

Marine Chemistry 63 (1999) 293-309

MARINE CHEMISTRY

Biomarkers as organic-carbon-source and environmental indicators in the Late Quaternary Arctic Ocean: problems and perspectives

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Abstract

In order to examine the variation in marine and terrigenous sources of the organic matter during the last 15,000 Cal. yr BP, hydrogen index values, C/N ratios, and specific biomolecules (short- and long-chain *n*-alkanes, short-chain fatty acids, sterols, alkenones, and pigments) were determined in three sediment cores from the Laptev Sea continental margin. The results show that the interpretation of the biomarker data is much more complicated and less definitive in comparison to similar data sets from low-latitude open-ocean environments. This is mainly caused by the complexity of the Arctic Ocean system, which is characterized by a high seasonality of sea-ice cover and primary productivity, sea-ice sediment transport and a high fluvial supply of freshwater (aquatic) organic matter. A combination of organic geochemical, organic petrographic and micropaleontological data may yield to a more precise identification of organic-carbon input controlled by river discharge seems to be predominant during the last about 10,000 Cal. yr BP. Maximum supply of terrigenous organic carbon was reached in the Early Holocene (i.e., about 9000–10,000 Cal. yr BP). Further offshore at the upper continental slope (core PS2458-4), a major change in organic-composition occurred near 10,000 Cal. yr BP. During this period hydrogen indices as well as the amounts of short-chain *n*-alkanes, short-chain fatty acids, dinosterol and brassicasterol significantly increased, indicating increased relative proportions of marine organic matter preserved in the later time interval. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: marine and terrigenous organic carbon; biomarker; paleoproductivity; Laptev Sea; Arctic Ocean

1. Introduction

The present state of the Arctic Ocean and its influence on the global climate system strongly depends on river discharge (see Stein (1998) for review). The freshwater balance of the Arctic Ocean, which receives 10% of the global runoff (Aagaard and Carmack, 1989), plays a key role in controlling sea-ice extent and intermediate/bottom water formation in the Northern Hemisphere, as well as Arctic Ocean surface-water conditions. The major Arctic rivers also supply huge amounts of suspended inorganic (detrital) and organic matter to the shelves and the detrital component of Arctic shelf sediments,

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thus, largely consists of riverine material. The annual discharge of suspended sediments by the Lena River, for example, is presently 17.6×10^6 tons (Martin et al., 1993). Concerning the sources and fate of organic matter within the Arctic system, Arctic rivers which discharge large quantities of terrigenous organic matter, but also nutrients, into the system, are of considerable importance. Dissolved and particulate organic matter supplied by the Lena River is estimated at 3.6×10^6 tons/yr and 1.3×10^6 tons/yr, respectively (Rachold et al., 1996). The riverine nutrient supply may cause enhanced surface-water productivity. This is reflected by elevated chlorophyll a concentrations and phytoplankton cell numbers in the Lena River plume (Heiskanen and Keck. 1996). The concentrations of dissolved silica are high throughout the year within the Lena River $(43-108 \mu M)$, whereas nitrate and phosphate are low $(1.4-16 \ \mu M \text{ and } 0.1-0.8 \ \mu M$, respectively) (Létolle et al., 1993; Cauwet and Sidorov, 1996; Gordeev et al., 1996). Within the Lena River phytoplankton productivity, thus, seems to be limited by nutrients other than silica (Heiskanen and Keck, 1996). This may suggest that the linkage between riverine nutrient supply and enhanced productivity is not necessarily a simple direct relationship.

Most of the organic matter accumulates in coastal zones; however, significant amounts of this material are transported further offshore by different processes such as sea-ice, ocean currents, and turbidity currents (Stein and Korolev, 1994; and further references therein). Eolian input is only of very minor importance for the sedimentary budget of the Arctic Ocean. Macdonald et al. (1998) estimated the eolian flux in the Mackenzie shelf area, reaching 1.4×10^4 tons/yr. Based on studies of snow samples from the western central Arctic Ocean an eolian flux of 3.3-14.0 μ g/cm² and year was calculated (Darby et al., 1974, 1989). Even if all this material would be released during summer melting and would reach the sea floor (which is not very realistic), this would result in an average sedimentation rate of 0.02–0.09 mm/kyr, i.e., about 1-5% of the bulk sedimentation rate. In our study area, the Laptev Sea continental margin where Holocene bulk sedimentation rates increase to values of about 15 to 800 cm/kyr (Stein and Fahl, 1998), the eolian input then becomes even much less important.

