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15. ORGANIC GEOCHEMISTRY OF GREENISH CLAY AND ORGANIC-RICH SEDIMENTS SINCE THE EARLY MIOCENE FROM HOLE 985A, NORWAY BASIN[1]

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ABSTRACT

Dark, organic-rich sediments were recovered from the lower Miocene section (~16.6 Ma) in Hole 985A in the Norway Basin during Ocean Drilling Program Leg 162. Organic carbon and total sulfur contents of the dark sediments showed a maximum concentration of 5.6 and 26.1 wt%, respectively. Sulfur enrichment in the sediments indicates that these dark layers were formed under anoxic conditions in bottom water. Four dark and eight greenish gray sediment samples, ranging in age from early Miocene to Pleistocene, were analyzed for lipid-class compounds (aliphatic hydrocarbons, fatty alcohols, and sterols) using gas chromatography (GC) and GC/mass spectrometry to better understand the formation processes of the organic-rich dark layers and to reconstruct the paleoenvironmental changes. The molecular distributions of *n*-alkanes and fatty alcohols indicate that terrigenous organic matter largely contributed to both types of sediments. Significant amounts of hopanoid hydrocarbons, such as diploptene and hop-17(21)-ene, however, were detected characteristically in the dark sediments, which suggests that prokaryotes such as methane-oxidizing bacteria or cyanobacteria may have significantly contributed to the formation of these organic-rich, dark sediments. These results indicate that the bottom waters of the Norway Basin had been subjected to anoxic conditions during the early Miocene.

INTRODUCTION

The high-latitudinal oceans are key regions for understanding the global climate system and its changes throughout geological time. The deep-water convection in these areas, for example, is a major driver of the global thermohaline circulation that controls global heat transport and climate. Recently, lipid-class compounds such as alkanes and fatty alcohols have been studied in deep-sea sediments to better understand paleoenvironmental changes associated with biological activities. Because some of these biomarkers are chemically stable during early diagenesis, they are useful in the reconstruction of long-term paleoceanographic and paleoclimatologic changes. For example, *n*-alkanes and fatty alcohols studied in the black shales and/or adjacent rocks recovered by the Deep Sea Drilling Project (DSDP) and the Ocean Drilling Program (ODP) have provided some paleoenvironmental signatures of climate changes (e.g., Meyers et al., 1984; Simoneit, 1986; Deroo et al., 1979; Rinna et al., 1996; Stein and Stax, 1996). Pristane/phytane (Pr/Ph) ratios of sediments have also been used to indicate bottom-water redox conditions (e.g., Didyk et al., 1978).

Here we report organic geochemical studies of dark, organic-rich sediments collected from ODP Hole 985A to better understand the formation mechanism of dark/black sediment layers in relation to biological activities. Site 985 is a part of a paleoenvironmental transect from Norway to Greenland, designed to study the history of advection of temperate saline Atlantic waters into the Norwegian-Greenland Sea. Dark, organic-rich sediments have rarely been recovered from previous DSDP and ODP sites in the northern North Atlantic. Therefore, organic geochemical analyses of these dark layers may provide information about the origin of the organic matter in the Norway Basin and about the state of bottom-water conditions since the early Miocene.

SAMPLES AND METHODS

Sediment Samples and Age Controls

We recovered six layers of dark, organic-rich sediments from Hole 985A (66°56.490′N, 66°27.012′W, 2788 m water depth), which was drilled on the eastern slope of the Iceland Plateau in the Norway Basin (Fig. 1). The organic-rich layers were observed in Core 162-985A-37X (338–347 meters below seafloor [mbsf]). Carbonate contents in these layers were found to be nearly zero (Shipboard Scientific Party, 1996). Shipboard age controls of Hole 985A were based primarily on magnetic polarity events and biostratigraphy (Shipboard Scientific Party, 1996). In this paper, we used the shipboard age controls, and the approximate age of the dark sediments ranged from 16.52 to 16.67 Ma (early Miocene). Unfortunately, the paleomagnetic data were unreliable in the sediments below 155 mbsf; thus, biostratigraphic information from the rare, nonbarren intervals provides the only shipboard age control for the lowermost portion of this hole (Shipboard Scientific Party, 1996). Ages of the section older than 14.40 Ma (278.79 mbsf) may be revised in the future to older ages.

Lipid Isolation, Gas Chromatography (GC), and GC/Mass Spectrometry Analysis

A total of 12 selected samples (Table 1), including four dark, organic-rich sediments, were studied for the molecular distributions of lipid-class compounds. The frozen sediment samples were thawed and the outer rims were removed to avoid potential contamination. The samples were dried and ground to a fine powder in an agate pestle. Before organic solvent extraction, dry samples (7–8 g for greenish gray sediments and 1–2 g for dark sediments) were spiked with two internal standards (1.43 µg of *n*-C_{19} fatty alcohol and 2.47 µg of *iso*-C_{21} fatty acid). Lipids were extracted three times with methanol/dichloromethane (3:1), dichloromethane/methanol (10:1), and dichloromethane/methanol (10:1) using an ultrasonic homogenizer. The extracts were isolated by a centrifuge, washed with 50 mL of 0.15-M HCl to remove salts contained in the sediments, and were then saponified with 30 mL of 0.5-M KOH/methanol for 2 hr under a reflux. Neutral components were separated by extraction with

