

34. HYDROCARBON AND KEROGEN STUDIES

John M. Hunt, Department of Chemistry, Woods Hole Oceanographic Institution,
Woods Hole, Massachusetts

ABSTRACT

Three core samples from Hole 217 and one from Hole 218 were analyzed for organic carbon, C₁ to C₇ and detailed C₄ to C₇ hydrocarbons, C₁₅+ hydrocarbon and nonhydrocarbons, and visual kerogen. In the C₁ to C₇ range only methane was present in amounts greater than 1 ppm. However, a detailed analysis showed 10 hydrocarbons present in the C₄ to C₇ range from the Hole 218 sample cored at 769 meters. The C₁₅+ saturates in all samples contained about 90% naphthenes. The paraffins had CPI's ranging from 1.4 to 1.8. The deepest samples in Holes 217 and 218 contained well-preserved coarse to medium woody plant debris.

INTRODUCTION

The objective of this work was to evaluate diagenetic changes in organic matter leading to the formation of C₄ to C₇ hydrocarbons and the alteration of C₁₅+ hydrocarbons and kerogen. Such information is valuable in understanding the depths at which petroleum hydrocarbons originate and the types of organic matter from which they may form. The samples analyzed are listed in Table 1, along with their geologic information, organic carbon contents, and kerogen description. The organic carbon yields, which were determined by the standard Leco method, are probably minimal because some solubilized carbon is lost during the washing process. All of these samples, however, are probably in the range from 0.05 to 0.15 weight percent. The kerogen, which is obtained after removal of the mineral matter by standard palynological techniques, is examined microscopically at 100 X magnification. Marine organic matter is predominantly amorphous and sapropellic in appearance, whereas continental material is woody and herbaceous.

METHODS OF ANALYSIS

The analyses were carried out by G. S. Bayliss of GeoChem Laboratories using his own modifications of known techniques.

C₁ to C₇ and Detailed C₄ to C₇ Hydrocarbon Analysis

The apparatus used for both these analyses was a Varian Aerograph 1400 gas chromatograph fitted with a Porapak Q, 5' X 1/8" o.d., 304 ss column, for the C₁-C₇ analysis, and the same instrument fitted with a 200', 0.01-inch i.d. HHK (Hexadecene-hexadecane-Kel F) capillary column, for the detailed C₄-C₇ analysis. The gasoline range hydrocarbons were concentrated before analysis by passing relatively large volumes of gas through a 1/16" i.d. ss sample loop attached to a backflush valve.

An unknown volume of frozen core material (still frozen) was placed into a microblender fitted with a

polytron pulsating blade assembly and after completely filling with water, a known volume of helium was introduced to form a gas cap. The blender container was placed in a boiling water bath for 10 minutes, blended for 1 minute, and replaced in the bath for 20 minutes. (In a test case, the temperature of the contents of the container was measured at 95° C±.) The sample treated in this manner was used for both the C₁-C₇ hydrocarbon and the detailed C₄-C₇ hydrocarbon analysis.

C₁-C₇ Hydrocarbon Analysis

One milliliter of gas was withdrawn from the gas space and injected directly onto the Porapak Q column operating isothermally at 200°C. The detector response for the C₁, C₂, C₃, iC₄, and nC₄ components was integrated and the ppm values computed against known standards. The C₅'s, C₆'s, and C₇'s were shown as composite peaks. This initial analysis, besides giving the data points for the C₁ through C₄ hydrocarbon contents, also served to determine what volume of gas would be required for a detailed capillary analysis of the C₄-C₇ hydrocarbon.

Detailed C₄-C₇ Gasoline Range Hydrocarbon Analysis

A measured volume of gas was withdrawn from the blender gas cap by water displacement and pressure injected through the septum attachment fitted to the sample loop cooled in liquid nitrogen. This procedure could effectively, and reproducibly, concentrate the C₄-C₇ hydrocarbons present in 10 to 150 ml of gas.

Following concentration, the sample loop was switched to the column position, the liquid nitrogen trap was removed, and the sample loop was heated in order to inject the C₄-C₇ hydrocarbon onto the capillary column. No column splitter was used, so the entire sample concentrate was analyzed in each case. After resolution of the individual compounds from methane (C₁) through toluene (C₇), the column was backflushed to remove the C₈+ compounds.