Comparison of sedimentological and organic-geochemical proxies in surface sediments reflecting the surface water productivity and terrigenous organiccarbon flux with physical and biological parameters provides a means to identify the most important processes controlling the organic-carbon accumulation in the Arctic Ocean (e.g., Fahl and Stein, 1997; Schubert and Stein, 1997; Stein et al., 1998). Interpretation of vertical profiles in sediment cores in the context of these findings will then yield information on changes in the organic-carbon cycle of the Arctic Ocean through time. These data may, in turn, yield important insights into the role of the Arctic Ocean during global climate change.

The use of specific organic-geochemical tracer compounds (biomarkers) as (paleo-) environmental proxies is a well established tool in low- and midlatitude open-ocean areas (e.g., Farrimond et al., 1990; ten Haven et al., 1990; Prahl et al., 1994; Hinrichs et al., 1995). When using biomarkers as (paleo-) indicators of spatial and temporal changes in organic-carbon sources for high-latitude ice-covered regions, such as the Laptev Sea continental margin and adjacent deep sea, it is important to consider the complex factors controlling the organic-carbon flux in these areas. First, the strong fluvial supply may provide freshwater (aquatic) organic matter as well as terrestrial organic matter. Second, due to the more or less closed sea-ice cover, phytoplankton productivity in the Arctic Ocean is very low and represents a mixed signal of surface-water productivity and productivity of sea-ice communities. Third, the organic matter deposited on the Laptev Sea shelf, which is a mixture of terrigenous higher plant material, freshwater organic material and, to a limited extent, marine organic matter, may be incorporated into the sea-ice and further transported offshore. Thus, terrigenous organic matter may be deposited far away from the source area.

The major goal of this study is (1) to discuss the problems of using biomarkers as organic-carbonsource indicators in Arctic Ocean sediments, (2) to identify organic-carbon sources (i.e., marine vs. aquatic vs. terrigenous), and (3) to reconstruct changes in composition and flux of organic carbon in relation to climate change and sea-level rise at the Laptev Sea continental margin during the last \sim 15,000 Cal. yr BP.

2. Sediments and stratigraphy

The three sediment cores described in this study, PS2458-4, PS2725-5, and KD9502-14 (Fig. 1, Table

1), were obtained during RV *Polarstern* Expedition ARK-IX/4 1993 (Fütterer, 1994), RV *Polarstern* Expedition ARK-XI/1 1995 (Rachor, 1997), and TRANSDRIFT-III Expedition 1995 with RV *Kapi*-



Fig. 1. Location of cores KD9502-14, PS2725-5, and PS2458-4 from the Laptev Sea and the continental margin. Grey arrows indicate the Transpolar Drift System (Pfirman et al., 1989).

Table 1

Position, water depth and recovery of sediment cores taken during the 1993 and 1995 RV Polarstern and Kapitan Dranitsyn cruises

Core	Gear	Position		Water depth (m)	Recovery (m)
		Inner Laptev Sea			
KD9502-14	Vibro corer	76°11.52′ N	133°06.99'E	46	2.30
		Western East Siberian	n Sea		
PS2725-5	Gravity corer	78°39.36' N	144°08.1' E	77	4.78
	•	Eastern Laptev Sea			
PS2458-4	Kastenlot	78°09.95′ N	133°23.86′ E	983	8.00

tan Dranitsyn (Kassens, 1997), respectively. The sampling was carried out using a Kastenlot, gravity corer, and vibro corer.

2.1. Inner Laptev Sea shelf

Core KD9502-14 from the Laptev Sea shelf east of the New Siberian Islands (Table 1) consists of olive gray silty clay (Kassens, 1997). Based on AMS-¹⁴C dating, the sedimentary sequence probably represents the last ~ 8000 Cal. yr BP (Bauch et al., 1996).

2.2. East Siberian Sea

Core PS2725-5 was obtained from the shelf of the western East Siberian Sea, north of the New Siberian Islands (Table 1). The 4.8 m long sedimentary sequence is dominated by very dark gray, dark olive, and black silty clay with common to abundant black spots/layers between 30 and 178 cmbsf (Rachor, 1997). The lowermost 40 cm contain significant amounts of sand. Based on AMS-¹⁴C dating performed on bivalves, the sediments represent the last \sim 10,000 Cal. yr BP (Stein and Fahl, 1998).

