interpret the freshwater alginite determined in the studied cores as a signal for freshwater supply, although the portions are small (< 4 %). Based on radiocarbon datings on Core PS2458 from the eastern slope this event took place at ~9.8 - 9.7 ka. In the cores PS2476 and PS2742 from further west maximum values of freshwater alginite are recorded at ~9.4 - 9.1 ka as based on interpolated ages. An enlarged river discharge to the slope at this time is supported by a distinct increase of smectite (Müller 1999) as shown in Figure 5.6 and a study on heavy mineral distribution (Behrends 1999) indicating an increased supply of freshwater from the western Laptev Sea. Due to the lack of a large ice sheet in the Laptev Sea area other sources for the huge freshwater supply have to be considered. Melting of small glaciers and snow fields in the Siberian hinterland caused by the post-glacial warming together with the increased precipitation in Holocene times (Monserud 1998) may explain the enlarged freshwater supply. Additionally, the shallow Laptev Sea shelf (50-60 m) became flooded for the first time after the LGM. This transgression may have amplify defrosting of the permafrost soils on the shelf, leading to a release of large meltwater quantities. Moreover, high sedimentation rates at the eastern Laptev Sea continental slope (up to 200 cm/calky) and high accumulation rates of organic carbon (up to 2.0 gC/cm²/ky) in the early Holocene (Boucsein et al. in press) can be related to the increased fluvial supply of sediments and OM.

Based on our data we cannot directly determine the source of the freshwater alginite found in the Holocene sediments of Core PS2742-5. As a possible source for high smectite contents found in Holocene sediments of a nearby sediment record (PS2741) at the continental slope north-east of Severnaya Zemlya the Kara Sea shelf is discussed. The formation of dense brines on the Kara Sea shelf that

cascaded downslope and carried fine-grained suspension as contour current along the continental slope is discussed as possible explanation for the transport of Kara Sea material towards the core position (Knies et al. 2000). Thus, we suggest the Kara Sea with the Ob and Yenisei rivers as possible source for the freshwater alginite found in Core PS2742-5. During the Holocene further increases in the amounts of freshwater alginite are recorded in cores PS2476 and PS2742. This increase probably reflects an intensification of the freshwater supply from the Kara and western Laptev Sea towards the continental margin at ~ 5.0 and ~ 2.5 ka (interpolated ages).

Between 8.0 - 9.0 ka extremely high sedimentation rates of 100-500 cm/ka were reported in the inner and south-eastern parts of the St. Anna Trough, and explained by an increased sediment input from the Siberian rivers and/or coastal erosion during post-glacial sea-level rise (Herlihy 1996; Kolstad 1996; Polyak et al. 1997; Stein et al., subm.). However, in the studied sediment records from the St. Anna Trough area the signal for freshwater supply is relatively small. Nevertheless, in Core PL9460 increased amounts of freshwater alginite are found at ~8.5 and ~5.0 ka (interpolated ages) and in Core PL9408 the amounts of freshwater alginite started to increase in the upper part of the Holocene sediments. As reported by studies on surface sediments of the southern Kara Sea (Matthiessen 1999; Polyakova 1999) the main portions of freshwater algae and freshwater diatoms are deposited in the estuaries of the Ob and Yenisei rivers, decreasing towards the open ocean. This could be an explanation for the reduced freshwater signal in the studied cores of St. Anna Trough area in the northern Kara See. Thus, for the increased amounts of freshwater alginite recorded in the upper part of the Holocene sediments in Core PL9408 we rather suggest sea-ice transport than fluvial transport from the Ob and Yenisei rivers.

### b) Marine signal

Knies et al. (2000) previously reported an intensification of Atlantic water inflow in the Holocene at the northern Barents Sea continental margin indicated by peaks in the accumulation of MOM. Our data show that this signal can be traced towards the eastern Laptev Sea continental margin. In the early Holocene (since ~9.5 ka) a remarkable increase in the amounts of MOM (up to 20%) and dinoflagellate cysts (Fig.5.7) was determined in the sediments of the Eurasian continental margin. Additionally, the dinoflagellate cyst *Operculodinium centrocarpum* was found, indicating the influence of Atlantic water masses. We interpret this time interval of higher portions in MOM as enhanced surface-water productivity triggered by the inflow of warmer Atlantic water masses, partly ice-free conditions and an adequate nutrient supply by the Siberian rivers. For comparison, relatively high productivity rates (200 mgCm<sup>-2</sup>d<sup>-1</sup>) are reported for the ice free area of the Laptev Sea during recent summers and, especially, near the ice-edge at the shelf break (Boetius and Damm 1998). This primary productivity signal is preserved in the surface sediments as reported from organic-geochemical and palynological studies (e.g. Boetius et al. 1996; Fahl and Stein 1997; Kunz-Pirrung 1999). Additionally, maceral data revealed that 20-40 % of the POM preserved in the surface sediments near the continental margin is of marine origin (Boucsein and Stein 2000).

In Core PS2458 the increase in primary productivity was recorded from ~9.5 ka to ~7.5 ka as based on radiocarbon datings. In the cores further west an increase in the amounts of MOM is documented from ~9.4 – 9.1 ka to ~7.6 – 7.3 ka (interpolated ages). An enhanced primary productivity in the sediments of the eastern Laptev Sea continental slope during that time is confirmed by organic-geochemical data, showing a distinct increase in the concentrations of marine biomarkers (short-chain fatty acids, dinosterols, brassicasterol) (Fahl and Stein 1999). This time slice of increased primary productivity seems to be approximately concurrent with the Holocene climatic optimum in northern central Siberia occurring in the Boreal period from 9.2 to 8.0 ka (Hahne and Melles 1997).

