37. C_2–C_8 HYDROCARBONS IN SEDIMENTS FROM DEEP SEA DRILLING PROJECT LEG 75, HOLES 530A, ANGOLA BASIN, AND 532, WALVIS RIDGE[1]

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ABSTRACT

A series of C_2–C_8 hydrocarbons (including saturated, aromatic, and olefinic compounds) from deep-frozen core samples taken during DSDP Leg 75 (Holes 530A and 532) were analyzed by a combined hydrogen-stripping/thermovaporization method. Concentrations representing both hydrocarbons dissolved in the pore water and adsorbed on the mineral surfaces vary in Hole 530A from about 10 to 15,000 ng/g of dry sediment weight depending on the lithology (organic-carbon-lean calcareous oozes versus "black shales"). Likewise, the organic-carbon-normalized C_2–C_8 hydrocarbon concentrations vary from 3,500 to 93,100 ng/g C_{org}, reflecting drastic differences in the hydrogen contents and hence the hydrocarbon potential of the kerogens. The highest concentrations measured of nearly 10^5 ng/g C_{org} are about two orders of magnitude below those usually encountered in Type-II kerogen-bearing source beds in the main phase of petroleum generation. Therefore, it was concluded that Hole 530A sediments, even at 1100 m depth, are in an early stage of evolution. The corresponding data from Hole 532 indicated lower amounts (3,000–9,000 ng/g C_{org}), which is in accordance with the shallow burial depth and immaturity of these Pliocene/late Miocene sediments.

Significant changes in the light hydrocarbon composition with depth were attributed either to changes in kerogen type or to maturity related effects.

Redistribution pheonomena, possibly the result of diffusion, were recognized only sporadically in Hole 530A, where several organic-carbon lean samples were enriched by migrated gaseous hydrocarbons.

The core samples from Hole 530A were found to be severely contaminated by large quantities of acetone, which is routinely used as a solvent during sampling procedures on board *Glomar Challenger*.

INTRODUCTION

The geochemistry of low-molecular weight hydrocarbons in Deep Sea Drilling Project (DSDP) cores has been studied in detail by Hunt (1974, 1975, 1978), Faber et al. (1978), Hunt and Whelan (1978a, b; 1979), Whelan and Hunt (1978, 1979, 1980), Whelan (1979), Whelan and Sato (1980), Whelan et al. (1980), and Schaefer et al. (1983). One of the main conclusions of their comprehensive studies was that these compounds (C_1–C_7 molecular range) are generated from the kerogen by *in situ* low-temperature reactions and, therefore, represent a very sensitive indicator for the degree of thermally controlled hydrocarbon generation starting at sedimentary interface temperatures. The exception is methane, which can, in addition, be formed in large quantities by bacterial action. Recently, the formation of trace quantities of C_4–C_7 hydrocarbons (including olefins) from bacterial degradation of naturally occurring terpenoids has been demonstrated in laboratory experiments (Hunt et al., 1980). Whelan et al. (1982) found small amounts of volatile organic compounds in macroalgae in concentrations high enough to suggest that the seaweeds are a source for some of the volatile hydrocarbons identified in recent marine sediments. It is, however, not yet clear if these sources may account for a sizable proportion of the total light hydrocarbon fraction encountered in low mature or immature ancient sediments. A dual origin of low-molecular weight hydrocarbons in these sediments appears possible.

Furthermore, the study of light hydrocarbons is a valuable tool for recognizing redistribution or migration in the subsurface. This is because light hydrocarbons are more water soluble than their higher homologues. Also, among the various compound classes such as aromatics, saturated cyclic, branched, and straight-chain alkanes there are greater variations in the degree of mobility through the water-saturated pore space of the sediments.

Holes 530A and 532, DSDP Leg 75, off the southwestern margin of Africa, penetrated a sequence of organic-carbon-rich strata. Therefore, light hydrocarbon generation could be anticipated. It was one objective of the present study to recognize if and to what extent low molecular weight hydrocarbons have been generated as a function of the maturity and type of organic matter present in those sediments. Secondly, we hoped to recognize the possible redistribution of light hydrocarbons between adjacent layers of organic-rich "black shales" and organic-carbon-lean strata.

During the cruise of the *Glomar Challenger* in the South Atlantic (August, 1980) 58 core samples (37 from Hole 530A, and 21 from Hole 532) were collected for this study in sealed vials and were deep-frozen on board. The stratigraphic distribution of these samples turned out to be ideal for the first objective, since every core was sampled at regular intervals. However, this sample set was less well suited to meet the second objective—examination of redistribution phenomena. Only at four

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[1] Hay, W. W., Sibuet, J.-C., et al., *Init. Repts. DSDP,* 75: Washington (U.S. Govt. Printing Office).

intervals were adjacent organic-carbon-rich and lean layers available for comparison (Hole 530A).

METHOD

Fifty-eight small sediment samples (approximately 10 g) were collected on board immediately after the cores had been cut into sections. Samples were stored in aluminum-foil sealed, 20-ml screw-capped glass flasks in a deep freezer, where they remained in a deep-frozen condition (approx. −20°C) until the analyses were performed in the laboratory at KFA Julich. The low-molecular-weight hydrocarbons (molecular range C_2–C_8) were analyzed by a slightly modified, combined hydrogen-stripping/thermovaporization method described in detail by Schaefer et al. (1978). The method was modified since all core samples from Hole 530A turned out to be extensively contaminated by acetone. Similar contamination effects have been detected in samples from Site 511 of Leg 71 (Schaefer et al., 1983). As in Leg 71, this contamination is introduced during sampling procedures. On board *Glomar Challenger*, acetone is routinely used for sealing each 1.5-m length core section in the plastic core liner by rinsing both plastic caps with this solvent before they are pressed on both ends. Obviously, the excess acetone penetrates and contaminates the cores. This contamination effect is severe. In all samples from Hole 530A, the concentration of acetone by far exceeded that of the total light hydrocarbons. One of the most critical possible consequences of this contamination might be the introduction into the cores of other volatile compounds, including hydrocarbons, if the acetone used is not absolutely pure. The samples analyzed from Hole 532, which was hydraulic piston cored, did not contain any acetone.

The analytical method used in this study utilizes the extraction of hydrocarbons from the rock and subsequent capillary gas chromatography in a single-step procedure carried out in a closed gas-flow system (Schaefer et al., 1978). Briefly, a small portion of the freshly crushed sediment sample (generally between 0.1 and 1.0 g) is placed in the flow system of a capillary gas chromatograph, the hydrogen carrier gas serving as the stripping gas. Simultaneously the rock sample is heated to 110°C for 5 minutes in a hydrogen flow of 5 ml/min. We have indications that the yields obtained by this procedure represent nearly the absolute quantities of hydrocarbons present, both dissolved in the pore water and adsorbed on mineral surfaces. Hence, the concentration values obtained cannot easily be compared with light hydrocarbon data from other techniques, e.g., from headspace analyses.

Prior to chromatographic separation, the mobilized compounds are passed through a small section of a mixture of dry $CaCl_2$ and silica gel (for details see Schaefer et al., 1983) in order to prevent the pore water and the acetone from entering the gas chromatographic column. The analysis is carried out using a modified Perkin Elmer 3920 gas chromatograph (GC), equipped with a 45 m length, 0.5 mm i.d. S.C.O.T. column with squalane stationary phase and hydrogen carrier gas, run isothermally at 55°C and connected to a flame-ionization detector. The GC detector output is connected to a chromatography data system (Datachrom II, Kratos Instem Ltd., Stone, England) run on a PDP11/10 computer (Digital Equipment Corp.). This on-line system generates partially processed data (peak areas and retention times) on punched tape for off-line calculations of retention indices and compound concentrations. The latter are based on a daily calibration of the gas chromatography with n-butane in hydrogen (50 ppm by volume) as the external standard.

Organic carbon contents of the sediments have been measured on the stripped samples after treatment with hot 6N HCl by a combustion method (LECO Carbon Analyzer IR 112).

Data on kerogen qualities (hydrogen indices) were obtained for samples from Hole 530A (Cores 91 through 104) by application of the Rock-Eval pyrolysis procedure (Espitalié et al., 1977).

RESULTS AND DISCUSSION

Generation of Low-Molecular Weight Hydrocarbons

Hole 530A

Low-molecular-weight hydrocarbons (38 compounds identified in the C_2–C_8 molecular range) were analyzed in 37 core samples covering the depth interval 764 to 1088 m (Cores 68 to 104). The concentrations, normalized to dry weight sediment, are listed in Table 1. The compounds are arranged in sequence of increasing retention on squalane as the stationary GC phase.

The total light-hydrocarbon concentrations in Hole 530A (sum of all compounds identified except the olefins) are plotted against depth in Figure 1, both in absolute and organic-carbon-normalized units (ng/g of dry weight sediment and ng/g of organic carbon, respectively). As also shown on this figure, the organic-carbon content (measured on the identical samples) ranges from about 0.06 to 0.2% in most samples. Only in lithologic Unit 8 (red and green claystone and marlstone with interbedded black shales) were the following samples with elevated organic carbon contents ($>1.0\%$ C_{org}) available for study: A black shale sample from Core 95, Section 2, 93–94 cm with 24.6% C_{org}; two samples from Core 97: Section 2, 56–58 cm and Section 4, 48–50 cm, which have 15.5 and 4.45% C_{org}, respectively; and a sample from Core 96, Section 6, 8–9 cm, where C_{org} was 1.37%. These are samples of the 260 beds of organic-rich black-shale layers (1–60 cm thick) penetrated by Hole 530A in a sequence of 165 m of Late Cretaceous pelagic, fine-grained turbiditic basinal sediments.

