39. C₂-C₈ HYDROCARBONS IN SEDIMENTS FROM DEEP SEA DRILLING PROJECT LEG 71, SITE 511, FALKLAND PLATEAU, SOUTH ATLANTIC¹

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ABSTRACT

 C_2-C_8 hydrocarbons (36 compounds identified) from 56 shipboard sealed, deep-frozen core samples of DSDP Leg 71, Site 511, Falkland Plateau, South Atlantic, were analyzed by a combined hydrogen stripping-thermovaporization method. Concentrations, which represent hydrocarbons dissolved in the pore water and adsorbed to the mineral surfaces of the sediment, vary from 24 ng/g of dry weight sediment in Lithologic Unit 4 to 17,400 ng/g in Lithologic Unit 6 ("black shale" unit). Likewise, the organic carbon normalized C_2-C_8 hydrocarbon concentrations range from 10⁴ to 3.5×10^5 ng/g C_{org} . The latter value is more than one order of magnitude lower than expected for petroleum source beds in the main phase of oil generation. The low maturity at 600 meters depth is further supported by light hydrocarbon concentration ratios. The change of the kerogen type from Lithologic Unit 5 (Type III) to 6 (Type II) is evidenced by changes in the C_6 and C_7 hydrocarbon composition. Redistribution phenomena are observed close to the Tertiary–Cretaceous unconformity and at the contact between the "black shale" unit and the overlying Cretaceous chalks and claystones. Otherwise, the low molecular weight hydrocarbons in Hole 511 are formed *in situ* and remain at their place of formation.

The core samples turned out to be contaminated by large quantities of acetone, which is routinely used as a solvent during sampling procedures onboard *Glomar Challenger*.

INTRODUCTION

The ubiquitous occurrence of low molecular weight hydrocarbons in DSDP cores has been studied in detail by Hunt (1975), Hunt and Whelan (1978), Faber et al. (1978), Whelan and Hunt (1978), Whelan (1979), Whelan and Hunt (1979), Whelan and Sato (1980), and Whelan and Hunt (1980). One conclusion from these studies was that C1 to C7 range compounds are formed from kerogen by in situ low-temperature degradation reactions in low-maturity sediments. The exception is methane, which can also be formed by bacterial action. The main objective of the present study was to obtain additional data for the formation of low molecular weight hydrocarbons as a function of the maturity and type of the organic matter. Furthermore, by closely spaced (decimeter, centimeter) sampling over the relevant depth interval, it was intended to recognize possible redistribution phenomena of light hydrocarbons between the Aptian "black shale" and the overlying Albian-Turonian organic carbon lean strata.

During the cruise of *Glomar Challenger* in the South Atlantic, Falkland Plateau (January, 1980), 56 core samples were sealed and deep-frozen onboard. Low molecular weight hydrocarbon analysis of the frozen cores was carried out by application of a recently developed single-step hydrogen stripping-thermovaporization method.

The sediment samples were collected from the cores immediately after they had been cut into sections on deck. Samples were stored in Teflon-sealed 30-ml aluminum containers in a deep freezer and remained in deep-frozen condition (approx. -20° C) until the analysis was performed in the laboratory at KFA Jülich. The low molecular weight hydrocarbons were measured by a slightly modified, combined hydrogen-stripping-thermovaporization method described in detail by Schaefer et al. (1978). Modification of the method was necessary, since the samples turned out to be extensively contaminated by acetone (see detailed description and discussion about shipboard contamination of sediment samples by acetone at the end of this chapter). The analytical method comprises both extraction of hydrocarbons from the rock and subsequent capillary gas chromatography (GC) in a single-step procedure carried out in a closed gas-flow system. Briefly, a small portion of the crushed sediment sample (generally, between 0.1 and 1.0 gram) is placed in the flow system of a capillary gas chromatograph, the carrier gas serving as the stripping gas. The rock sample is heated to 110°C for 5 min. in a hydrogen flow of 5 ml/min. Therefore it is assumed that the analytical data obtained represent the absolute quantities of hydrocarbons both dissolved in the pore water and adsorbed on the mineral surface. Hence the concentration values obtained cannot easily be compared to other light hydrocarbon data (e.g., from head-space analyses). Splitless introduction of the hydrocarbons accumulated in a cold trap ensures a high sensitivity.

Lowest detectable quantity (e.g., for *n*-butane) is 0.01 ppb (weight per weight of rock for 1-g sample.) Owing to analytical limitations, the method does not include the measurement of methane. Evaporation losses during sample pretreatment and the inefficiency of the cold trap render the methane concentrations inaccurate. Isothermal GC analysis allows the application of Kováts retention indices for compound identification. The chromatograms are obtained using a 45-m 0.5 mm ID support-coated open tubular column with squalane stationary phase and hydrogen carrier gas, run isothermally at 55° C, connected to a flame ionization detector. The GC detector output is linked to a chromatography data system (Datachrom II, Kratos-In-

METHOD

¹ Ludwig, W. J., Krasheninnikov, V. A., et al., *Init. Repts. DSDP*, 71: Washington (U.S. Govt. Printing Office).

stem Ltd., Stone, England) run on a PDP 11/10 computer (Digital Equipment Corp.). This on-line system outputs partially processed data (peak areas and retention times) on punched tape for off-line calculations of retention indices and compound concentrations.

Organic carbon contents were measured on the stripped sediment samples after treatment with hot 6N HCl by a combustion method (LECO carbon analyzer IR 112). Selected samples from Cores 56 to 68 were measured by the Rock-Eval pyrolysis method (Espitalié et al., 1977).

RESULTS AND DISCUSSION

Generation of Low Molecular Weight Hydrocarbons

The low molecular weight (C_2 - C_8 range) hydrocarbon concentrations of 56 core samples covering the depth interval 159 to 605 meters (Cores 18-68) are summarized in Table 1. The compounds are arranged in sequence of increasing retention on squalane as the stationary GC phase.

The hydrocarbon quantities in Hole 511 are shown in Figures 1 and 2. In these diagrams the sum of low molecular weight hydrocarbons (Table 1) is plotted against depth, both in absolute (i.e., ppb rock-weight-based) and organic-carbon-normalized units, respectively.