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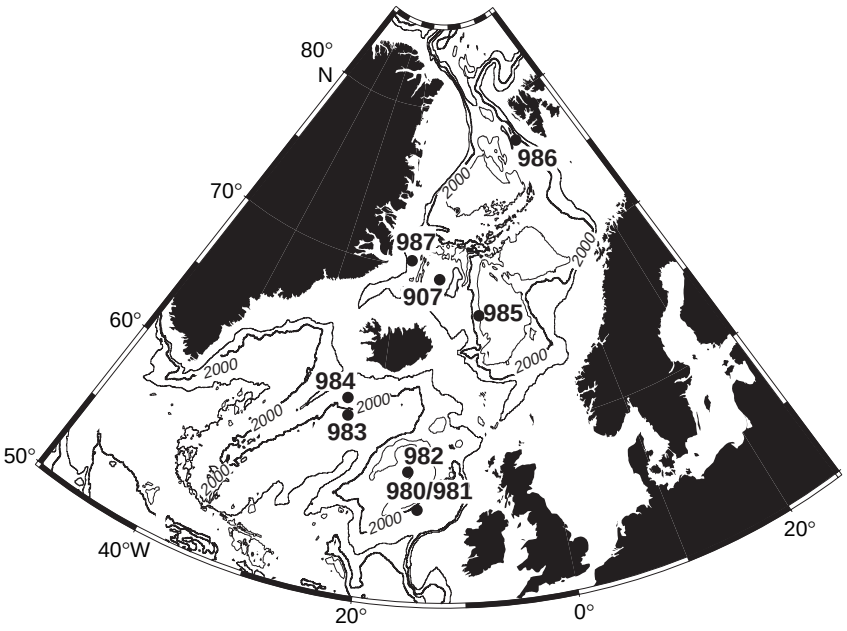

Figure 1. Location map of Site 985 in the Norway Basin. Contours are shown in meters below sea level.

Table 1. Sample list and elemental compositions of sediments from Hole 985A, Norway Basin.

Core, section, interval (cm)	Depth (mbsf)	Age (Ma)	Epoch	Lithology	TOC (wt%)	TN (wt%)	TS (wt%)	C/N molar ratio
162-985A-								
1H-3, 79-84	3.79	0.14	Pleistocene	Clayey nannofossil ooze	0.46	0.06	0.12	9.03
9H-3, 78-82	77.98	2.90	late Pliocene	Dark greenish gray silty	—	—	—	—
15H-3, 79-84	134.99	5.92	late Miocene	Dark greenish gray silty clay	—	—	—	—
19X-3, 78-82	168.48	7.68	late Miocene	Dark greenish gray clay	—	—	—	—
22X-3, 79-84	197.19	9.43	late Miocene	Dark greenish gray clay	0.28	0.06	0.47	5.24
26X-3, 79-84	235.59	11.77	middle Miocene	Dark greenish gray clay	—	—	—	—
36X-3, 79-84	331.89	16.16	early Miocene	Dark greenish gray clay	0.36	0.06	0.51	7.22
36X-3, 79-84	341.49	16.48	early Miocene	Dark greenish gray clay	0.19	0.04	0.00	5.37
37X-4, 24-27	342.44	16.52	early Miocene	Dark layer	3.83	0.28	9.98	15.9
37X-5, 82-84	344.53	16.58	early Miocene	Dark layer	3.99	0.30	19.9	15.3
37X-6, 16-18	345.37	16.61	early Miocene	Dark layer	5.64	0.39	26.1	17.0
37X-7, 31-34	347.02	16.67	early Miocene	Dark layer	4.38	0.37	18.0	14.0

Note: TOC = total organic carbon, TN = total nitrogen, TS = total sulfur, — = not measured.

dichloromethane/*n*-hexane (10:1) twice, whereas acidic components were extracted with dichloromethane three times after the remaining solution was acidified with 7 mL of 6-M HCl to pH < 2. The neutral fraction was further separated into four subfractions in a Pasteur pipette column packed with a silica gel (BIO-SIL A, 200–400 mesh), which was deactivated with 1% water (Kawamura, 1995). Aliphatic hydrocarbons (N-1), polynuclear aromatic hydrocarbons (N-2), ketones and aldehydes (N-3), and fatty alcohols and sterols (N-4) were eluted with *n*-hexane, *n*-hexane/dichloromethane (2:1), dichloromethane, and dichloromethane/methanol (95:5), respectively. The N-4 fraction was treated with bis-trimethyl-silyl-trifluoroacetamide (BSTFA) before gas chromatographic analysis.

GC analyses of the N-1 and N-4 fractions were performed with a Carlo Erba 5160 gas chromatograph installed with a cold on-column injector, a HP-5 fused silica capillary column (30 m × 0.32 mm internal diameter; 0.25-µm film thickness), and a flame ionization detector (FID). The FID temperature was maintained at 330°C. Hydrogen was used as a carrier gas, and the column oven temperature was programmed from 70° to 120°C at 30°C/min and from 120° to 320°C (30–40 min) at 6°C/min. The GC peaks were processed using a Shimadzu Chromatopac C-R7A integrator. GC/mass spectrometry analyses were performed with a Finnigan Mass Lab MD-1000 system installed with a DB-5 fused silica capillary column (60 m × 0.25 mm internal diameter; 0.25-µm film thickness). Helium was used as a carrier gas, and the gas chromatograph oven temperature was programmed from 50° (1 min) to 310°C (40 min) at 6°C/min.