From Figure 1 it is apparent that hydrocarbon concentrations vary over the whole depth range by more than three orders of magnitude—i.e., between about 10 for the organic-carbon-lean samples and 14,400 ng/g dry weight sediment for the black shale of Core 97 (Sample 530A-97-2, 56–58 cm). This drastic variation is also evident from Figure 2, where the hydrocarbon concentrations of all samples are plotted vs. their organic carbon contents. The general trend, apart from significant data scatter particularly among the organic-carbon-lean samples, deviates only slightly from a linear relationship (diagonal in log/log plot) indicating that, generally, these hydrocarbons are formed *in situ* by low-temperature degradation of organic matter. To eliminate the influence of fluctuations in organic carbon contents, the hydrocarbon concentrations are also shown in Figure 1 in carbon-normalized units (black circles). There is still a considerable variation despite this normalization step. Values vary from about 3,500 to 93,100 ng/g of organic carbon. Fluctuations are, however, of a greater magnitude in Unit 8 than in the overlying section. They are probably caused by the pronounced variation in kerogen quality in this sample set. As shown in Table 1, the hydrogen index, which characterizes kerogen quality, varies in Unit 8 between 10 and 625 mg hydrocarbons/g C_{org}. Such drastic changes in the hydrogen content of the kerogen indicate significant differences in potential for generating low-molecular-weight hydrocarbons. As expected, therefore, the highest hydrogen index black-shale sample (530A-97-2, 56–58 cm) has the highest light-hydrocarbon yield of nearly 10^5 ng/g C_{org}. However, as is obvious from Figure 1 and Table 1, some samples have high hydrocarbon concentrations (organic carbon normalized units) despite their low organic carbon contents and low hydrogen indices—e.g., Sample 530A-96-2, 7–8 cm, where 74,000 ng/g C_{org} are reached. It is thought that this sample is,

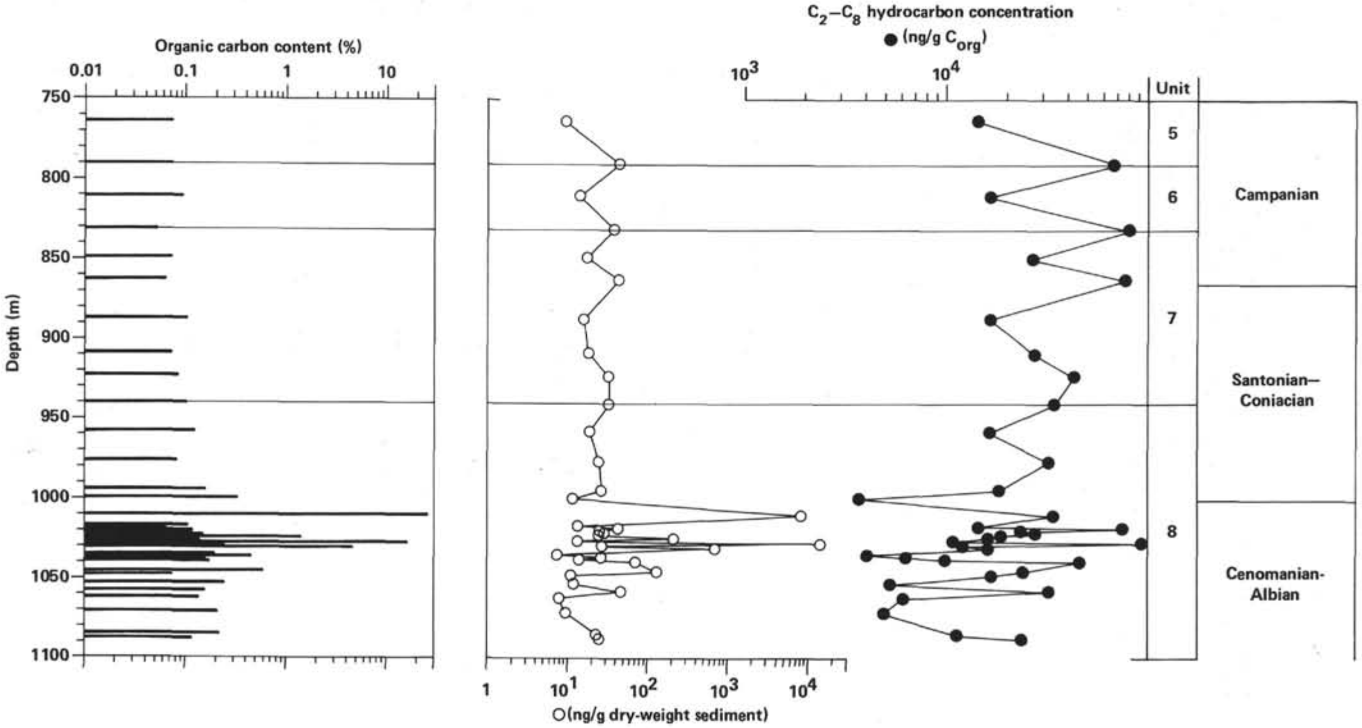

Figure 1. Organic carbon and low-molecular-weight hydrocarbon content (sum of all C_2 to C_8 hydrocarbons identified in Table 1, except olefins) vs. depth for sediment samples from DSDP Hole 530A, Leg 75. Lithologic Units 5 to 8 and stratigraphy as defined by Leg 75 shipboard scientists. (Revisions of stratigraphic ages are given in Steinmetz et al., this volume.)

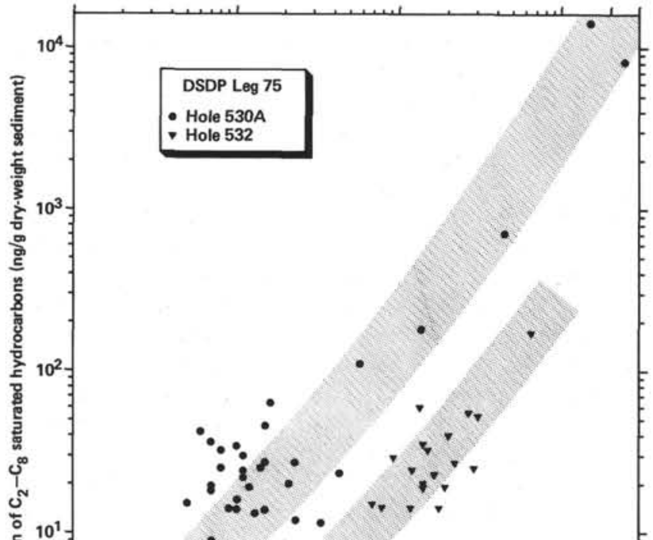

Figure 2. C_2–C_8 saturated hydrocarbon concentration in ng/g of dry-weight sediment vs. organic-carbon content for core samples from DSDP Holes 530A and 532, Leg 75. (Estimated trend marked by stippled signature.)

at least to some degree, enriched by migrated gaseous hydrocarbons. Criteria for differentiation between *in situ* formed versus migrated light hydrocarbons will be discussed below. In Figure 1 no regular increase of light hydrocarbon concentrations with depth, reflecting a generation trend with maturity increase, can be established. This is thought to be because the sampled interval of less than 350 m is too short in view of a low maturity gradient.

In Figure 3, the total light hydrocarbon concentrations of Leg 75 samples are compared to those of Jurassic–Aptian black shales from Leg 71 and also to those of three good-quality petroleum source rock units of different maturities (Schaefer et al., in press). The concentrations reached in the black shales of Hole 530A indicate that considerable quantities of gasoline-range hydrocarbons have indeed been generated. However, as is also obvious from Figure 3, values of about 10^5 ng/g C_{org} are far below those typically encountered in mature ($\overline{R}_o = 0.8$ to 0.9%) Type-II kerogen-bearing source rocks. The concentrations of total C_2–C_8 saturated hydrocarbons (organic-carbon normalized units) measured in three black shale samples (4% minimum organic carbon content) are compared to those of the following:

1) Jurassic–Aptian black shales of Site 511, Leg 71, Falkland Plateau (mean organic carbon content = 3.4%; mean hydrogen index (I_H) = 278 mg/g C_{org}; $\overline{R}_o = 0.4$ to 0.5% (see Schaefer et al., 1983).

2) Toarcian shales from northwest Germany (mean C_{org} = 9.6%; mean I_H = 890 mg/g C_{org}; $\overline{R}_o = 0.41$%;

Table 1. Summary of low-molecular-weight hydrocarbon concentrations, organic carbon contents, and Rock-Eval pyrolysis hydrogen indices of core samples from DSDP Hole 530A, Leg 75.