It is apparent from Figure 1 that hydrocarbon concentrations vary over the whole interval by almost three orders of magnitude. Roughly, the section can be subdivided into two main intervals. There are low hydrocarbon concentrations (20-300 ng/g dry weight sediment) in Lithologic Units 2A, 2B, 3, 4, and 5, whereas considerable amounts occur in the major part of Unit 6, particularly in samples with elevated organic carbon contents. (For lithologic units and stratigraphy, see the site chapter, this volume.) For example, almost 20,000 ng/g occur in Core 66 at 585 meters depth. This depth corresponds to a measured vitrinite reflectance \overline{R}_{o} = 0.4% (von der Dick et al., this volume). To eliminate the influence of fluctuations in organic carbon contents, we show the corresponding values in a carbon-normalized form (Fig. 2). Concentrations vary from about 10⁴ to 3×10^5 ng/g of organic carbon. The highest values are found, as expected, at the bottom of the hole; however, three samples of Lithologic Unit 3 also reveal quite similar values (almost 3×10^5 ng/g of organic carbon). It is striking that the whole section down to a depth of 230 meters appears to be enriched by low molecular weight hydrocarbons, compared to the lower section of Unit 4-in particular, to the samples from 260 to 340 meters, where less than 20,000 ng/g Corg occurs. One explanation for this phenomenon will be discussed in the next section. From approximately 300 to 605 meters, an exponential (a straight line in the semilog plot) trend of increasing hydrocarbon concentrations is observed. This indicates generation of these compounds from kerogen with increasing thermal stress. A change of the type of organic matter in this interval from Lithologic Unit 5 to 6 (see the following) has only a minor influence on the parameter plotted in Figure 2. It has been shown by Leythaeuser et al. (1979) that Type III kerogen generates predominantly C_2 to C_4 hydrocarbons, whereas Type II kerogen, at the same maturity, favors the formation of the C_5 to C_8 hydrocarbons. Therefore, in the plot of the

 C_2 to C_8 hydrocarbons versus depth (Fig. 2) the influence of kerogen type is to a large extent obliterated.

Major deviations from the generation trend in Figure 2 are observed at the contact between Lithologic Units 5 and 6. Whereas the upper section of Unit 6 (490-520 m) shows significantly lower values than the general trend, part of Unit 5, represented by two extremely organiccarbon-lean samples from Core 51, reveal drastically elevated organic-carbon-normalized values. The concentrations in the lower section of the Unit 6 indicate that despite a relatively low maturity level (vitrinite reflectance 0.4-0.5%, see von der Dick et al., this volume), considerable quantities of gasoline-range hydrocarbons have been generated. However, values of about 3×10^5 ng/g Corg are, according to our experience, still well below those concentrations encountered in mature ($\overline{R}_o =$ 0.8-0.9%) Type II or III kerogen source beds. Organic matter of both types, in the main phase of oil generation, yields about $10^7 \text{ ng/g } C_{\text{org}}$. The low maturity is further supported by a detailed comparison of light-hydrocarbon maturity-sensitive parameters, although these parameters are also source-type-dependent, thus limiting their universal application for the assessment of maturity. The n-hexane/methylcyclopentane ratio (Jonathan et al., 1975), for example, ranges from 0.76 to 0.85 in Core 68-typical for low maturity organic matter. This conclusion is also indicated by isobutane/n-butane ratios greater than unity (1.01-1.14) in Cores 66 and 68. Another maturity-sensitive low molecular weight hydrocarbon parameter, introduced by Thompson (1979), leads to a somewhat different conclusion. The so-called "heptane-value," which is calculated as the n-heptane content in a specified boiling range of the hydrocarbon mixture, (i.e., between cyclohexane and methylcyclohexane) reveals a mean of 19.4% in Core 68. This corresponds to a present-day subsurface temperature of 145°C in the Tertiary section of the Gulf of Mexico. Such a temperature was never reached in the sediments in Hole 511 and is not in agreement with the aforementioned parameters.

In Hole 511 the significant change in the type of organic matter at the contact between Lithologic Units 5 and 6 is demonstrated by Figure 3. 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. It is obvious that Lithologic Units 2, 3, 4, and 5 produce a fairly homogeneous depth pattern for C₆ hydrocarbon composition. Benzene contents of 20 to 45% (mean value around 35%) can be associated with Type III kerogen throughout this interval (Leythaeuser et al., 1979; Schaefer and Leythaeuser, 1980). Some data scatter occurs at the Tertiary-Cretaceous unconformity at about 200 meters depth, but we observe no particular difference in type of organic matter between the Tertiary and the Cretaceous. A significant change from Type III to Type II kerogen is observed between 495 and 520 meters. Benzene contents decrease drastically from about 40% to less than 10%-or even less than 5%-at 530 meters (Core 60). The data scatter near the contact between Lithologic Units 5 and 6 is partly due to sample selection. Both organic-carbon-rich "black shales" and organic-carbon-lean sediment samples were selected in this interval to study possible redistribution phenomena (see next section).

The type of organic matter in Lithologic Unit 6 was studied by Rock-Eval pyrolysis measurements. The same samples that were used for light hydrocarbon analyses were subsequently pyrolyzed, so that the light hydrocarbon parameters discussed earlier could be correlated with the hydrogen content of the kerogen (i.e., the hydrogen index; Table 1). The complete pyrolysis data are summarized in Figure 4, in which both the hydrogen and the oxygen indices are plotted into a van Krevelentype diagram (Espitalié et al, 1977). According to these data, all samples fall between Type II and Type III kerogen evolution paths. The shallowest black shale analyzed in this study (514.60 m depth, Sample 511-58, CC, organic carbon content 4.3%) reveals a maximum hydrogen index of 433 mg/g C_{org} . All other samples have lower hydrogen indices and, therefore, reflect either the maturity increase (e.g., Core 66 at 585 m depth) or the change to a more hydrogen-lean kerogen (e.g., Sample 511-58-2, 105-107 cm). Because of the high liptinite content in the black shales, generally, high organic carbon contents of the samples are associated with high hydrogen indices.