2.3. Eastern Laptev Sea

Core PS2458-4 taken from the upper eastern Laptev Sea continental slope (Table 1), consists of a 8 m long sedimentary sequence of very dark olivegray silty clay of dominantly terrigenous origin (Fütterer, 1994). The upper 25 cm are of dark brown to very dark brown color. Small bivalves occasionally occur, and these bivalves were used for AMS-¹⁴C dating (Spielhagen et al., 1996). Based on these dates, the sediments of core PS2458-4 represent the last ~ 15,000 Cal. yr BP. At a depth of 100 cmbsf, there is evidence of a hiatus lasting 6–8000 years; the upper 100 cm are probably not older than 100–200 Cal. yr BP (Spielhagen et al., 1996).

3. Methods

The bulk parameters (total nitrogen and organiccarbon contents) were determined by means of a Heraeus CHN-analyzer (for details concerning the method see Stein, 1991). C/N ratios were calculated as 'total organic carbon/total nitrogen ratios' based on weight percentage. The Rock–Eval parameters hydrogen index (HI in mg HC/g TOC) and oxygen index (OI in mg CO₂/g TOC) were determined as described by Espitalié et al. (1977).

For the lipid analyses the sediment samples were stored at -80° C or in dichloromethane:methanol (2:1, by vol.) at -23° C until further treatment. The sediment (8 g) 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 *n*-alkanes, sterols and alkenones.

3.1. n-Alkanes

The alkanes were separated from the other fractions by column chromatography using hexane as eluent. The composition of this fraction was analysed with a Hewlett Packard gas chromatograph (HP 5890, column 50 m \times 0.25 mm; film thickness 0.25 µm; 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 was 1 µl (Cold Injection Sys-

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tem: $60^{\circ}C$ (5 s), $300^{\circ}C$ (60 s), rate: $10^{\circ}C/s$). Helium was used as carrier gas. The composition was verified by comparison with a standard mixture; for the quantification squalane was added before any analytical step.

3.2. Alkenones

The alkenones were separated from the other fractions by column chromatography using hexane: ethylacetate (95:5 and 90:10, by vol.) as eluent. A saponification step with 1 M potassium hydroxide in 95% methanol for 2 h at 90°C followed. The fraction was analysed by means of a Hewlett Packard gas chromatograph (as described for the *n*-alkane analysis) using a temperature program as follows: 60°C (1 min). 270° C (rate: 20° C/min). 320° C (rate: 1°C/min). 320°C (20 min isothermal). The injection volume was 1 µl (Cold Injection System: 60°C. $105^{\circ}C$ (rate: $3^{\circ}C/s$), $320^{\circ}C$ (rate: $10^{\circ}C/s$), $320^{\circ}C$ (60 s isothermal). The identification of the alkenones was carried out by means of retention time. For quantification octacosanoic acid methyl ester was used as an internal standard.

3.3. 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 h at 80°C. After extraction with hexane, the composition was analysed with a Hewlett Packard gas chromatograph (HP 5890, column 30 m \times 0.25 mm; film thickness 0.25 μ m; 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 ul. The fatty acids and alcohols were identified by a standard mixture (Marinol standard was kindly made available by J.R. Sargent, Scotland). For quantification, an internal standard (19:0 fatty acid methyl ester) was added.

3.4. Sterols

An aliquot of the total extract was silvlated with $100 \mu l$ BSTFA (bis-trimethylsilyl-trifluoroacet-

amide) (60°C for 2 h). After extraction with hexane. the composition was analysed by GC/MS, which consists of a gas chromatograph (HP 5890, column 30 m \times 0.25 mm; film thickness 0.25 µm; liquid phase: HP 5) and a mass spectrometer (MSD, HP 5972, 70 eV electron-impact-ionisation. Scan 50-650 m/z, 1 scan/s, ion source temperature 175°C). GC analysis was performed with the following temperature program: 60°C (1.55 min), 200°C (rate: 20°C/min), 300°C (rate: 5°C/min). The injection volume is 1 µl (splitless). Helium was used as carrier gas (1.2 ml/min at 60°C). The identification of the sterols was carried out on basis of GC retention time and MS fragmentation pattern. For quantification, cholest-5-en-3 β -ol-2,2,3,4,4,6- d_6 (internal standard) was added before any analytical step. Note that only the 4α -23,24-trimethyl- 5α -cholest-22*E*-en-3B-ol (dinosterol) and 24-methylcholesta-5.22 Edien-3B-ol (brassicasterol) were used for interpretation.

3.5. Pigments

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

3.6. Carbon-reference-index (CPI)

The relation of odd-to-even chain length of the *n*-alkanes as an estimate for the thermal maturity of the terrigenous organic matter was calculated as $CPI = (C_{21} + C_{23} + C_{25} + C_{27} + C_{29} + C_{31})/(C_{22} + C_{24} + C_{26} + C_{28} + C_{30} + C_{32})$ (after Bray and Evans, 1961).

