MASTER

ABSTRACT

Well cuttings from two offshore Gulf Coast stratigraphic test wells (South Padre and Mustang Island) have been analyzed for C_7 - C_{15} hydrocarbon distributions by thermal distillation-pyrolysis GC, for C_1 - C_7 hydrocarbons by headspace analysis and for C_{15+} hydrocarbons by extraction. The results from the South Padre well show that the threshold of intensive hydrocarbon generation starts around 10,000 feet and peaks around 14,000 feet. The distribution of individual homologs within each hydrocarbon group indicates that the more volatile members are migrating upward from the generation zone. Thus, n-pentane (C_5) peaks at 10,000 feet, and the higher homologs, C_5 , C_6 , C_7 , C_8 and C_{10} peak at successively greater depths to 15,000 feet. Benzene also peaks before toluene which peaks before the xylenes. This phenomena was not observed in the Mustang Island well where organic carbon contents and hydrocarbon yields were lower, apparently too low to induce migration.

C_1 - C_7 hydrocarbon distributions also were studied by the headspace technique in offshore samples from the East Coast, Gulf of California and Gulf of Maine. Hydrocarbon yields from wells east of Cape Hatteras and on the Blake-Bahama Plateau were much lower than in most other areas analyzed to date. Some Gulf of California samples had high gas yields due to hydrothermal intrusions and igneous dikes raising sediment temperatures. Gulf of Maine samples were unique in having no aromatic hydrocarbons.

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

REA

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ORGANIC GEOCHEMISTRY OF CONTINENTAL MARGIN SEDIMENTS

Report Submitted to the Department of Energy on Research
Conducted Under Contract EG-77-S-02-4392

1. PERSONNEL

Dr. John M. Hunt
Dr. Jean K. Whelan
Dr. A. Y. Huc
Ms. Marcia Pratt

2. RESEARCH PERIOD

November 1, 1978 - October 31, 1979

3. INTRODUCTION

Our basic research on the origin and accumulation of hydrocarbons of continental margin sediments has concentrated on four areas during the past year.

- A. Gulf of Mexico
- B. East Coast of the U.S.A.
- C. Gulf of California
- D. Gulf of Maine

The Gulf of Mexico study, which will be completed in September, involved the determination of C_7-C_{14} hydrocarbons by thermal distillation and pyrolysis, the C_1-C_6 hydrocarbons by the headspace technique and the C_{15+} hydrocarbons by extraction. The first technique is described in DoE Report Number COO-4392-1, while the second and third techniques are described in the analytical section of this report. For the other three areas listed above, the C_1-C_6 hydrocarbon analyses have been completed and the C_7-C_{14} analyses are being initiated. Our results and conclusions to date are discussed by area.

4. RESULTS AND DISCUSSION

A. Gulf of Mexico

Well cuttings samples were obtained from two Coastal Offshore Stratigraphic Test (COST) wells in the Texas Gulf Coast through the courtesy of the Phillips Petroleum Company. The location of the wells is shown in Figure 1. Also shown is the location of known gas production. In this report, the two COST wells will be referred to as South Padre Island and Mustang Island wells.

The organic carbon content of cuttings from the two wells is shown in Figure 2. The lines drawn between the two sections indicate stratigraphically equivalent units based on paleontology. Organic carbon contents are generally higher in the South Padre Island well with the highest values being in the 12,000-15,000 foot depth range. Organic carbon contents for the South Padre Island well average about 1% and for the Mustang Island well about 0.7%.

The South Padre Island well penetrated a thick clastic sequence of massive marine shale with occasional streaks of silty sand and very thin limey sections, mostly of Tertiary age. The Pleistocene section extends to 2,550 feet, the Pliocene to 4,860 feet, and the Miocene to 15,763 feet (total depth).

Figure 3 is a plot of formation temperatures in °C indicating an average geothermal gradient of about 2.6°C/100 m (1.4°F/100 feet).

The sandy sections in the well were confined mostly to the Pleistocene where permeabilities were recorded as high as 2 darcys. In the Miocene section below 10,000 feet, the permeabilities ranged between 0.01 and 0.7 millidarcys. Pressures in the South Padre Well were slightly above hydrostatic to a depth of about 9,000 feet where the overpressure zone is encountered (Figure 4). Porosities in this zone range from 20-30%.

In the Mustang Island well, the Pleistocene section extends to 1,550

WELL LOCATIONS

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

feet, the Pliocene to 2,180 feet, and the Miocene to 13,000 feet (TD). Sandy intervals extend to about 5,380 feet with the deeper sections being essentially all shale.

A typical example of the cuttings analysis from the Mustang Island well is shown in Figures 5, 6 and 7. About 20 mg of crushed wet cuttings are heated at a rate of 30°C/minute from room temperature to 800°C in a helium stream. Figure 5 shows the recording by the flame ionization detector (FID). This measures the total yield of hydrocarbon components versus temperature. The P_1 peak, which represents thermal distillation (actually a steam distillation), gives off adsorbed hydrocarbons at temperatures generally below 150°C. The P_2 peak, the pyrolysis or cracking peak, represents the hydrocarbons formed by the breakdown of kerogens at temperatures generally above 450°C.

Gas chromatograms showing the individual hydrocarbons in P_1 and P_2 are shown in Figures 6 and 7. Due to the nature of the column, it is not possible to determine the hydrocarbons very quantitatively below C_7 or above C_{15} . The aromatic hydrocarbons, benzene, toluene and the xylenes are present in relatively high concentrations, even at this great depth. This indicates the hydrocarbon mixture is in an early stage of generation. Young, relatively immature oils tend to have high percentages of aromatics.

The quantity of hydrocarbons present is determined by analyzing known mixtures of hydrocarbons with both the FID column and the gas chromatograph. The precision of these instruments is excellent. Duplicate run generally trace almost exactly the same pattern on both the FID and GC curves. However, it is not possible to determine absolute values very accurately since synthetic standards made in the laboratory cannot really duplicate the adsorption conditions of hydrocarbons occurring in a natural shale. Also, differences in response factors of the FID and GC detectors will cause some variation in absolute amounts. Consequently, although we are quoting much of our data quantitatively, it more accurate to make comparisons on a relative basis rather than to think in absolute terms of yields. Some comparative yields of the P_1 peak

MUSTANG ISL.
9,750 FT.

FIGURE 5

FIGURE 6

MUSTANG ISL.
9,750 FT.
P₂

FIGURE 7

by FID and GC at different depths in South Padre Island are shown in Table 1. C_o equals organic carbon.

Table 1

<u>Depth</u>	<u>mg HC/g C_o</u>	
	<u>GC</u>	<u>FID</u>
4,800	0.5	2
7,200	2	3.5
9,030	5	5
10,200	12	13
11,700	8	7
12,600	13	15
14,600	28	23
15,600	20	29

Figure 8 illustrates the way the area and shape of the pyrograms change as the depth of burial changes at South Padre Island. P_1 representing the hydrocarbons formed naturally shows its greatest increase at depths beyond 9,000 feet. As P_1 increases, P_2 decreases because there is less hydrocarbon available from cracking the kerogen at greater depths. Nature has partially cracked the kerogen in the deeper samples, so less is available to crack in the laboratory operation.

Figures 9 and 10 show the gas chromatograms of South Padre Island samples at 12,570 feet. There is a smooth decrease in the yield of the n-alkanes

SOUTH PADRE ISL.