A detailed discussion of Rock-Eval data in connection with organic petrography covering the complete depth interval of Hole 511 is given by von der Dick et al. (this volume).

Redistribution of Low Molecular Weight Hydrocarbons

In general, light hydrocarbons of the molecular range considered in this chapter, exhibit a high degree of mobility as compared to the remaining organic constituents of the rocks. Therefore it can be assumed that they are readily redistributed in a sedimentary column.

It has been shown in the previous section that major deviations from the general generation trend of C_2-C_8 hydrocarbons (Fig. 2) are observed between 160 m and 225 meters depth as well as close to the contact between Lithologic Units 5 and 6. The elevated carbon-normalized hydrocarbon concentrations in Cores 18 to 28and especially in Lithologic Units 2B and 3 (approx. 183-210 m depth)-appear to coincide with the Tertiary-Cretaceous unconformity at 196 meters. For example, the highest concentrations are encountered in Lithologic Unit 3 and are characterized by the occurrence of chert pebbles in gray calcareous and zeolitic foraminiferal oozes. Elevated sand contents of up to 25% occur between 186 and 225 meters. Movement of hydrocarbon-bearing compaction waters through this section and subsequent adsorption at the clay mineral surfaces may account for the elevated organic-carbonnormalized hydrocarbon concentrations.

The other interval that exhibits a significant deviation from the general generation trend in Figure 2 is from 495 to 520 meters. In this section, carbon-normalized values of C_2 - C_8 hydrocarbon concentrations exhibit a significant reduction compared to the overall generation trend by a factor of approximately five. Although the type of kerogen changes from Type II in the lower part to predominantly Type III in the upper part of Lithologic Unit 6, the change cannot account for the drastic differences in hydrocarbon concentrations. This is exemplified by two black shale samples of high organic carbon content, high hydrogen index values, and almost equal maturity. Whereas Sample 511-58,CC (514.60 m depth, C_{org} 4.3%, I_{H} = 433 mg/g C_{org}) contains 3.5 × 10⁵ ng C_2 - C_8 hydrocarbons/g C_{org} , Sample 511-59-4, 143-145 cm (523.93 m depth, C_{org} = 6.0%, I_{H} = 371 mg/g C_{org}) has a C_2 - C_8 hydrocarbon content of 1.3 × 10⁶ ng/g C_{org} . This difference is interpreted as a preferential loss of low molecular weight hydrocarbons from the upper part of Lithologic Unit 6 and a redistribution, probably into the overlying strata. Therefore the lowermost part of Lithologic Unit 5, represented by samples from Cores 51 and 54 as well as 56 (Samples 511-56-2, 90-92 cm and 511-56-3, 75-77 cm) exhibits elevated concentrations which exceed the generation trend just defined (Fig. 2).

In this study we applied Whelan's (1979) approach to redistribution processes: an in situ origin for light hydrocarbons is assumed for depth intervals in which concentration trends for individual compounds run parallel (so called "in-phase variation"). Conversely, intervals with "out-of-phase" variations are explained as a result of light hydrocarbon redistribution. For most homologs of the alkane families considered here, as well as for isomers of individual carbon numbers, concentration trends run nearly parallel with depth (Table 1). However, the depth interval 490-505 meters is clearly exceptional: (1) Concentration trends of n-, and neopentane (2.2-dimethylpropane) reveal a pronounced out-of-phase variation with depth (Fig. 5). (2) There is a pronounced relative enrichment of toluene compared to the intervals above and below, as illustrated by the toluene/n-heptane ratio plotted against depth in Figure 6.

These observations are tentatively interpreted as a result of light hydrocarbon redistribution processes. The out-of-phase variation of these pentane isomers (Fig. 5) appears to indicate preferential loss of neopentane from the shales of the interval between 490 and 505 meters. This can be explained as a diffusion effect, since neopentane has a higher diffusivity than *n*-pentane. Whelan and Sato (1980) observed preferential enrichment of neopentane in the fractured and coarse-grained sandy intervals of Holes 434, 439, 440, and 441, DSDP Legs 56 and 57. Interval 490-505 meters of Hole 511, however, reflects diffusive loss of neopentane, since the interval contains a uniform lithology, with respect to grain size.

The trend of increasing relative proportions of toluene from about 520 to 495 meters appears to reflect a preferential up-section enrichment in toluene up to a maximum value of 13.0 (i.e., four times above background). The sediments unaffected by this process have light hydrocarbon compositions with uniformly low toluene/*n*-heptane ratios (below 3.0).

We propose a tentative mechanism for the origin of this toluene enrichment; a higher-than-normal flux of compaction water passing through the interval. It is asTable 1. Summary of low molecular weight hydrocarbon concentrations, organic carbon contents (and Rock-Eval pyrolysis hydrogen indices for selected samples of Lithologic Unit 6) of core samples for DSDP Hole 511.