4. Biomarkers as organic-carbon source and environmental indicators

Several biomolecules are frequently used as biomarkers indicative for the origin of organic matter in sediments in order to derive information about the (paleo-) environmental conditions. The distribution and significance of these molecular fossils are quite well established in temperate low and mid-latitude regions and oceanic areas subject to minor fluvial influence (e.g., Farrimond et al., 1990; ten Haven et al., 1990; Prahl et al., 1994; Hinrichs et al., 1995). When using biomarkers in the Laptev Sea and the adjacent Arctic Ocean, the different transport processes, which are dominated by river discharge, seaice transport, downslope transport, and vertical and lateral transport through the water column, have to be considered. The unambiguous importance of the Siberian rivers is reflected by the high input of terrigenous (higher-plant and aquatic) organic matter onto the shelf and into the adjacent slope and deep sea area. Accordingly, up to 98% of the TOC represents terrigenous organic carbon on the Laptev Sea shelf (Boetius et al., 1996), with this proportion decreasing offshore where marine productivityespecially at the ice margin-becomes more important (Fahl and Stein, 1997). The interpretation of the biomarker signals are thus much more complex than in low-latitude regions characterized by minor fluvial input and the lack of sea-ice influence. In these latter areas the complex mixing of lipids from diverse sources typical for our study area, can be largely excluded.

In the Laptev Sea continental margin and similar environments biomarkers such as short-chain *n*-alkanes, alkenones, short-chain fatty acids, sterols, and pigments may derive from aquatic (freshwater) algae as well as from marine phyto- and zooplankton (see Table 2). Consequently a pronounced algal signature is not necessarily marine in origin, and all data have to be interpreted cautiously. Whereas the long-chain fatty acids are almost exclusively of terrigenous origin, derived from specific terrestrial higher plants (Eglinton and Hamilton, 1963; Madureira et al., 1995), the short-chain (saturated and mono/polyunsaturated) compounds are commonly related to a marine source (e.g., Kates and Volcani, 1966: Ackman et al., 1968: Harrington et al., 1970: Pohl and Zurheide, 1979; Falk-Petersen et al., 1987; Fraser et al., 1989; Volkman, 1989; Fahl and Kattner, 1993). Specific fatty acid compositions have been described for marine diatoms, different ice algae (Kates and Volcani, 1966; Fahl and Kattner, 1993), marine Dinophyceae (Mayzand et al., 1976; Fraser et al., 1989; Ahlgren et al., 1992), as well as Haptophyceae (Sargent et al., 1985, Conte et al., 1994). Shortchain fatty acids, however, are also found in lacustrine / freshwater environments (Ahlgren et al., 1992; Léveillé et al., 1997). As a result, short-chain fatty acids cannot be used to distinguish between aquatic and marine inputs (Table 2). The same is true for pigments (Table 2), short-chain *n*-alkanes (e.g., Eglinton and Hamilton, 1963; Venkatesan et al., 1987; Madureira et al., 1995) and the investigated sterols. 4α -23,24-Trimethylcholest-22 *E*-en-3β-ol (dinosterol) is well known as a biosynthetic product of dinoflagellates (Boon et al., 1979; de Leeuw et al., 1983) and other marine sources (Nichols et al., 1990; Volkman et al., 1993), but also occurs in lacustrine organisms (Table 2) and aquatic environments (Yunker et al., 1995). Robinson et al. (1984) and Thiel (1993), for example, determined high concentrations of dinosterol in the water column as well as in the sediments of Lake Van (Turkey) and Lake

Table 2

List	of	different	biomarkers	from	marine	and	freshwater	origin
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Compounds	Marine	Freshwater/non-marine	
Short-chain <i>n</i> -alkanes $(C_{15} + C_{17} + C_{19})$	Hinrichs et al., 1995	McKirdy et al., 1986	
Long-chain <i>n</i> -alkanes $(C_{27} + C_{29} + C_{31})$		Yunker et al., 1995	
Short-chain fatty acids (C_{12} to C_{24})	Fahl and Kattner, 1993	Kates and Volcani, 1966	
	Nichols et al., 1984	Ahlgren et al., 1992	
4α -23,23-Trimethyl-5 α -cholest-22 <i>E</i> -en-3 β -ol	Nichols et al., 1984	Tayler, 1987	
(Dinosterol)		Thiel, 1993	
24-Methylcholesta-5,22 E-dien-3β-ol	Nichols et al., 1984	Tayler, 1987	
(Brassicasterol)		Thiel, 1993	
		Yunker et al., 1995	
Long-chain alkenones $(C_{37\cdot4} + C_{37\cdot3} + C_{37\cdot2})$	Conte et al., 1994	Thiel et al., 1997	
Chlorophyll <i>a</i> , <i>b</i> , <i>c</i>	Stryer, 1987	Stryer, 1987	