Following completion of the C₁-C₇ and detailed C₄-C₇ hydrocarbon analyses, the microblender was opened and

TABLE 1
Location and Description of Analyzed Samples

Sample	Interval (cm)	Age	Depth (m)	Lithology	Organic Carbon (wt.%)	Kerogen Description
217-16-4	10-30	Paleocene	416	Nannofossil-Chalk	0.04	Amorphous, Herbaceous
217-24-0	20-41	U. Maastrichtian	487	Micrite	0.02	Amorphous, Herbaceous
217-33-2	0-20	M. Maastrichtian	587	Biomicrite	0.14	Woody, Amorphous
218-27-2	0-10	M. Miocene	769	Clayey Silt	0.14	Woody, Herbaceous

the contents washed into a drying pan. The water was allowed to evaporate, the solid was oven dried at 50°C, and the amount of sample was weighed. (Composite samples collected in this manner were used for the remaining geochemical analyses.)

The results of the detailed C₄-C₇ hydrocarbon analyses are shown in Table 2. The values are expressed in ppb on a volume/weight basis, with each peak having been identified against a known standard. Benzene was used as an internal standard for peak comparison in the C₄-C₇ analysis.

TABLE 2
C₄ Through C₇ Hydrocarbons in Holes 217 and 218

Compound	Hydrocarbon (ppb) ^a			
	217-16-4	217-24-0	217-33-2	218-27-2
Isobutane	63	119	99	102
<i>n</i> -Butane	89	55	117	125
Isopentane	9	37	39	106
<i>n</i> -Pentane	28	29	19	84
Cyclopentane		4		84
2-Methylpentane				531
3-Methylpentane				534
<i>n</i> -Hexane				82
<i>n</i> -Heptane				115
Methylcyclohexane				52
Total	189	244	288	1,815

^aParts per billion by volume.

C₁₅+ Soxhlet Extraction and C₁₅+ Adsorption Chromatographic Separation

Soxhlet Extraction

The composite dry samples, used for the organic carbon and the light hydrocarbon analyses, were completely homogenized by grinding in a Bantam Micro Pulverizer (100% through 60 mesh sieve; 75% through 120 mesh, 10% through 250 mesh). A weighed aliquot (100 g) of each sample was transferred to a prewashed cellulose thimble and soxhlet extracted with 10:1 benzene:methanol for 16 hours. All solvents were redistilled prior to use, and soxhlet extractions using thimbles only showed no detectable C₁₅+ residues. Following extraction, the solvent was evaporated to small bulk (1-2 ml) by heating on a steam bath. The C₁₅+ extract was then deasphalted by the addition of 40 ml normal pentane (Spectro quality solvent) and separated into a C₁₅+ pentane-soluble fraction and an asphaltene fraction by filtration through a prewashed column (45 cm

× 1 cm diameter) of Hyflo Supercel (5.0 gm). The asphaltene was recovered from the column by 10:1 benzene:methanol elution.

Adsorption Chromatography

Only one sample, 218-27-1, contained sufficient C₁₅+ normal pentane-soluble material for a complete detailed liquid chromatographic separation. This sample was independently separated into the C₁₅+ saturate hydrocarbon, the C₁₅+ aromatic hydrocarbon, and the C₁₅+ NSO (nitrogen-sulfur-oxygen containing) nonhydrocarbon by elution through a combined alumina/Silica-gel column (45 cm × 1 cm diameter, 7 g Alcoa F-20 grade alumina; 7 g Davidson Silica-gel grade 62, 60-200 mesh) using normal pentane (40 ml; 2.5 bed volumes), benzene (30 ml; 5 bed volumes) and 50:50 methanol:benzene (60 ml, 3.75 bed volumes).

The remaining three samples were all subjected to microchromatography with the ppm values for the C₁₅+ saturate and the C₁₅+ aromatic hydrocarbon contents being computed from quantitative gas chromatographic analysis. The liquid chromatographic separation procedure used on the micro scale was an exact duplication of the normal procedure with correspondingly smaller amounts of adsorbents and solvents being used.

A small disposable pipette was charged with Silica-gel (1.0 g) and alumina (1.0 g) and, after washing with normal pentane, the C₁₅+ normal pentane-soluble fraction of the C₁₅+ extractable material was transferred onto the column. Elution was carried out with pentane, benzene, and 50:50:methanol:benzene and each fraction collected in a clean glass vial. No weighings were carried out in this separation because of the very small amounts of C₁₅+ pentane-soluble material available. In order to measure the ppm values for the isolated C₁₅+ hydrocarbon fractions, the gas chromatographic analysis, discussed in the following section, was quantified against known standard concentrations. The compositional data are recorded in Table 3.

