55. LOW-MOLECULAR-WEIGHT HYDROCARBONS IN SEDIMENTS OF DEEP SEA DRILLING PROJECT LEG 93, HOLE 603B, OFF THE EAST COAST OF NORTH AMERICA[1]

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ABSTRACT

C_2–C_8 hydrocarbon concentrations (about 35 compounds identified, including saturated, aromatic, and olefinic compounds) from 27 shipboard-sealed, deep-frozen core samples of DSDP Hole 603B off the east coast of North America were determined by a gas-stripping/thermovaporization method. Total yields representing the hydrocarbons dissolved in the pore water and adsorbed on the mineral surfaces of the sediments vary from 22 to 2400 ng/g of dry-weight sediment. Highest yields are measured in the two black shale samples of Core 603B-34 (hydrogen index of 360 and 320 mg/g C_{org}, respectively). In organic-carbon-normalized units these samples have hydrocarbon contents of 12,700 and 21,500 ng/g C_{org}, respectively, indicating the immaturity of their kerogens. Unusually high organic-carbon-normalized yields are associated with samples that are extremely lean in organic carbon. It is most likely that they are enriched by small amounts of migrated light hydrocarbons. This applies even to those samples with high organic-carbon contents (1.3–2.2%) of Sections 603B-28-4, 603B-29-1, 603B-49-2, and 603B-49-3, because they have an extremely low hydrocarbon potential (hydrogen index between 40 and 60 mg/g C_{org}). Nearly all samples were found to be contaminated by varying amounts of acetone that is used routinely in large quantities on board ship during core-cutting procedures. Therefore, 48 samples from the original set of 75 collected had to be excluded from the present study.

INTRODUCTION

Hole 603B of DSDP Leg 93 was drilled in May 1983 by the crew of *Glomar Challenger* in 4633 m water depth on the lower North American continental rise 270 n. mi. east of Cape Hatteras, North Carolina (35°29.71′N; 70°01.71′W, see Fig. 1). Despite various operational problems at this site, a comprehensive sedimentary sequence was recovered which characterizes Mesozoic and late Cenozoic sedimentation along this passive margin at the interface between continental and deep-sea environments.

In this chapter we analyze the low-molecular-weight hydrocarbon fraction (C_2–C_8 molecular range) of 27 selected core samples from 911 to 1443 m sub-bottom depth to characterize the stage to which hydrocarbon-generation processes have advanced and to examine if migration effects are detectable for these compounds (cf. Leythaeuser et al., 1980, 1982, 1983).

As shown in previous studies (see, e.g., Whelan and Hunt, 1981, 1982; Schaefer et al., 1983a, b; Schaefer and Leythaeuser, 1984; Jasper et al., 1984; Schaefer et al., 1984, and references cited therein), quantity and composition of hydrocarbons of this molecular-weight range can be followed to monitor the progress of thermally controlled hydrocarbon-generation reactions and of migration processes in low-maturity sediments.

METHODS

Seventy-five core samples (approximately 10 g) were stored on board in aluminum-foil sealed, 20-ml screw-capped glass vials in a deep freezer (approximately −20°C) until the analyses were performed in the laboratory at KFA Jülich. Blank runs revealed an adequate purity of the sampling vials used for this study. The low-molecular-weight hydrocarbons (molecular range C_2–C_8) were determined by a slightly modified, combined gas-stripping/thermovaporization method (Schaefer et al., 1978) described in detail in our previous studies of DSDP Leg 71, 75, 79, and 89 sediments (Schaefer et al., 1983a, b; Schaefer and Leythaeuser, 1984; Schaefer et al., 1984; Schaefer and Leythaeuser, in press). The relative standard deviation of hydrocarbon stripping yields was determined to be around 10% for core samples containing relatively low light hydrocarbon concentrations (Schaefer et al., 1978). It is assumed, however, that the standard deviation for thermovaporization yields is somewhat higher. The modification of the method (i.e., by applying a mixture of $CaCl_2$ and silica gel to the thermovaporized hydrocarbon fraction) was necessary because nearly all samples from Hole 603B turned out to be drastically contaminated on board ship by varying amounts of acetone. Therefore, the analytical results of only 27 core samples could be included in our study.

The occurrence of large amounts of acetone, which is usually applied during core-cutting procedures on board the *Glomar Challenger*, in the light hydrocarbon fraction of DSDP cores causes problems because of the following two reasons. First, it is possible that the acetone used on board ship is not absolutely pure and that, therefore, other organic compounds may contaminate the core samples. Second, the acetone peak in the gas chromatograms interferes with various compounds that are of geochemical interest.

Organic-carbon contents of the sediments were measured by a combustion method (LECO Carbon Analyzer IR 112) after treatment with hot 6*N* HCl on the same samples used for low-molecular-weight hydrocarbon determination. The accuracy of the organic-carbon determination is still rather high at organic-carbon levels of 0.1% or even less (10% relative standard deviation). Data on kerogen type were obtained for selected whole rock samples from Hole 603B by Rock-Eval pyrolysis (Espitalié et al., 1977).

RESULTS AND DISCUSSION

Organic Carbon Contents and Pyrolysis Yields

The sample series, comprising the interval from 911 to 1443 m sub-bottom depth (Cores 603B-11 to 603B-68), mainly consists of silty and/or zeolite-bearing claystones or siltstones. Black carbonaceous claystones occur in Core 603B-34 (two samples). Samples 603B-28-4, 100–101 cm and 603B-57-5, 36–38 cm are sandstones.