FIGURE 8

FIGURE 9

FIGURE 10

which are shown as C_7 , C_8 , C_9 , etc. In this sample, the $n-C_8$ is present in highest concentration (about 1000 mg/g C_0). The double peaks which show clearly at the n -alkane positions of Figure 10 indicate the presence of olefins which are products of high temperature cracking in the laboratory. These olefins were later confirmed by gas chromatography-mass spectrometry. In nature, these olefins may form, but they would be quickly reduced to alkanes since the buried sediments are almost always reducing. Olefins are not found in crude oil, except in trace amounts, and they are rarely encountered in the hydrocarbons extracted from ancient sediments. Figure 11 shows the distributions of hydrocarbons at 15,690 feet in P_1 , South Padre Island. Note that the hydrocarbon peak has shifted from C_8 to C_{11} (compare Figures 9 and 11). The C_{11} concentration at 15,690 feet is approximately 1,450 mg/g C_0 .

Most of these generation reactions are first order, that is, the reaction rate approximately doubles for every 10°C rise in temperature. This causes an exponential increase in the concentration of hydrocarbons within the source rocks. This exponential increase can be observed by plotting the production index, which is the ratio of the area under P_1 to the combined areas of $P_1 + P_2$. This is shown in Figure 12. The first 10,000 feet of sediments are organically immature, that is, the time and temperature has not been adequate to initiate intense hydrocarbon generation. At depths beyond 10,000 feet, there is a well-defined increase in hydrocarbon concentration indicating that generation is increasing toward a peak in the range of 15,000-16,000 feet. The horizontal lines in Figure 12 represent the range of values obtained from analyzing several samples while the dots represent the mean. This increase also can be observed by plotting the yield of C_6 - C_{15} hydrocarbons with depth for P_1 which is the free adsorbed hydrocarbons formed by natural cracking (Figure 13).

As part of the generation and migration process, there is a well-defined increase in total n -alkanes with depth and decrease in single ring aromatics (benzene, toluene, xylenes). This is shown in Figure 14. The lines drawn were calculated by the least squares method. The n -alkanes would be expected to increase with depth because thermodynamically they are the most stable of

FIGURE 11

FIGURE 12

FIGURE 13

SOUTH PADRE ISL.

FIGURE 14

the hydrocarbons. Also, it requires more energy (higher temperatures) to crack the straight chains compared to the branched and cyclic hydrocarbons. The decrease in aromatics could be a combination of generation and migration processes. Some aromatic hydrocarbons are formed early, particularly those derived from tree resins. Condensates found at shallow depths in the Western Canada Basin tend to be high in aromatics. Since the aromatic hydrocarbons are about 1000 times more soluble than the alkanes, they would tend to move out of a basin with the compacting waters more rapidly than the relatively insoluble hydrocarbons. This would cause an increased concentration of aromatics at the shallower depths.

This distribution difference can also be seen in a triangular plot of the major hydrocarbon groups, aromatics, cycloalkanes and normal plus branched alkanes. Figure 15 shows this change in concentration with depth. The shallow samples are relatively high in aromatics, while the deeper samples contain more of the branched and cycloalkanes.

The fact that the low molecular weight n-alkanes peak at a shallower depth than the high molecular weight n-alkanes as indicated in Figures 9 and 11 is shown even more clearly in Figure 16 where histograms of the n-alkanes are plotted from heptane (C_7) through tetradecane (C_{14}). At 10,200 feet, n-heptane is dominant. At 12,570 feet, C_8 is in highest concentration, at 14,610 feet it is C_{10} , and at 15,690 feet C_{11} . This shift to the higher molecular weight hydrocarbons with depth is also apparent within the group of single ring aromatics (Figure 17). Benzene is observed to peak at the shallowest depth, toluene intermediate and the xylenes at the greatest depth.

This phenomena of the peaking of the higher molecular weight compounds at greater depths has several possible explanations as follows:

1. Generation of lighter hydrocarbons at shallower depths than heavier hydrocarbons. This might be possible if there is a wide variation in the organic matter precursors of the different hydrocarbons with depth.

FIGURE 15

SOUTH PADRE ISL.
n-ALKANES
P₁

FIGURE 16

SOUTH PADRE ISLAND

CHANGE IN AROMATIC HYDROCARBONS WITH DEPTH

P_1 (mg/g C org.)

FIGURE 17

However, if the kerogen matrix is similar down the hole, thermodynamic considerations would normally expect the large molecules to form first, and the small molecules last. A reservoir mixture of hydrocarbons is not in thermodynamic equilibrium, but is constantly moving in the direction of smaller molecules. This is why crude oils tend to become lighter with depth, eventually changing to condensates and gas. The phenomena being observed here is moving in the opposite direction.

2. A qualitative difference in the organic matter. Organic carbon concentrations are slightly higher at depths below 13,000 feet in the South Padre Island well compared to shallower samples. However, we have no real evidence that the organic matter is different. In fact, the hydrocarbon concentrations in the P_2 peak suggest that the kerogen is fairly similar at all depths. Figures 18 and 19 show that the shift in the molecular weight of the hydrocarbon peak with depth does not occur in the hydrocarbons obtained from the thermal degradation of kerogen (P_2). Figure 18 shows the change in concentration of C_6-C_{10} (light gasoline and kerosene) compared with the $C_{11}-C_{15}$ hydrocarbons (heavy kerosene and gas oil) in P_2 . The lighter hydrocarbons are present in somewhat higher concentrations than the heavier ones at all depths. If there was a difference in the kerogen precursor above and below 12,000 feet, it should show up in P_2 of this figure. Figure 19 is a histogram of individual hydrocarbon concentrations with depth which may be compared with Figure 16. Clearly Figure 19 does not show the shift in peaking observed in Figure 6.
3. The influence of the mineral matrix. There is some evidence that the mineral matrix can be involved in the qualitative and quantitative release of products during thermal distillation and pyrolysis. The effect seems to be greater with the P_2 peak than the P_1 peak (Espitalie et al., 1978). In the South Padre Island well, the clay mineralogy changes somewhat with depth. In order to check the

SOUTH PADRE ISL.

mg HC / g C₀

FIGURE 18

SOUTH PADRE I.
n-ALKANES
P₂

FIGURE 19

interaction of the mineral matter and organic matter, we mixed two samples, one from 10,200 feet with a low yield of hydrocarbon and a distribution centered in the low molecular weight range (Figure 16) and the second from 13,950 feet, with a high yield of hydrocarbons and a relatively flat distribution. If the mineral matter at 10,200 feet is involved in the distribution of the released hydrocarbons, one would expect it would alter the pattern of the hydrocarbon distribution at 13,950 feet. We found that the GC pattern of the 13,950 foot sample was not altered when mixed with the sample at 10,200 feet indicating that any mineral effect on hydrocarbon retention was negligible in the thermal distillation (P_1 peak).

4. Upward migration of the lighter hydrocarbons. This is the most plausible of the four suggested explanations. The low molecular weight compounds are known to migrate more easily than those of a higher molecular weight. The lighter components diffuse faster and are more soluble in formation fluids. Petroleum geochemists have frequently observed hydrocarbons diffusing short distances from reservoir accumulations.

In such examples the methane diffuses the furthest distance followed by ethane, propane, butane, etc. If the same phenomena is operating from a zone of generation in the shale source bed around 12,000 ft., it would create the hydrocarbon distributions observed in Figures 16 and 17.

The over-pressured zones may be involved in the migration process. Figure 4 shows that the under-compacted over-pressured section occurs at depths generally greater than 10,000 feet. Fluids in these over-pressured zones would escape updip and along vertical faults to the shallower more normally pressured zones. This directionality of the major fluid movement could orient hydrocarbon distributions by diffusion with the lighter components at shallower depths.