Reference no.	Core-Section (interval in cm)	68-2, 82–84	71-1, 18–20	73-2, 29–31	75-3, 15–17	77-2, 64–66	78-5, 8–10	81-2, 74–76	83-4, 43–45	85-1, 105–107	87-1, 65–67	89-1, 4–6
	Depth (m)	763.82	790.18	810.79	831.15	849.14	862.58	887.24	908.93	923.05	940.65	958.04
	Organic carbon content (% dry weight sediment)	0.07	0.07	0.09	0.05	0.07	0.06	0.10	0.07	0.08	0.10	0.12
	Hydrogen index [mg HC/g C_{org}]	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.
Hydrocarbon concentration (ng/g dry weight sediment)												
1	Ethene	0.52	1.5	0.67	0.24	0.78	1.3	0.78	1.0	0.70	0.95	0.80
2	Ethane	2.0	5.6	3.5	0.35	5.3	7.6	3.1	3.6	6.3	6.0	3.7
3	Propene	0.37	2.5	1.1	0.29	—	1.9	0.81	1.7	1.6	—	1.2
4	Propane	2.7	10.0	4.4	1.6	3.9	12.5	5.6	7.1	9.6	11.0	6.8
5	Methylpropane	0.58	4.1	1.3	1.5	1.8	3.6	1.9	2.0	2.2	2.6	2.4
6	Methylpropene + 1-Butene	0.89	6.6	2.1	2.2	1.8	3.2	2.2	3.5	1.8	2.9	4.6
7	n-Butane	0.88	5.5	1.9	3.0	3.0	7.0	2.3	2.6	5.5	4.9	3.0
8	trans-2-Butene	0.14	0.83	0.35	0.46	0.37	0.57	0.34	0.53	0.38	0.63	0.52
9	2, 2-Dimethylpropane	—	0.06	—	—	—	—	—	—	—	0.05	—
10	cis-2-Butene	0.13	0.77	0.29	0.44	0.30	0.50	0.30	0.42	0.31	0.56	0.42
11	Methylbutane	0.54	2.2	0.66	1.4	0.72	2.1	0.93	0.90	1.4	1.6	1.1
12	n-Pentane	0.71	3.7	1.2	2.8	1.4	4.6	1.2	1.3	3.4	3.1	1.5
13	2, 2-Dimethylbutane	0.01	0.04	0.02	0.02	—	0.12	—	—	0.04	0.06	0.02
14	Cyclopentane	<0.1	0.18	0.05	0.12	<0.1	0.19	<0.1	<0.1	0.17	0.14	<0.1
15	2, 3-Dimethylbutane	—	—	—	—	—	—	—	—	—	—	—
16	2-Methylpentane	0.13	0.63	0.16	0.52	0.19	0.61	0.18	0.20	0.51	0.51	0.10
17	3-Methylpentane	0.10	0.43	0.10	0.41	0.18	0.38	0.12	<0.1	0.33	0.40	<0.1
18	n-Hexane	0.34	2.0	0.56	2.0	0.69	2.3	0.50	0.56	2.1	2.6	0.24
19	Methylcyclopentane + 2, 2-Dimethylpentane	<0.1	0.23	0.10	0.22	0.21	0.31	0.11	—	0.25	0.29	0.10
20	2, 4-Dimethylpentane	—	—	—	—	—	—	—	—	—	—	—
21	Benzene	0.51	0.53	0.31	0.41	0.36	0.31	0.16	0.56	0.12	0.25	0.19
22	Cyclohexane	—	—	—	—	—	—	—	—	—	0.25	—
23	2-Methylhexane	—	0.15	—	—	—	—	—	—	<0.1	<0.1	—
24	2, 3-Dimethylpentane + 1, 1-Dimethylcyclopentane	—	—	—	—	—	—	—	—	<0.1	<0.1	—
25	3-Methylhexane	0.10	0.15	—	0.18	—	0.17	—	—	<0.1	<0.1	—
26	1, cis-3-Dimethylcyclopentane	0.10	—	—	—	—	—	—	—	—	—	—
27	1, trans-3-Dimethylcyclopentane	—	—	—	—	—	—	—	—	—	—	—
28	1, trans-2-Dimethylcyclopentane	—	—	—	—	—	—	—	—	—	—	—
29	n-Heptane	0.39	0.54	0.42	0.72	0.42	0.52	0.16	0.29	0.25	0.28	0.19
30	1, cis-2-Dimethylcyclopentane	—	—	—	—	—	—	—	—	—	—	—
31	Methylcyclohexane	<0.1	0.15	—	0.12	—	—	—	—	0.12	—	—
32	2, 5-Dimethylhexane	—	—	—	—	—	—	—	—	—	—	—
33	Ethylcyclopentane	—	—	—	—	—	—	—	—	—	—	—
34	1, trans-2, cis-4-Trimethylcyclopentane	—	—	—	—	—	—	—	—	—	—	—
35	1, trans-2, cis-3-Trimethylcyclopentane	—	—	—	—	—	—	—	—	—	—	—
36	Toluene	0.70	10.9	0.14	25.0	0.18	3.8	—	—	1.7	—	—
37	2-Methylheptane	—	—	—	—	—	—	—	—	—	—	—
38	n-Octane	—	—	—	—	—	—	—	—	—	—	—

Note: — = Concentration below or near detection limit; n.m. = not measured.

3) The Triassic Botneheia formation, Svalbard (mean $C_{org} = 4.4\%$; mean $I_H = 261$ mg/g C_{org}; maturity interval $\overline{R}_o = 0.66$ to 0.72%);

4) Jurassic shales, Porcupine Basin, offshore Ireland (mean $C_{org} = 1.5\%$; mean $I_H = 300$ mg/g C_{org}; maturity interval $\overline{R}_o = 0.78$-0.94%).

This comparison supports the conclusion that the organic matter in Hole 530A is immature, i.e. the maturity of the black shales from Site 511 ($\overline{R}_o = 0.4$ to 0.5%) is barely reached in Hole 530A. This conclusion agrees well with maturity data based on vitrinite reflectance by Rullkötter et al. (this volume). Furthermore, our conclusions are also supported by a comparison with light-hydrocarbon data from Holes 361 and 364, Leg 40, the Cape Basin off Capetown and the Angola Basin, respectively (Hunt, 1978). Although his analytical method is different, data on light hydrocarbon concentrations compare remarkably well. Hunt found for two Late Cretaceous organic-carbon-rich samples ($C_{org} = 4.5$ and 3.6%, respectively) of a maturity equivalent to $\overline{R}_o = 0.47\%$ (Kendrick et al., 1978) in Hole 361 about 10^5 ng C_4–C_7 hydrocarbons per gram of organic carbon. In Hole 364, which penetrated a stratigraphically similar section as Hole 530A, an organic-carbon-rich shale ($C_{org} = 1.4\%$) of Albian–Aptian age and a maturity of 0.28% $\overline{R}_o$ had about 18,000 ng/g C_{org}.

The effects of changes in type of organic matter on light-hydrocarbon composition in Hole 530A are examined in Figure 4. This diagram shows the relative composition of the C_6 hydrocarbons (sum of n-hexane, C_6 isoalkanes, C_6 cycloalkanes, and benzene normalized to 100%) as a function of depth. There are several samples and/or intervals that are characterized by drastic changes in the composition of the C_6 hydrocarbons, e.g., the relative proportion of benzene. This parameter is known to be controlled by two processes: changes in the type of organic matter (Leythaeuser et al., 1979) and redistribution effects, e.g., caused by drainage of compaction water (Schaefer et al., in press). In the geochemical study of Site 511, DSDP Leg 71, it was shown (Schaefer et al., 1983) that intervals bearing Type-III kerogens contained 20–45% benzene (as a fraction of total C_6 hydrocarbons). On the other hand, in the black shales of Site 511, which have a Type-II kerogen, the benzene proportion ranged from 4 to 8% at a maturity range of 0.4 to 0.5% vitrinite reflectance (von der Dick et al., 1983). This source-controlled effect is also seen in Figure 4. All black-shale samples reveal uniformly low benzene contents between 1 and 8%, whereas most other samples contain at least 20% (maximum of 45% in the uppermost sample, 530A-68-2, 82–84 cm). However, it is interesting to note that relatively low benzene contents are also observed with every major change in lithology, i.e., around the contacts between lithologic Units 5 and 6, 6 and 7, as well as 7 and 8. Deciding whether changes in the type of organic matter at these contacts (and of a magnitude undetectable by Rock-Eval pyrolysis data) or redistribution as a result of moving subsurface waters caused these effects is not yet possible.

As also shown in Figure 4, the proportion of C_6 cycloalkanes varies widely with depth, i.e., between 4% and about 40% (mean value, 11%). In two samples, C_6

Table 1. (Continued).

