# 26. GEOCHEMISTRY OF CARBON: DEEP SEA DRILLING PROJECT LEG 43

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## INTRODUCTION

Six frozen core sections were obtained through the JOIDES Organic Geochemistry Panel, and one unfrozen organic-carbon-rich section was received via Northern Louisiana State University. These samples for organic geochemical study were from Leg 43, Site 386, on the Central Bermuda Rise, 140 km south-southeast of Bermuda (Figure 1). The core sections were described and then analyzed for organic carbon content. The terrestrial or marine origin of the sedimentary organic matter and its degree of diagenesis were then investigated.

## SAMPLING AND PROCEDURES

The six cores were frozen in dry ice on shipboard and kept frozen until initiation of the organic analysis. As discussed in the Initial Reports for Leg 38 (Erdman and Schorno, 1976) all cores received by our laboratory are inspected for possible drilling disturbance and are photographed while still frozen. These particular cores were friable and were received badly fragmented. Thus, the procedure used to determine drilling disturbance, that is, visual inspection of each half section of core was not possible; however, the portions used for analysis appeared to be homogeneous. Black and white photographs of each section and lithological descriptions are given in Figures 2 through 7. The samples, freed of contaminants to the extent feasible, were freeze-dried and characterized according to the scheme shown in Figure 8.

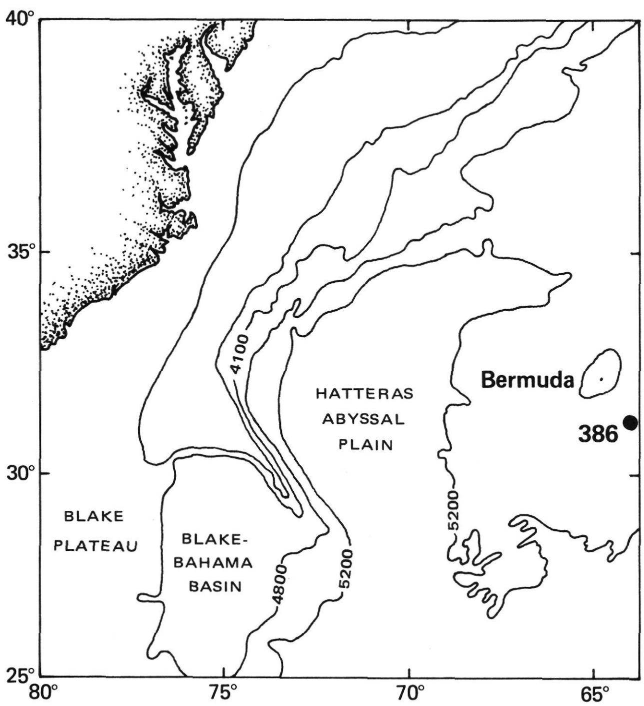



Figure 1. *Location of hole from which samples were obtained for geochemical study.*

## RESULTS

The organic and inorganic compositional data obtained from the homogenized core, along with subbottom depth and age, are given in Table 1. Table 2 contains the results of the organic analyses of the lipid. For some samples this fraction was very small. In such cases priority was given to determination of the isotopic composition of the total lipid, then the subfractions; that is, the saturates, aromatics, and asphaltics; then their carbon isotopic compositions (excluding the saturates); and finally, the *n*-alkane distribution. The *n*-alkane distributions for five of the seven samples are given in Figures 9, 10, and 11.

All the samples are from Cretaceous sediments. The six frozen core sections are upper Aptian-lower Albian to upper Albian, and span the depth interval from 937.2 to 857.8 meters. The unfrozen section is from the Cenomanian at 740.6 meters. All seven samples are predominantly gray to black mudstones or shales. Small fragments of fish bone were observed in several cores.