During the experimental procedures, we checked the recovery of lipids by using both internal and external standards. Internal standard recovery averaged 83.7% ± 12.2% (1σ, N = 12) for *n*-C_{19} alcohol. The concentrations reported for the lipid compounds contained in the N-4 fractions were corrected for the recoveries described above. However, the concentrations of aliphatic hydrocarbons were not corrected for the recovery because the recoveries of this fraction were >90% during these procedures (Ohkouchi, 1995). Triplicate analyses of composite sediments showed that the analytical errors in the experiments were 6.2% for C_{31} *n*-alkane and 5.6% for C_{24} fatty alcohol. Blank experiments performed in parallel with sample analyses showed no serious contamination peaks. The blank:sample ratios are usually <3% for C_{25} *n*-alkane.

Measurements of Total Organic Carbon, Total Nitrogen, and Total Sulfur

Wet sediments (~1 g) were dried at 105°C for 24 hr. The dried samples were ground to a fine powder in an agate pestle. Total organic carbon (TOC), total nitrogen (TN), and total sulfur (TS) were measured with a Carlo Erba CNS elemental analyzer (NA1500). The analytical error is <0.01% for each element.

RESULTS AND DISCUSSION

Bulk Compositions

Figure 2 shows the shipboard and shore-based results of elemental analysis of sediments from Hole 985A. Except for several organic-rich layers, total organic carbon ranged from 0 to 2.30 wt% (N = 140) with an averaged value of 0.35 wt% for the whole sequence. However, the averaged TOC content (0.71 wt%) in the middle interval (177–276 mbsf: middle Miocene–late Miocene) is considerably higher than that (0.28 wt%) of the other intervals (Shipboard Scientific Party, 1996). A similar TOC enrichment was observed between 14 and 15 Ma in Holes 642B and 643A, which were drilled on the Vøring Plateau (Hölemann and Henrich, 1994). Total nitrogen contents are generally low in Hole 985A (0.03–0.15 wt%; Fig. 2); however, TN peaks are shown at the organic carbon-rich layers. Total sulfur values show a similar trend, with an average of 0.32 wt% (Fig. 2).

In the dark, organic-rich sediments (N = 4), TOC contents vary in a range between 3.83 and 5.64 wt%, ~10 times larger than those of the greenish gray sediments (Fig. 2; Table 1). TN and TS are also higher in these sediments, with concentration ranges from 0.28 to 0.39 wt% and 9.98 to 26.1 wt%, respectively (Fig. 2; Table 1). These values are extremely high compared with those of the other sequence. In particular, TS in the dark layers is ~50 times more concentrated than in the greenish gray sediments. The chemical form of the sulfur is probably pyritic sulfur because of the occurrence of significant amounts of pyrite in these layers (Shipboard Scientific Party, 1996).

A TOC vs. TS diagram (Fig. 3) provides information about the depositional environment. Sulfur is abundantly present as sulfate in seawater; thus, the limiting factor for pyrite formation under oxic seawater conditions is the amount of organic matter. In such an environment, there is a positive correlation between sulfur and organic carbon contents (e.g., Berner, 1984). Under anoxic seawater conditions, H_2S exists in the seawater. Thus, framboidal pyrite is initially formed in the water column, resulting in a surplus of sulfur in the organic carbon vs. sulfur diagram (Leventhal, 1983). Figure 3 shows an extreme enrichment of sulfur in the dark sediments. This suggests that the depositional environments were very anoxic, probably resulting from an increased productivity of the ocean and/or restricted deep-water ventilation in the Norway Basin region during the early Miocene.

Molecular Characteristics of Organic-Rich Sediments

Normal and Isoprenoid Hydrocarbons and Fatty Alcohols

Homologous series of C_{13}–C_{37} *n*-alkanes were detected in the sediments (Fig. 4), as well as pristane and phytane. Total concentrations of the *n*-alkanes ranged between 342 and 3360 ng/g dry sediments (Table 2). Molecular distributions of long-chain C_{25}–C_{35} *n*-alkanes in most samples showed an odd carbon-number predominance with a maximum at C_{29} or C_{31} (Fig. 4). The carbon preference indexes (CPI: ratio of the amounts of odd-carbon *n*-alkanes to those of even-carbon *n*-alkanes) for C_{25}–C_{34} *n*-alkanes vary from 2.84 to 5.77 in the greenish gray sediments and from 2.37 to 2.88 in the dark sediments, respectively (Fig. 5; Table 2). Mean carbon numbers (MC#: the concentration-weighted, mean carbon-chain length; Peltzer and Gagosian, 1989) for C_{25}–C_{35} *n*-alkanes vary from 28.6 to 30.0 in the greenish gray sediments and from 30.1 to 30.5 in the dark sediments, respectively (Fig. 5; Table 2).

Concentrations of pristane and phytane in the 12 samples ranged from 3.84 to 44.6 ng/g dry sediments and from 1.97 to 29.7 ng/g dry sediments, respectively. Pristane/phytane (Pr/Ph) ratios ranged from 1.0 to 2.6 (Fig. 5; Table 2). The Pr/Ph ratios of three dark sediments (Samples 162-985A-37X-5, 82–84 cm; 37X-6, 16–18 cm; and 37X-7, 31–34 cm) are nearly unity, suggesting that these dark sediments may have been deposited under anoxic conditions in bottom water.