91-1, 66–68 976.66	93-4, 6–8 994.56	94-1, 76–78 999.76	95-2, 93–94 1010.43	96-1, 7–8 1017.07	96-2, 7–8 1018.57	96-3, 8–9 1020.08	96-4, 8–9 1021.58	96-5, 8–9 1023.08	96-6, 8–9 1024.58	97-1, 56–58 1026.56	97-2, 56–58 1028.06	97-3, 48–50 1029.48	97-4, 48–50 1030.98	98-1, 20–21 1035.20	98-2, 20–21 1036.70
0.08	0.15	0.33	24.6	0.10	0.06	0.11	0.11	0.14	1.37	0.13	15.5	0.23	4.45	0.19	0.43
412	60	10	191	37	86	30	39	23	49	45	625	33	359	59	14
1.1	1.6	0.72	3.3	0.74	0.99	1.6	1.3	1.3	0.77	0.87	10.6	0.67	1.7	0.17	0.65
5.8	5.6	2.2	185	3.1	8.8	4.5	6.6	5.1	2.8	2.7	39.8	6.9	4.4	0.45	4.3
1.8	2.7	1.0	7.8	0.71	1.8	1.8	1.6	1.3	2.9	1.3	14.1	0.94	3.5	0.10	0.69
7.6	9.3	3.3	738	4.9	12.1	5.7	10.5	7.5	9.9	3.4	431	8.2	42.9	0.89	8.0
1.9	4.5	1.1	726	1.4	3.9	2.0	3.2	2.2	4.0	0.85	704	2.2	99.8	0.61	2.4
1.7	10.2	3.4	10.6	1.4	2.2	1.8	3.6	2.1	2.9	1.7	20.3	1.1	7.8	0.58	1.8
4.0	3.9	1.5	864	1.9	6.2	3.1	4.6	3.6	7.7	1.8	821	3.5	122	1.1	3.5
0.56	0.95	0.34	1.0	0.26	0.66	0.68	0.65	0.55	0.79	0.35	2.3	0.29	0.71	0.16	0.36
—	—	—	4.6	—	0.06	0.04	—	—	0.14	—	4.8	—	0.74	—	—
0.52	0.80	0.30	0.29	0.18	0.58	0.60	0.58	0.45	1.0	0.27	0.72	0.18	0.35	0.09	0.32
1.0	1.3	0.55	765	0.70	2.4	1.2	1.4	1.5	13.5	0.70	1020	1.2	130	0.78	1.2
2.5	1.6	1.0	1120	0.85	4.0	2.4	2.4	2.3	23.5	1.3	1390	2.2	125	1.4	1.8
0.05	—	—	4.9	0.01	0.09	—	—	0.02	0.13	0.01	5.5	0.02	0.37	0.02	0.01
0.10	<0.1	<0.1	70.1	<0.1	0.24	0.11	<0.1	0.10	2.1	<0.1	87.7	0.15	12.1	0.11	0.12
—	—	—	73.6	—	<0.1	<0.1	—	—	2.6	—	142	—	7.0	—	—
0.25	<0.1	0.14	856	0.16	0.68	0.38	<0.1	0.40	25.1	0.20	1480	0.38	47.4	0.20	0.29
0.21	<0.1	0.10	90.3	0.1	0.48	0.40	<0.1	0.26	3.6	0.25	178	0.22	6.5	0.15	0.18
1.2	0.21	0.79	577	0.35	2.1	1.3	0.50	1.2	18.0	0.75	1140	1.3	22.6	0.62	0.80
0.22	—	0.14	376	<0.1	0.44	0.22	0.15	0.20	15.3	0.14	891	0.28	48.4	0.13	0.14
—	—	—	30.6	—	—	—	—	—	0.86	—	80.9	—	0.70	—	—
0.33	0.11	0.26	187	0.14	1.1	—	0.25	0.28	7.3	0.41	129	0.35	1.3	0.24	0.13
—	—	—	46.7	—	0.13	—	—	—	1.8	—	78.7	—	4.8	—	—
—	—	—	62.9	—	0.13	—	—	0.10	2.2	0.1	167	—	0.64	<0.1	—
—	—	—	129	—	<0.1	—	—	<0.1	4.6	0.1	358	—	2.3	<0.1	—
—	—	—	71.5	—	0.13	0.14	—	0.10	2.8	0.1	203	<0.1	0.79	<0.1	—
—	—	—	91.9	—	<0.1	0.27	—	—	5.6	—	449	—	5.0	<0.1	—
—	—	—	86.3	—	<0.1	<0.1	—	—	5.2	—	394	—	4.3	<0.1	—
—	—	—	146	—	<0.1	<0.1	—	—	8.2	—	608	—	6.7	<0.1	—
0.44	0.34	0.65	389	0.35	0.57	1.3	—	0.69	6.6	0.80	869	0.44	1.7	0.31	0.13
—	—	—	45.1	—	—	—	—	—	3.0	—	278	—	2.7	—	—
—	—	—	195	—	0.13	<0.1	—	0.20	8.7	—	628	0.15	5.2	0.15	—
—	—	—	5.6	—	—	—	—	—	—	—	22.5	—	—	—	—
—	—	—	54.6	—	—	—	—	—	2.2	—	241	—	1.2	—	—
—	—		31.5	—	—	—	—	—	0.89	—	244	—	0.22	—	—
—	—	—	21.6	—	—	—	—	—	0.51	—	165	—	0.15	—	—
0.11	0.33	0.39	50.8	0.24	0.63	1.6	0.25	0.33	28.0	0.30	486	<0.1	<0.1	0.15	4.0
—	—	—	121	—	—	<0.1	—	—	0.51	—	421	—	0.15	—	—
—	—	—	108	—	—	0.77	—	—	0.51	—	279	—	—	—	—

cycloalkanes could not be identified because of peak overlap, resulting from residual acetone contamination. The composition of the majority of the samples, therefore, can be classified as paraffinic. This agrees well with light hydrocarbon data from DSDP Hole 364 (Hunt, 1978). These observations, however, are not in agreement with the "paraffinic stage" in light hydrocarbon diagenesis as defined by Thompson (1979). Typical paraffinic compositions of the light hydrocarbon mixture, as found in Hole 530A, would require sediment temperatures exceeding 90°C. Such high temperatures have never been reached in DSDP Hole 530A. Therefore, it is suspected that the differentiation between the "napththenic" and "paraffinic stages" in light-hydrocarbon evolution is strongly source-type dependent and hence cannot be referred to in such a general manner.

Isobutane/*n*-butane ratios remain below unity in all samples (mean 0.66) except for a value of 1.15 in Sample 530A-93-4, 6–8 cm, supporting the previously made conclusion of a low maturity of the organic matter in this hole. A tendency in the isobutane/*n*-butane ratio to increase with depth becomes evident when one compares the upper with the lower half of the sampled interval. An increase of this ratio with increasing maturity is a general feature for initial maturation stages (Hunt et al., 1980).

Neopentane (2, 2-dimethylpropane) remains a rare constituent of the light-hydrocarbon fraction over the whole interval. It was detected in about 30% of the samples, and *n*-pentane/neopentane ratios varied between about 40 and 300. The lowest values are possibly associated with samples enriched by migrated gaseous compounds (see discussion to follow).

Significant amounts of olefins, i.e., ethene, propene, methylpropene + butene-1 (not resolved in the gas chromatogram), trans-butene-2, and cis-butene-2 could be detected in nearly all samples. The most abundant peak was the unresolved methylpropene + butene-1, which even exceeded the concentration of n-butane and methylpropane in some of the organic-carbon-lean samples. Trans- to cis-butene-2 ratios vary from 1.1 to 1.3 in most of the organic-carbon-lean samples. In the black shales with more than 4% organic carbon, this ratio is however between 2 and 3, indicating that the formation of the trans-isomer appears to be favored. These values are more consistent with the thermodynamic equilibrium (3.18 at 25°C, 2.27 at 100°C). Ratios of 1.1 to 1.3, as measured in most of the samples, clearly show the kinetically controlled preferential formation of the cis-isomer. Similarly low trans-/cis-butene-2 ratios (generally between 1.0 and 1.4) has also been measured in samples from Site 511. Only some black shales revealed values of about 2 (Schaefer et al., 1983).

Hole 532

Low-molecular-weight hydrocarbons have been analyzed in 21 core samples (HPC) covering the depth interval 132 to 235 m (Cores 32 to 58). The concentrations, normalized to dry weight sediment, are listed in Table 2. The total hydrocarbon concentrations in Hole 532 (sum of all compounds identified, except the olefins) are plotted against depth in Figure 5, both in absolute (ng/g)

Table 1. (Continued).