The organic carbon content in these cores is relatively high for DSDP samples. The lowermost upper Aptian-lower Albian sample contains 6.1 percent. The

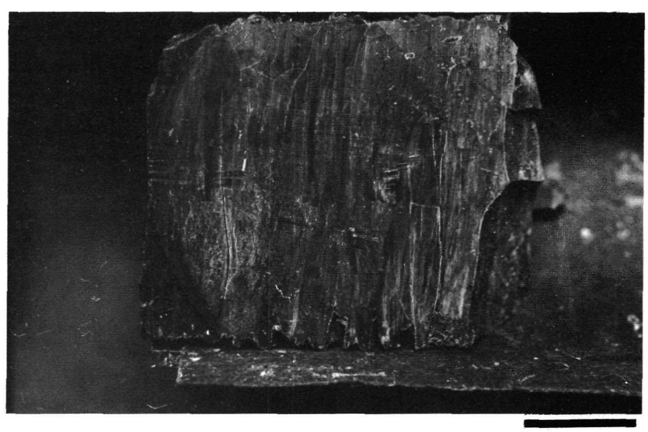



Figure 2. *Section 386-54-5. Shale, dark gray (N3), fissile, micaceous on parting surfaces (subconchoidal).*

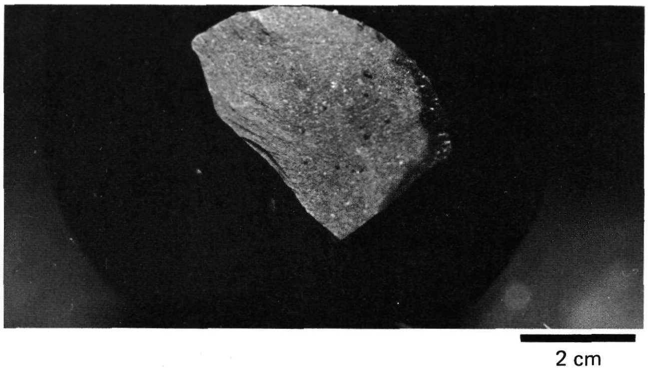



Figure 3. *Section 386-56-3. Mudstone, calcareous, grayish black (N2). Contains brown skeletal debris (bones or siliceous spines) and soft white blebs of clay or carbonate up to 1 mm diameter. Scattered quartz grains (subrounded) to 200 μm. Occasional 500-100 μm pyrite.*

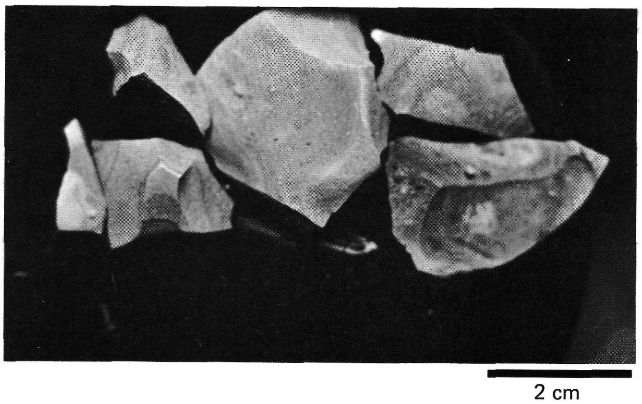



Figure 4. *Section 386-57-3. Mudstone dark gray (N3). Conchoidal fracture. Scattered brown siliceous or bony skeletal debris (spines, flattened plates up to 1 mm).*

concentration then decreases to 0.89 percent in the upper Albian. The Cenomanian sample contains 9.5 percent. The content of carbon as carbonate varies within the depth interval studied from a low of less than 0.1 percent to a high of 4.4 percent (0.8 to 37 percent as calcium carbonate) with no apparent trends with depth.

The amount of the organic carbon present as lipid varies from 0.56 percent in the middle Albian to 9.6 percent in the upper Albian. The average value for all unconsolidated DSDP samples studied in this laboratory is 2.0 percent. For those samples with a total organic carbon content in excess of 1 percent, the average content of lipid is somewhat higher (3.0 percent). Expressed in terms of dry weight of sediment, the lipid fraction is 0.064 percent in the upper Aptian-lower Albian, decreases to 0.005 percent in upper Albian, and then increases to a high value of 0.49 percent in the Cenomanian.