During the Holocene two further events of higher primary productivity can be interpreted in cores PS2476 and PS2742 at ~4.2 – 4.5 ka (interpolated ages) and ~2.5 – 2.7 ka (interpolated ages) (Fig.5.7). At this time the portions of MOM and dinoflagellate cysts are increased and, moreover, the occurrence of the dinoflagellate cysts *Operculodinium centrocarpum* (see Fig.5.7) verifies the influence of Atlantic-water inflow during that time. Unfortunately, this time intervals are not recorded in the sediments of Core PS2458 due to a hiatus lasting 6 – 8.0 ka.

In contrast in the sediment cores from the St. Anna Trough area higher portions of MOM are recorded since deglaciation time as discussed before and, are explained by a continuous influence of Atlantic water masses. Nevertheless, in the southern core PL9460 maximum values are reached at the beginning of the Holocene from ~9.4 ka to ~7.6 ka (interpolated ages) (Fig.5.7) and can be interpreted as a intensification of warmer Atlantic water inflow and, ice-free conditions together with an adequate fluvial nutrient supply similar to the environmental conditions described for the Eurasian continental margin. Moreover, the occurrence of the dinoflagellate cysts *Operculodinium centrocarpum* in core PL9460 indicates an increased Atlantic water influence at ~7.6 and ~3.8 ka (interpolated ages).

## 5.7 Summary and conclusions

- During the Last Glacial the environment of the St. Anna Trough area was affected by grounded glacier ice as documented by the widespread occurrence of diamictons. The OM in the diamictons is characterized by reworked organic matter and the absence of MOM. Deglaciation started at ~13.3 ka and was completed near ~ 10.0 ka. MOM started to accumulate during deglaciation time, which is explained by increased primary productivity triggered by Atlantic water inflow. Furthermore, freshwater alginites give evidence for active draining rivers into the Kara Sea delivering freshwater and OM to the St. Anna Trough.
- The large Laptev Sea shelf and the Vilkitzky Strait are supposed to be fallen dry because of the lowered sea-level during the Last Glacial and were not icecovered during that time. At ~13.5 ka MOM and freshwater alginite were deposited at the eastern Laptev Sea continental margin and are interpreted as a first sign for warming and freshwater supply. First evidence for Atlantic water masses reaching the eastern Laptev continental margin has been determined at ~10.4 ka, indicated by an increase in MOM and the occurrence of the dinoflagellate cyst Operculodinium centrocarpum.

At the beginning of the Holocene an enlarged fluvial supply from the Kara and Laptev Seas can be confirmed by an increase of freshwater alginite. This correlates with the extremely high sedimentation rates described for the Kara and Laptev seas and can be explained by an increased freshwater and sediment discharge by the Siberian rivers. This freshwater signal has been found in the sediment records of the Laptev Sea continental margin at ~9.8 – 9.1 ka, ~5.0 and ~2.5 ka. In the Kara Sea an increase in freshwater supply has been recorded ~8.5 ka and ~5.0 ka. Additionally, surface-water productivity caused by an intensification of Atlantic water inflow, temporary ice-free conditions and fluvial nutrient supply is documented in the increased accumulation of MOM and dinoflagellate cysts and can be followed in the Holocene sediments along the Kara and Laptev Sea continental margin at ~9.5 – 7.3 ka, ~ 4.4 – 3.8 ka and ~2.7 – 2.5 ka.

# 6. Perspectives and open questions

The study showed that the use of petrographical data reveals helpful information about the environmental conditions in marine environments. The data sets contribute to our understanding of organic matter deposition and give detail insights in the type and sources of the particulate organic matter.

As discussed in this case study the strong river discharge into the marine systems of the Laptev and Kara seas hampered classical methods for characterization of the organic-matter sources. The supply of terrestrial and aquatic organic material into the marine system lead to complications in characterization of the organic matter sources in marine sediments. The results from the sediment core PS2458-4 (Chapter 4) have shown that the parameters hydrogen indices, n-alkanes and short-chain fatty acids cannot be used for distinguishing between freshwater, terrestrial and marine material. In spite of these problems the results show, moreover, a good correlation between specific biomarkers (dinosterols, brassicasterol) and the data sets from maceral analysis and palynology. Thus, in order to prevent contradictory interpretations, future work on the organic matter contents in marine sediments of the Eurasian shelf seas should always comprises a multi-parameter approach, including specific biomarkers, palynology and maceral analysis. The described problems in using single organic-geochemical parameters for studies on organic matter should be also considered in other coastal-near shelf areas.

Further work on material from sediment traps is needed in the Arctic seas for a better understanding of this complex marine system and its organic carbon cycle. The strong seasonality of surface-water salinity, fluvial discharge and primary productivity lead to discrepancies between the signals obtained from the surface-water layer and the surface sediments as the results from the Kara Sea expedition in 1997 have shown (Matthiessen et al. 1999). Thus, calculations of the paleoproductivity by using organic carbon data, obtained from geological records, are not possible without a better knowledge of the modern mechanisms controlling the organic matter deposition. Especially for the study area, more

surface sediments and sediment records from the Kara Sea have to be investigated for the organic carbon contents and palynomorph assemblages. A multi-parameter approach including maceral analysis, palynology and biomarkers should be performed on the same surface samples for a better understanding of the modern situation, but also, to enable a comparison with the data sets from sediment record PS 2458-4. A transect from the estuaries towards the continental margin would give more information about the oceanographic conditions. Moreover, studying of further geological records with a high stratigraphical resolution would allow to interpret the climatic variability, paleoenvironmental changes and paleoceanography from the Last Glacial to the Holocene.

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