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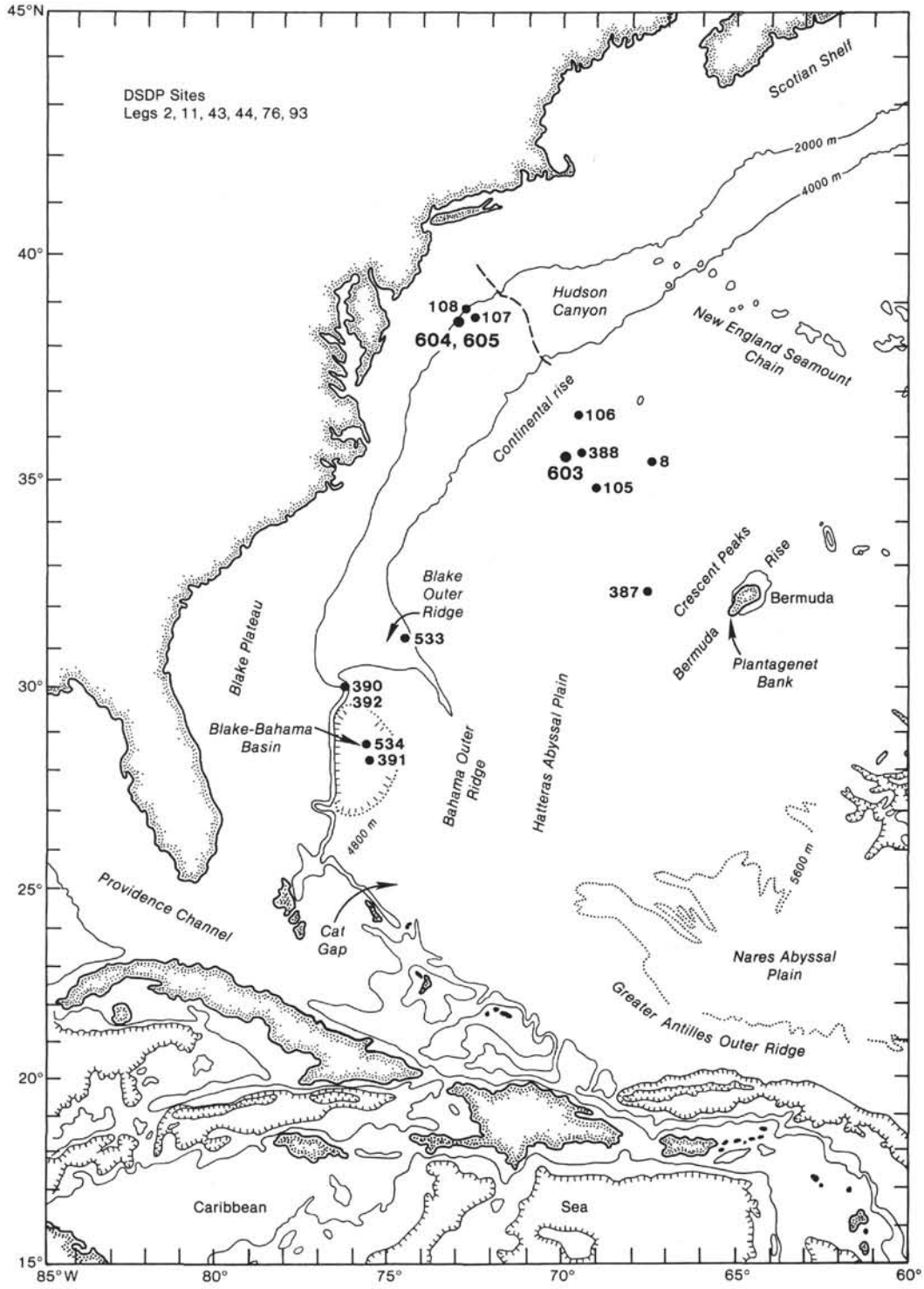

Figure 1. Location of DSDP Leg 93, Site 603.

Organic-carbon contents are very variable in the studied sample series (Table 1, Fig. 2). They range from virtually zero (0.05% or less) in the silt- and zeolite-bearing claystones of Core 603B-29 (lower Senonian) to 8.9 and 11.1% in the black shales of Core 603B-34 (Cenomanian, 1128.02 and 1130.36 m depth). Elevated organic-carbon contents (0.7–2.2%) occur in seven samples from Cores 603B-11, -28, -29, and -49. All other samples are relatively poor in organic carbon (between 0.1 and 0.2%).

The results of the Rock-Eval pyrolysis (Table 1) of selected samples (organic-carbon contents higher than 0.7%) classify the organic matter as kerogen Type III (hydrogen index I_H less than 100 mg/g C_{org}) except for the two black shales of Core 603B-34, which exhibit a mixed type II/III kerogen quality (I_H = 357 and 323