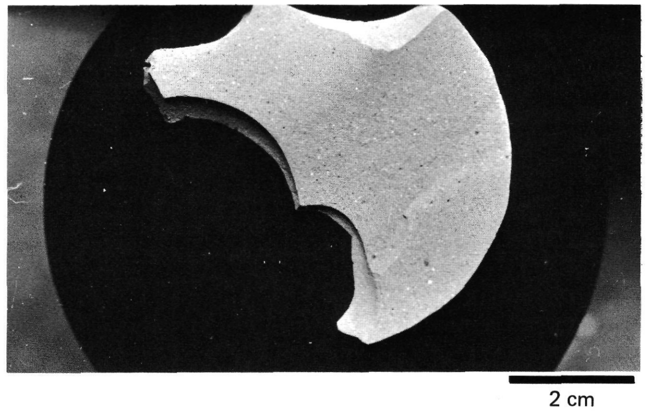



Figure 5. *Section 386-58-5. Mudstone, slightly calcareous, grayish black (N2). Subconchoidal fracture. White calcareous angular shell fragment 5 mm across.*

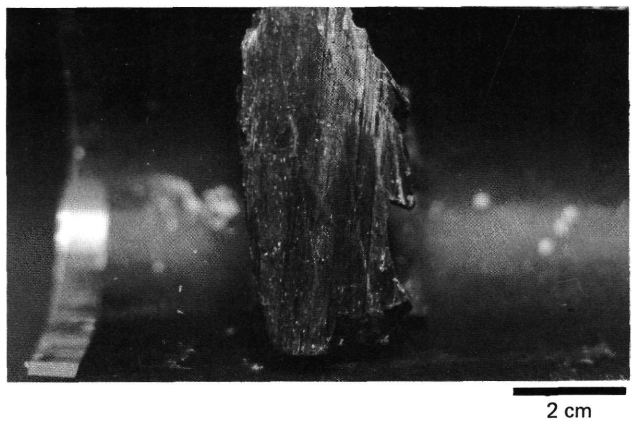



Figure 6. *Section 386-60-5. Shale, grayish black (N2). Fissile. Interbeds 2-5 mm thick of slightly calcareous, more tightly cemented shale. Scattered brown skeletal debris. 1 mm blebs of lighter clay scattered throughout.*

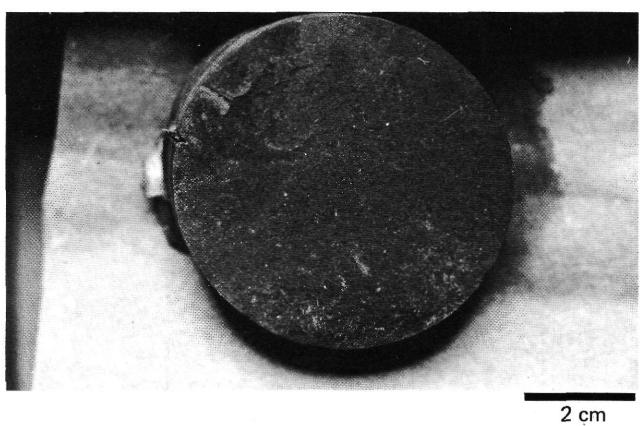



Figure 7. *Section 386-63-1. Shale, silty, grayish black (N2). Fish vertebrae to 5 mm diameter, smaller bones. Abundant blebs of pale green clay. Fissile.*