Reference no.	Core-Section (interval in cm)	98-3, 20–21	98-4, 20–21	99-2, 34–35	99-3, 107–108	100-1, 44–45	100-4, 50–51	101-1, 35–37	102-1, 53–54	104-1, 39–40	104-3, 22–23
	Depth (m)	1038.20	1039.70	1045.84	1048.07	1053.44	1058.00	1062.35	1071.53	1085.39	1088.22
	Organic carbon content (% dry weight sediment)	0.15	0.16	0.57	0.07	0.23	0.15	0.13	0.20	0.21	0.11
	Hydrogen index [mg HC/g C_{org}]	63	23	33	31	15	17	20	12	19	27
Hydrocarbon concentration (ng/g dry weight sediment)											
1	Ethene	0.68	2.6	1.8	0.57	0.74	2.7	0.47	0.45	1.0	0.73
2	Ethane	1.8	8.9	4.1	1.5	2.7	6.7	1.9	1.8	3.4	3.4
3	Propene	1.1	3.1	2.0	0.56	0.95	3.9	0.47	0.60	0.72	1.1
4	Propane	3.5	17.0	7.1	2.2	3.5	10.4	1.9	2.7	3.6	4.6
5	Methylpropane	1.3	6.4	2.2	1.0	1.0	4.6	0.58	0.77	1.1	1.0
6	Methylpropene + 1-Butene	1.3	10.8	2.3	0.76	0.90	10.9	0.60	0.72	0.85	3.6
7	n-Butane	2.3	7.9	3.2	1.0	1.7	5.6	1.1	1.0	2.1	2.1
8	trans-2-Butene	0.40	1.5	0.66	0.19	0.27	1.4	0.20	0.20	0.24	0.27
9	2, 2-Dimethylpropane	—	—	—	—	—	0.11	—	—	0.03	—
10	cis-2-Butene	0.33	1.3	0.68	0.17	0.26	1.3	0.12	0.13	0.20	0.25
11	Methylbutane	0.82	4.0	4.2	0.56	0.54	2.7	0.34	0.43	0.68	0.77
12	n-Pentane	2.1	5.0	7.7	0.71	1.1	4.3	0.68	0.53	1.7	1.4
13	2, 2-Dimethylbutane	0.03	0.01	0.07	—	0.01	0.02	0.02	—	0.04	0.08
14	Cyclopentane	0.1	0.35	1.2	<0.1	<0.1	0.21	<0.1	<0.1	<0.1	<0.1
15	2, 3-Dimethylbutane	—	—	1.2	—	—	0.12	—	—	<0.1	0.1
16	2-Methylpentane	0.26	1.1	12.2	0.11	0.15	1.1	<0.1	0.12	0.38	0.31
17	3-Methylpentane	0.24	1.0	2.3	<0.1	<0.1	1.1	0.12	<0.1	0.38	0.49
18	n-Hexane	0.90	3.9	10.9	0.37	0.55	3.2	0.40	0.49	1.2	1.0
19	Methylcyclopentane + 2, 2-Dimethylpentane	0.15	0.56	7.8	—	<0.1	0.40	<0.1	<0.1	0.21	0.23
20	2, 4-Dimethylpentane	—	—	0.86	—	—	<0.1	—	—	<0.1	<0.1
21	Benzene	0.18	3.9	3.8	<0.1	0.24	2.9	0.18	0.29	1.1	1.0
22	Cyclohexane	—	0.28	0.70	<0.1	—	—	—	<0.1	—	—
23	2-Methylhexane	—	0.55	2.3	<0.1	<0.1	0.33	<0.1	<0.1	0.23	<0.1
24	2, 3-Dimethylpentane + 1, 1-Dimethylcyclopentane	—	0.28	4.7	—	<0.1	0.33	—	—	0.38	0.26
25	3-Methylhexane	—	0.55	2.8	<0.1	<0.1	0.33	<0.1	—	0.33	0.21
26	1, cis-3-Dimethylcyclopentane	—	0.33	4.4	—	<0.1	0.14	—	—	0.10	<0.1
27	1, trans-3-Dimethylcyclopentane	—	<0.1	4.2	—	—	0.10	—	—	<0.1	<0.1
28	1, trans-2-Dimethylcyclopentane	—	0.28	6.4	—	—	0.14	—	—	<0.1	<0.1
29	n-Heptane	0.35	2.8	10.1	1.3	0.25	2.4	0.35	0.18	3.2	3.5
30	1, cis-2-Dimethylcyclopentane	—	—	2.3	—	—	—	—	—	<0.1	—
31	Methylcyclohexane	—	0.20	7.7	—	<0.1	0.32	—	—	0.26	0.14
32	2, 5-Dimethylhexane	—	—	0.25	—	—	—	—	—	—	—
33	Ethylcyclopentane	—	<0.1	1.6	—	—	0.15	—	—	0.10	—
34	1, trans-2, cis-4-Trimethylcyclopentane	—	—	1.4	—	—	—	—	—	—	—
35	1, trans-2, cis-3-Trimethylcyclopentane	—	—	0.94	—	—	—	—	—	—	—
36	Toluene	0.71	6.0	15.0	2.7	0.19	0.10	0.17	1.2	2.0	2.9
37	2-Methylheptane	—	<0.1	0.63	—	—	0.10	—	—	0.16	0.17
38	n-Octane	—	1.7	0.63	—	—	0.17	—	—	0.83	1.5

and organic-carbon-normalized units (ng/g C_{org}). Also included is a depth plot of the organic-carbon content (measured on the identical samples). It ranges from 6.5 to 0.7%, with a clear tendency to decrease with increasing depth. Likewise, the total C_2–C_8 hydrocarbon concentrations decrease by one order of magnitude from 305 ng/g at 132 m to 31 ng/g at 235 m depth. Only one sample (Sample 532-40-2, 47–49 cm) deviates considerably from the general trend (only 12 ng/g), despite a relatively high organic carbon content of 2.2%.

The total light-hydrocarbon concentration vs. organic-carbon content relationship for samples from Hole 532 is also shown in Figure 2. Concentrations are clearly below those of Hole 530A, i.e., approximately by one order of magnitude. This is interpreted as reflecting the significantly lower maturity of the Pliocene/late Miocene sediments penetrated by Hole 532 ($\overline{R}_o = 0.31\%$ at 150 m depth according to Rullkötter el al. (this volume). In order to eliminate variations in the organic-carbon content we also show the concentrations in carbon-normalized form. Except for the one sample at 163 m mentioned previously, the light-hydrocarbon concentrations reveal only minor scatter. Concentrations of this size (3,000 to 9,000 ng/g C_{org}) are in our experience typical for sediments that are definitely in the immature evolution stage. This is also obvious from Figure 3, where the saturated hydrocarbon concentrations are compared to those in DSDP Holes 530A and 511 and several petroleum source rocks of different maturity.

The composition of the C_6-hydrocarbons reveals the highly "aromatic nature" in all samples from Hole 532 (Fig. 6). The benzene content (relative to all C_6 hydrocarbons) varies from about 30 to nearly 60%. Similarly high benzene contents have been recognized as a widespread phenomenon and classified as the initial stage of light-hydrocarbon evolution in diagenetically young sediments starting from sedimentary interface temperatures ("aromatic stage," Thompson, 1979).

Redistribution of Low-Molecular Weight Hydrocarbons

Light hydrocarbons in the molecular range considered here exhibit a high degree of mobility in the water-saturated pore system as compared to other organic constituents from the sediment. Therefore, their variations with depth are more likely to reflect redistribution or migration phenomena than those of other compounds.

The light-hydrocarbon data of Holes 530A and 532 as previously discussed, however, lead to the conclusion that in most of the samples analyzed hydrocarbons were formed *in situ* and remained at their place of origin. No clear indications for, for example, enrichment of the organic-carbon-lean samples by the interbedded black shales could be observed. According to our experience from the study of Site 511, DSDP Leg 71 (Schaefer et al., in press), the lack of evidence of this kind most probably reflects inadequacies in the sampling of Leg 75. At Site 511 a short-distance migration was only recognized by analysis of very closely spaced samples taken in decimeter or even centimeter intervals. However, samples with this spacing were unfortunately not available from Holes 530A and 532.

Nevertheless, several samples from Hole 530A exhibited very high hydrocarbon concentrations which significantly exceed the indigenous level at this maturity, as

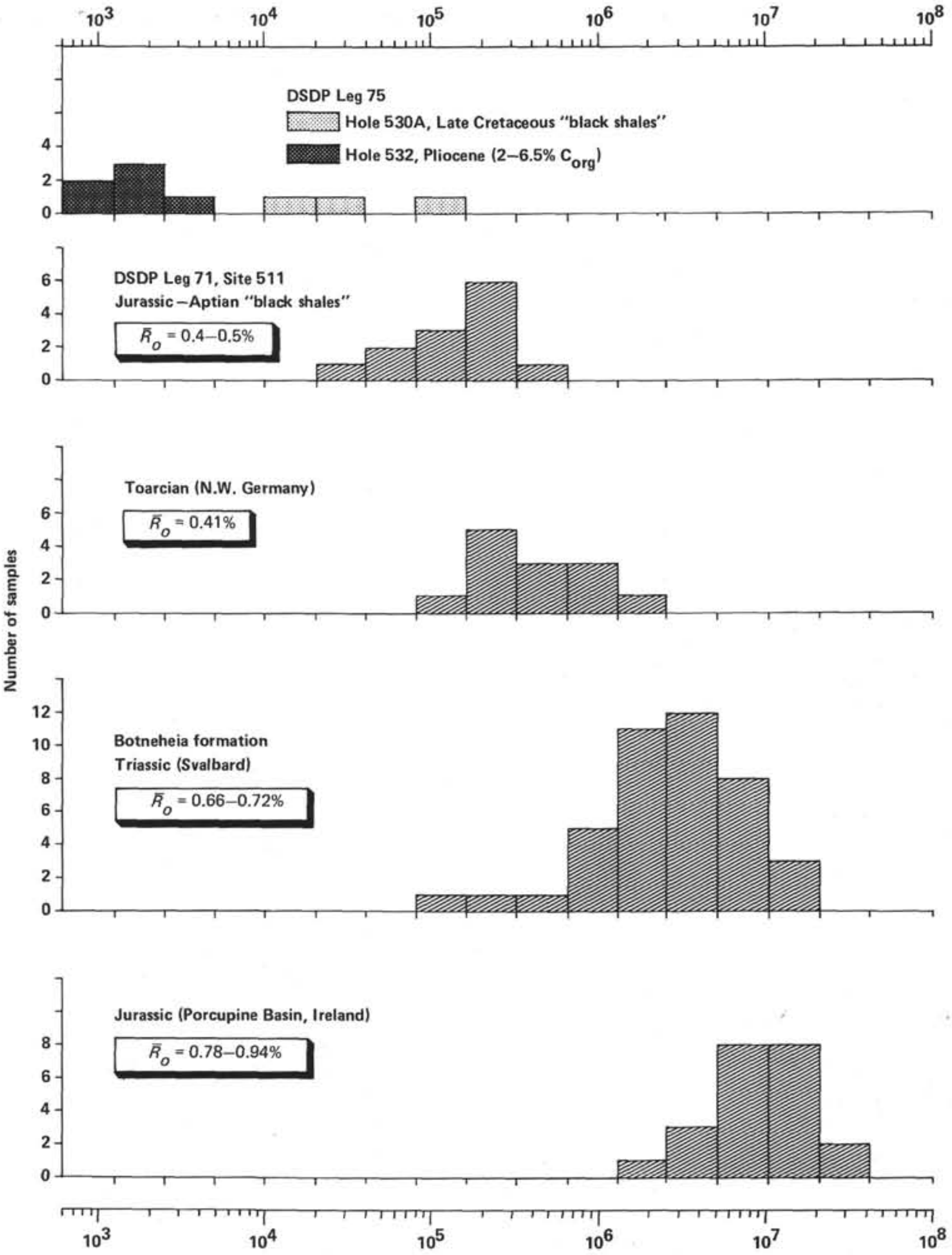

Figure 3. C_2–C_8 saturated hydrocarbon concentrations (in ng/g C_{org}) of organic-carbon-rich sediment samples (organic-carbon content exceeding 2%) from DSDP Holes 530A and 532, Leg 75, compared to those of Jurassic–Aptian black shales from DSDP Site 511, Leg 71, and potential oil source rocks of different maturity. This comparison indicates the immaturity of the organic matter in Holes 530A and 532.

established at our laboratory. As has been discussed (Fig. 1), exceptionally high organic-carbon-normalized values appear to coincide with the contacts between the lithologic units as defined by the shipboard scientists, in particular between Units 5 and 6, and 6 and 7. Also, exceedingly high carbon-normalized concentrations occur in several other organic-carbon-lean samples. It is surprising that the depth variation of the proportion of benzene in the C_6-hydrocarbon mixture (Fig. 4) correlates inversely with that of the total light hydrocarbon concentrations, particularly in Units 5, 6, and 7. The reason for this is not yet known.