	Sample (interval in cm)	511-18-2 99-101	511-20-2 12-14	511-21-1 4-6	511-24-1 28-30	511-24-1 70-72	511-24-1 146-148	511-24-2 70-72	511-24-3 146-148	511-25-1 12-14	511-25-1 44-46	511-27-1 38-40	511-27-2 30-32	511-27-2 48-50	511-28-3 10-12	511-28-3 40-42	511-30-3 42-44	511-30-3 147-149	511-31-1 31-34	511-31-2 77-79
	Depth [m]	139.49	1//.02	103.34	204.18	205.20	205.90	200.70	208.90	209.12	209.44	219.36	220.81	220.99	220.00	220.90	243.92	240.97	232.31	234.27
No.	Hydrocarbon	(ng/g dry weight sediment)																		
1	Ethane	21.7	23.9	35.5	14.9	35.8	10.0	13.0	8.4	15.5	16.2	9.4	3.3	16.6	9.1	22.6	4.8	10.3	7.4	1.9
2	Propane	33.2	51.8	56.1	20.9	52.6	21.6	17.2	12.6	35.0	32.4	20.8	5.5	19.9	18.3	35.0	9.8	15.8	11.3	3.6
3	Methylpropane	10.4	14.5	20.6	7.3	20.0	7.9	4.6	5.7	14.9	12.5	8.8	2.3	6.3	8.2	11.8	5.0	5.7	4.6	1.9
4	Methylpropene + 1-butene	20.0	16.5	8.8	5.6	12.2	7.6	3.3	6.0	9.9	11.8	6.2	2.4	10.3	19.1	16.6	16.3	12.0	12.7	5.5
5	n-butane	18.3	27.4	30.4	11.9	28.0	11.1	8.6	7.6	16.6	15.3	10.4	3.2	12.9	10.7	18.9	5.8	9.0	6.5	2.4
6	trans-2-butene	3.2	4.2	2.3	1.3	4.8	1.8	0.88	1.5	2.4	1.9	1.5	0.42	1.7	1.2	2.1	1.1	0.91	1.0	0.39
7	2,2-dimethylpropane		< 0.5	_	_	< 0.5		-			-	< 0.2	-	-		-		-	—	
8	cis-2-butene	2.5	3.6	2.0	1.1	3.9	1.5	0.69	1.2	1.9	1.5	1.2	0.35	1.4	1.0	1.7	1.0	0.77	0.91	0.31
9	Methylbutane	8.3	13.3	11.3	5.4	13.9	5.9	3.2	4.3	9.5	6.8	5.2	1.6	5.0	6.0	8.5	4.3	4.9	3.0	1.7
10	n-pentane	10.8	21.3	18.5	5.7	17.4	5.8	4.3	5.8	8.9	8.5	5.9	2.1	9.5	7.1	12.4	3.6	6.2	4.4	2.2
11	2,2-dimethylbutane	0.16	0.17	0.24	0.06	0.28	0.09	0.04	0.08	0.16	0.17	0.05	+	+	+	0.12	0.03	0.08	0.05	+
12	Cyclopentane	2.9	1.2	0.48	0.20	0.96	0.36	0.27	0.28	0.38	0.35	0.26	0.11	0.43	0.45	0.45	0.27	0.24	0.25	0.13
13	2,3-dimethylbutane	+	+	-1.5	0.08	~0.5	0.13	0.07	< 0.1	0.16	< 0.1	< 0.1	< 0.1	0.19	0.15	~0.2	0.07	0.11	+	0.01
14	2-methylpentane	5.7	2.9	3.4	2.0	4.7	1.6	0.91	1.1	2.4	2.1	1.4	0.46	2.0	1.6	2.7	0.93	1.2	1.1	0.48
15	3-methylpentane	3.7	3.8	2.7	1.8	4.4	1.6	0.94	1.4	2.2	1.6	1.2	0.41	2.1	1.7	2.7	0.51	1.2	0.58	0.37
16	n-hexane	9.3	11.6	12.4	7.0	13.6	4.9	3.7	4.4	7.3	6.5	4.5	1.4	7.6	5.0	9.2	2.5	5.1	3.6	1.8
17	Methylcyclopentane + 2,2-dimethylpentane	1.1	1.4	1.2	0.63	1.9	0.58	0.37	0.53	0.89	0.63	0.43	0.24	1.5	0.87	1.1	0.49	0.57	0.49	0.27
18	2,4-dimethylpentane	+	+	+	_	< 0.1	+	< 0.1	+	~0.4	~0.2	+	+	0.11	+	+	+		_	+
19	Benzene	7.1	13.7	14.2	4.6	10.8	6.2	4.2	4.9	6.8	7.1	5.1	1.3	6.5	5.7	7.7	3.3	3.8	3.4	1.1
20	Cyclohexane	2.0	0.42	0.30	0.34	0.39	0.43	< 0.1	2.1	0.26	0.17	1.2	0.23	0.86	1.2	0.71	0.70	2.9	3.9	1.5
21	2-methylhexane	1.2	1.4		0.86	1.4	+	~0.3	0.51	0.87	0.71	0.43	0.17	1.5	0.86	0.91	0.41	0.55	0.40	0.31
22	2.3-dimethylpentane +																			
	1.1-dimethylcyclopentane	0.57	0.66	()	0.52	0.78	+	< 0.1	0.32		0.16	0.15	-	+	+	0.36	0.20	0.18	0.23	-
23	3-methylhexane	1.1	+	<1	0.86	1.4	+	~0.3	0.62	_	_	0.13	0.19	1.5	0.73	· · · · ·	0.61	0.22	0.51	0.20
24	1.cis-3-dimethylcyclopentane	+	0.98	<1	1.0	1.6	0.50	< 0.1	0.51	+	+	0.36	0.08	0.47	0.41	0.63	< 0.1	0.20	0.40	< 0.1
25	1, trans-3-dimethylcyclopentane	+	0.36	<1	0.69	0.78	< 0.1	< 0.1	0.12	+	+	+	+	0.33	0.17	0.13	< 0.1	0.05	0.11	< 0.1
26	1, trans-2-dimethylcyclopentane	+	0.63	<1	0.69	1.2	< 0.1	< 0.1	0.12	+	+	+	+	0.52	0.28	0.29	< 0.1	0.20	0.22	< 0.1
27	n-heptane	17.1	18.0	11.1	5.5	9.8	5.0	3.1	4.3	6.8	12.2	6.3	2.3	10.6	20.4	8.6	2.0	4.2	4.0	2.5
28	1.cis-2-dimethylcyclopentane			—	_		_	-			_		_			_	_		_	-
29	Methylcyclohexane	2.6	1.3	1.3	0.65	0.98	0.13	0.25	0.27	0.47	0.17	0.01	+	1.1	0.53	0.27		0.05	~ -1	
30	2,5-dimethylhexane	-	_	-	-		-	-		-	-	-	_		-	-	_		-	
31	Ethylcyclopentane		1.3	_	-	+	+	+		+	+		_	0.74	+	+		+	-	
32	1.trans-2.cis-4-trimethylcyclopentane		_	_	\sim	<u>14</u>	-	- <u>2</u> -1		<u></u>	- <u>-</u>		-	_	_	- <u>-</u> -			-	
33	1.trans-2-cis-3-trimethylcyclopentane			-	-	_	-	-			-	_	-		-	-	-		_	
34	Toluene	70.7	79.0	29.1	6.0	37.1	13.4	9.2	7.5	40.3	31.9	16.1	3.5	16.7	6.4	65.5	17.3	30.9	37.0	1.9
35	2-methylheptane	-	0.000	_	0.75		0.50			1.7	1.4		_			1.1	_	0.47	_	
36	n-octane	13.2	15.0	5.4	2.7	6.2	2.6	2.5	3.1	11.0	8.8	2.6	0.64	2.2	1.3	5.3	2.4	4.3	2.6	
37	Organic carbon content (%dry wt.)	0.41	0.39	0.12	0.11	0.11	0.13	0.11	0.13	0.06	0.06	0.11	0.14	0.14	0.25	0.61	0.34	0.61	0.73	0.27
38	Hydrogen index (mg/g Corg)																			

Note: - = concentration below or near detection limit; + = not determined because of peak overlapping; n.m. = not measured.