The headspace analyses for the hydrocarbon range below C_7 provides additional support for the proposed migration mechanism. Figure 20 shows the distribution of n-pentane, n-hexane and n-heptane with depth in the South Padre Island well. In the immature section shallower than 8,000 feet the hydrocarbon distributions were erratic. At 8,100 ft. there was a pronounced dominance of the n- C_5 over the C_6 and C_7 n-alkanes. This C_5 predominance occurred to about 11,000 ft. From 11,500 to 12,600 ft. the n- C_6 was the predominant alkane. Beyond 13,000 ft. the n- C_7 took over and continued as the dominant hydrocarbon to total depth of 15,630 ft. This shift from the low molecular weight C_5 predominance in the shallow samples to the higher molecular weight C_7 predominance in the deeper samples mirrors the changes previously discussed in the higher molecular weight ranges. The most plausible explanation for these differences is a migration mechanism.

In Figure 21, the C_6 and C_7 saturated hydrocarbons determined by headspace analysis are grouped in their three major types, branched alkanes, cycloalkanes and normal alkanes. The normal alkanes predominate at the greater depth. This could be the result of migration, since the n-alkanes are the least soluble. It could also be explained as generation however, since the n-alkanes require higher temperatures to form from the kerogen.

It had been previously reported by Hunt et al. (1978) that the ratio of iso- C_5 /n- C_5 in Black Sea sediments showed an increase from the surface to maximum depth where the temperature was around 50°C. Data for Paris Basin sediments by Durand et al. (1971) shows a similar increase but with less slope to a bottom hole temperature approaching 100°C. Equilibrium calculations however, show that the ratio should decrease in high temperature regimes beyond 100°C (Figure 22). In this figure, 1, 2, and 3 are best fit lines for data from Holes 397A, 380A and 381 in the Black Sea. Line 4 is the Paris Basin and 5 is calculated from equilibrium values. We plotted the data for this C_5 ratio for the South Padre Island samples and found that they followed the same change with depth as the observed and calculated values of both Hunt and Durand. The only difference was that the entire ratio was shifted to somewhat lower values.

DISTRIBUTION OF C₅-C₇ n-ALKANES WITH DEPTH

SOUTH PADRE ISLAND

FIGURE 20

CHANGE IN C₆-C₇ HYDROCARBON TYPE DISTRIBUTION WITH DEPTH, SOUTH PADRE ISLAND

- < 10,000 FT
- ▲ > 10,000 FT
< 13,800 FT
- > 13,800 FT

FIGURE 21

•nc

FIGURE 22

The reason for the change in this ratio is not related to migration since these two pentanes have about the same coefficient of diffusion and about the same solubility. Also, it occurs at a shallower depth than the generation and migration evidence (see Figure 3). It appears to be the result of differences in precursors available for generation and in early reaction mechanisms. Our studies of deep sea surface sediments over the last several years have shown n-pentane to be very common at the surface probably due to straight chain biological precursors. With burial however, carbonium ion reactions are favored at low temperatures which tend to yield primarily branched alkanes. This causes a shift in the early predominance of n-alkanes to branched alkanes. Eventually, as temperatures increase beyond 100°C the cracking reactions begin to dominate. These are free radical reactions which tend to yield more straight chain alkanes than branched alkanes. Consequently, the former compounds begin to dominate and continue to do so as long as hydrocarbons are generated. This is one of the causes for the shift to n-alkane predominance in deep samples that was observed in Figure 21.

Figure 23 shows hydrocarbon distribution changes with depth for the entire hydrocarbon range from C₂ up through C₁₅₊ using three different analytical techniques, headspace analysis, thermal distillation and extraction. The data show that in all hydrocarbon ranges there is a pronounced increase in yield, known as the threshold of intense hydrocarbon generation around 10,000 feet. The lower molecular weight ranges show more scatter and a shallower increase in yield than the higher molecular weight ranges. This would be expected if the generation is being accompanied by migration.

The analysis of Mustang Island samples provided an interesting contrast with South Padre because in the former, the quantity of hydrocarbons formed appears to be too small for migration to occur. Organic carbon contents at Mustang Island (P₁) were significantly lower than at South Padre (Figure 2). Also, the quantity of hydrocarbons generated at Mustang Island was one-half to two-thirds the quantity at South Padre. These amounts may be borderline or below the minimum required to cause migration. Momper (1978) has pointed out

SOUTH PADRE ISLAND

HYDROCARBON DISTRIBUTION CHANGES WITH DEPTH

(PLOTTED AS PERCENT OF HIGHEST VALUE)

FIGURE 23

that a minimum amount of hydrocarbons must be generated for appreciable migration to occur. Figure 24 shows the Production Index for Mustang Island samples. When compared with South Padre (Figure 12) the index is similar except that it only barely begins to show the increase that occurs at the threshold of intense generation. This threshold is probably at or near the bottom of the hole. Consequently, the entire section to 11,000 feet is immature with evidence of generation just beginning before the hole is terminated.

Figure 25 is the depth-concentration plot for the C_6-C_{10} and $C_{11}-C_{15}$ hydrocarbon fractions from P_1 and P_2 (compare with Figure 18 for South Padre). Note that the pattern for the two molecular weight ranges is essentially the same in contrast to South Padre where the lighter hydrocarbons appear at shallower depths. This is further substantiated from the histogram of individual n-alkane distributions for P_1 shown in Figure 26. There is no significant shift in the predominance of the low molecular weight alkanes to the high molecular weight ranges with depth as occurs at South Padre (Figure 16). We also plotted the distribution of single-ring aromatics (benzene, toluene and xylenes) as shown in Figure 27. Unfortunately, the data do not go deep enough to show concentration peaks but the beginning of the curves suggest that peaking will be uniform for these different molecular weight ranges.

Clearly the molecular weight shift with depth observed at South Padre Island does not occur in the samples from Mustang Island. The best explanation appears to be that the yields are too low to induce primary migration.

Our study of these COST wells has shown that hydrocarbons are forming, the depth at which intense hydrocarbon generation is initiated and hydrocarbon distribution variations caused by generation and migration. In order to verify these results and to extend the investigation to greater depths, we are proposing to obtain samples from additional offshore wells further to the north in the vicinity of Louisiana and Mississippi.

FIGURE 24

MUSTANG ISLAND

mg HC/g C₀

FIGURE 25

MUSTANG ISLAND
n-ALKANES
P₁

37.

6,510 FT.

12,300 FT.

10,160 FT.

12,740 FT.

11,540 FT.

12,920 FT.

FIGURE 26

MUSTANG ISLAND

CHANGE IN AROMATIC HYDROCARBONS WITH DEPTH

P_1 (mg/g C org.)

FIGURE 27

B. East Coast of U.S.A.

In our DOE report, COO-4392-1, we indicated that we could quantitatively measure the adsorbed and cracked hydrocarbons in the molecular weight range from 1 to 20 carbon atoms with our thermal distillation-pyrolysis unit. The system shown in that report involved trapping the C_1 to C_6 hydrocarbons in alumina after trapping the C_7 to C_{20} hydrocarbons in Tenax. Unfortunately, the C_1 - C_6 trapping disrupted quantification of all other data (area of P_1 and P_2 and amount of C_7 - C_{15} hydrocarbons) when the alumina and Tenax traps were placed in series. After several frustrating experiments, we decided to use the thermal distillation only for the C_{7+} hydrocarbon range and determine C_1 to C_6 hydrocarbons by our well-established headspace technique. Also, we found some variability in the C_{15} to C_{20} range and decided to drop further investigation of this until we would have the time to work on the analytical procedure. Consequently, all the data in this report covers the ranges which are quantitatively reproducible, namely, C_1 to C_6 by headspace and C_7 to C_{15} by thermal distillation and pyrolysis.

Since our single thermal distillation unit has been tied up with the Gulf of Mexico samples, our work in the other areas has concentrated to date on headspace analyses for the C_1 to C_6 hydrocarbons.