In Figure 7 the light-hydrocarbon gas chromatograms of three samples from lithologic Unit 8 are compared which are less than 10 m apart: two organic carbon lean Type-III kerogen-bearing samples (A = Sample 530A-96-2, 7–8 cm, B = Sample 530A-97-1, 56–58 cm) and a typical black shale (C = Sample 530A-97-2, 56–58 cm). It was suspected that light hydrocarbons were redistributed into the organic-carbon-lean sample B from the black shale (1.5 m below), which has generated considerable quantities of hydrocarbons. The hydrocarbon concentration and composition measured in sample B, however, do not support this assumption. A

Table 2. Summary of low-molecular-weight hydrocarbon concentrations and organic carbon contents of core samples from DSDP Hole 532, Leg 75.

Ref. no.	Core-Section (interval in cm)	32-1, 20–21	33-2, 97–99	34-2, 53–55	37-1, 68–70	40-2, 47–49	41-2, 51–53	42-2, 115–116	43-3, 43–45	44-3, 107–108
	Depth (m)	132.00	137.67	141.23	151.28	162.77	167.21	172.25	177.43	182.47
	Organic carbon content (% dry weight sediment)	6.45	1.34	3.05	1.41	2.15	1.50	1.65	2.92	2.00
	Hydrocarbon concentration (ng/g dry weight sediment)									
1	Ethene	1.9	1.1	1.5	0.81	0.48	1.3	2.2	1.1	1.9
2	Ethane	7.8	12.4	5.0	3.3	1.5	4.1	3.5	1.5	6.8
3	Propene	0.98	1.1	1.6	0.75	0.24	1.1	1.6	0.62	1.0
4	Propane	6.2	15.1	9.9	4.4	1.7	6.7	4.6	2.4	9.8
5	Methylpropane	3.0	4.1	3.1	0.96	0.25	1.9	0.95	0.44	2.2
6	Methylpropene + 1-Butene	1.5	1.8	3.2	0.68	0.43	1.6	2.9	1.2	2.1
7	n-Butane	3.3	6.5	4.1	1.5	0.44	2.3	1.5	0.80	3.4
8	trans-2-Butene	0.51	0.49	0.61	0.22	0.03	0.32	0.29	0.12	0.45
9	2, 2-Dimethylpropane	—	0.11	—	—	—	0.11	—	—	—
10	cis-2-Butene	0.25	0.39	0.38	0.15	0.03	0.22	0.25	0.11	0.34
11	Methylbutane	6.6	3.5	8.8	1.3	0.35	1.5	1.1	2.1	1.4
12	n-Pentane	5.6	4.6	5.2	1.4	0.41	3.5	1.4	1.6	2.5
13	2, 2-Dimethylbutane	0.09	0.06	0.07	0.01	0.01	0.02	0.01	0.02	0.01
14	Cyclopentane	0.90	0.31	0.55	0.10	<0.1	0.15	0.64	0.27	0.25
15	2, 3-Dimethylbutane	2.1	<0.1	—	—	—	<0.1	—	—	—
16	2-Methylpentane	3.8	1.4	2.8	0.59	0.17	0.66	0.90	1.4	1.1
17	3-Methylpentane	4.7	0.73	0.90	0.19	<0.1	0.42	0.42	0.48	0.50
18	n-Hexane	4.0	2.9	3.4	0.97	0.18	1.5	1.5	1.8	2.1
19	Methylcyclopentane + 2, 2-Dimethylpentane	4.0	0.79	1.6	0.31	<0.1	0.39	0.45	0.68	0.55
20	2, 4-Dimethylpentane	0.11	<0.1	0.15	<0.1	—	<0.1	<0.1	0.11	—
21	Benzene	11.1	2.4	3.7	1.5	0.45	1.9	2.2	3.4	3.0
22	Cyclohexane	3.3	0.22	0.36	0.42	—	0.52	0.32	0.80	0.75
23	2-Methylhexane	1.0	0.31	0.34	0.12	—	0.32	0.32	0.30	0.29
24	2, 3-Dimethylpentane + 1, 1-Dimethylcyclopentane	7.2	0.16	<0.1	0.11	—	0.26	0.32	0.21	0.15
25	3-Methylhexane	3.5	0.31	0.24	0.17	—	0.53	0.37	0.44	0.39
26	1, cis-3-Dimethylcyclopentane	0.99	0.31	1.1	0.16	—	0.19	0.30	0.20	0.15
27	1, trans-3-Dimethylcyclopentane	0.44	0.20	0.53	0.11	—	0.19	0.25	0.21	0.15
28	1, trans-2-Dimethylcyclopentane	0.34	0.20	0.22	0.11	—	0.25	0.25	0.29	0.25
29	n-Heptane	94.8	2.0	3.0	1.0	0.23	2.2	1.8	3.0	2.3
30	1, cis-2-Dimethylcyclopentane	0.37	0.12	0.22	<0.1	—	0.11	—	0.21	—
31	Methylcyclohexane	0.96	0.39	0.44	0.56	—	1.2	0.65	1.4	1.1
32	2, 5-Dimethylhexane	<0.1	—	—	—	—	0.11	—	0.17	—
33	Ethylcyclopentane	0.37	0.39	0.22	<0.1	—	0.37	<0.1	0.45	0.30
34	1, trans-2, cis-4-Trimethylcyclopentane	—	—	—	—	—	<0.1	—	—	—
35	1, trans-2, cis-3-Trimethylcyclopentane	—	—	—	—	—	0.19	—	—	—
36	Toluene	123	13.7	35.8	33.1	6.4	52.4	35.6	121	60.5
37	2-Methylheptane	2.1	0.78	1.2	0.39	—	0.82	0.49	1.2	0.84
38	n-Octane	3.9	1.9	2.8	0.44	—	1.7	0.49	2.3	1.5

Note: — = Concentration below or near detection limit.

value of 10,700 ng/g C_{org} is not exceptional, and the front-biased hydrocarbon distribution, i.e., favoring the gas compounds, is typical for generation from hydrogen-lean kerogens. On the other hand, sample A from Core 96, although also bearing a type-III kerogen, shows extremely high organic-carbon-normalized hydrocarbon concentrations (74,000 ng/g C_{org}), mainly as a result of the abundance of the most mobile gas compounds, e.g., 14,600 ng/g C_{org} for ethane and 20,100 ng/g C_{org} for propane. For comparison, the values in sample B are 2,080 and 2,630 ng/g C_{org}, respectively. Therefore, it is concluded that sample A is enriched by migrated gases. The mechanism of this process is most likely diffusion through the water-saturated pore space since this process favors the movement of the gaseous compounds. This explanation is also supported by the fact that sample A has the highest neopentane concentration of the whole sample series (100 ng/g C_{org}). Concentrations of neopentane were found to vary drastically in previously analyzed DSDP cores (Whelan and Hunt, 1978; Whelan, 1979; Whelan and Sato, 1980). Generally, higher abundance of this compound seemed to correlate with either fractured or coarse-grained sediments. This relative enrichment in neopentane was explained to be either indicative of terpene-derived aerobically altered organic matter or caused by preferential movement of this nearly spherical molecule by diffusion. The diffusion coefficient for neopentane is higher than that of its less branched isomers (Sahores and Witherspoon, 1970). Thus, any diffusion of C_5 hydrocarbons should favor neopentane, as observed in sample A of Hole 530A. It is interesting to note that above sample A the nearest layer of black shales occurs at about the same interval spacing as sample B is separated from sample C. In Core 96 layers of black shales are encountered 3 m below and 1 m above sample A. Obviously the conditions for redistribution in this interval were more complicated than simple diffusion in the vertical direction.

For samples of Hole 532 no redistribution phenomena of this type were recognized.

CONCLUSIONS

Data on light hydrocarbons from Holes 530A and 532 clearly show that their organic matter is immature in terms of classical hydrocarbon-generation mechanisms. Light hydrocarbons from the interval of Pliocene/late Miocene calcareous and siliceous marls and oozes between 132 and 235 m in Hole 532 are in a very initial evolutionary phase. This was obvious both from the very low hydrocarbon concentrations and from their composition, which is of a highly aromatic nature. An increase of organic-carbon-normalized total light-hydrocarbon concentrations by about one order of magni-

Table 2. (Continued).