Priest Pot (England). High contents of 24-methylcholesta-5,22 E-dien-3B-ol (brassicasterol) were also measured in this lacustrine / freshwater environment (Thiel et al., 1997; Table 2), reflecting the presence of diatoms, dinoflagellates or haptophytes (Conte et al., 1994). For the long-chain *n*-alkanes a terrigenous origin from higher plants is generally accepted (Salasoo, 1987; Villanueva et al., 1997). The synthesis of long-chain *n*-alkanes by some special sulfatereducing bacteria seems to be of minor importance for the marine environments (Davis, 1968). The lithology of the investigated cores displays a change from dark brown (oxic) to dark olive colours between 20 and 30 cmbsf indicating a reducing milieu in the lower core section. Thus, the influence of sulfate-reducing bacteria cannot be excluded. Even the long-chain unsaturated alkenones, usually regarded as a prominent marine coccolithophorid indicator (e.g., Volkman et al., 1980; Brassell et al., 1986; Prahl et al., 1989; Farrimond et al., 1990; Sikes et al., 1991; Jasper and Gagosian, 1993), were also detected in lacustrine sediments (e.g., Thiel et al., 1997). In our study area, however, the alkenones are present only in low abundances (Fahl and Stein, 1997; Stein et al., 1998).

In the Mackenzie river estuary (Canadian Arctic) the biomarker distribution also indicates a significant aquatic contribution (Yunker et al., 1995) as suggested for the Lena River.

Based on the arguments outlined above it appears to be clear that the exclusive use of biomarkers to distinguish between marine and terrigenous/aquatic sources is questionable, especially in the Laptev Sea and the adjacent continental slope. In order to solve this problem and to allow more precise statements about the organic-carbon origin and its (paleo-) environmental significance, it is necessary to combine the organic-geochemical results with micropaleontological and sedimentological data. In addition, future work on stable carbon isotopic composition of biomarkers could yield more information about the origins of organic carbon and its deposition.

5. Biomarker records in the Laptev Sea continental margin area

In order to understand the sedimentary processes controlling organic-carbon deposition, as well as the

(paleo-) environmental changes in the Laptev Sea and the adjacent continental margin through time, the three sediment cores, KD9502-14, PS2725-5 and PS2458-4, were investigated for the distribution of bulk parameters (TOC, HI values, and C/N ratios) and biomarkers (long/short-chain *n*-alkanes, shortchain fatty acids, dinosterol, brassicasterol, and pigments).

The depth profiles of the two shelf cores KD9502-14 and PS2725-5, which span the last \sim 8000-1000 Cal. yr BP, show TOC contents between 1 and 1.6% (Figs. 2 and 3). HI values of < 100 mgHC/g TOC occur throughout the entire records. In a HI vs. OI ('van-Krevelen-type') diagram, all data points plot into the 'Krevelen-type III' field (Fig. 4A and B), reflecting the high proportion of immature/fresh terrigenous organic carbon. The biomarker composition supports the predominantly terrigenous character of the organic carbon in both cores (Figs. 2 and 3). In general, the concentrations of long-chain *n*-alkanes $(C_{27} + C_{29} + C_{31})$ are high $(300-400 \ \mu g/g \text{ TOC})$, comprising more than 50% of the total *n*-alkanes. The concentrations of the corresponding short-chain *n*-alkanes (10 μ g/g TOC) and pigments are rather low on the shelf as expected. In general, the *n*-alkane composition showing a terrigenous predominance is similar to the ice-free New England continental margin (Venkatesan et al., 1987), the Gulf of Mexico (Jasper and Gagosian, 1993), and the coastal zone off Washington State influenced by Columbia River supply (Prahl and Muehlhausen, 1989), as well as for the permanent ice-covered Arctic Ocean (Schubert and Stein, 1996). In all these environments the ratio of long- to short-chain *n*-alkanes ranges between 25 and 40. The CPI is high, varying between 1.8 and 4.3, which also supports the predominance of fresh terrigenous material in the cores (cf. Bray and Evans, 1961). According to Brassell et al. (1978) and Hollerbach (1985), fresh terrigenous organic matter shows a CPI of 3 to 10, whereas fossil material varies around 1 depending on the state of decomposition and thermal alteration.