Table 1. (Continued).

	Sample (interval in cm) Depth [m]	511-31-4 142-145 257.92	511-31-6 6-8 259.56	511-31-6 12-14 259.62	511-36-4 31-33 304.31	511-40-4 52-54 342.52	511-41-2 72-75 349.22	511-46-2 75-77 396.75	511-51-1 3-5 442.03	511-51-1 125-126 443.25	511-54-6 84-86 478.84	511-55-4 80-82 485.30	511-56-2 90-92 491.90	511-56-3 75-77 493.25	511-56-3 112-114 493.62	511-56-4 2-4 494.02	511-56-4 44-46 494.44	511-56-4 141-143 495.41	511-56-5 6-8 495.56	511-56-5 56-58 496.06
Ref. No.	Hydrocarbon		Concentration (ng/g dry weight sediment)																	
1	Ethane	5.6	5.9	8.5	5.3	9.6	6.7	8.4	16.6	9.9	11.3	2.7	4.6	11.3	12.4	11.0	21.8	46.5	12.2	13.4
2	Propane	11.0	10.3	13.9	11.0	19.6	8.9	18.4	28.8	14.7	15.0	7.4	8.0	8.4	21.6	14.2	61.5	57.5	19.0	16.2
3	Methylpropane	4.4	3.8	4.3	4.6	6.4	3.1	7.2	9.4	5.0	4.3	3.5	4.1	2.9	8.0	5.6	21.8	18.6	8.4	6.3
4	Methylpropene + 1-butene	10.7	10.3	4.4	6.7	7.0	6.5	15.4	11.5	5.7	3.3	3.0	2.1	2.2	4.5	5.6	16.8	5.4	4.4	2.9
5	<i>n</i> -butane	5.8	5.4	8.2	5.9	8.8	4.9	8.2	13.0	7.2	8.2	4.5	4.3	3.8	10.5	8.8	27.0	27.2	10.1	8.6
6	trans-2-butene	0.98	0.73	1.1	0.79	1.1	0.68	1.5	2.4	1.0	0.47	0.59	0.61	0.37	1.3	1.6	3.3	1.7	1.6	1.0
7	2,2-dimethylpropane	_		-			-	< 0.2	< 0.2	—		< 0.1	0.26	0.08	—	< 0.2	< 0.2	0.26	< 0.2	0.17
8	cis-2-butene	0.79	0.60	0.90	0.71	0.90	0.56	1.3	1.9	0.82	0.37	0.46	0.57	0.30	0.97	1.3	2.5	1.4	1.2	0.88
9	Methylbutane	7.9	4.6	3.0	8.6	5.3	2.9	4.3	6.3	3.5	6.1	3.1	2.8	3.4	5.3	4.3	13.3	13.8	6.0	5.8
10	n-pentane	4.1	3.6	4.9	4.7	4.9	3.5	4.6	6.8	4.4	5.5	2.5	2.7	2.4	5.4	6.5	12.7	17.0	6.8	6.6
11	2,2-dimethylbutane	0.07	0.05	0.10	< 0.1	0.01	0.02	< 0.1	< 0.1	0.07	0.08	< 0.1	0.01	0.06	0.07	+	+	-	0.06	< 0.1
12	Cyclopentane	0.17	0.15	0.27	0.16	0.33	0.14	0.24	0.42	0.19	0.13	0.14	0.11	0.24	0.27	0.27	0.83	1.3	0.02	0.44
13	2,3-dimethylbutane	0.07	0.02	0.11	< 0.1	< 0.1	< 0.1	0.02	< 0.1	0.10	0.10	0.08	0.05	0.04	< 0.1	0.27	+	~1	0.06	0.06
14	2-methylpentane	0.77	0.60	1.1	0.79	1.7	0.75	0.87	1.8	0.89	0.85	0.74	0.59	0.46	1.3	2.6	3.2	11.1	1.8	4.9
15	3-methylpentane	0.93	0.79	1.3	0.78	1.2	0.75	0.74	2.1	0.98	0.90	0.51	0.54	0.49	1.1	1.9	3.1	4.4	1.2	2.0
16	n-hexane	2.8	2.6	4.5	2.9	3.8	2.6	3.5	5.6	3.0	3.8	1.7	1.8	1.7	4.1	4.9	9.8	12.2	5.1	5.2
17	Methylcyclopentane + 2,2-dimethylpentane	0.29	0.27	0.60	0.33	0.62	0.35	0.47	0.69	0.45	0.34	0.29	0.21	0.21	0.44	1.6	1.1	8.1	0.70	3.9
18	2,4-dimethylpentane	+	+	_	+		-			—		+	< 0.1	+		+	+	-0.4	~0.1	0.02
19	Benzene	2.2	1.9	3.4	2.7	5.0	2.0	3.5	6.5	2.3	2.8	2.1	2.1	1.4	3.7	4.0	17.1	10.4	3.5	3.2
20	Cyclohexane	0.91	0.78	1.2	1.4	0.84	0.32	0.89	0.75	0.13	0.18	0.33	0.14	0.32	0.38	1.6	0.98	2.1	1.5	4.5
21	2-methylhexane	0.22	0.26	0.47	0.22	0.40	0.19	0.41	0.88	0.31	0.39	0.24	0.19	0.18	0.41	0.78	0.81	2.4	0.52	0.88
22	2,3-dimethylpentane +																			
	1,1-dimethylcyclopentane	0.09	0.15	0.31	0.08	0.32	0.07	0.46	0.56	0.17			0.09		0.16	-	0.61	2.4	0.24	1.4
23	3-methylhexane	-	0.19	0.64	-	0.47	0.28	0.28		—		0.14	—	+	~0.2	-	0.50	4.8	-	1.3
24	1,cis-3-dimethylcyclopentane	< 0.1	0.23	-0.08	< 0.1	0.40	< 0.1	< 0.1	0.57	< 0.1	< 0.1	0.14	< 0.1	< 0.1	~0.2	< 0.1	0.12	3.1	+	1.4
25	1,trans-3-dimethylcyclopentane	< 0.1	~0.02	0.08	< 0.1	~0.12	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.3	1.2	1.7	~0.15	1.1
26	1,trans-2-dimethylcyclopentane	< 0.1	0.02	0.17	< 0.1	0.12	< 0.1	< 0.1	-0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	1.0	0.42	5.5	-0.3	3.2
27	n-heptane	5.6	1.8	5.1	2.1	2.9	2.6	5.9	7.8	2.0	2.3	2.3	1.5	1.6	3.5	4.4	7.3	11.3	4.0	4.0
28	1,cis-2-dimethylcyclopentane	-	-	-			_			-			-	-	_		0.27	1.8		0.98
29	Methylcyclohexane	-	+	0.36	0.11	0.13	—	~0.2	+	0.22	0.13	0.11	0.05	0.07	+	1.2	0.49	7.7	0.49	3.7
30	2,5-dimethylhexane	\rightarrow		-					-	-			-	+	-			0.11		+
31	Ethylcyclopentane	-	-	-		-	_		_	-	+		_		_	+	0.06	2.9	+	1.2
32	1,trans-2,cis-4-trimethylcyclopentane	_		+		+	\rightarrow	+		_			-		-	+	—	1.7	-	1.1
33	1,trans-2-cis-3-trimethylcyclopentane	-		-		-	_		_	—	-	_	-	177	_	+		3.7		2.0
34	Toluene	22.4	12.6	17.2	25.5	44.2	8.4	11.2	19.4	8.3	4.0	3.9	9.4	8.0	9.4	44.6	54.4	34.3	25.2	52.5
35	2-methylheptane		-	0.46	-	0.39	-	—		-	-	-			—		0.95	3.3		2.0
36	n-octane	1.3	1.3	2.9	1.9	2.8	2.0	2.2	4.9	2.0	2.0	0.90	1.1	2.1	2.6	2.0	6.0	7.9	3.1	4.1
37	Organic carbon content (%dry wt.)	0.29	0.30	0.66	0.69	0.64	0.12	0.35	0.06	0.03	0.06	0.04	0.03	0.08	0.09	0.34	0.13	0.56	0.16	0.44
38	Hydrogen index (mg/g Corg)															n.m.	n.m.	n.m.	n.m.	n.m.