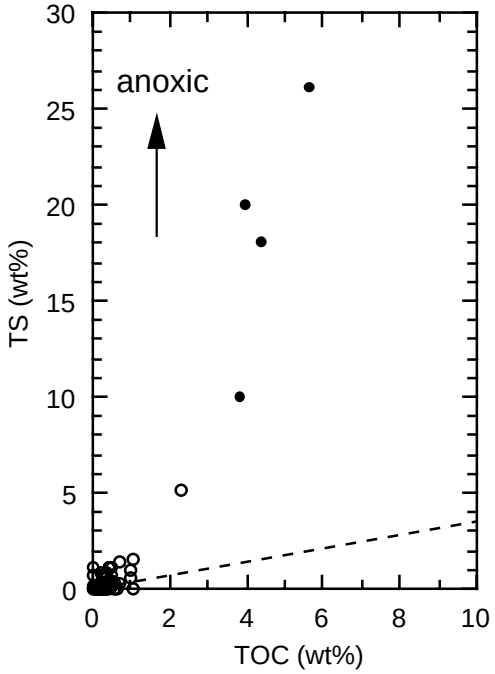

Figure 3. TOC vs. TS diagram from Hole 985A. Open circles indicate greenish gray clay; solid circles indicate dark sediments. The dashed line shows a C/S ratio of 2.8, which is an average for normal marine detrital sediments from the Quaternary (Berner, 1984).

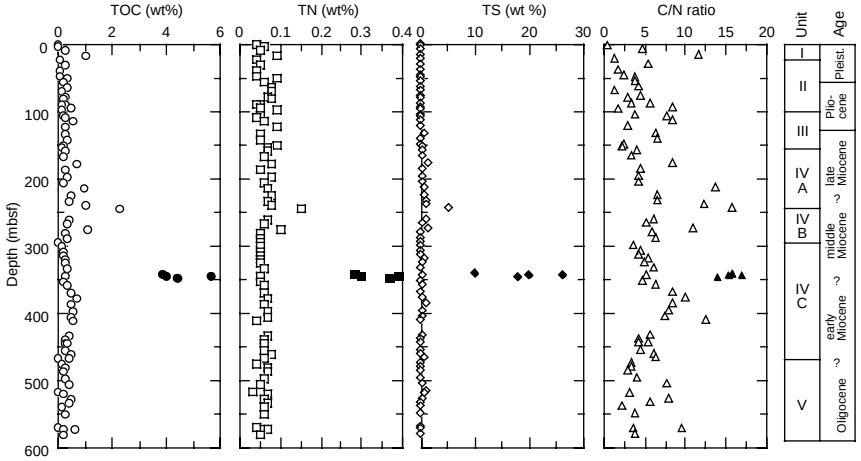

Figure 2. Total organic carbon (TOC), total nitrogen (TN), and total sulfur (TS) contents and TOC/TN (C/N) molar ratios, lithostratigraphic units, and ages from Hole 985A. Open symbols show data from greenish gray sediments; solid symbols show data from dark sediments.

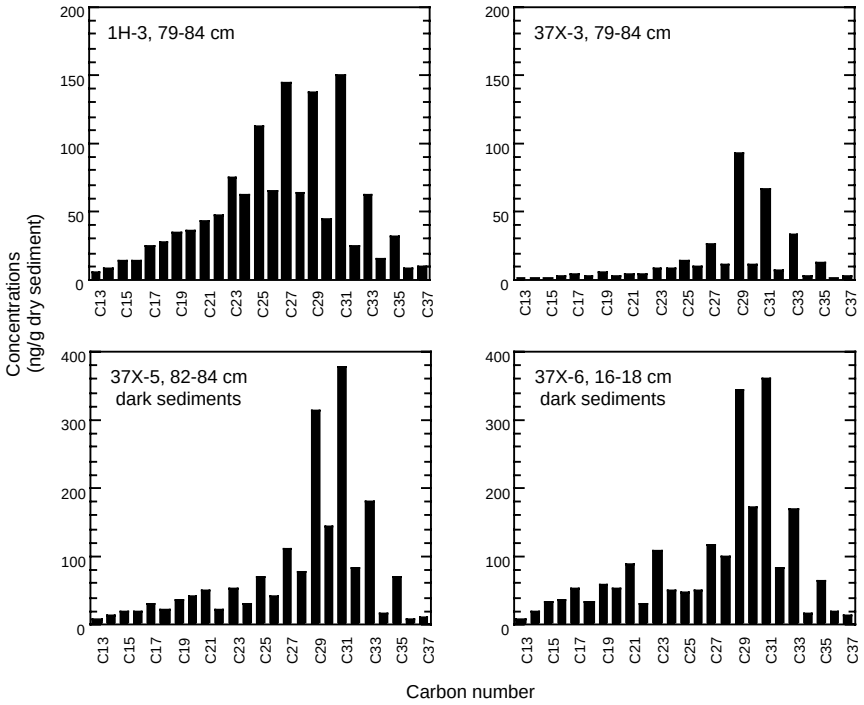

Figure 4. Chain-length distributions of *n*-alkanes in two greenish gray sediments (Samples 162-985A-1H-3, 79–84 cm; and 37X-3, 79–84 cm) and two dark, organic-rich sediments (Samples 162-985A-37X-5, 82–84 cm; and 37X-6, 16–18 cm).

Table 2. Analytical results of hydrocarbons in sediments from Hole 985A.