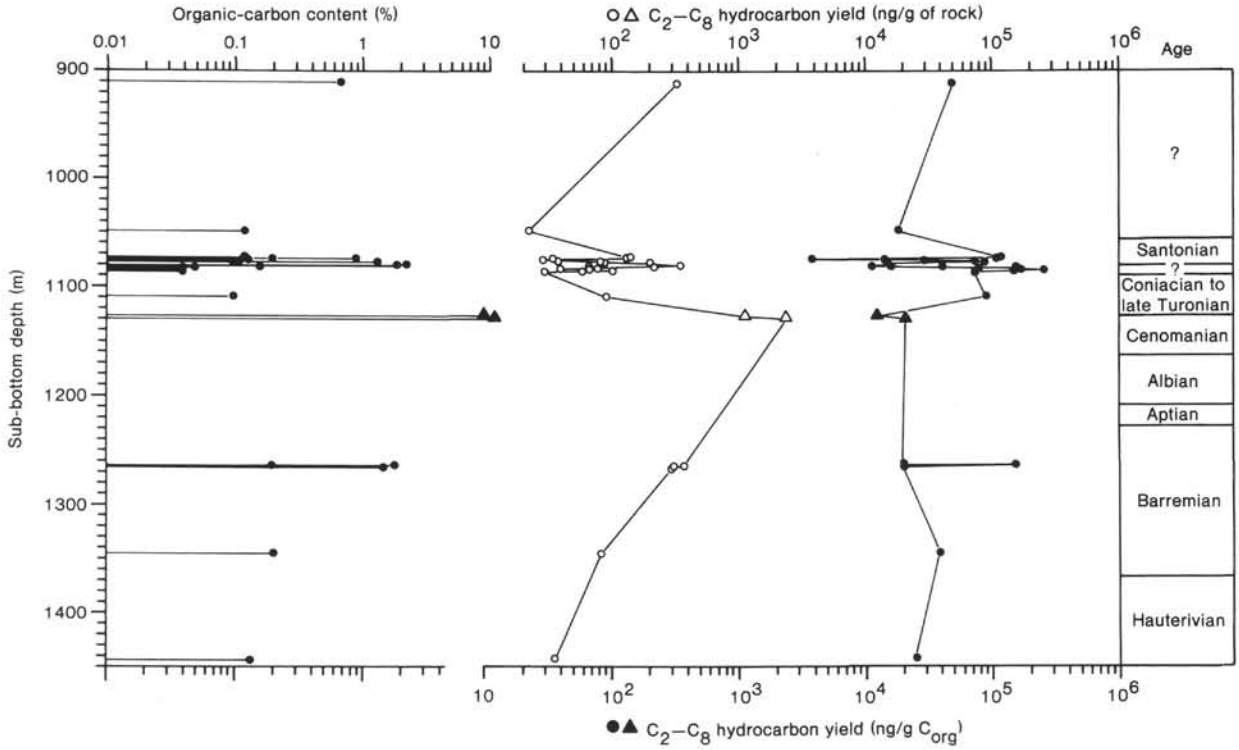

Figure 2. Organic-carbon content and low-molecular-weight hydrocarbon yield (sum of all C_2–C_8 hydrocarbons identified in Table 1, except the olefins) versus depth for sediment samples from DSDP Hole 603B, Leg 93. Triangles indicate black shale samples of Core 603B-34.

mg/g C_{org}, respectively). T_{max} values of these two samples are about 410°C, indicating kerogens that are definitely in an immature evolutionary stage. T_{max} values in all other samples are quite variable (between 422 and 471°C). The high values of about 470°C are associated with very hydrogen lean kerogens (I_H between 36 and 60 mg/g C_{org}) in Cores 603B-28 and -29 that are lithologically described as sandstone and silty claystones (turbidites). It is questionable, however, whether the high T_{max} values are indicative of a high maturity of these samples, because their pyrolytic yields are very low and T_{max} values may therefore be caused by an artifact effect.

Light Hydrocarbon Contents

As shown in Figure 2, light hydrocarbon yields (sum of total C_2–C_8 molecular range, see Table 1, except the olefins) are quite variable in the samples studied . Rock-weight-based values vary by more than two orders of magnitude from 22 (Sample 603B-25-2, 36–37 cm) to nearly 2400 ng/g dry-weight sediment in the black shale Sample 603B-34-2, 135–137 cm, reflecting the different potential for generating light hydrocarbons in terms of organic richness and hydrogen content of the kerogens. As expected, such high light hydrocarbon yields, as in the two black shale samples (i.e., 1130 and 2390 ng/g of rock) are not reached by any other sample of the series. Organic-carbon-rich, type-III kerogen-bearing samples (C_{org} content between 1.3 and 2.2%) have yields of about 200 to 360 ng/g rock. In all other samples (with the exception of Samples 603B-11-2, 67–68 cm; 603B-28-1, 35–36 cm, and 603B-28-1 100–101 cm) light hydrocarbon yields are about or less than 100 ng/g of rock.

Organic-carbon-normalized yields are again very variable (i.e., by about two orders of magnitude). Highest values of more than 10^5 ng/g C_{org} occur in samples with very low organic-carbon contents (0.04–0.2%). The two black shale samples of Core 603B-34 exhibit much lower yields of 12,700 and 21,500 ng/g C_{org}, respectively. Provided that these hydrocarbon contents are indigenous, the conclusion is warranted that the organic matter of the black shales is immature. According to Rullkötter et al. (this volume), Cenomanian-age sediments at Site 603 have a vitrinite reflectance of about 0.3%, which supports our conclusion. Concentration values of about 2 $\times$ 10^4 ng/g C_{org} compare well with those of corresponding Cenomanian-age black shale samples of DSDP Hole 530A of Leg 75 (Angola Basin, cf. Schaefer and Leythaeuser, 1984) where a slightly higher vitrinite reflectance (about 0.4%) was measured (Rullkötter et al., 1984).

Redistribution of Light Hydrocarbons

To detect samples or intervals that are enriched in hydrocarbons, in Figure 3 we plotted the total light hydrocarbon yields in (A) rock-weight and (B) organic-carbon-content-normalized units versus the organic carbon contents of the sediment samples. Based on these data and following the concepts for recognition of redistribution or migration phenomena (i.e., by comparing light hydrocarbon yields in closely spaced samples of different lithology and kerogen type or samples with equal

Table 1. Summary of low-molecular-weight hydrocarbon yields, organic-carbon contents, and Rock-Eval pyrolysis data of core samples from DSDP Hole 603B.