Table 1. (Continued).

	Sample (interval in cm)	511-56-5 127-129	511-57-4 42-44	511-57-4 47-49	511-58-2 97-98	511-58-2 105-107	511-58,CC	511-59-3 108-110	511-59-4 15-17	511-59-4 143-145	511-60-2 133-135	511-60-5 90-92	511-61-2 129-131	511-63-3 17-18	511-66-1 44-46	511-66-1 61-64	511-68-1 119-122	511-68-1 127-129	511-68-2 36-38
	Depth [m]	496.77	503.92	503.97	510.97	511.05	514.60	522.08	522.65	523.93	530.33	534.40	539.79	559.17	584.94	585.11	604.69	604.77	605.36
Ref. No.	Hydrocarbon		Concentration (ng/g dry weight sediment)																
1	Ethane	29.0	4.8	60.7	6.5	41.5	139	88.7	47.9	479	9.6	322	251	46.9	131	255	18.0	117	504
2	Propane	31.6	8.9	59.4	9.7	23.3	85.3	72.3	45.6	369	24.5	308	328	186	495	667	64.1	332	790
3	Methylpropane	8.9	4.6	19.6	1.9	5.9	23.6	31.2	27.5	169	21.2	178	222	353	864	1010	88.4	541	936
4	Methylpropene + 1-butene	6.6	2.8	4.9	1.5	1.3	7.0	4.5	2.4	9.4	1.8	3.3	7.1	12.9	14.9	12.3	2.4	9.3	6.6
5	<i>n</i> -butane	17.4	5.0	27.8	4.9	12.0	40.8	59.3	54.4	322	40.3	328	365	392	863	996	80.4	489	821
6	trans-2-butene	1.7	1.2	1.5	0.57	0.40	2.3	1.9	1.1	1.6	1.5	4.2	1.9	3.1	1.4	3.2	0.45	1.9	2.9
7	2.2-dimethylpropane	0.51	< 0.5	1.5	_	0.77	8.6	2.8	2.5	10.1	1.4	8.7	3.1	2.9	6.3	6.6	0.39	3.1	4.9
8	cis-2-butene	1.5	0.91	1.3	0.44	0.38	2.0	1.3	0.93	0.89	1.5	2.9	0.99	2.1	0.83	1.9	0.27	1.1	1.5
9	Methylbutane	10.6	2.7	28.6	2.6	11.2	41.8	49.9	54.6	234	37.8	230	256	600	1370	1420	94.0	657	931
10	n-pentane	12.7	2.7	24.4	3.3	12.5	55.6	108	107	554	91.6	546	536	746	1500	1640	114	776	1110
11	2.2-dimethylbutane	0.25	_	0.30	-	0.13	1.5	0.54	0.71	4.0	0.57	29	2.6	33	57	6.4	0.63	3.4	4.2
12	Cyclopentane	1.3	0.04	4.0	0.13	1.9	6.4	9.0	8.5	45.7	6.6	44 3	45.5	51.7	97.6	108	7.9	54.3	81.0
13	2 3-dimethylbutane	0.90	_	-4	~0.1	1.7	8 3	~ 9	~ 8	- 35	-6	~ 30	~ 30	~ 60	131	135	~7	~ 50	~ 70
14	2-methylpentane	9.5	0.40	43.6	0.97	16.5	63.2	105	105	511	86.7	419	403	670	1310	1350	76.4	574	769
15	3-methylpentane	4.2	0.66	10.5	0.66	4.4	15.5	20.7	19.4	92.4	14.7	70.6	62.4	98.8	264	258	12.8	94 1	127
16	n-hexane	9.7	1.7	16.5	2.4	10.2	71.5	109	112	551	103	491	430	659	1170	1250	66.4	482	628
17	Methylcyclopentane + 2.2-dimethylpentane	8.0	0.33	34.6	0.40	14.2	40.9	66.2	67.2	336	57.6	315	327	546	1120	1180	78.3	587	823
18	2 4-dimethylpentane	0.40	-	2.0	< 0.1	0.88	4.8	7.1	6.9	32.6	5.9	26.3	26.0	37.7	64.3	62.9	4.0	32.1	41.6
19	Benzene	5.6	2.6	9.7	1.8	5.9	34.4	18.4	16.8	80.0	9.8	67.9	73.9	111	195	217	18.6	129	199
20	Cyclohexane	1.6	-	10.7	0.32	9.0	38.9	17.2	23.0	54.5	11.3	46.7	71.2	297	98.2	122	9.8	98.9	83.1
21	2-methylberane	2.1	_	7.0	0.21	3.0	15.2	30.4	23.5	110	21.5	87.2	71.5	130	195	202	11.2	87.8	106
22	2 3-dimethylpentane +	2.1		1.0	0.21	2.0	12.12	2014		110	2110	07.2	7112	100		202		0110	
~~	1.1-dimethylcyclopentane	2.8	0.00	14.6	+	6.5	49.4	35.7	40.4	139	23.1	96.6	84 4	137	297	273	15.6	103	134
23	3-methylhexane	_	-	12.5	0.26	4.3	36.3	35.5	39.5	175	29.2	110	78.7	138	245	237	13.5	105	141