Core, section, interval (cm)	Depth (mbsf)	Age (Ma)	Pristane (ng/g ds)	Phytane (ng/g ds)	Pr/Ph	Total *n*-alkanes (ng/g ds)	$C_{17–20}$ *n*-alkanes (ng/g ds)	$C_{25–35}$ *n*-alkanes (ng/g ds)	CPI (C_{25}–C_{34})	MC# (C_{25}–C_{35})
162-985A-										
1H-3, 79-84	3.79	0.14	42.6	27.1	1.58	1260	122	852	2.84	28.9
9H-3, 78-82	77.98	2.90	13.7	6.76	2.03	2230	99.4	1720	4.52	28.6
15H-3, 79-84	134.99	5.92	35.0	13.4	2.61	3360	207	2490	3.70	28.6
19X-3, 78-82	168.48	7.68	12.8	8.04	1.59	750	52.3	601	4.30	29.4
22X-3, 79-84	197.19	9.43	10.8	7.28	1.48	928	50.9	765	4.45	29.0
26X-3, 79-84	235.59	11.77	42.7	24.2	1.77	2310	161	1940	3.71	29.8
36X-3, 79-84	331.89	16.16	10.8	6.72	1.60	680	48.5	549	3.06	30.0
37X-3, 79-84	341.49	16.48	3.84	1.97	1.96	342	16.0	289	5.77	29.8
37X-4, 24-27	342.44	16.52	44.6	29.7	1.50	3300	261	2660	2.37	30.5
37X-5, 82-84	344.53	16.58	11.7	11.1	1.05	1850	128	1490	2.88	30.1
37X-6, 16-18	345.37	16.61	18.9	17.4	1.09	2110	196	1520	2.47	30.1
37X-7, 31-34	347.02	16.67	8.30	8.36	0.99	2590	97.1	2280	2.54	30.1

Notes: ds = dry sediments, Pr/Ph = pristane/phytane ratio. CPI = carbon preference index (the ratio of the amounts of odd-carbon *n*-alkanes to those of even-carbon *n*-alkanes [Peltzer and Gagosian, 1989]). MC# = mean carbon number (the concentration-weighted, mean carbon-chain length [Peltzer and Gagosian, 1989]).

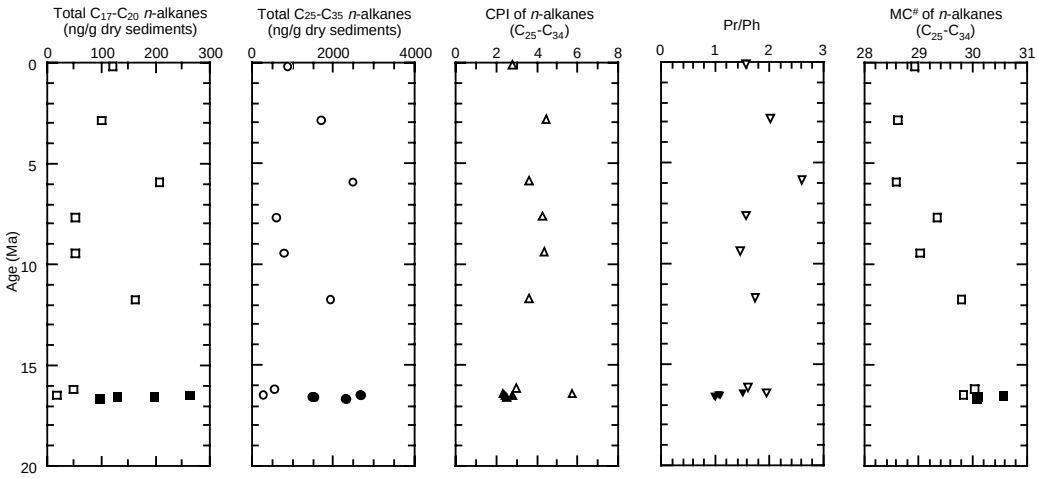

Figure 5. Concentrations of total C_{17}–C_{20} *n*-alkanes and total C_{25}–C_{35} *n*-alkanes in sediments from Hole 985A vs. age, together with CPIs (C_{25}–C_{34}), Pr/Ph ratios, and MC#s (see text for abbreviations). Symbols as in Figure 2.

Pr/Ph ratios of oils or bitumens have been used to indicate the redox potential of the source sediments (Didyk et al., 1978). Pr/Ph <1 indicates anoxic deposition, particularly when accompanied by high porphyrin and sulfur contents. Oxic conditions are indicated by Pr/Ph >1.

We also detected fatty alcohols and sterols in the greenish gray and dark sediments. Homologous series of saturated C_{12}–C_{30} fatty alcohols were detected in the sediments, as well as cholesterol (cholest-5-en-3ß-ol), ß-sitosterol (24-ethyl-cholest-5-en-3ß-ol), and dinosterol (4,23,24-trimethyl-5α[H]-cholest-22-en-3ß-ol). Total concentrations of C_{24}–C_{30} fatty alcohols varied between 280 and 6770 ng/g dry sediments (Table 3). Fatty alcohols show a strong even carbon-number predominance with a peak at C_{28} or C_{30}. Relatively short-chain, C_{12}–C_{20} alcohols are thought to be mainly derived from marine organisms and bacteria, whereas the C_{24}–C_{30} alcohols are mainly derived from vascular plants (e.g., Eglinton and Hamilton, 1967; Tulloch, 1976; Simoneit, 1977; Brassell et al., 1980). As shown in Figure 6, concentrations of C_{24}–C_{30} fatty alcohols in the dark sediments are higher than those of the near and overlying greenish gray sediments, which suggests a greater contribution of terrestrial higher plants to the sediments. CPIs for C_{23}–C_{30} fatty alcohols show no typical trend with age. MC#s for C_{23}–C_{30} fatty alcohols vary from 26.5 to 28.6 in the entire sequence (Fig. 6; Table 3). Concentrations of total sterols ranged from 16.3 to 534 ng/g dry sediments (Table 3). These concentrations are distinctly lower than fatty alcohols.