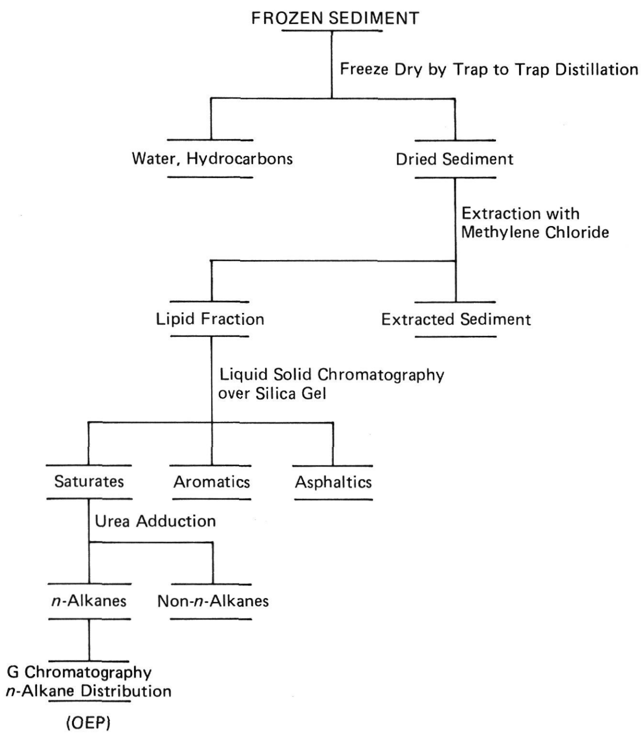



Figure 8. *Flow sheet for the separation and characterization of organic matter from DSDP cores from Leg 43.*

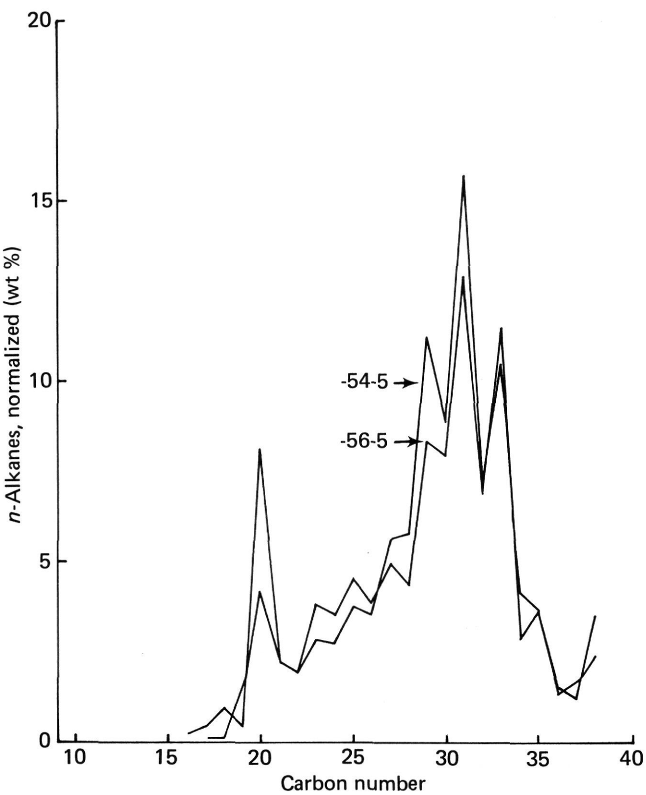



Figure 9. *Plots of normalized* n-*alkane composition versus carbon number for the upper and middle Albian Sections 386-54-5 and 386-56-3.*