We did carry out thermal distillation-pyrolysis for three samples from Hole 386 of the Deep Sea Drilling Project off the coast of North Carolina. The results are shown in Table 2 in comparison with samples from the South Padre Island well in the Gulf of Mexico. Both the P_1 and P_2 peaks showed a much lower hydrocarbon yield for the three samples on the East Coast compared to the three in the Gulf of Mexico. The interpretation is that both the adsorbed hydrocarbons and the hydrocarbons available from cracking kerogen are low by an order of magnitude from the East Coast compared to the Gulf Coast. More samples should be run to verify this initial conclusion. However, no samples from South Padre Island gave yields as low as the three from Hole 386.

TABLE 2.

Hydrocarbon Yield by Thermal Distillation
in mg HC/g C_o

<u>DSDP Leg 43, Hole 386</u>			<u>S. Padre Island</u>		
Depth m,	P ₁	P ₂	Depth, m	P ₁	P ₂
740	0.088	22	470	3	60
872	0.113	1.3	1,460	2	20
913	1.25	7.6	2,200	3.5	35

DSDP Hole 388A was drilled on the lower part of the continental rise about 350 miles due east of Cape Hatteras. Table 3 shows hydrocarbon data obtained at two depths in this well. The samples shown in this and succeeding tables were obtained as cores in the DSDP Project which were frozen on shipboard and kept frozen until analyzed. Nevertheless, the values for methane and ethane are probably suspect since they have much higher vapor pressures than the other hydrocarbons. At the bottom of the table we have summed the ethane and propane in one group and the butanes through heptanes in another. The total yield of hydrocarbons in these two samples is very low compared to other sites we have analyzed around the world. For example, it is two orders of magnitude lower than samples at a comparable sediment depth in the Black Sea. It is three orders of magnitude lower than samples from the Angola and Cape Basins off southwest Africa. The hydrocarbon spectrum is typical of the hydrocarbons formed very early in immature sediments. Some hydrocarbons dominate far out of proportion to others because of variations in the precursors. Thus, isopentane represents about 30% of the C_4 to C_7 hydrocarbons and the aromatics about 9%.

Holes 391A and 391C were drilled in the Blake-Bahama Basin about 350 miles due east of Orlando, Florida. C_1 - C_7 hydrocarbon data are shown over a depth range from 150 to 1,392 m in Tables 3, 4 and 5. All of these samples are in the immature, pre-generation stage. They show the erratic distribution that occurs from variations in biological precursors and a lack of migration. Samples from two depths, 354 and 654 m had almost no hydrocarbons. The highest yields were from the deepest sample. On the average, yields were noticeably higher in all samples deeper than 1,000 m. Aromatics were dominant in the shallower samples with toluene representing more than 40% of the C_4 - C_7 hydrocarbons in samples at 150, 641, and 654 m. High toluene concentrations have also been observed in Walvis Bay off southwest Africa in a highly reducing sediment.

Individual hydrocarbon distributions become somewhat more uniform in the deeper samples indicating that the hydrocarbon mixture is moving toward the composition of petroleum. However, due to the low temperatures, probably not

TABLE 3.
C₁-C₇ Hydrocarbons - DSDP Leg 44

Sample No.	388A-5-0-0-20	388A-11-0-20-50	391A-3-4-0-28	391A-9-0-0-50	391A-11-0-0-27	391A-13-0-20-35
Sediment Depth	246 m	332 m	150 m	354.5 m	411 m	526 m
Lithology	Silty Clay	Clay	Calcareous Clay	Marly Clay	Intraclastic Chalk	Silaceous Mudstone
Age	U. Miocene	M. Miocene	U. Miocene	Miocene	Miocene	L. Miocene
Hydrocarbons	Concentration in ng/g dry wt. sediment					
Methane	0.4	1.1	0.30	0	5.4	2.2
Ethane	0.6	0.1	0.52	0	1.7	0.25
Propane	3	0.47	1.91	0	16.4	2.7
i-Butane	0.8	0.35	0.21	0	52.4	0.38
n-Butane	1.0	0.38	0.33	0	42.3	0.15
Neopentane	0.17	0.15	0.03	0	0	0.63
i-Pentane	3.1	3.47	0.24	0	0	0.83
n-Pentane	0.81	0.57	0.15	0	0	1.06
Cyclopentane	0.06	0.09	0	0	0	0.005
2,2-Dimethylbutane	0.05	0.26	0.21	0	0	0.83
2,3-Dimethylbutane	0.02	0.23	0.08	0	0.005	0.74
2-Methylpentane	0.14	0.38	0.07	0.10	0.10	0.56
3-Methylpentane	0.04	0.15	0.035	0.035	0.035	0.13
n-Hexane	0.08	0.30	0.07	0.14	0.10	0.17
Methylcyclopentane	0.17	0.29	0.08	0.07	0.07	0.03
2,2-Dimethylpentane	0.005	0.14	0	0	0	0.80
Benzene	0.74	0.04	0.85	0.03	0.06	0.11
2,4-Dimethylpentane	0.02	0.12	0	0	0	0.78
2,2,3-Trimethylbutane	nd	nd	nd	nd	nd	nd
Cyclohexane	0.13	0.40	0.005	0	0.007	1.22

TABLE 3. (Cont.)

Sample No.	388A-5-0-0-20	388A-11-0-20-50	391A-3-4-0-28	391A-9-0-0-50	391A-11-0-0-27	391A-13-0-20-35
3,3-Dimethylpentane	0.10	0	0	0	0.005	0
1,1-Dimethylcyclopentane	0.15	0.01	0	0	0	0.005
2-Methylhexane	0.49	0.13	0.02	0	0	0.086
2,3-Dimethylpentane	0.88	0.31	0.04	0	0.08	1.04
1-C-3-Dimethylcyclo- pentane	0	0	0	0.005	0	0
3-Methylhexane	0.14	0.34	0.08	0	0.05	0.25
1-Trans-3-Dimethylcyclo- pentane	0.06	0.2	0	0	0	0
1-t-2-Dimethylcyclopentane	0.04	0.12	0	0	0	0.008
3-Ethylpentane	0	0.005	0.04	0	0	0.005
n-Heptane	0.14	0.54	0.49	0	0	0.26
1-C-2-Dimethylcyclo- pentane	0	0.005	0	0	0.20	0
Methylcyclohexane	0.41	1.16	0.12	0	0	1.39
Toluene	0.10	0.96	6.76	1.58	0.64	3.98
ΣC_2+C_3 (ng/g dry wt.)	3.6	0.57	2.43	0	18.1	2.95
ΣC_4-C_7 (ng/g dry wt.)	9.8	11.1	9.91	1.96	96.0	15.4
Total Carbon	0.6	0.8	11.1	9.0	9.1	4.2
% C ₀	0.4	0.4	0.6	0.2	0.2	1.4

TABLE 4.