Gas Chromatographic Analysis

The C₁₅+ saturate hydrocarbon and the C₁₅+ aromatic hydrocarbon fractions, isolated from the extractable bitumen material by liquid chromatography, were individually analyzed by gas chromatography using a 20' × 1/8" o.d., 304 ss column packed with 5% eutectic (LiNO₃, NaNO₃, KNO₃) on 60-80 mesh chromasorb G. Column conditions for the analysis were initial 160° temperature programmed at 20°/minute to 350°C, using helium (20

TABLE 3
C₁₅+ Hydrocarbons in Holes 217 and 218

Sample	217-16-4	217-24-0	217-33-2	218-27-1
Depth (m)	416	487	574	769
Organic Carbon (Wt. %)	0.04	0.02	0.14	0.14
C ₁₅ + Extracts (ppm):				
Saturate HC	10	9	11	32
Aromatic HC	6	6	6	13
Total HC	16	15	17	45
Asphaltics	184	189	300	162
N, S, O Compounds	8	6	7	24
Total Non-HC	192	195	307	186
Ratio HC/Non-HC	0.08	0.08	0.06	0.24
Saturate Analysis				
% Paraffins	7.5	9.9	11.3	8.8
% Isoprenoid	0.5	1.5	1.0	1.1
% Naphthenes	92	88.6	87.7	90.1
Pristane/Phytane	0.50	1.0	0.53	0.86
CPI ^a	1.4	1.7	1.6	1.8

^aSee text for calculation.

ml/minute) as carrier gas. A solid inlet probe system was used to preconcentrate the C₁₅+ saturate hydrocarbon (dissolved in chromatographic-grade normal heptane) prior to injection.

In order to determine the ppm concentrations of the C₁₅+ saturate hydrocarbons isolated from the first three samples in Table 1, the analysis was carried out under stringent dilution/injection/instrument sensitivity conditions. The total area above baseline was used to compute the ppm values against a known standard.

The odd-even carbon preference, CPI, was calculated in the following manner:

$$\text{CPI} = \frac{\frac{C_{25}+C_{27}+C_{29}+C_{31}}{C_{26}+C_{28}+C_{30}+C_{32}} + \frac{C_{25}+C_{27}+C_{29}+C_{31}}{C_{24}+C_{26}+C_{28}+C_{30}}}{2}$$

RESULTS AND DISCUSSION

Methane yields for all samples varied from 7 to 9 ppm, and no other hydrocarbon was present in amounts greater than 1 ppm. This would be expected from the low organic content of the sediments. The most significant result in Table 2 is the appearance of several common gasoline range hydrocarbons in the clayey silt at 769 meters in Hole 218.

The 2- and 3-methylpentanes may be breakdown products of iso- and anteisobiogenic hydrocarbons. Cyclopentane and methylcyclohexane are common gasoline range naphthenes, but the depths at which they originate are still poorly defined. These results are intriguing, but they need verification by analyses to corresponding depths in other DSDP holes. The C₄-C₇ hydrocarbons in Sample 218-27-2 cannot be ascribed to a seep because the ratios of hydrocarbon to organic carbon (45/1400) and of total extract to organic carbon (231/1400) are much too low in comparison with other presumed seeps. For example, McIver reported a hydrocarbon to organic carbon ratio of 0.26 for the Shatsky Rise enrichment which was believed to be a seep (McIver, 1971).

Data on the C₁₅+ hydrocarbons show a low ratio of hydrocarbons to nonhydrocarbons (asphaltic and nitrogen, sulfur, oxygen compounds) as would be expected from biogenic organic matter which has undergone very little alteration. Sample 218-27-2, which indicates the beginning of hydrocarbon generation in the C₄-C₇ range, also shows a marked increase in the ratio of hydrocarbons to nonhydrocarbons in the C₁₅+ range.

The saturate analysis, however, shows no clear change with depth. The naphthenes constitute 90% of the saturate fraction at all depths, which is rather surprising since the paraffins usually dominate in the saturate fraction of surface sediments. The CPI, or ratio of odd to even chain length paraffins, varies between 1.4 and 1.8, with the deepest sample having the highest value. These differences are undoubtedly caused by variations in the contribution of continental paraffins, since these are the paraffins showing the odd predominance in the C₂₅+ range.

Although the organic carbon and hydrocarbon contents of these samples are generally low compared to areas like the Gulf of Mexico, California basins, and Orinoco Delta, they do suggest that some hydrocarbon formation is occurring in the clay-silt sample at 769 meters. Also, the two deepest samples contain well-preserved continental woody material, whereas the shallower carbonate cores have largely amorphous organic material of marine origin.

REFERENCE

- McIver, R. D., 1971. Evidence of Migration of Hydrocarbons in Pleistocene Sediments of the Shatsky Plateau, Western Pacific Ocean. *In* Fischer, A. G., Heezen, B. C., et al., Initial Reports of the Deep Sea Drilling Project, Volume VI: Washington (U. S. Government Printing Office), p. 1327-1329.