Core-Section (interval in cm) Sub-bottom depth (m)	11-2, 67–68 910.97	25-2, 36–37 1049.47	28-1, 35–36 1073.56	28-1, 100–101 1074.21	28-2, 35–36 1075.06	28-2, 100–101 1075.71	28-3, 35–36 1076.56	28-3, 100–101 1077.21
Lithology	Mica-bearing claystone	Silt-rich claystone	Silt-bearing claystone	Silt-bearing claystone	Silt-bearing claystone	Silt-bearing claystone	Silt-bearing claystone	Silt-bearing claystone
C_{org} (%)	0.67	0.12	0.12	0.12	0.90	0.20	0.13	0.11
Hydrogen index (mg hydrocarbons/g C_{org})	71				36			
Oxygen index (mg CO_2/g C_{org})	186				315			
T_{max} (°C)	427				470			
Hydrocarbon concentration (ng/g dry-weight sediment)								
Ethene	2.3	0.82	2.0	1.1	2.3	1.9	1.9	8.4
Ethane	3.4	1.5	16.1	9.8	3.8	1.6	2.6	2.8
Propene	3.5	2.0	2.9	6.9	2.8	1.8	2.2	16.5
Propane	12.9	2.6	27.9	19.8	4.8	3.2	5.2	5.9
Methylpropane	8.3	2.1	13.5	13.1	2.1	2.0	4.3	6.3
Methylpropene + 1-butene	4.7	2.3	5.1	7.0	2.9	2.5	3.2	25.2
n-Butane	4.8	1.6	14.3	10.2	2.9	2.0	3.1	4.8
Methylbutane	35.0	1.0	9.4	8.2	1.5	1.2	2.0	1.9
n-Pentane	75.3	2.0	8.4	11.2	3.7	1.7	2.1	5.7
2,2-Dimethylbutane	<0.01	0.05	?	—	?	0.09	<0.01	0.14
Cyclopentane	?	<0.1	0.68	<0.1	<0.1	<0.1	<0.1	0.43
2,3-Dimethylbutane	2.5	—	0.21	0.28	—	—	<0.1	<0.1
2-Methylpentane	?	0.30	2.6	1.9	0.41	0.29	0.42	1.2
3-Methylpentane	4.5	0.27	1.3	1.2	0.49	0.22	0.30	?
n-Hexane	10.7	1.4	5.3	5.5	2.7	1.4	1.7	5.8
Methylcyclopentane + 2,2-dimethylpentane	12.3	0.27	1.1	0.90	0.21	0.30	—	0.88
2,4-Dimethylpentane	1.5	—	—	<0.1	—	—	—	0.38
Benzene	21.4	0.95	7.3	5.2	2.5	0.94	1.8	9.4
Cyclohexane	10.9	<0.1	—	<0.1	—	—	—	0.40
2-Methylhexane	3.9	0.46	0.90	1.0	<0.1	0.65	<0.1	1.2
2,3-Dimethylpentane + 1,1-dimethylcyclopentane	4.0	0.26	0.38	0.66	—	0.25	<0.1	1.1
3-Methylhexane	4.5	0.55	0.59	1.1	—	0.65	<0.1	1.1
1,cis-3-Dimethylcyclopentane	4.8	—	—	<0.1	0.23	<0.1	—	?
1,trans-3-Dimethylcyclopentane	4.6	—	—	<0.1	—	—	—	<0.1
1,trans-2-Dimethylcyclopentane	4.3	—	—	<0.1	—	—	—	0.70
n-Heptane	15.7	1.0	4.5	3.2	1.7	1.4	2.0	4.6
1,cis-2-Dimethylcyclopentane	1.6	—	—	—	—	—	—	—
Methylcyclohexane	33.3	—	—	<0.1	—	—	—	—
2,5-Dimethylhexane	<0.1	—	—	—	—	—	—	—
Ethylcyclopentane	2.2	—	—	—	—	—	—	—
1,trans-2,cis-4-Trimethylcyclopentane	0.59	—	—	—	—	—	—	—
1,trans-2,cis-3-Trimethylcyclopentane	1.7	—	—	—	—	—	—	<0.1
Toluene	39.3	4.9	27.2	38.6	5.2	9.8	11.3	17.6
n-Octane	6.2	<0.1	0.28	<0.1	1.8	0.47	0.86	5.2

Note: — = value below or near detection limit; ? = value uncertain due to peak overlappng.

kerogen type at different depth levels; cf. Schaefer et al., 1983a; Schaefer and Leythaeuser, 1984; Jasper et al., 1984; Schaefer and Leythaeuser, in press), it appeared that two depth intervals should be considered in more detail.

1074–1087-m Depth Interval

Organic-carbon contents and C_2–C_8 hydrocarbon yields (both rock-weight-based and normalized to organic-carbon contents of the rock) are plotted versus depth for 16 samples in Figure 4. Comparing the organic-carbon-normalized yields with those of the two hydrogen-rich-kerogen-bearing black shales of Core 603B-34 (Figs. 2 and 3B), we conclude that all samples included in Figure 4 are enriched in hydrocarbons (except Sample 603B-28-2, 35–36 cm). In view of the extremely low hydrocarbon potential, even the yields of the three samples with high organic-carbon contents from 1078.71, 1081.11, and 1081.81 m depth are much higher than expected at this maturity level (15,400; 16,100; 11,600 ng/g C_{org}). In this respect it is very unlikely that these samples are the source of the hydrocarbon impregnation of the other organic-carbon-lean samples of this interval. Instead, we believe that possible sources for these hydrocarbons are hydrogen-rich-kerogen-bearing claystones, such as the black shales of Core 603B-34. To support this hypothesis we plotted the rock-weight-based yields of three *n*-alkanes (ethane, propane, *n*-butane) for this depth interval (Fig. 5). As can be seen in this figure, there is no clear relationship between hydrocarbon yields, molecular size, and organic richness of the rocks. Compare, for instance, the hydrocarbon yields of the organic-carbon-rich samples (1.3–2.2% C_{org}) with those of only 0.04% C_{org} at 1084.81, 1085.61, and 1086.31 m depth; their hydrocarbon yields are quite similar. The most probable explanation for this observation is to assume that hydrocarbons have been redistributed within the sedimentary column. The degree of enrichment at any given level would be controlled by adsorption phenomena of the mineral surfaces and the available pore space of the rock.

1264–1266-m Depth Interval

Three samples with organic-carbon contents of 1.8, 0.2, and 1.5% are considered. In particular, the first two closely spaced samples (only 8 cm apart) represent an ideal pair to examine potential redistribution effects. It is obvious from Figure 2 that total light hydrocarbon yields in rock-weight-based units are very similar in these

Table 1 (continued).