The *n*-alkane distributions in dark sediments and greenish gray samples are dominated by long-chain homologs derived from epicuticular waxes of terrestrial higher plants (Eglinton and Hamilton, 1967). MC#s of *n*-alkanes and fatty alcohols show relatively higher values in the lowermost section (early Miocene) and a decrease toward the upper section (Figs. 5, 6). Rinna et al. (1996) reported a similar result for Hole 909C, Fram Strait, which is the boundary region between the Arctic Ocean and the North Atlantic. They interpreted the higher MC#s in the sediments to indicate a warmer climate (or supply of organic matter from a continental area with a warmer climate) in the Miocene. We found that MC#s of plant leaf *n*-alkanes are higher (31.4–31.5) in an equatorial region (4°N) than those (28.9–29.6) in mid latitudes (27°–43°N) (Kawamura et al., 1998). Therefore, these results from Hole 985A may suggest that the climate conditions in the northern North Atlantic were warmer than in the Pliocene and/or that low- to high-latitudinal atmospheric transport of terrestrial materials was enhanced during the early Miocene.

The CPI values are known to be 5–10 for terrestrial higher plant waxes and unity for petroleum hydrocarbons and combustion residues of fossil fuels (Simoneit and Mazurek, 1982). Thus, the CPI index indicates that the lipid compounds of greenish gray sediments in

Table 3. Analytical results of *n*-fatty alcohols and sterols in sediments from Hole 985A.

Core, section, interval (cm)	Depth (mbsf)	Age (Ma)	*n*- Fatty alcohols				Sterols
			C_{12}–C_{20} (ng/g ds)	C_{24}–C_{30} (ng/g ds)	CPI (C_{23}–C_{30})	MC# (C_{23}–C_{30})	Total (ng/g ds)
162-985A-							
1H-3, 79-84	3.79	0.14	49.8	489	4.57	27.0	57.2
9H-3, 78-82	77.98	2.90	296	4040	4.81	26.6	202
15H-3, 79-84	134.99	5.92	217	4070	4.43	26.5	284
19X-3, 78-82	168.48	7.68	82.0	1150	6.42	26.8	55.0
22X-3, 79-84	197.19	9.43	71.4	1940	5.66	26.9	110
26X-3, 79-84	235.59	11.77	193	6770	5.06	27.2	361
36X-3, 79-84	331.89	16.16	32.6	488	7.23	28.1	32.9
37X-3, 79-84	341.49	16.48	26.4	280	5.76	28.1	16.3
37X-4, 24-27	342.44	16.52	363	2060	4.32	28.5	238
37X-5, 82-84	344.53	16.58	365	1440	7.30	28.6	534
37X-6, 16-18	345.37	16.61	773	1260	4.90	28.4	464
37X-7, 31-34	347.02	16.67	436	2210	5.56	28.6	359

Notes: ds = dry sediments. CPI = carbon preference index (the ratio of the amounts of even-carbon *n*-alcohols to those of odd-carbon *n*-alcohols [Peltzer and Gagosian, 1989]). MC# = mean carbon number (the concentration-weighted, mean carbon-chain length [Peltzer and Gagosian, 1989]). Sterols = cholesterol + ß-cholestanol + stigmasterol + ß-sitosterol + dinosterol.

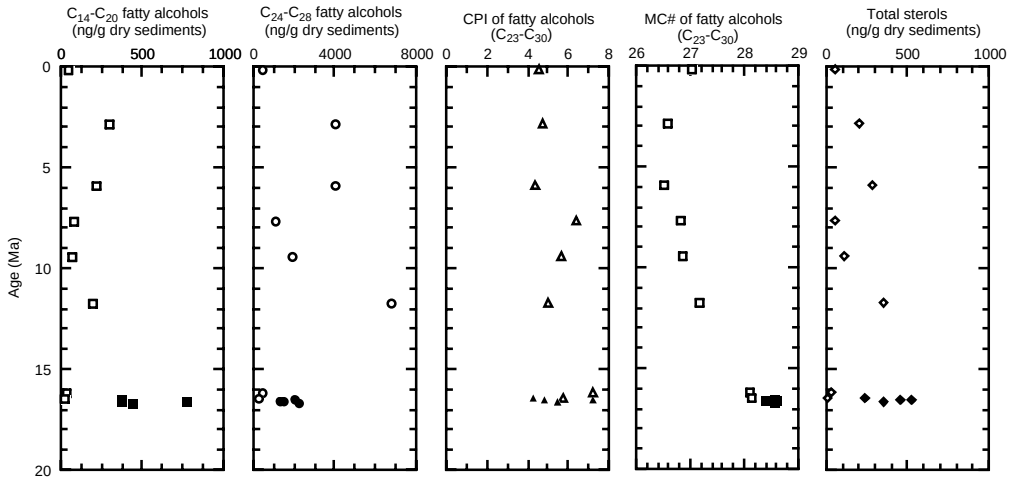

Figure 6. Concentrations of total C_{14}–C_{20} and C_{24}–C_{28} fatty alcohols, CPIs of C_{23}–C_{30} fatty alcohols, MC#s of C_{23}–C_{30} fatty alcohols, and concentrations of total sterols in the sediments from Hole 985A. Symbols as in Figure 2.