45-1, 53–55	46-2, 128–130	48-2, 108–110	49-1, 50–52	50-1, 46–48	51-1, 100–101	52-2, 60–62	54-3, 63–69	55-2, 60–61	56-1, 69–71	57-1, 80–82	58-1, 51–53
183.33	189.58	198.18	200.10	204.06	208.60	213.70	223.63	226.10	228.69	232.20	235.31
1.21	2.22	1.88	1.39	1.76	2.66	1.39	0.92	1.17	0.79	0.68	1.14
1.4	1.4	1.6	2.1	1.3	1.9	0.66	1.4	1.3	1.1	1.0	0.51
4.1	3.7	2.4	7.4	3.1	4.9	1.3	5.1	2.0	3.3	1.2	0.51
1.3	1.2	1.4	1.4	0.49	2.1	0.41	1.2	0.87	0.57	0.74	0.30
5.3	5.6	3.9	7.8	2.2	10.4	1.8	9.4	2.7	4.3	2.1	0.81
1.2	1.4	0.72	1.5	0.31	2.3	0.59	2.7	0.77	0.77	0.45	0.35
1.7	2.4	1.5	2.0	0.41	3.6	0.63	2.1	1.6	0.83	1.1	0.95
2.3	1.7	1.1	3.0	0.48	2.8	0.86	3.3	1.0	1.2	0.66	0.53
0.34	0.30	0.14	0.41	0.05	0.47	0.11	0.39	0.15	0.12	0.13	0.10
—	0.04	—	—	—	—	—	—	—	—	—	—
0.27	0.33	0.12	0.33	0.08	0.36	0.07	0.33	0.10	0.08	0.08	0.10
0.67	1.8	0.68	1.7	0.26	5.9	1.0	1.3	0.89	0.51	0.91	0.84
2.0	2.2	0.95	2.7	0.68	5.1	1.8	1.8	1.1	0.67	0.82	1.2
0.01	0.01	—	0.01	—	0.02	0.01	0.01	0.01	—	—	—
0.11	0.22	0.23	0.27	0.16	1.6	0.40	0.14	0.27	<0.1	0.96	<0.1
—	—	—	—	—	<0.1	<0.1	—	—	—	—	—
0.34	0.83	0.89	0.76	0.43	2.6	1.0	0.46	0.49	0.18	0.38	0.27
0.27	0.45	0.26	0.50	0.19	0.82	0.45	0.19	0.16	<0.1	0.22	0.20
1.3	1.4	1.2	1.7	0.94	3.5	1.9	1.1	0.94	0.48	0.89	0.60
0.17	0.39	0.37	0.48	0.33	1.6	0.66	0.20	0.38	0.10	0.48	0.17
—	<0.1	<0.1	0.10	<0.1	0.12	<0.1	<0.1	<0.1	—	<0.1	<0.1
1.5	2.4	2.2	3.3	3.0	5.6	2.5	1.8	1.7	0.83	2.5	1.1
0.35	0.54	0.43	0.50	0.29	0.59	0.34	0.27	0.30	0.17	0.32	0.14
0.16	0.23	0.19	0.33	0.16	0.46	0.32	0.10	0.15	<0.1	0.25	0.10
0.16	0.18	0.15	0.24	0.11	0.39	0.23	0.12	<0.1	<0.1	0.19	0.10
0.27	0.25	0.25	0.45	0.25	0.42	0.40	<0.1	0.15	<0.1	0.43	0.17
0.16	0.26	0.24	0.24	0.21	0.66	0.30	0.12	0.22	<0.1	0.21	<0.1
0.11	0.18	0.12	0.15	0.11	0.20	0.14	<0.1	<0.1	<0.1	0.18	<0.1
0.11	0.26	0.13	0.24	0.18	0.20	0.14	<0.1	<0.1	0.10	0.18	<0.1
1.2	1.9	2.0	2.1	1.6	3.5	2.2	1.2	1.0	0.63	1.4	0.72
—	<0.1	<0.1	—	0.11	0.19	0.12	—	—	—	—	—
0.54	0.93	0.81	1.1	0.76	1.0	0.78	0.33	0.22	0.21	1.3	0.34
—	—	<0.1	—	<0.1	<0.1	<0.1	—	—	—	<0.1	—
0.16	0.20	0.18	0.27	0.14	0.26	0.12	<0.1	<0.1	—	0.18	<0.1
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
23.9	64.9	54.7	47.5	39.3	60.6	32.1	26.6	22.7	17.0	42.6	22.0
0.54	0.59	0.62	0.73	0.55	2.0	0.98	0.25	0.44	0.21	0.42	0.10
0.81	1.3	0.82	0.97	0.63	2.1	1.4	0.99	0.59	0.77	0.63	0.35

tude was observed in the Cenomanian black shales of Hole 530A if compared to the organic-carbon-rich samples from Hole 532 (Pliocene 2.0–6.5% C_{org}). This was interpreted to reflect a significant maturity increase. However, light-hydrocarbon concentrations in the black shales of Hole 530A are still about two orders of magnitude lower than usually measured in typical petroleum source beds in the main phase of hydrocarbon generation (0.8-0.9% $\overline{R}_o$). Therefore, it is concluded that the maturity of the black shales in Hole 530A is not exceeding the equivalent of about 0.4% vitrinite reflectance. The data on light-hydrocarbon concentration and composition of this study are remarkably similar to those from DSDP Holes 361 and 364, Leg 40, Cape Basin off Capetown and Angola Basin, respectively (Hunt, 1978).

Source-dependent changes in the light-hydrocarbon composition were observed in Hole 530A when comparing organic-carbon-lean Type-III kerogen-bearing samples with adjacent black shales. The latter revealed, for instance, uniformly low relative benzene contents between 1 and 8%, whereas the former contained 20 to 45% as a fraction of the total C_6 hydrocarbons. The same observation has been made for DSDP Site 511, Leg 71 (Schaefer et al., 1983).

Migration effects could not be studied in an ideal way with the available sample set (i.e., inadequate sampling intervals and frequency). Redistribution processes, most probably by diffusion, could only be recognized in a few samples from Hole 530A. These samples exhibited very high hydrocarbon concentrations which drastically exceeded the indigenous level commonly measured at the corresponding maturity. Enrichment was most intense by the gaseous compounds, i.e., ethane, propane, and the butane isomers. In some of these cases neopentane was also an abundant constituent of the C_5 saturated hydrocarbons. It was concluded that the process which caused the enrichment is most probably diffusion through the water-saturated pore space. However, conditions for redistribution in the studied interval were obviously more complicated than simple diffusion in the vertical direction.

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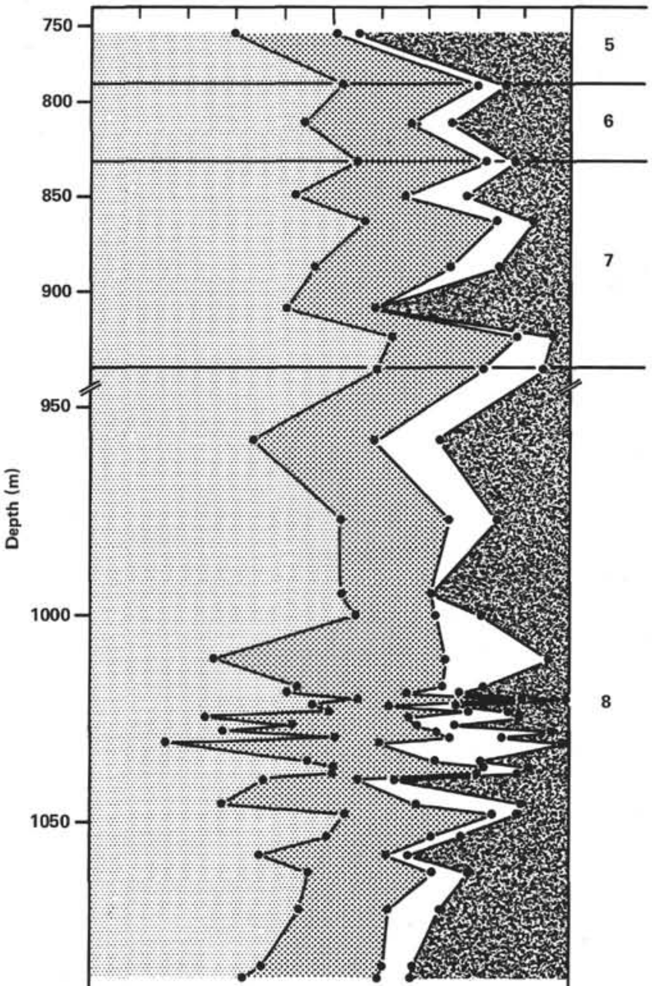

Figure 4. C_6 hydrocarbon relative composition (sum of n-hexane, isoalkanes, cycloalkanes, and benzene, normalized to 100%, plotted from left to right) vs. depth for sediment samples from DSDP Hole 530A, Leg 75.