24	1.cis-3-dimethylcyclopentane	3.3	-	14.6	0.12	61	20.9	38.8	37.3	211	31.3	147	138	184	363	373	23.8	191	250
25	1.trans-3-dimethylcyclopentane	29		14.9	0.08	61	23.2	40.4	39.5	202	30.4	134	127	171	361	357	22.1	178	238
26	1.trans-2-dimethylcyclopentane	6.7		33.9	0.12	13.1	35.2	80.1	78.4	394	56.4	231	190	223	720	671	24.9	214	277
27	n-heptane	9.4	1.1	14.1	1.3	10.5	97.5	97.0	98.7	495	116	501	406	680	1040	1200	42.2	324	412
28	1.cis-2-dimethylcyclopentane	2.0		7.0		3.0	8.8	19.6	20.2	97.8	18.8	85.9	73.1	80.5	141	148	9.1	73.3	94.7
29	Methylcyclohexane	8.1	+	37.9	+	16.1	65.7	77.5	76.7	346	52.6	231	209	343	1280	1090	39.0	321	427
30	2.5-dimethylhexane	1.2	-	1.2	_	0.04	2.3	2.4	2.6	13.7	2.3	8.1	5.9	12.7	22.4	19.3	1.1	9.2	10.8
31	Ethylcyclopentane	25	-	13.4		5.2	21.1	36.5	37.6	180	33.2	141	115	197	382	377	20.8	167	205
32	1 trans-2 cis-4-trimethylcyclopentane	2.0		10.7		3.8	19.6	35.7	36.2	169	27.4	104	78.0	118	255	237	13.1	113	142
33	1.trans-2-cis-3-trimethylcyclopentane	3.6	-	19.6	_	6.8	32.5	68.3	69.9	323	44.8	148	67.1	106	334	284	11.1	95.0	121
34	Toluene	115	8.8	51.3	7.0	46.4	310	56.0	125	969	113	185	154	923	543	774	109	586	501
35	2-methylheptane	3.9	-	26.5		10.4	76.0	72.8	73.8	372	78.2	265	185	367	549	543	26.2	223	280
36	n-octane	6.4	0.79	11.1	1.3	8.7	64.1	59	55.9	298	79.5	335	232	465	648	607	20.7	172	209
37	Organic carbon content (%dry wt)	0.56	0.13	1.4	0.09	0.97	4.3	1.8	1.8	6.0	0.99	3.2	3.6	46	4.8	5 5	0.39	2.9	4 1
38	Hydrogen index (mg/g Corg)	174	n.m.	131	n.m.	67	433	312	135	371	263	322	287	n.m.	336	311	n.m.	223	209



Figure 1. C_2-C_8 hydrocarbon (sum of all compounds, except olefins, identified in Table 1 and Fig. 8) concentration in ng/g dry weight sediment vs. depth in DSDP Hole 511. Lithologic units on the right.



Figure 2. C_2-C_8 hydrocarbon (sum of all compounds, except olefins, identified in Table 1 and Fig. 8) concentration in ng/g of organic carbon vs. depth in DSDP Hole 511. Lithologic units on the right. Generation trend marked by stippled signature.



Figure 3. C_6 hydrocarbon relative composition (G6 = n-hexane, I6 = sum of C_6 isoalkanes, N6 = sum of C_6 cycloalkanes, A6 = benzene, normalized to 100%) vs. depth in DSDP Hole 511. Lithologic units on the right.



Figure 4. Rock-Eval pyrolysis data (hydrogen index I_H vs. oxygen index I_O , according to Espitalié et al. (1977)) for selected sediment samples of Lithologic Unit 6 in DSDP Hole 511. Numbers in circles are core numbers.



Figure 5. n-Pentane and neopentane (2.2-dimethylpropane) concentrations in ng/g of dry weight sediment for depth interval 440 to 560 meters in DSDP Hole 511. Letters A to H on the right-hand side refer to the following lithologies (extracted from Initial Core Descriptions): A = muddy calcareous shale, B = calcareous claystone, C = (muddy) nannofossil chalk, D = claystone, E = "black shale," F = zeolitic claystone, G = including laminae of calcilutite + calcarenite + shell debris, H = nannofossil claystone, void = no core recovery.