C₁-C₇ Hydrocarbons - DSDP Leg 44

Sample No.	391A-20-2-13-26	391A-21-4-2-50	391A-21-4-87-124	391C-6-3-100-120	391C-7-2-125-130	391C-8-2-115-143
Sediment Depth	641 m	654 m	654.4 m	691 m	727.8 m	784.6 m
Lithology	Variegated Silty Claystone	Claystone-Silty Claystone	Darker Claystone Layer	Claystone & Silt Laminae	Silty Clay	Clay
Age	L. Miocene	L. Miocene	L. Miocene	U. Albian	U. Albian	U. Albian
Hydrocarbons	Concentration in ng/g dry wt. sediment					
Methane	7.1	0	0.75	0.54	1.13	0.37
Ethane	1.18	0	0.16	0.55	0.26	0.25
Propane	1.28	0	0.16	0.54	1.75	0.28
i-Butane	0.12	0	0.01	0.09	0.14	0.14
n-Butane	0.45	0	0.18	0.18	0.14	0.20
Neopentane	0	0	0.14	0.18	0	0.04
i-Pentane	0.69	0	0	0.17	0.09	0.11
n-Pentane	0.45	0	0.02	0.16	0.06	0.07
Cyclopentane	0	0	0.005	0	0	0.005
2,2-Dimethylbutane	0.14	0	0.42	0.005	0.21	0.4
2,3-Dimethylbutane	0	0	0.35	0.002	0.005	0.005
2-Methylpentane	0.42	0	0.18	0.038	0.07	0.01
3-Methylpentane	0.14	0	0.07	0.004	0.01	0.16
n-Hexane	0.53	0.018	0.02	0.013	0.03	0.10
Methylcyclopentane	0.21	0	Trace	0.007	0.005	0.005
2,2-Dimethylpentane	0.03	0	2.73	0	0	0
Benzene	0.13	0.019	Trace	0.01	0.20	0
2,4-Dimethylpentane	0.24	0	2.1	0	0	0
2,2,3-Trimethylbutane	nd	nd	nd	0	0	0
Cyclohexane	0.32	0	0.42	0.023	0.05	0.005

TABLE 4. (Cont.)

Sample No.	391A-20-2-13-26	391A-21-4-2-50	391A-21-4-87-124	391C-6-3-100-120	391C-7-2-125-130	391C-8-2-115-143
3,3-Dimethylpentane	0.005	0	0	0	0	0
1,1-Dimethylcyclopentane	0.005	0	0	0	0	0
2-Methylhexane	1.22	0	2.40	0.32	0	0
2,3-Dimethylpentane	3.06	0	2.40	0.29	0	0
1-C-3-Dimethylcyclopentane	0	0	0	0	0	0
3-Methylhexane	4.20	0	0.45	0.08	0.15	0.15
1-Trans-3-Dimethylcyclopentane	2.49	0	0	0.005	0.10	0.005
1-t-2-Dimethylcyclopentane	1.88	0	0	0.005	0	0
3-Ethylpentane	0.08	0	0	0	0	0
n-Heptane	10.0	0	0.005	0.14	0.27	0.005
1-C-2-Dimethylcyclopentane	Trace	0	0	0	0	0
Methylcyclohexane	1.14	0	2.45	0.24	0.28	0.18
Toluene	23.9	0	7.78	1.04	1.2	0.86
ΣC_2+C_3 (ng/g dry wt.)	2.46	0	0.32	1.09	2.01	0.53
ΣC_4-C_7 (ng/g dry wt.)	51.8	0.037	19.7	3.0	3.0	2.45
Total Carbon	0.5	0.1	0.3	0.6	0.7	0.4
% C _O	0.5	0.1	0.3	0.6	0.6	0.3

TABLE 5 .
C₁-C₇ Hydrocarbons - DSDP Leg. 44

Sample No.	391C-10-3-138-142	391C-12-4-0-30	391C-21-3-110-138	391C-30-2-118-131	391C-48-2-146-50	391C-52-2-17-34
Sediment Depth	901 m	958 m	1090 m	1184 m	1355 m	1392 m
Lithology	Claystone	Interbedded	Limestone	and	Claystone	
Age	Aptian-Albian	U. Barrem-Aptian	U. Valanginian - L. Barremian		L. Tithonian	
Hydrocarbons	Concentration in ng/g dry wt. sediment					
Methane	0.57	0.16	4.9	4.5	0.44	2.0
Ethane	0.34	0.05	0.68	1.2	0.61	2.5
Propane	1.96	0.08	1.5	3.2	0.79	1.7
i-Butane	0.26	0.02	0	2.0	0.13	0.62
n-Butane	0.38	0.03	1.0	1.9	0.26	0.85
Neopentane	0.27	0.004	0	0.10	0	0.27
i-Pentane	0.48	0.03	0	3.4	0.24	1.20
n-Pentane	0.27	0.015	0.005	2.0	0.16	0.66
Cyclopentane	0.002	0.004	0	0.2	0.063	0.03
2,2-Dimethylbutane	0.30	0.03	nd	0.04	0.02	0.03
2,3-Dimethylbutane	0.01	0.01	0.21	0.21	0.036	0.07
2-Methylpentane	0.18	0.03	0.28	1.2	0.056	0.39
3-Methylpentane	0.02	0.01	0.21	0.22	0.081	0.21
n-Hexane	0.10	0.01	0.39	0.82	0.053	0.35
Methylcyclopentane	0.02	0.065	0.49	0.80	0.052	0.24
2,2-Dimethylpentane	0	0	0.08	0.01	0.10	0
Benzene	0.06	0.003	0.22	0.57	1.05	0.35
2,4-Dimethylpentane	0	0	0.04	0.11	0.10	0.41
2,2,3-Trimethylbutane	nd	nd	nd	nd	nd	0
Cyclohexane	0.14	0	0.24	0.32	0.01	0.21

TABLE 5. (Cont.)

Sample No.	391C-10-3-138-142	391C-12-4-0-30	391C-21-3-110-138	391C-30-2-118-131	391C-48-2-146-50	391C-52-2-17-34
3,3-Dimethylpentane	0.005	0	0	0.006	0	0.12
1,1-Dimethylcyclopentane	0.005	0	0	0.018	0	0.005
2-Methylhexane	0.096	0	0	0.21	0.37	2.8
2,3-Dimethylpentane	0.48	0.016	1.35	0.65	0.37	2.8
1-C-3-Dimethylcyclopentane	0	0	0	0	0	0
3-Methylhexane	0.09	0	0.08	0.37	0.09	2.8
1-Trans-3-Dimethylcyclopentane	0.05	0	0	0.16	0.03	0.05
1-t-2-Dimethylcyclopentane	0	0	0.20	0.13	0.06	0.12
3-Ethylpentane	0.04	0	Trace	0	0.07	0.02
n-Heptane	0.28	0	0.20	0.87	0.07	3.8
1-C-2-Dimethylcyclopentane	0	0	0	0.05	0	0.03
Methylcyclohexane	0.35	0.005	1.06	0.30	0.07	5.8
Toluene	1.07	0.005	1.88	0.52	0.08	9.1
ΣC_2+C_3 (ng/g dry wt.)	2.3	0.13	2.18	4.4	1.40	4.2
ΣC_4-C_7 (ng/g dry wt.)	4.91	0.42	7.93	17.2	3.25	33.3
Total Carbon	4.6	2.0	5.5	10.0	3.8	2.7
% C ₀	1.0	1.7	0.5	0.1	0.3	0.6

more than 50°C at the bottom, these sediments are still a long way from reaching the threshold of intense hydrocarbon generation. Also, there does not seem to be any evidence of migration in this very early stage.

C. Gulf of California

The C₁-C₇ hydrocarbon data from five holes drilled on IPOD Leg 64, plus two piston cores are shown in Tables 6, 7, and 8. Holes 474 and 476 were drilled on the edge of the continental rise at the entrance to the Gulf of California. Holes 477, 478 and 479 were drilled in the Guaymas Basin in the center of the Gulf. This is an area of high heat flow with hydrothermally altered terrigenous muds and dolomite intrusions in the deeper sections.