28-4, 35-36 1078.06 Silt-bearing claystone	28-4, 100-101 1078.71 Sandstone	29-1, 31-32 1081.11 Silt-rich claystone	29-1, 100-101 1081.81 Silt-rich claystone	29-2, 31-32 1082.61 Silt-rich claystone	29-2, 100-101 1083.31 Silt- and zeolite-bearing claystone	29-3, 31-32 1084.11 Silt- and zeolite-bearing claystone	29-3, 100-101 1084.81 Silt- and zeolite-bearing claystone	29-4, 31-32 1085.61 Silt- and zeolite-bearing claystone	29-4, 100-101 1086.31 Silt- and zeolite-bearing claystone	29-5, 31-32 1087.11 Silt- and zeolite-bearing claystone
0.10	1.33 60 65 471	2.22 40 58 471	1.90 48 49 470	0.16	0.05	0.05	0.04	0.04	0.04	0.04
2.3	3.4	5.2	2.3	1.7	2.1	2.4	2.6	3.2	2.2	2.5
2.3	6.8	4.3	5.6	11.4	4.8	3.7	4.7	5.0	6.5	2.3
3.3	4.6	6.9	4.3	2.5	3.4	3.2	3.7	4.0	2.8	3.9
13.2	12.5	6.9	15.8	14.6	12.1	6.0	10.8	12.7	10.4	3.7
8.5	8.7	4.0	6.6	4.6	6.4	3.1	4.5	6.3	4.7	2.4
5.0	4.3	6.3	4.9	3.0	4.6	3.6	5.7	5.8	3.9	4.6
7.0	6.6	4.6	8.3	6.3	6.5	3.3	5.7	7.4	5.4	2.4
5.6	8.8	10.3	8.7	2.5	4.3	2.3	3.1	3.8	3.2	1.2
4.2	23.5	53.7	30.6	4.4	2.9	2.4	6.3	7.3	5.5	2.1
0.05	0.12	3.7	0.23	<0.01	0.07	0.14	0.43	0.04	0.04	0.12
<0.1	?	<0.1	<0.1	0.26	<0.1	0.25	<0.1	0.20	<0.1	<0.1
0.23	—	<0.1	0.26	<0.1	—	<0.1	—	<0.1	—	<0.1
1.4	2.4	2.9	2.2	0.70	0.82	0.63	0.55	0.80	0.75	0.38
0.87	1.3	2.4	0.92	0.55	0.46	0.63	0.64	1.0	0.42	0.93
3.4	4.8	7.8	5.3	3.2	2.5	2.3	11.4	11.1	2.2	1.4
0.66	1.2	2.1	1.3	0.61	0.41	0.28	0.31	0.46	0.23	<0.1
—	0.21	0.30	0.20	0.12	—	—	<0.1	—	—	0.11
6.0	10.5	19.6	20.4	3.4	5.2	4.2	3.6	18.3	4.3	4.2
<0.1	0.78	2.2	1.0	<0.1	—	—	—	—	—	<0.1
1.1	1.5	2.5	1.3	0.94	0.47	0.26	0.80	0.77	0.36	—
0.48	0.94	2.2	1.1	0.32	<0.1	<0.1	0.30	<0.1	0.22	—
1.0	1.8	3.7	1.7	1.0	0.40	0.26	0.88	0.84	0.26	—
0.41	0.49	2.5	0.74	<0.1	<0.1	0.24	0.71	0.31	<0.1	—
—	0.43	0.95	0.33	<0.1	—	—	—	—	—	—
—	0.32	1.0	0.44	<0.1	—	—	—	—	—	—
3.4	4.6	7.3	4.7	3.0	2.5	1.7	1.7	3.4	1.4	1.5
—	<0.1	0.54	—	—	—	—	—	—	—	—
—	2.1	7.4	2.4	—	—	—	—	—	—	—
—	—	<0.1	—	—	—	—	—	—	—	—
—	<0.1	0.11	—	—	—	—	—	—	—	—
—	—	<0.1	—	—	—	—	—	—	—	—
—	—	<0.1	<0.1	—	—	—	—	—	—	—
28.0	103.0	199.0	96.0	8.6	27.7	7.5	9.5	21.8	12.2	7.2
<0.1	<0.1	4.4	2.0	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

three samples (376, 315, and 305 ng/g of rock). Likewise, the organic-carbon-normalized values vary from about 20,000 ng/g C_{org} (Samples 603B-49-2, 50–52 cm and 603B-49-3, 64–66 cm) to about 160,000 ng/g C_{org} in the siltstone with only 0.2% of organic carbon (603B-49-2, 58–61 cm). It appears that these three samples are, in terms of their total light hydrocarbon contents, equilibrated to a certain extent by a redistribution process. However, an examination of individual compounds (see Table 1) in Sample 603B-49-2, 50–52 cm (C_{org} = 1.8%) and Sample 603B-49-2, 58–61 cm (C_{org} = 0.2%) reveals that the C_2–C_4 hydrocarbons are more abundant in the latter, whereas C_5–C_7 hydrocarbon yields are higher in the former. In this respect it is questionable if these data reflect simple equilibration of the compounds between the sediment layers. Instead, the general predominance of the gaseous hydrocarbons in Sample 603B-49-2, 58–61 cm might be caused by preferential diffusion of the most mobile compounds into this layer. On the other hand, in view of the significant difference in organic-carbon contents of these two samples by nearly one order of magnitude, it is not surprising that the concentrations of individual hydrocarbons, particularly in the C_5–C_7 molecular range, are not identical in both samples. This might, for instance be caused by different adsorption activities of their organic matter and mineral surfaces.

As discussed before, however, even C_2–C_8 hydrocarbon yields of 20,000 ng/g C_{org} are much too high in view of the extremely low hydrocarbon potential of the two organic-carbon-rich samples (hydrogen index 49 and 44 mg/g C_{org}, respectively) at the corresponding maturity level. Again, as concluded from the results in the 1074–1087-m depth interval, the source of the hydrocarbons that caused the enrichment is most probably hydrogen-rich-kerogen-bearing claystones such as black shales from Core 603B-34.

CONCLUSIONS

The conclusions reached in this study were of a somewhat limited nature because after all samples received were analyzed, only 27 samples yielded reliable data that could be included in this interpretation. This was because of the severe acetone contamination of most samples. It is emphasized, however, that even for these 27 samples the quality of the data is not ideal. Therefore, the conclusions drawn here are mainly based on total C_2–C_8 hydrocarbon yields.

Table 1 (continued).