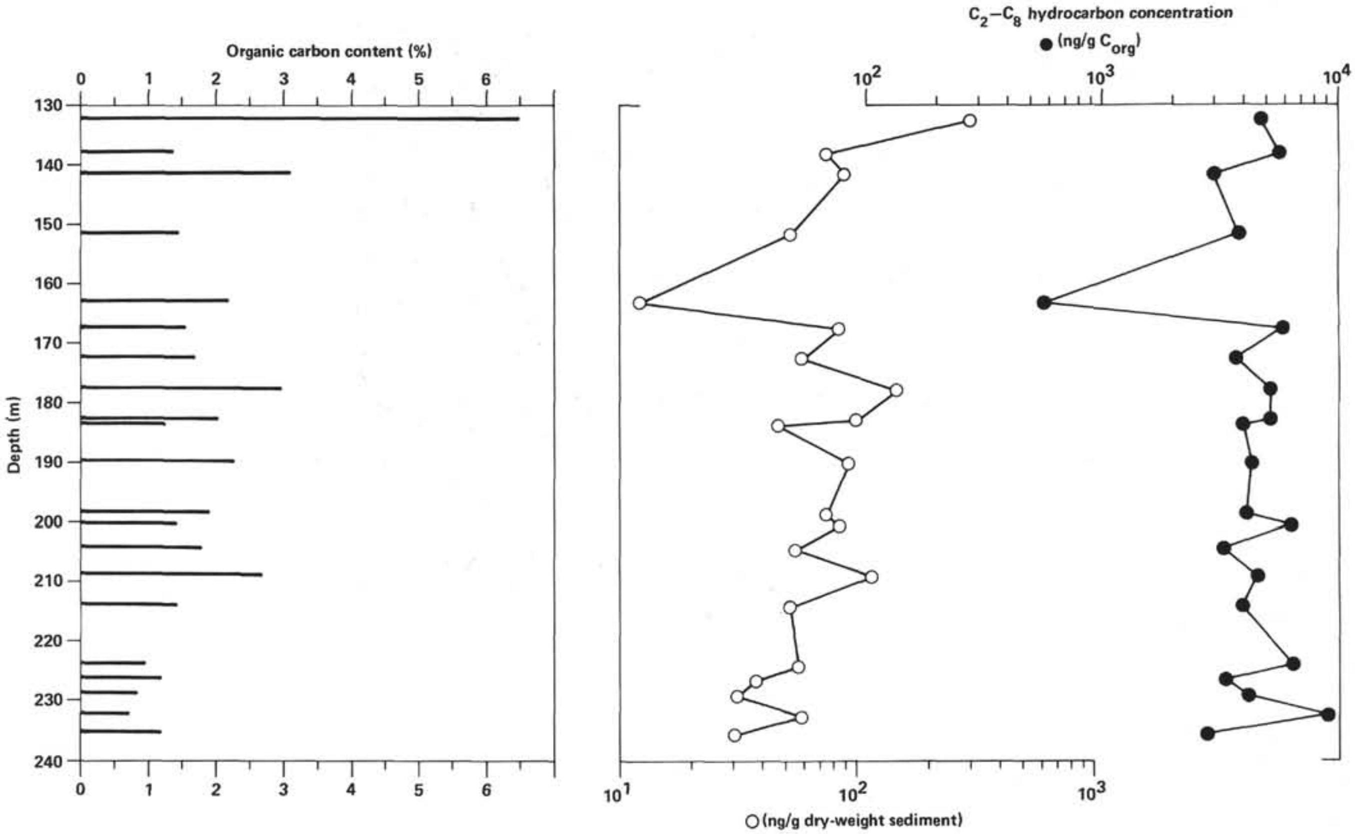

Figure 5. Organic carbon and low-molecular-weight hydrocarbon content (sum of all C_2 to C_8 hydrocarbons identified in Table 2, except olefins) vs. depth for Pliocene/late Miocene age sediments from DSDP Hole 532, Leg 75.

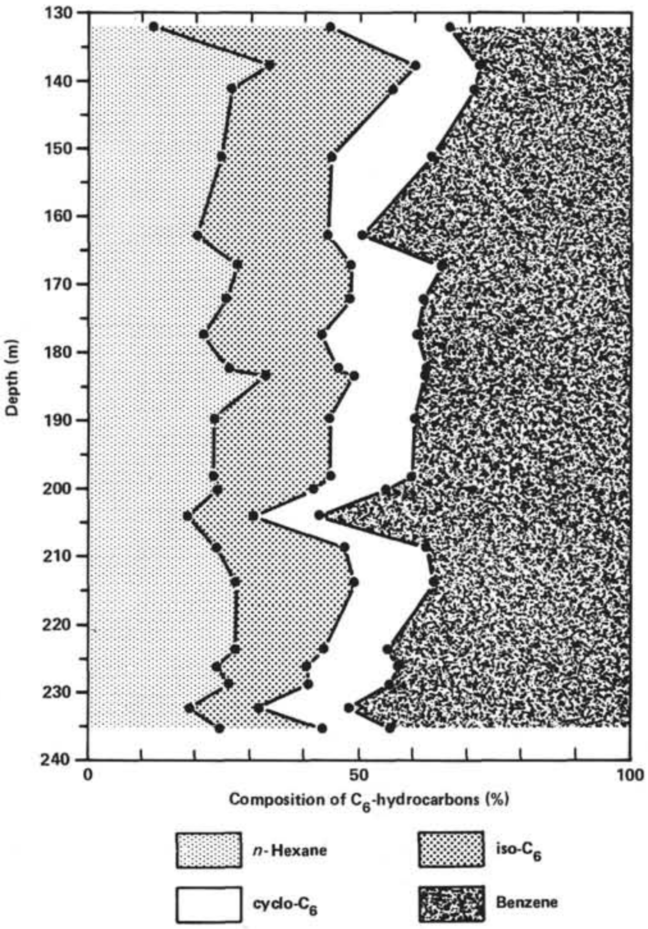

Figure 6. C_6 hydrocarbon relative composition (sum of *n*-hexane, isoalkanes, cycloalkanes, and benzene, normalized to 100%, plotted from left to right) vs. depth for sediment samples from DSDP Hole 532, Leg 75.

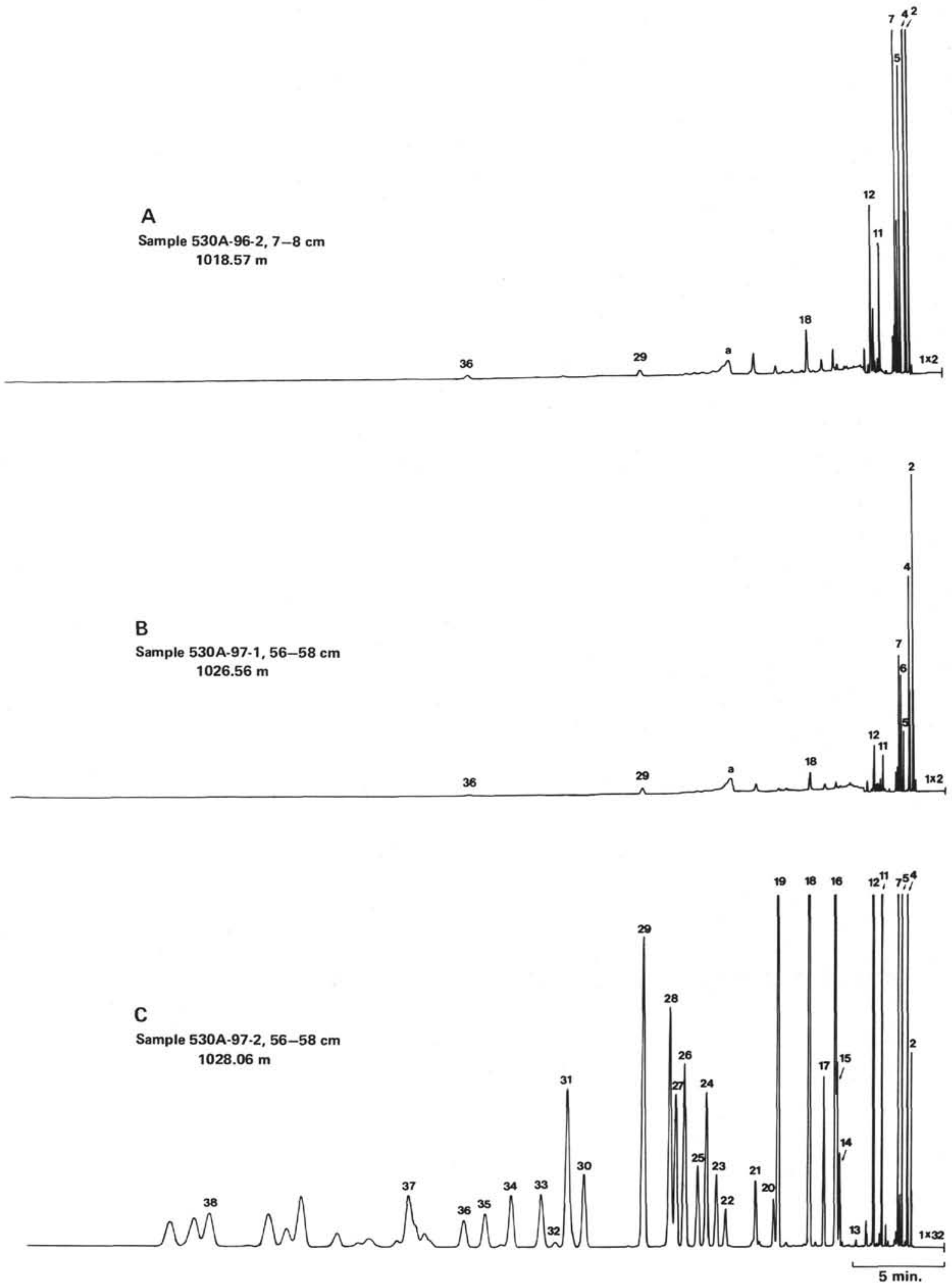

Figure 7. Capillary gas chromatograms of three selected samples from lithologic Unit 8 of DSDP Hole 530A, Leg 75. Peak numbers refer to compounds listed in Table 1. (Note: 16-fold attenuation of chromatogram C in comparison with A and B. a = residual acetone contamination after special treatment of the samples.)