In contrast to the short-chain *n*-alkanes, the contents of the short-chain fatty acids 16:0, 16:1(n-7), 16:1(n-5), 18:0, 18:1(n-9), and 18:1(n-7) are surprisingly high (300 μ g/g TOC; Figs. 2 and 3, Table 3). These values are similar to those from the Santa Barbara Basin and the New England continental



Fig. 2. Organic-geochemical bulk parameters and specific biomarkers in the sedimentary sequence of core KD9502-14: total organic-carbon contents (%), total organic carbon/total nitrogen (C/N) ratios, hydrogen index values (mg HC/g TOC), long- and short-chain *n*-alkanes (μ g/g TOC), short-chain fatty acids (μ g/g TOC), brassicasterol (μ g/g TOC), dinosterol (μ g/g TOC), and pigment absorbance values. AMS-¹⁴C ages according to Bauch et al. (1996).



Fig. 3. Organic-geochemical bulk parameters and specific biomarkers in the sedimentary sequence of core PS2725-5: total organic-carbon contents (%), total organic carbon/total nitrogen (C/N) ratios, hydrogen index values (mg HC/g TOC), long- and short-chain *n*-alkanes (μ g/g TOC), short-chain fatty acids (μ g/g TOC), brassicasterol (μ g/g TOC), dinosterol (μ g/g TOC), and pigment absorbance values. AMS-¹⁴C ages according to Stein and Fahl (1998).



Fig. 4. Hydrogen index vs. oxygen index ('van-Krevelen-type') diagram of cores KD9502-14 (A), PS2725-5 (B) and PS2458-4 (C). Roman numbers mark different kerogen types: I and II marine, III terrigenous organic matter (classification after Espitalié et al., 1977; Peters, 1986).

margin (Table 3), where they have been interpreted as a marine organic-carbon source indicators. The same interpretation was published by ten Haven et al. (1990) for the upwelling area off Peru, but there the concentrations of the short-chain fatty acids are 10 times higher than in the Laptev Sea (Table 3), as expected for high-productivity environments characterized by high marine organic-carbon flux. Ze-

Table 3

Concentrations of biomarkers in sediments from different environments

Area		Type of environment
Lake Van, Turkey		Freshwater environment
(Thiel, 1993)		(water depth: 451 m)
Long-chain <i>n</i> -alkanes	362 μg/g TOC	
Dinosterol	128 μg/g TOC	
Brassicasterol	380 µg/g TOC	
Columbia River		High fluvial supply
(Prahl and Muehlhausen, 1989)		
Long-chain <i>n</i> -alkanes	$277\pm87~\mu g/g~TOC$	
Gulf of Mexico		High fluvial supply, hemipelagic
(Jasper and Gagosian, 1993)		environment
Long-chain <i>n</i> -alkanes (odd)	164 µg/g TOC	(water depth: 2260 m)
Peru Upwelling Area		High productivity
(Farrimond et al., 1990; ten Haven et al., 1990)		upwelling environment
Long-chain <i>n</i> -alkanes	51 μg/g TOC *	(water depth: 461 m)
Short-chain <i>n</i> -alkanes	8 μg/g TOC *	
Short-chain fatty acids	5000 μg/g TOC	
Dinosterol	34 µg∕g TOC∗	
Brassicasterol	235 µg/g TOC*	
Santa Barbara Basin		Semi-closed basin with high surface-
(Hinrichs et al., 1995; Stein and Rack, 1995)		water productivity and suboxic bottom
Long-chain <i>n</i> -alkanes	91 μg/g TOC	water
Short-chain <i>n</i> -alkanes	31 µg/g TOC	(water depth: 577 m)
Short-chain fatty acids	140–250 μg/g TOC	
Dinosterol	42 μg/g TOC	
Brassicasterol	40 µg/g TOC	
Cont. margin, New England		Continental margin, ice-free
(Venkatesan et al., 1987)		(water depth: 1280 m)
Long-chain <i>n</i> -alkanes	60.6 µg/g TOC	
Short-chain <i>n</i> -alkanes	2.4 μg/g TOC	
Fatty acids (C12–C32)	454 µg/g	
Dinosterol	136 µg/g TOC	
North Atlantic, Biscay Abyssal Plain		Open ocean, ice-free
(Madureira et al., 1995)		(water depth: 4105 m)
Long-chain <i>n</i> -alkanes	75 µg/g TOC	
Total sterols	150 µg/g 10C	
Arctic Ocean		Open ocean, permanent sea-ice
(Schubert and Stein, 1996)	100 700 / 500	cover
Long-chain <i>n</i> -alkanes	$400 - 700 \ \mu g/g \ TOC$	(water depth: 1500–4000 m)
Short-chain <i>n</i> -alkanes	10-20 µg/g TOC	
Laptev Sea shelf		Shelf, seasonal sea-ice cover,
(1 his paper, average values)	255 (70.5	nigh fluvial supply
Long-chain <i>n</i> -alkanes	355 μg/g TOC	(water depth: 46 m)
Short-chain <i>n</i> -alkanes	$9 \mu g/g TOC$	
Snort-chain fatty acids	$300 \ \mu g/g \ TOC$	
Diriosterol	$4 \mu g/g TOC$	
DIASSICASIEIOI	/ µg/g 10C	