Core-Section (interval in cm)	32-2, 53-54	34-1, 51-53	34-2, 135-137	49-2, 50-52	49-2, 58-61	49-3, 64-66	57-5, 36-38	68-2, 10-11
Sub-bottom depth (m)	1109.50	1128.02	1130.36	1264.41	1264.49	1266.05	1345.57	1443.31
Lithology	Silt-rich claystone	Black carbonaceous claystone	Black carbonaceous claystone	Siltstone	Siltstone	Nannofossil-rich claystone	Sandstone	Sandy siltstone
C_{org} (%)	0.10	8.94	11.10	1.83	0.20	1.49	0.21	0.14
Hydrogen index (mg hydrocarbons/g C_{org})		357	323	49		44		
Oxygen index (mg CO_2/g C_{org})		67	64	161		156		
T_{max} (°C)		409	412	423		422		
Hydrocarbon concentration (ng/g dry-weight sediment)								
Ethene	2.3	15.2	39.2	5.8	6.1	6.1	2.4	0.89
Ethane	5.1	103.0	55.8	23.0	52.6	17.9	9.8	4.4
Propene	2.7	12.9	33.3	7.3	10.5	9.5	3.9	1.3
Propane	12.6	109.0	87.9	23.7	61.4	16.6	12.0	4.6
Methylpropane	6.1	141.0	95.7	8.6	27.8	9.2	6.2	2.4
Methylpropene + 1-butene	4.3	7.7	14.1	4.0	6.9	5.9	3.9	1.3
n-Butane	6.4	35.3	39.9	12.5	35.0	8.5	6.5	2.7
Methylbutane	3.8	?	251.0	23.0	18.8	24.6	5.2	1.7
n-Pentane	3.1	81.4	443.0	89.4	23.2	89.4	5.4	2.3
2,2-Dimethylbutane	<0.01	2.3	9.2	?	0.20	0.53	0.41	0.07
Cyclopentane	<0.1	44.4	407.0	<0.1	2.9	?	0.70	0.22
2,3-Dimethylbutane	—	—	12.7	—	0.81	1.2	0.28	<0.1
2-Methylpentane	0.83	110.0	140.0	6.3	4.9	5.3	1.6	0.69
3-Methylpentane	0.71	16.1	21.9	4.2	3.4	2.6	1.1	0.42
n-Hexane	3.1	21.7	50.1	70.4	13.6	11.2	3.9	1.7
Methylcyclopentane + 2,2-dimethylpentane	1.2	114.0	129.0	7.1	2.9	10.4	1.7	<0.1
2,4-Dimethylpentane	0.40	8.5	10.3	—	—	0.51	—	—
Benzene	5.6	16.1	33.1	10.0	10.3	7.4	3.4	2.7
Cyclohexane	0.30	10.0	24.1	6.0	0.60	4.5	0.65	0.15
2-Methylhexane	3.2	12.6	22.7	2.6	2.1	2.3	0.64	0.47
2,3-Dimethylpentane + 1,1-dimethylcyclopentane	1.2	30.3	46.3	2.7	0.95	2.9	0.32	0.32
3-Methylhexane	3.7	10.9	25.1	3.5	2.0	3.3	0.68	0.53
1,cis-3-Dimethylcyclopentane	0.24	53.2	81.1	1.9	0.68	2.3	0.30	0.37
1,trans-3-Dimethylcyclopentane	0.40	41.1	57.1	2.0	0.48	2.7	0.28	<0.1
1,trans-2-Dimethylcyclopentane	0.20	20.0	29.9	2.3	1.5	14.9	0.60	0.34
n-Heptane	3.5	17.5	40.1	6.5	7.8	6.1	2.6	1.5
1,cis-2-Dimethylcyclopentane	—	19.7	27.7	0.32	<0.1	1.2	—	—
Methylcyclohexane	<0.1	36.7	69.1	11.2	0.72	<0.1	0.85	0.59
2,5-Dimethylhexane	—	3.6	<0.1	—	—	—	—	—
Ethylcyclopentane	—	19.0	28.2	0.32	<0.1	—	—	—
1,trans-2,cis-4-Trimethylcyclopentane	—	16.5	16.0	1.3	<0.1	5.5	—	—
1,trans-2,cis-3-Trimethylcyclopentane	—	4.7	3.6	5.4	<0.1	9.6	—	—
Toluene	29.3	21.8	120.0	52.1	36.5	42.8	17.0	7.7
n-Octane	<0.1	9.8	7.3	<0.1	0.14	<0.1	1.4	<0.1

1. Highest rock-weight-based C_2–C_8 hydrocarbon yields are measured in the two black shale samples of Core 603B-34 (1130 and 2390 ng/g of rock). The corresponding organic-carbon-normalized values (12,700 and 21,500 ng/g C_{org}) are typical for indigenous concentration levels of immature hydrogen-rich-kerogen-bearing claystones. Similar values were measured, for instance, in corresponding Cenomanian-age black shales of DSDP Hole 530A (Angola Basin).

2. Organic-carbon-normalized yields of most other samples of this study are of similar magnitude or even higher despite greatly inferior kerogen qualities.

The highest yields occur in samples with 0.2 or less organic-carbon contents (more than 10^5 ng/g C_{org}). It is most likely that they are enriched with small amounts of low-molecular-weight hydrocarbons. Because of their very low organic-carbon contents, the organic-carbon-normalized values indicate in an extremely sensitive fashion even traces of migrated hydrocarbons. On the other hand, it could be shown that even samples richer in organic carbon and bearing Type III kerogen (603B-28-4, 100–101 cm; 603B-29-1, 31–32 cm; 603B-29-1, 100–101 cm; 603B-49-2, 50–52 cm; and 603B-49-3, 64–66 cm) are also enriched in hydrocarbons that were generated in potential hydrocarbon sources, such as the black shales of Core 603B-34.

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REFERENCES

Espitalié, J., Laporte, J. L., Madec, M., Marquis, F., Leplat, P., Paulet, J., and Boutefeu, A., 1977. Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. *Rev. Inst. Fr. Pet.*, 32:23–42.

Jasper, J. P., Whelan, J. K., and Hunt, J. M., 1984. Migration of C_1 to C_8 volatile organic compounds in sediments from the Deep Sea Drilling Project, Leg 75, Hole 530A. *In* Hay, W. W., Sibuet, J.-C., et al., *Init. Repts. DSDP*, 75, Pt. 2: Washington (U.S. Govt. Printing Office), 1001–1008.