Hydrocarbon yields and compound distributions are comparable to those on the east coast except for a very high yield of gases. Again, most of these sediments are immature but a few have been raised to a high temperature by the hydrothermal fluids. For example, the very high yields of methane, ethane, propane and butanes at 126 m in Hole 477 indicate such generation. Since the total sediment column here is late Quaternary in age, there has not been sufficient time to generate large amounts of hydrocarbons except by hot intrusions. Nearly all of the Guaymas Basin samples show a much higher methane content than the samples from Hole 474 and 476 at the mouth of the Gulf. The previously mentioned sample at 126 m from Hole 477 is particularly interesting because it was taken just below a dolomite sill. The high yields of methane through butanes are almost certainly due to the high temperatures caused by the sill. Geologically, this event would be very recent since there is no evidence of migration upward into the shallower sediments at 15 and 31 m except possibly for the methane. Methane migrates much more easily than the higher alkanes so it could be causing the higher concentrations observed at shallower depths in this hole. If such migration is occurring, it has not yet affected the ethane and propane appreciably since their concentrations are reversed at the 31 and 126 m depths. Of course, some of this methane may be biological, but one would expect to see higher concentrations in Hole 478 if

TABLE 6.

C₁-C₇ Hydrocarbons - IPOD Leg 64

Sample No.	474-4-2-40-49	474-5-3-115-120	476-2-2-73-79	476-3-4-37-41	476-7-2-113-117	477-3-1-135-140
Sediment Depth	23 m	35 m	11 m	22 m	59 m	15 m
Lithology		Diatomaceous Ooze With H ₂ S			Diatom Ooze, Silty Clay	
Age		Pleistocene			Quaternary	
Hydrocarbons	Concentration in ng/g dry wt. sediment					
Methane	464	285	7.6	6.2	5.6	858
Ethane	1.58	2.0	1.7	0.86	1.08	0.41
Propane	1.76	2.9	2.6	0.85	1.22	0.45
i-Butane	0.39	1.1				
n-Butane	0.50	1.13		0.22		0.26
i-Pentane	4.0	5.4				
n-Pentane	0.43	2.1	1.6			
Cyclopentane	0.49	0.7				
2,2-Dimethylbutane				0.1		
2,3-Dimethylbutane	0.33	0.10		0.2	0.15	0.01
2-Methylpentane	0.46	0.10	0.24	0.4	0.40	0.01
3-Methylpentane	0.84	0.8	0.04		0.2	0.04
n-Hexane	0.24		0.50	0.8	3.0	
Methylcyclopentane	0.10		0.1	0.05	0.46	
2,2-Dimethylpentane	0.05			0.14	0.15	
Benzene	} 0.29		} 0.15	} 0.14	} 0.47	
2,4-Dimethylpentane						
2,2,3-Trimethylbutane	0.13					
Cyclohexane				0.13	0.2	

TABLE 6. (Cont.)

Sample No.	474-4-2-40-49	474-5-3-115-120	476-2-2-73-79	476-3-4-37-41	476-7-2-113-117	477-3-1-135-140
1,1-Dimethylcyclopentane		0.16				
2-Methylhexane			} 0.2			
2,3-Dimethylpentane					0.4	
3-Methylhexane		0.10				
1-Trans-3-Dimethylcyclopentane		0.03			0.01	
1-t-2-Dimethylcyclopentane					0.01	
3-Ethylpentane			0.1	0.07	0.01	
n-Heptane	0.05	0.10	0.38	1.47	0.5	
Methylcyclohexane	0.05			0.2		
Toluene	0.7	0.12	2	3.8	0.18	1.2
ΣC_2+C_3 (ng/g dry wt.)	3.34	4.9	4.3	1.71	1.30	0.86
ΣC_4-C_7 (ng/g dry wt.)	9.05	11.9	5.3	7.72	5.94	1.52
Total Carbon						
% C _O		2.75	1.45	2.66	1.85	

TABLE 7 .

C₁-C₇ Hydrocarbons - IPOD Leg 64

Sample No.	477-5-1-115-120	477-17-1-140-145	478-2-1-7-18	478-2-4-102-113	478-2-5-49-55	479-1-2-37-42
Sediment Depth	31 m	126 m	3.6 m	9 m	10 m	2 m
Lithology	Diatomaceous Ooze and Turbidites					
Age	Late Quaternary					Pleistocene
Hydrocarbons	Concentration in ng/g dry wt. sediment					
Methane	587	1719	7.29	1.86	19.9	477
Ethane	2.0	200	1.94	0.26	3.3	6.6
Propane	2.99	109	1.92	0.24	3.0	2.4
i-Butane	1.03	8.62				
n-Butane	1.11	17.4		0.26		
i-Pentane	4.34	2.50				
n-Pentane	1.36	2.38	0.01			0.01
Cyclopentane	0.77	1.64				
2,2-Dimethylbutane		0.15				
2,3-Dimethylbutane	0.2	0.15	0.66	0.37	1.42	0.77
2-Methylpentane	0.3	0.9	1.04	0.41	2.04	0.56
3-Methylpentane	0.1	0.53	0.22	0.83	0.25	
n-Hexane	0.35	0.94	0.94	0.67	1.21	0.23
Methylcyclopentane	0.40	1.12	0.2	0.5	0.1	
2,2-Dimethylpentane			0.2	0.1	0.1	
Benzene	} 1.72	} 11.0	0.2	0.28		
2,4-Dimethylpentane			0.2	0.19	0.1	
2,2,3-Trimethylbutane			0.49	1.63	0.64	0.09
Cyclohexane	0.08					

TABLE 7. (Cont.)

Sample No.	477-5-1-115-120	477-17-1-140-145	478-2-1-7-18	478-2-4-102-113	478-2-5-49-55	479-1-2-37-42
1,1-Dimethylcyclopentane	} 0.43	0.09	0.5		0.6	
2-Methylhexane		0.24				
2,3-Dimethylpentane	0.18					
3-Methylhexane		0.35				
1-Trans-3-Dimethyl- cyclopentane		0.15				
1-t-2-Dimethylcyclo- pentane		0.15				
3-Ethylpentane						
n-Heptane	0.06	0.44	1.0	0.5	1.2	0.2
Methylcyclohexane	0.28	0.24	0.2			
Toluene	0.38	1.1	4.7	8	0	2.2
ΣC_2+C_3 (ng/g dry wt.)	4.99	309	3.86	0.50	6.3	9.0
ΣC_4-C_7 (ng/g dry wt.)	13.1	50.1	10.6	13.7	7.7	4.1
Total Carbon						
% C _o	2.64	0.73	3.1		3.1	3.6

TABLE 8.

C₁-C₇ Hydrocarbons - IPOD Leg 64

Sample No.	479-3-1-67-74	479-5-5-8-23	479-6-1	P3-2-31-46	P10-2-45-55
Sediment Depth	13.2 m	37.6 m	41 m	6.6 m	44.7 m
Lithology	Diatomaceous Ooze				
Age	Pleistocene			Quaternary	
Hydrocarbons	Concentration in ng/g dry wt. sediment				
Methane	636	1240	1025	304	198
Ethane	1.38	6.2	11.9	0.96	0.16
Propane	1.76	4.6	12.2	1.07	0.55
i-Butane		1.3	2.37	0.52	
n-Butane		0.70	2.95	0.11	
i-Pentane		3.9	12.5		
n-Pentane		0.64	4.91		
Cyclopentane		2.22	1.0		
2,2-Dimethylbutane	1.1				
2,3-Dimethylbutane	0.34		1.42		
2-Methylpentane	0.38		1.53		
3-Methylpentane	0.17		0.2		
n-Hexane	0.34		0.79		0.25
Methylcyclopentane	0.13		0.18		0.29
2,2-Dimethylpentane			0.44		0.29
Benzene	} 0.97		} 0.60		} 0.07
2,4-Dimethylpentane					
2,2,3-Trimethylbutane	0.10		0.25		0.16
Cyclohexane			0.26		

TABLE 8. (Cont.)