Hole 985A contain a large contribution from terrestrial higher plant waxes (e.g., Eglinton and Hamilton, 1967; Simoneit, 1978).

Hopanoid Hydrocarbons

Various hopanoid hydrocarbons were detected in the dark sediments by mass chromatography at m/z 191 (Fig. 7A). Their abundances are similar to those of higher molecular weight *n*-alkanes such as *n*-C_{31}. Oleane-12-ene (C_{30}), hop-17(21)-ene (C_{30}), and diploptene (17ß[H], 21ß[H]-hop-22[29]-ene) are dominant hopanoid hydrocarbons in these samples. Concentrations of oleane-12-ene and diploptene varied in the studied section, with a range of 10.0–897 ng/g dry sediments and 0.95–402 ng/g dry sediments, respectively (Fig. 8; Table 4). Although the hopanoid hydrocarbons were detected in the organic-lean greenish gray sediments, they are ~10 times more concentrated in the dark sediments than in greenish clay. In contrast, concentrations of hop-17(21)-ene are high in the dark sediments and range from 550 to 773 ng/g dry sediments (Fig. 8; Table 4). Their concentrations in the greenish clay, however, were below detection limits.

The dark sediments are characterized by high concentrations of hopanoid hydrocarbons and terrestrial biomarkers. In contrast, they are minor species in the greenish clay adjacent to the dark sediments. These hopanoids are generally synthesized by prokaryotes such as bacteria and cyanobacteria, with an exception of a few terrestrial eukaryotes like ferns or lichens (e.g., Ourisson et al., 1979, 1987; Rohmer et al., 1984). However, hopanoids in some terrestrial eukaryotes do not synthesize carbon skeletons >C_{30}. Bacteria appear to be the major source for the sedimentary hopanoids, such as diploptene or diplopterol (Rohmer et al., 1984). Therefore, prokaryotes, including methane-oxidizing bacteria and cyanobacteria, are responsible for the abundant presence of hopanoids in the dark sediments. These considerations led us to conclude that the bacterial activity was enhanced at the time of the formation of organic-rich sediments of the early Miocene.

Hopanes have been reported abundantly in petroleum and some sediments: the hopanoid precursors are important cellular membrane constituents of prokaryotes (e.g., Peters and Moldowan, 1993). These hopanes may have originated from prokaryotes, including cyanobacteria in the water column and methanotrophic bacteria in bottom sediments. Simoneit (1977) reported that the major hopanoid hydrocarbons detected in the Black Sea are trinorhopane, diploptene, and 17ß(H)-moret-22(29)-ene. Venkatesan (1988) also reported the presence of diploptene and hop-17(21)-ene in sediment cores from Brans-