Leythaeuser, D., Schaefer, R. G., and Pooch, H., 1983. Diffusion of light hydrocarbons in subsurface sedimentary rocks. *Am. Assoc. Pet. Geol. Bull.*, 67:889–895.

Leythaeuser, D., Schaefer, R. G., and Yükler, A., 1980. Diffusion of light hydrocarbons through near-surface rocks. *Nature* (London) 284:522–525.

_____, 1982. Role of diffusion in primary migration of hydrocarbons. *Am. Assoc. Pet. Geol. Bull.*, 66:408–429.

Rullkötter, J., Mukhopadhyay, P. K., and Welte, D. H., 1984. Geochemistry and petrography of organic matter in sediments from Hole 530A, Angola Basin, and Hole 532, Walvis Ridge, Deep Sea Drilling Project. *In* Hay, W. W., Sibuet, J.-C., et al., *Init. Repts. DSDP*, 75, Pt. 2: Washington (U.S. Govt. Printing Office), 1069–1087.

Schaefer, R. G., and Leythaeuser, D., 1984. C_2–C_8 Hydrocarbons in sediments from Deep Sea Drilling Project Leg 75, Holes 503A, Angola Basin, and 532, Walvis Ridge. *In* Hay, W. W., Sibuet, J.-C., et al., *Init. Repts. DSDP*, 75, Pt. 2: Washington (U.S. Govt. Printing Office), 1055–1067.

_____, in press. Low molecular weight hydrocarbons in sediments of Deep Sea Drilling Project Leg 89, Sites 585, East Mariana Basin, and 586, Ontong-Java Plateau. *In* Moberly, R., Schlanger, S. O., et al., *Init. Repts. DSDP*, 89: Washington (U.S. Govt. Printing Office), 577–588.

Schaefer, R. G., Leythaeuser, D., and Gormly, J., 1984. Generation and migration of low-molecular-weight hydrocarbons in sediments of Deep Sea Drilling Project Leg 79, Sites 544, 545, and 547, offshore Morocco. *In* Hinz, K., Winterer, E. L., et al., *Init. Repts. DSDP*, 79: Washington (U.S. Govt. Printing Office), 743–773.

Schaefer, R. G., Leythaeuser, D., and von der Dick, H., 1983a. Generation and migration of low-molecular-weight hydrocarbons in sediments from Site 511 of DSDP/IPOD Leg 71, Falkland Plateau, South Atlantic. *In* Bjorøy, M., et al. (Eds.), *Advances in Organic Geochemistry 1981*: Chichester (Wiley), pp. 164–174.

Schaefer, R. G., von der Dick, H., and Leythaeuser, D., 1983b. C_2–C_8 Hydrocarbons in sediments from Deep Sea Drilling Project Leg 71, Site 511, Falkland Plateau, South Atlantic. *In* Ludwig, W. J., Krasheninnikov, V., et al., *Init. Repts. DSDP*, 71: Washington (U.S. Govt. Printing Office), 1033–1043.

Schaefer, R. G., Weiner, B., and Leythaeuser, D., 1978. Determination of sub-nanogram per gram quantities of light hydrocarbons (C_2–C_9) in rock samples by hydrogen stripping in the flow system of a capillary gas chromatograph. *Anal. Chem.*, 50:1848–1854.

Whelan, J. K., and Hunt, J. M., 1981. C_1–C_8 Hydrocarbons in Leg 63 sediments from outer California and Baja California borderlands. *In* Yeats, R. S., Haq, B. U., et al., *Init. Repts. DSDP*, 63: Washington (U.S. Govt. Printing Office), 775–784.

_____, 1982. C_1–C_8 Hydrocarbons in Leg 64 sediments, Gulf of California. *In* Curray, J. R., Moore, D. G., et al., *Init. Repts. DSDP*, 64, Pt. 2: Washington (U.S. Govt. Printing Office), 763–780.

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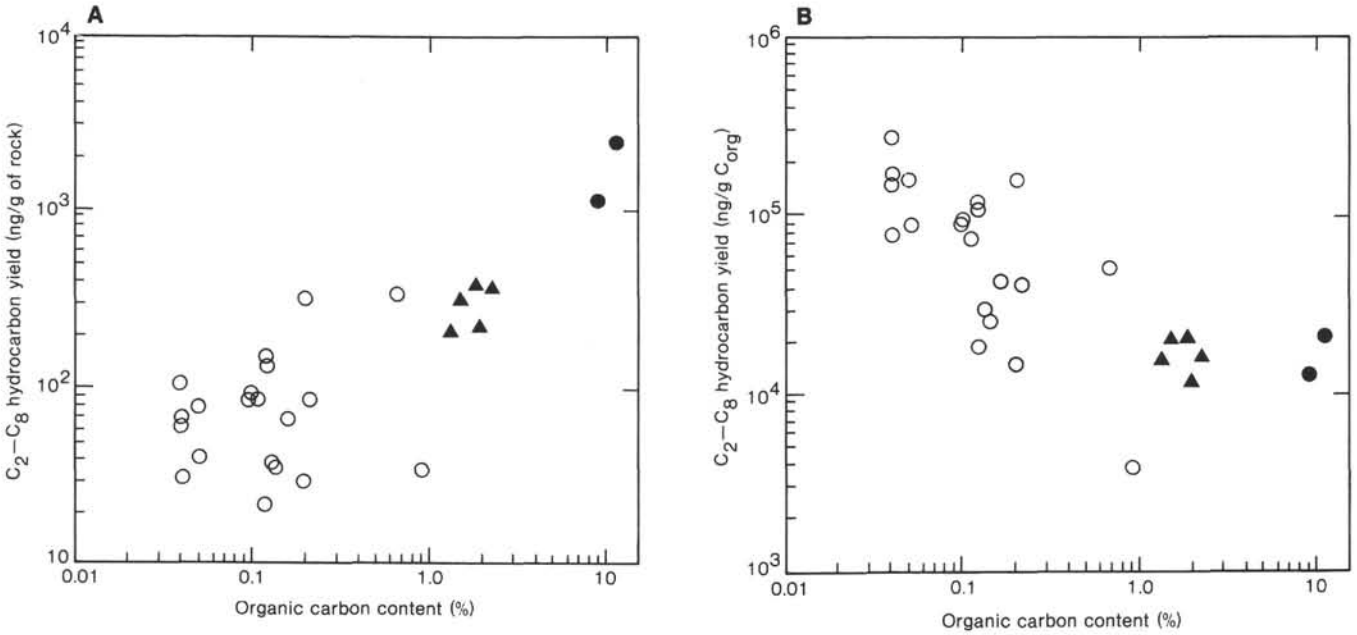