Sample No.	479-3-1-67-74	479-5-5-8-23	479-6-1	P3-2-31-46	P10-2-45-55
1,1-Dimethylcyclopentane					
2-Methylhexane			0.16		
2,3-Dimethylpentane			0.3		
3-Methylhexane			0.2		
1-Trans-3-Dimethyl- cyclopentane	0.06				
1-t-2-Dimethylcyclo- pentane	0.19		0.25		
3-Ethylpentane			0.25		
n-Heptane	0.59		0.52		
Methylcyclohexane			0.26		
Toluene	5.7		0.97		2.4
ΣC_2+C_3 (ng/g dry wt.)	3.14	10.8	24.1	2.03	0.71
ΣC_4-C_7 (ng/g dry wt.)	10.1	nd	32.3	nd	3.5
Total Carbon					
% C _O	2.8	2.7		4.3	2.1

this were the case since the two holes are only 12 km apart.

Several alkanes did not show up in the gas chromatograms of the two piston cores (blank spaces in all of these tables mean that the hydrocarbon was not detectable). Other functional groups such as alkenes (olefins), aldehydes, alcohols, etc. were observed in the surface piston cores. This is typical of what we have seen in other areas such as Walvis Bay and the Persian Gulf. These unsaturated hydrocarbons and oxidized compounds are reduced to hydrocarbons as they are buried deeper.

This is an interesting area because it contains hydrocarbons thermally generated by high temperatures at relatively shallow depth, plus the hydrocarbons formed by low temperature reactions near the surface that we have observed in other areas. We plan to carry out some thermal distillation - pyrolysis studies on these samples in order to clarify the interpretations from these early headspace analysis results.

D. Gulf of Maine

The Woods Hole Oceanographic Institution R/V Knorr took gravity cores at several stations in the Gulf of Maine and on the outer continental shelf. C_1 - C_7 hydrocarbon analyses for these surface samples are shown in Tables 9 and 10. The sediments in this area are mainly brown to olive-gray clays with a hydrogen sulfide odor. Stations 2 through 8 and 14 are on the continental shelf while the others are on the outer continental margin in deep water.

These sediments are somewhat unique in having no aromatics, that is, no toluene or benzene. Toluene has been absent in very few areas, notably those containing well-oxygenated waters and little or no diatomaceous input. Other hydrocarbons absent in these cores include neopentane, cyclopentane, 2,2,3-trimethylbutane, 2-methylhexane, 2,3-dimethylpentane and some of the dimethylcyclopentanes. There were a number of alkenes present which are not listed in this table. This included 2-methyl-2-butene plus other hexenes, cyclohexene,

TABLE 9.

C₁-C₇ Hydrocarbons - Gulf of Maine

KNORR 69-1 Station No.	2		3		4		5		7		8	
Sediment Depth (cm)	0-1	25-28	0-4	25-29	0-2	26-29	0-1	26-30	0-2	14 ⁺	0-2	6-10
Water Depth (m)	260			238			265		225		260	
Hydrocarbons	Concentration in ng/g dry wt. sediment											
Methane					2.13		1.08		2.05		4.50	0.22
Ethane					0.91		0.92		0.37		1.28	0.06
Propane	0.96	0.55	0.47		2.16	0.12	1.66		0.77	0.18	1.71	0.22
i-Butane			Trace									
n-Butane	9.43	3.79	0.80	2.84	6.78	0.35	3.99	0.38	3.38	2.33	1.87	0.22
i-Pentane												
n-Pentane	1.08	Trace			2.82		1.12		0.54	0.12	1.09	
2,2-Dimethylbutane		0.18							0.34			
2,3-Dimethylbutane		1.28			1.78	0.51	0.86	0.17	1.03		1.99	0.35
2-Methylpentane		1.44			1.16	0.41	0.71	0.11	0.59			0.15
3-Methylpentane				0.42		0.13	0.44					
n-Hexane	1.5			0.62	2.48	0.57	2.14	0.27	0.83	0.27		0.13
Methylcyclopentane		0.26		0.24								
2,2-Dimethylpentane	1.4			0.07	0.16							0.13
2,4-Dimethylpentane	0.49			0.23	0.60	0.28	2.07	0.13	0.29			
Cyclohexane				0.09								

TABLE 9. (Cont.)

KNORR 69-1 Station No.	2		3		4		5		7		8	
Sediment Depth (cm)	0-1	25-28	0-4	25-29	0-2	26-29	0-1	26-30	0-2	14 ⁺	0-2	6-10
3,3-Dimethylpentane				0.04								
1,1-Dimethylcyclopentane				0.17								
3-Methylhexane	0.08											
1-Trans-3-Dimethyl- cyclopentane				0.10								
1-t-2-Dimethylcyclopentane	0.05											
3-Ethylpentane					0.53							
n-Heptane	0.09				1.22							
Methylcyclohexane												
ΣC_2+C_3 (ng/g dry wt.)	0.96	0.55	0.47	0	3.07	0.12	2.58	0	1.14	0.18	2.99	0.28
ΣC_4-C_7 (ng/g dry wt.)	14.1	6.9	1.8	4.8	17.5	2.2	11.3	1.06	6.71	2.72	4.95	0.98
Total Carbon	2.1	2.0	2.19	2.15	2.19	1.96	2.07	2.17	1.16	0.55	1.14	1.18
% C _O	1.86	2.0	2.15	2.0	1.73	1.59	1.56	1.64	0.94	0.55	0.85	0.94

TABLE 10.
C₁-C₇ Hydrocarbons - Gulf of Maine

KNORR 69-1 Station No.	10		11		13		14	
Sediment Depth (cm)	0-2	10-14	0-2	10-14	0-2	18-22	0-2	22-26
Water Depth (m)	4195		1000		871		< 200	
Hydrocarbons	Concentration in ng/g dry wt. sediment							
Methane								
Ethane	0.02						1.04	0.06
Propane	0.11	0.09	0.04		0.19		1.89	0.37
i-Butane							1.48	
n-Butane	0.26	1.05	0.20		0.48	1.22	6.21	0.35
i-Pentane							0.51	
n-Pentane	Trace		0.34		0.16		0.94	
2,2-Dimethylbutane							5.04	
2,3-Dimethylbutane			0.72		0.39			
2-Methylpentane			0.51		0.25			
3-Methylpentane			0.32		0.13			
n-Hexane			0.80		0.20	0.40		
Methylcyclopentane							3.07	0.21
2,2-Dimethylpentane					0.22			
2,4-Dimethylpentane			0.64					
Cyclohexane								

TABLE 10. (Cont.)

KNORR 69-1 Station No.	10		11		13		14	
Sediment Depth (cm)	0-2	10-14	0-2	10-14	0-2	18-22	0-2	22-26
3,3-Dimethylpentane							0.34	
1,1-Dimethylcyclopentane							1.2	
3-Methylhexane								
1-Trans-3-Dimethylcyclopentane								
1-t-2-Dimethylcyclopentane								
3-Ethylpentane								
n-Heptane					0.17		0.72	
Methylcyclohexane							0.28	
ΣC_2+C_3 (ng/g dry wt.)	0.13	0.09	0.04	0	0.19	0	2.93	0.43
ΣC_4-C_7 (ng/g dry wt.)	0.26	1.05	3.53	0	2.00	1.62	19.8	0.56
Total Carbon	4.65	1.92	5.60	2.84	1.62	1.52	2.72	2.82
% C _O	0.66	0.49	0.77	0.58	0.80	0.77	2.23	2.31

methylcyclopentene, and dimethylcyclopentenenes. The larger variety of alkenes observed is very similar to some earlier studies we made of immature sediments in the Persian Gulf - Arabian Sea area.

Alkane and cycloalkane concentrations are low and have the type of erratic distribution characteristic of very young immature sediments. The organic precursors in this area seem to form n-butane easily since it is present in higher concentrations overall than was observed in the other areas.

These preliminary data indicate that the Gulf of Maine hydrocarbons represent the very earliest stage of hydrocarbon formation directly from biological precursors by low temperature reactions. There is no evidence in any of these analyses of migration within the cores or seepage from deeper horizons.