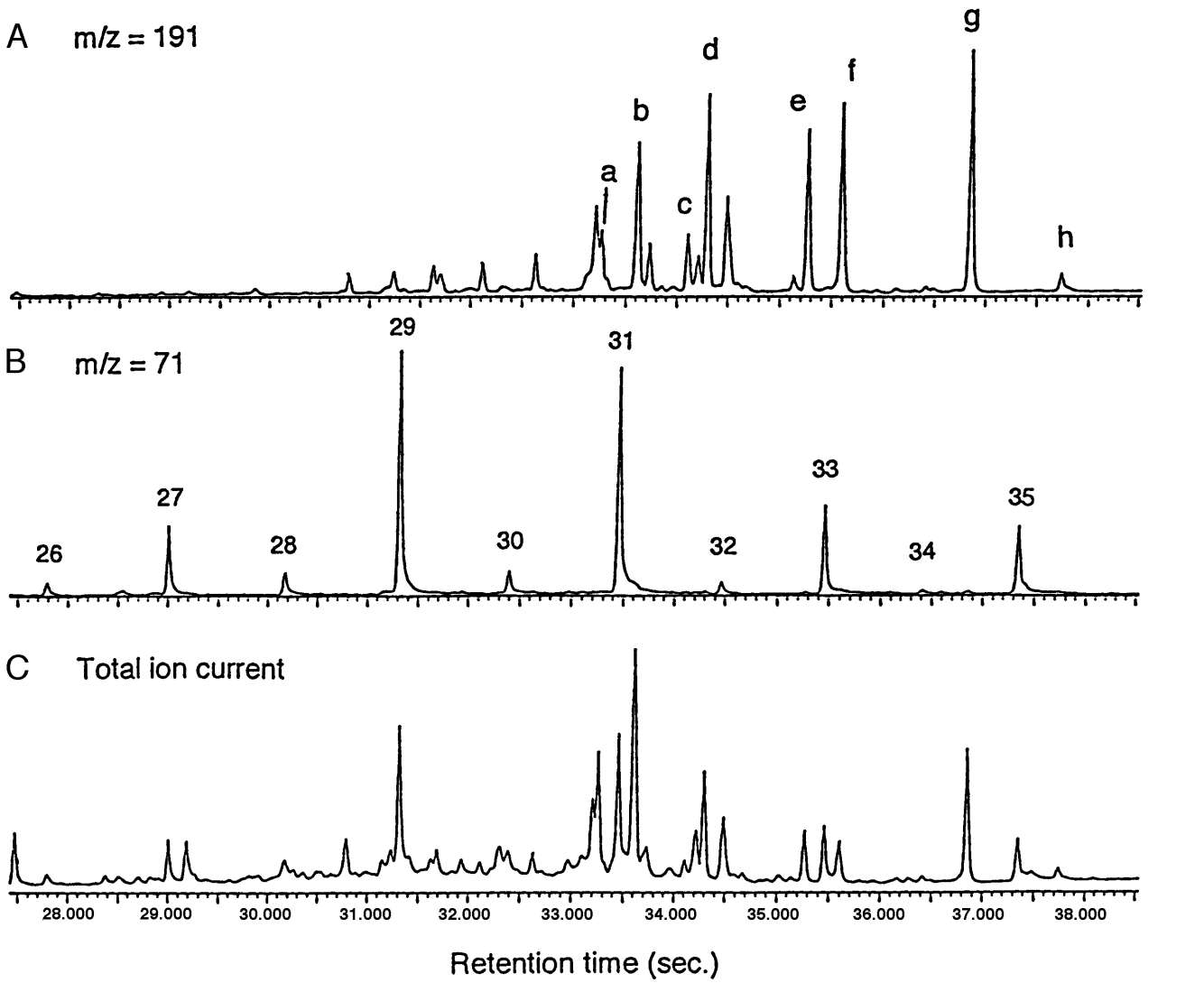

Figure 7. Partial ion chromatogram at **(A)** m/z 191 (hopanoid hydrocarbons), **(B)** m/z 71 (*n*-alkanes), and **(C)** total ion current of the aliphatic hydrocarbons separated from the dark sediments (Sample 162-985A-37X-6, 16–18 cm). Peaks: (a) olean-12-ene; (b) hop-17(21)-ene; (c) C_{30} αß-hopane; (d) diploptene; (e) C_{31} αß-hopane; (f) C_{30} ßß-hopane; (g) C_{31} ßß-hopane; and (h) C_{32} ßß-hopane.

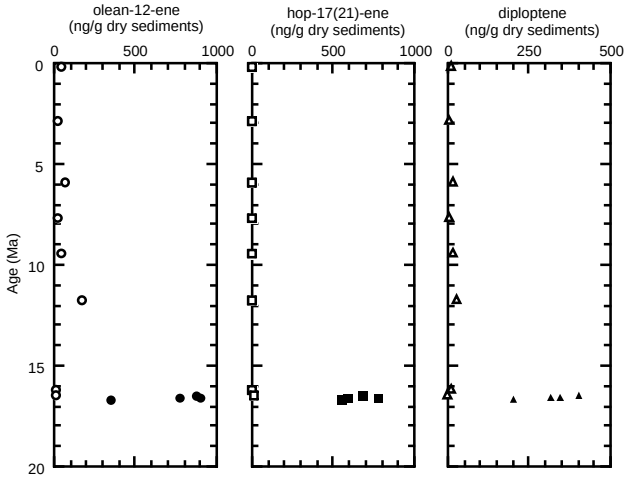

Figure 8. Concentrations of olean-12-ene, hop-17(21)-ene, and diploptene from all the sediments studied. Symbols as in Figure 2.

Table 4. Analytical results of hopanoid hydrocarbons in sediments from Hole 985A.

Core, section, interval (cm)	Depth (mbsf)	Age (Ma)	Olean-12-ene (ng/g ds)	Hop-17(21)-ene (ng/g ds)	Diploptene (ng/g ds)
162-985A-					
1H-3, 79-84	3.79	0.14	43.7	ND	13.6
9H-3, 78-82	77.98	2.90	26.3	ND	5.86
15H-3, 79-84	134.99	5.92	74.3	ND	18.7
19X-3, 78-82	168.48	7.68	17.7	ND	5.21
22X-3, 79-84	197.19	9.43	51.0	ND	14.5
26X-3, 79-84	235.59	11.77	171	ND	29.2
36X-3, 79-84	331.89	16.16	10.0	ND	11.3
37X-3, 79-84	341.49	16.48	11.2	7.14	0.95
37X-4, 24-27	342.44	16.52	877	677	402
37X-5, 82-84	344.53	16.58	897	581	315
37X-6, 16-18	345.37	16.61	765	773	344
37X-7, 31-34	347.02	16.67	349	550	199

Note: ds = dry sediments, ND = not detected.

field Strait and McMurdo Sound, Antarctica, and concluded that these hopanes are probably derived from phytoplankton and/or planktonic bacteria. Recently, Ohkouchi et al. (1997) reported that several hopanols and hopanoic acids occur abundantly in the Cretaceous (Cenomanian/Turonian boundary) black shales and proposed that the cyanobacteria could be a major source of organic matter in these shales.

SUMMARY AND CONCLUSIONS

Organic-rich dark sediments and organic-lean greenish gray sediments obtained from the Norway Basin (Hole 985A) from the lower Miocene–Pleistocene were analyzed for lipid-class compounds, including aliphatic hydrocarbons and fatty alcohols.

1. TOC, TN, and TS concentrations in the dark sediments are very high compared with those of organic-lean clay. Distributions of *n*-alkanes and fatty alcohols indicate that large amounts of terrestrial components contributed to the deposition of dark sediments during the early Miocene.
2. Pristane/phytane (Pr/Ph) ratios are nearly unity, and total sulfur concentrations are extremely high (9.98–26.1 wt%) in the dark sediments. This suggests that the dark layers formed under anoxic conditions in bottom water within the Norway Basin during the early Miocene.
3. Bacterially derived compounds, such as hopanoid hydrocarbons, are characteristically abundant in the dark sediments deposited in the early Miocene. This study indicates that prokaryotes, such as methane-oxidizing bacteria or cyanobacteria, may have significantly contributed to the formation of these organic-rich, dark sediments.

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