Figure 3. Low-molecular-weight hydrocarbon yield (A) in rock-weight and (B) in organic-carbon-content-normalized units, versus organic-carbon content of the sediment samples from DSDP Hole 603B, Leg 93. Solid circles indicate black shale samples of Core 603B-34. Triangles indicate samples with high organic-carbon contents (1.3–2.2%) of Cores 603B-28, -29, and -49.

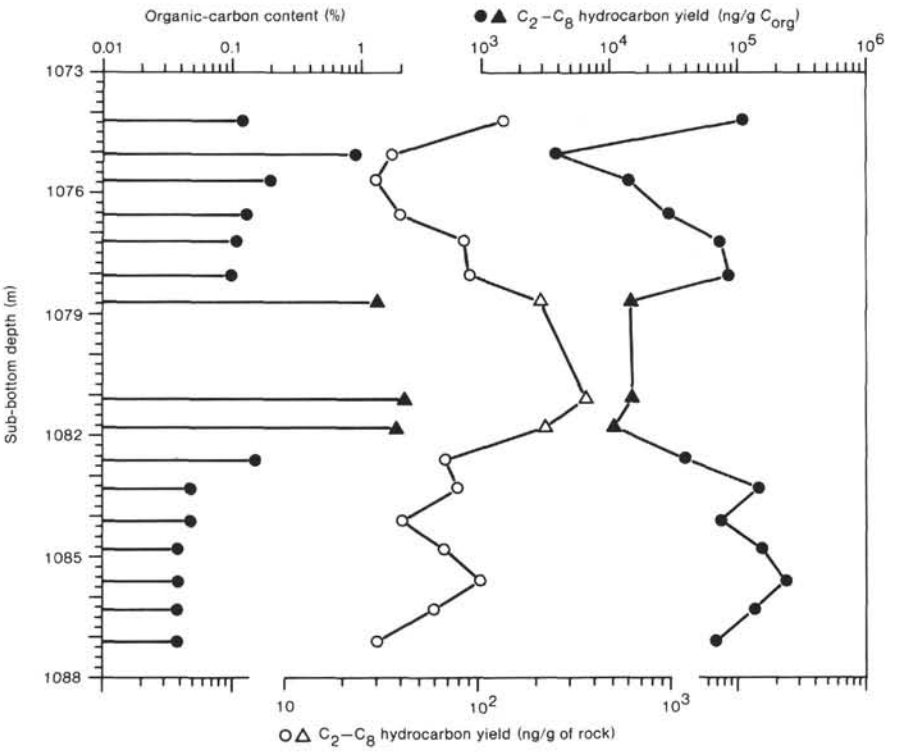

Figure 4. Organic-carbon content and low-molecular-weight hydrocarbon yield (as in Fig. 2) versus depth for the 1074-1087-m interval of DSDP Hole 603B, Leg 93. Triangles indicate samples with high organic-carbon contents (1.3–2.2%) of Cores 603B-28 and -29.

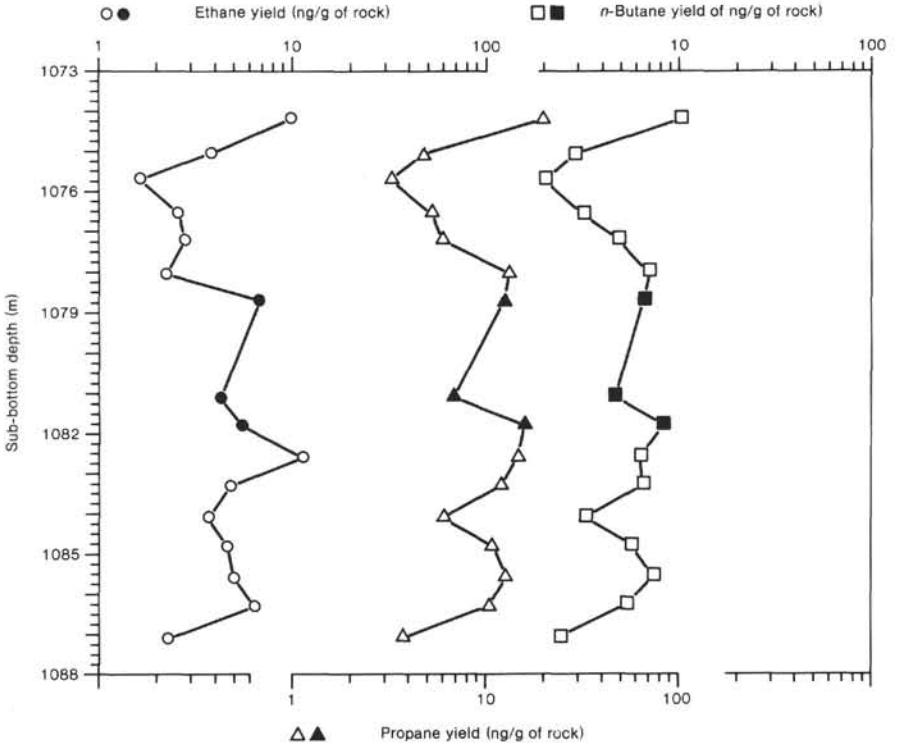

Figure 5. Ethane, propane, and *n*-butane yield (ng/g dry-weight sediment) versus depth for the 1074-1087-m interval of DSDP Hole 603B, Leg 93. Solid symbols indicate samples with high organic-carbon contents (1.3–2.2%) of Cores 603B-28 and -29.