E. Analytical Procedures and Developments

The thermal distillation-pyrolysis technique for C_7 to C_{14} hydrocarbons was described in DoE Report No. COO-4392-1. The headspace technique for analyzing C_1 to C_7 hydrocarbons is as follows.

Part of the frozen sediment is weighed into a #2 can which is equipped with two holes to which a silicone rubber septum has been glued with silicone rubber cement. The can is completely filled with water and sealed. A helium headspace is then made by injecting 150 ml of helium into the can and withdrawing 150 ml of water. The can is then allowed to stand overnight while the sediment thaws. The can is shaken vigorously for 3 minutes on a commercial paint shaker and then heated in a 90°C water bath for 30 minutes.

C_1 - C_5 hydrocarbon analysis is carried out on a dual-column gas chromatograph (GC) equipped with dual flame-ionization (FID) detectors used in the compensation mode. The columns used (Durand and Espitalie, 1971) are $1/8'' \times 6'$ spherosil (40-100 mesh) attached to a $1/8'' \times 12'$ 20% OV-101 on Anakrom AS (100/110 mesh) with the spherosil at the front end of the columns. The sample to be analyzed

(5-10 ml of gas) is first concentrated by injection into a 1/8" x 12" stainless steel loop packed with activated alumina as described by Swinnerton and Linnembom (1967). The loop is attached to the gas chromatograph via a Carle micro-volume switching valve. For C_1 - C_5 analysis, the loop is cooled in liquid nitrogen and the gas swept onto the loop with a helium stream. After the sample has been frozen in the loop, the loop is sealed via toggle valves and then heated for one minute in a 90-100°C water bath. The Carle valve is then switched to inject the contents of the loop into the carrier gas stream of the GC. GC analysis is carried out by programming the column from 60-200°C at 8°C/min. and by measuring peak areas with an electronic integrator.

Many other columns have been described in the literature for separation of light hydrocarbons, and several were tried in this work before this method was chosen for the following reasons. First, the analysis can be carried out at normal GC temperatures rather than in the more problematical cryogenic range. Secondly, this column gives good separation of ethylene, propylene and the butenes from the saturated C_1 - C_5 alkanes, an attribute not possessed by any other column we tried. However, we did not test all of the new polymeric GC supports after we found that this column met our separation requirements.

The third advantage of this column is that the separation of methane and ethane is good so that small amounts of ethane can be analyzed in the presence of larger amounts of methane, a common situation in sediment gas analyses. If the methane peak does become so big that small C_2 - C_5 peaks are "lost" in the methane tail, the sample is injected into the sample loop cooled in dry ice. The loop is then swept with helium before heating and turning the Carle valve. In this way, most of the methane is removed while higher hydrocarbons are retained.

C_4 - C_7 analysis is carried out on a 0.01" x 200' capillary column coated with hexadecane-hexadecane-kel F as described by Schwartz and Brasseaux (1963). This column was designed specifically to separate all of the saturated C_4 -

C₇ hydrocarbon isomers. A gas sample from the can headspace, 5-50 ml depending on levels of hydrocarbons shown by the packed column analysis, is injected into an empty 15" x 1/16" x 0.03 ID stainless steel loop immersed in a liquid nitrogen trap. The loop is attached to a Carle microvolume sampling valve. The Carle valve is then switched into the GC carrier gas line and the sample introduced, via the heating loop, into a one inch "U" made in the front of the capillary column. The capillary "U" is heated in a 90°C water bath so that the whole sample goes into the column as a "slug" without splitting. Amounts of each compound are measured with a computing integrator (Columbia Scientific Instruments Supergrator 3).

Even though a modification of this procedure has been used by oil companies in source rock studies, there is no published literature on its precision. We have tested the method on a standard mixture containing all of the saturated hydrocarbons for which we are analyzing. The standard is injected into the 150 ml helium headspace of a canned water sample and then analyzed as described above. The coefficient of variation for the standards is 5% for replicate samples over three orders of magnitude in the concentration range comparable to those found in sediments. Only in the most dilute standards, near to the detection limits of the methods, do corrections have to be made for sample recovery because of hydrocarbon solubility in water. Even in these very dilute standards, ratios of peak areas show very good precision, a coefficient of variation of 6%.

The standards prepared as described above are used in determining GC response factors so that any solubility or absorption effects inherent in the method are minimized. The quantitative limit of detection of the method is about 1 ng of each hydrocarbon in the GC sample.

The C₁₅₊ extraction involves placing 10 to 20 grams of dry, finely crushed sediment in a beaker with chloroform. The beaker is placed on a heater with a magnetic stirrer and heated for 1 hour at 50°C. The chloroform dissolves the adsorbed C₁₅₊ hydrocarbons from the rock. After cool-

ing, the chloroform solution is filtered, evaporated into dryness, and the quantity of extract is determined on a micro-balance. The method has been described in some detail by Monin et al. (1978).

The gas chromatography analyses are used to identify the individual hydrocarbons in the various molecular weight ranges. However, GC retention times alone cannot be used to positively identify peaks. We use GC-mass spectrometry to confirm peak identities and to identify minor constituents which are often buried under larger GC peaks. We have two Finnigan GC-mass spectrometer-computer systems in use at Woods Hole. The one we have used most often is the conventional electron impact instrument. The other can be used either in the electron impact mode or in the chemical ionization mode which is extremely useful in the analysis of complex mixtures of compounds.

As previously discussed, these analytical methods have good precision and are very useful in making quantitative comparisons on a relative basis. However, we have some evidence that the thermal distillation technique recovers more of the absorbed hydrocarbons in a rock and thereby gives better quantitative results on an absolute basis than the headspace method. What we would like to do is to develop an instrument that will give us the C_1 through C_{20} hydrocarbon range entirely by thermal distillation-gas chromatography. Development of such an instrument will take some time and yet in the long run it will enable much more quantitative evaluations to be made of the hydrocarbon potential of sedimentary basins. Accordingly, we are proposing for the coming year that we do research and development on such an instrument and also continue a modest research program with offshore samples using our existing technique. This is discussed in more detail in our proposal.

5. REFERENCES

- Durand, B. and J. Espitalie, 1972. Formation et evolution des hydrocarbures de C, a C_{15} et des gaz permanents dans les argiles du Toarcien du Bassin de Paris. In: *Advances in Organic Geochemistry*, Ed. H. R. von Gaertner and H. Wehner, 455-468, Pergamon Press, Oxford.

- Espitalie, J., M. Madec and B. Tissot, 1978. Interaction of mineral matrix with organic matter during pyrolysis, presented at the joint annual meeting of the Geological Association of Canada and the Geological Society of America, October 23-26, 1978 in Toronto, Canada.
- Hunt, J. M. and J. K. Whelan, 1978. Dissolved gases in Black Sea sediments. Initial Reports DSDP, 42B: 661-665.
- Momper, J., 1978. Oil migration limitations: In: Physical and Chemical Constraints on Petroleum Migration. AAPG Short Course, Oklahoma City, Oklahoma.
- Morin, J. C., R. Pelet and A. Fevrier, 1978. Analyse geochemique de la matiere organique extraite du roches sedimentaires, IV. Extraction du roches en faibles quantites. Rev. Inst. Francais Petrole, 33: 223-240.
- Schwartz, R. D. and D. J. Brasseaux, 1963. Resolution of complex hydrocarbon mixtures by capillary gas liquid chromatography. Analytical Chemistry, 35: 1374-1382.
- Swinerton, J. W. and V. J. Linnenbom, 1967. Determination of C_1 to C_4 hydrocarbons in seawater by gas chromatography. Jour. Gas Chrom., 5: 570-573.