Table 3 (continued)

Area		Type of environment
Laptev Sea continental slope		Continental slope, seasonal sea-ice
(This paper, average values)		cover, high fluvial supply
799–360 cmbsf		(water depth: 948 m)
Long-chain <i>n</i> -alkanes	196 μg/g TOC	•
Short-chain n-alkanes	7 μg/g TOC	
Short-chain fatty acids	$17 \mu g/g TOC$	
Dinosterol	9 μg/g TOC	
Brassicasterol	22 μg/g TOC	
360–0 cmbsf		
Long-chain <i>n</i> -alkanes	150 μg/g TOC	
Short-chain n-alkanes	86 μg/g TOC	
Short-chain fatty acids	50 μg/g TOC	
Dinosterol	45 μg/g TOC	
Brassicasterol	100 µg/g TOC	

*Calculated with 3.5% TOC content (Suess et al., 1988).

Values are normalized to TOC content.

gouagh et al. (1996) assumed that the high amounts of short-chain fatty acids they measured in surface sediments from the Lena Delta and further offshore in the Laptev Sea (SPASIBA 2 Expedition, 1991) are marine in origin. However, based on the above arguments and the positive correlation with the high concentration of long-chain *n*-alkanes, as well as low hydrogen index values, we infer that the high concentration of short-chain fatty acids in our records probably derives from freshwater/aquatic algae (cf. Ahlgren et al., 1992; Léveillé et al., 1997).

The relative abundances of 4α -23,24-trimethyl- 5α -cholest-22*E*-en-3β-ol (dinosterol) and 24-methylcholesta-5,22 E-dien-3β-ol (brassicasterol) reach concentrations of 6 μ g/g TOC in both cores. These compounds are often used as indicators of marine inputs (e.g., Nichols et al., 1984), but here their presence also seems to be due to freshwater algae (Tayler, 1987; Thiel, 1993). First results of micropaleontological investigations and maceral analysis support this assumption. Low but significant amounts of freshwater algae occur throughout both shelf cores without high variabilities (Matthiessen, personal communication, 1997). In comparison with other oceanic regimes (Table 3), the concentrations of dinosterol and brassicasterol are rather low. Thus, in general, the organic-geochemical data of both cores indicate that the organic carbon which accumulates on the Laptev Sea shelf is mainly of terrigenous/

aquatic origin, most probably controlled by fluvial (Lena) discharge.

In the continental slope core PS2458-4 representing the last ~ 15,000 Cal. yr BP (Spielhagen et al., 1996), the sedimentary regime seems to be different. Although the TOC values are in the same range as those determined in the shelf cores (1-1.5%; Fig. 5), the composition of the organic carbon is much more variable, as indicated by the HI values, C/N ratios and the biomarker distributions. In the lower core section (790 to 360 cmbsf) low HI values and rather high concentrations of long-chain *n*-alkanes (C_{27} + $C_{29} + C_{31}$) (Fig. 5) indicate terrigenous organic matter. In general, also the high CPI indices of 2 to 3.5 and a position in the 'Krevelen-type III' field of HI vs. OI diagram (Fig. 4C) support the high content of fresh terrigenous organic material. The upper core section (360 to 0 cmbsf), on the other hand, is characterized by relatively high HI values (up to 200 mg HC/g TOC) suggesting a more marine character of the organic material. In the HI vs. OI diagram, these data points plot above the 'Krevelen-type III' line (i.e., a mixture of marine/terrigenous organic matter with, however, still a dominance of terrigenous organic material). The more marine character is also supported by higher concentrations of shortchain fatty acids, dinosterol, and brassicasterol, which are mainly derived from diatom and/or dinoflagellates (e.g., Kates and Volcani, 1966; Boon et al.,



Fig. 5. Organic-geochemical bulk parameters and specific biomarkers in the sedimentary sequence of core PS2458-4: total organic-carbon contents (%), total organic carbon/total nitrogen (C/N) ratios, hydrogen index values (mg HC/g TOC), long- and short-chain *n*-alkanes (μ g/g TOC), short-chain fatty acids (μ g/g TOC), brassicasterol (μ g/g TOC), dinosterol (μ g/g TOC), and pigment absorbance values. AMS-¹⁴C age according to Spielhagen et al. (1996).