Figure 6. Toluene/*n*-heptane ratio for depth interval 440 to 560 meters in DSDP Hole 511. (For abbreviations of lithologies on the right-hand side, see Fig. 5.)

sumed that these compaction waters carried high concentrations of toluene, which, because of its relatively higher solubility (compared to *n*-heptane, was preferentially dissolved from the black shale interval below. Most of this toluene was filtered out from the upward-moving compaction waters by preferential adsorption on clay mineral surfaces in rocks in the 490–505 meter interval. Preferential adsorption of toluene is a result of its higher polarity compared to *n*-heptane.

Another approach to short-range redistribution processes is to compare closely spaced samples from adjacent lithologic units of different organic richness. Figure 7A and B compares the compositions of the C₂ to C₈ light hydrocarbons of two shale samples from about 604 meters depth. Both samples are only 8 cm apart and differ in their organic carbon contents by a factor of 7.4 (0.39 vs. 2.9%). As evident from this figure, the light hydrocarbon composition of both samples is nearly identical, whereas their concentrations differ in accordance with their organic carbon contents. Based on the presently available evidence, we propose two alternative explanations for this fact: (1) If both samples bear an identical type of organic matter, the concentration difference reflects merely a dilution phenomenon, which implies an in situ origin for the light hydrocarbons in both samples. (2) If there is a significant difference in kerogen quality between the two samples (the leaner sample presumably bearing the lower quality kerogen), the compositional similarity can be interpreted to reflect a redistribution process.

Several closely spaced sample pairs from Hole 511 exhibiting similar compositional features were analyzed. Elemental analysis of kerogens in these samples, to resolve ambiguity in data interpretation, is in progress.

Shipboard Contamination of Core Samples by Acetone

During the initial stages of analysis of low molecular weight hydrocarbons from Hole 511, acetone in high concentrations was detected in many samples. The acetone was identified by both gas chromatographic retention index and its mass spectrum (Rullkötter, 1980, personal communication). Figure 8A represents a typical gas chromatogram in which the acetone peak interferes with some of the light hydrocarbon compounds. Both the very high concentration (in this example, approx. 580 ng/g of dry sediment) and the abundance of acetone at very different depths and lithologies led to the conclusion that it is not of natural origin. A careful examination of the sampling procedures revealed that onboard the Glomar Challenger acetone is routinely used during the preparation of core sections in rinsing the plastic caps. This explains why, generally, contamination is more pronounced at the ends of a section than in the middle. Also, the core catcher sample analyzed (511-58,CC) was extensively contaminated. We assume that all samples analyzed (159-605 m depth) were contaminated by varying amounts of acetone.

In order to eliminate the acetone from the sediment samples prior to analysis, the hydrogen stripping-thermovaporization method (Schaefer et al., 1978) had to be modified in the following way. Usually a small section





of the extraction tube containing the sediment sample is filled by $CaCl_2$ to prevent the pore water from entering the gas chromatographic column. It has been found that a mixture of $CaCl_2$ and silica gel (macroporous type 500, for thin-layer chromatography, E. Merck, Darmstadt) in the ratio 100:1 (w/w) is able to act simultane-

ously as an adsorbant for both pore water and acetone. This procedure yielded gas chromatograms (compare Fig. 8B with A) in which only traces of acetone could be detected. However, some samples were so extensively contaminated that the amount of silica gel was not sufficient (Fig. 8C). Nevertheless, approximately 21 μ g ace-



Figure 8. Occurrence of acetone (shipboard contamination) in the low molecular weight capillary gas chromatograms of samples from DSDP Hole 511. A. Sample 511-31-4, 142-145 cm (257.92 m), a = acetone. B. same sample as A, with acetone eliminated by modified hydrogen stripping-thermovaporization method. C. Sample 511-66-1, 61-64 cm (585.11 m), a = acetone. D. Same sample as C, with acetone eliminated. Numbers refer to compound names in Table 1.

tone/g of dry weight sediment could be measured in the Figure 8C sample. An increase in silica gel (CaCl₂/silica gel ratio = 33:1) was sufficient to produce an acetone-free gas chromatogram. However, other polar compounds—benzene (No. 19) and, particularly, toluene (No. 34)—are also affected and eliminated to a certain degree (compare Fig. 8D, with C).

All concentrations of toluene in Table 1 were corrected as necessary by comparison with the original, unaffected chromatogram and hence represent true concentrations. Owing to the high water solubility and low partial pressure of acetone in comparison to low molecular weight hydrocarbon compounds, other DSDP investigators using head space techniques for the analysis of volatile organic compounds may have overlooked the acetone. One of the most critical consequences of contamination by acetone is the introduction of other volatile compounds, including hydrocarbons, into the sediment cores if the acetone was not absolutely pure.

To avoid this type of contamination for future organic geochemical analysis of samples, we recommend discontinuing the use of acetone and introducing a contamination-free sealing procedure instead.

CONCLUSIONS

Light hydrocarbon data of Hole 511 indicate a gradual maturity increase in the organic matter throughout the sampled interval from 159 to 605 meters (Fig. 2). Considerable quantities of gasoline-range hydrocarbons have been generated, particularly in the lower part of Lithologic Unit 6 (black shales). However, organiccarbon-normalized concentrations are more than one order of magnitude lower than expected for Type II kerogen source beds in the main phase of oil generation. Therefore it is concluded that the organic matter of the black shale unit is of low maturity, a conclusion supported as well by maturity-sensitive light hydrocarbon parameters such as the isobutane/n-butane and the nhexane/methylcyclopentane ratios.

A significant change in the type of organic matter in Hole 511 from Type III kerogen (159 m to approx. 500 m depth) to predominantly hydrogen-rich Type II kerogen (below 500 m) is indicated by a change of the C_6 hydrocarbon composition (Fig. 3). Generally, low molecular weight hydrocarbons in Hole 511 are formed *in situ* and remain at their place of formation. Redistribution processes are discernible only at major stratigraphic or lithologic boundaries—that is, at the Tertiary–Cretaceous unconformity or at the transition from black shales to Cretaceous chalks and claystones. Redistribution phenomena have affected only comparatively narrow intervals of 10 to 30 meters.

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