1979; de Leeuw et al., 1983; Nichols et al., 1990; Fahl and Kattner, 1993; Volkman et al., 1993). The correlation coefficient (r^2) of 0.624 (for short-chain fatty acids) and 0.495 (for dinosterols) indicates a well supported correlation between the hydrogen index and these two biomarkers (Fig. 6A and B). The ratio of long- to short-chain *n*-alkanes, which reaches values of 2 to 6, is comparable to the calculated ratios from high-productivity upwelling areas, including the Santa Barbara Basin (Table 3). A high proportion of marine organic carbon is confirmed by micropaleontological and maceral data. Marine par-



Fig. 6. Hydrogen index (mg HC/g TOC) vs. short-chain fatty acids (μ g/g TOC) and hydrogen index (mg HC/g TOC) vs. dinosterol (μ g/g TOC) diagrams of core PS2458-4.

ticulate organic matter (lamalginites and dinoflagellate cysts) occur in significant amounts in this interval of core PS2458-4 (Boucsein, personal communication, 1997). This relative increase in the proportion of marine organic matter at the Laptev Sea continental slope occurred near 10,000 Cal. yr BP (Fig. 5), i.e., near the end of the last major post-glacial sealevel rise (cf. Fairbanks, 1989) when the Laptev Sea shelf became widely flooded. Since that time, the modern environmental situation appears to have been established.

Large volumes of sediments and associated organic matter, supplied by the major rivers such as the Lena, have accumulated on the Laptev Sea shelf. Modern (Holocene) accumulation rates of terrigenous organic matter reach high values of 0.2-2 g C $cm^{-2} kvr^{-1}$ at the location of core PS2725-5 (Stein and Fahl, 1998). During a short interval in the Early Holocene (i.e., near 9000-10.000 Cal. vr BP) when the Laptev Sea shelf became flooded and coastal erosion and/or river discharge distinctly increased, these values may have even reached 10-15 g C cm⁻² kyr⁻¹ (Stein and Fahl, 1998). Significant proportions of terrigenous organic matter, however, are also incorporated into the sea-ice and further transported offshore within the Transpolar Drift System (cf. Fig. 1). During melting processes, the organic (as well as inorganic) matter becomes released and settles to the deep-sea floor. Thus, in areas of the central Arctic Ocean characterized by very low phytoplankton productivity due to the more or less closed sea-ice cover (Subba Rao and Platt, 1984), the majority organic matter in the surface sediments may be of terrigenous origin (Stein et al., 1994; Schubert and Stein, 1996; Stein and Schubert, 1996). The n-alkane concentration in the central Arctic Ocean surface sediments, for example, are very similar to those determined in the Laptev Sea shelf sediments (Table 3).

6. Conclusion

* Total organic carbon, hydrogen index, C/N and biomarker records from the Laptev Sea continental margin provide information about variation in the input of terrigenous and marine organic carbon during the last 10,000–15,000 Cal. yr BP. * On the Laptev Sea shelf, (fluvial) terrigenous organic matter supply was most important throughout the last about 10,000 Cal. yr BP, with maximum values reached in the Early Holocene (i.e., 9000– 10,000 Cal. yr BP).

* On the upper continental slope a major increase in marine organic matter occurred near 10,000 Cal. yr BP, when the Laptev Sea shelf became largely flooded and the modern environmental situation established.

* The comparison of the river-dominated shelf cores (KD9502-14 and PS2725-5) with the continental slope core (PS2458-4), where marine productivity is enhanced, provides an excellent example of the possible problems and limitations in using biomarkers as terrigenous and marine organic-carbon-source indicators.

Acknowledgements

We especially thank M. Siebold for technical assistance. We thank T.I. Eglinton, J. Jasper, M. Yunker and one anonymous reviewer for numerous constructive suggestions and comments. This study was performed within the bilateral Russian–German multidisciplinary research project 'System Laptev Sea'. For discussion of the stratigraphic framework and further paleoenvironmental data obtained from Laptev Sea sediments, we would like to thank all colleagues from AWI and GEOMAR Kiel involved in this Laptev Sea-Project. The financial support by the Ministry for Education, Science, Research, and Technology (BMBF) is gratefully acknowledged. This is contribution No. 1444 of the Alfred-Wegener-Institute for Polar and Marine Research.

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