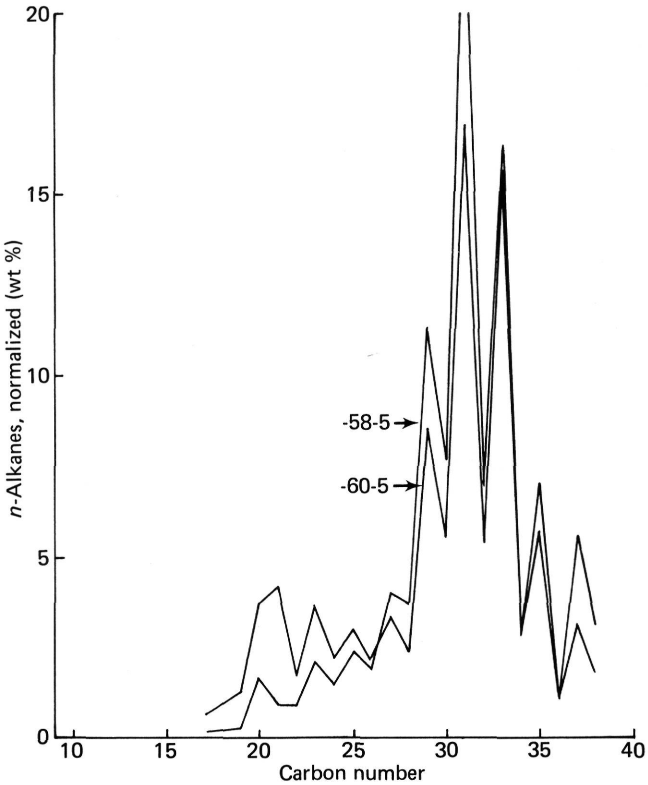



Figure 10. *Plots of normalized* n-*alkane composition versus carbon number for the middle Albian and upper Aptian-lower Albian Sections 386-58-5 and 386-60-5.*

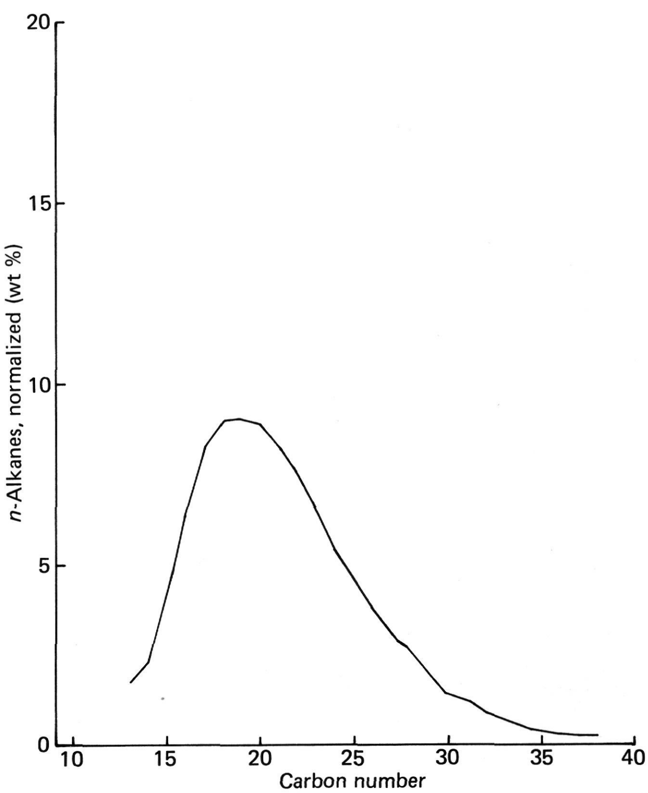



Figure 11. *Plot of the normalized* n-*alkane composition versus carbon number for the Cenomanian shale Section 386-43-3.*

**TABLE 1**
**Geochemical Characterization Data for Samples From DSDP Leg 43 for Total Homogenized Sediment**

| Site-Core-Section | Geologic Age | Sub-Bottom Depth (m) | Carbonate: Carbon (wt. %) | Carbonate: $CaCO_3$ (wt. %) | Organic Carbon: Total (wt. %) | Organic Carbon: Lipid (wt. %) | Nitrogen: Inorganic[a] (ppm) | Nitrogen: Organic[b] (ppm) | Kerogen Carbon: $\delta C^{13}$ PDB |
|---|---|---|---|---|---|---|---|---|---|
| 386-43-3[c] | Cenomanian | 740.6 | <0.10 | <0.83 | 9.50[c] | 0.485 | 34 | 2866 | -24.8 |
| 386-54-5 | Upper Albian | 857.8-857.9 | 0.45 | 3.75 | 0.89 | 0.005 | 200 | 100 | -24.6 |
| 386-56-3 | Upper Albian | 873.6-873.7 | 2.62 | 21.83 | 1.34 | 0.015 | 64 | 436 | -25.8 |
| 386-57-3 | Middle Albian | 883.2-883.3 | 0.34 | 2.83 | 0.89 | 0.005 | 73 | 227 | -25.2 |
| 386-58-5 | Middle Albian | 895.7-895.8 | 4.44 | 37.00 | 1.44 | 0.013 | 78 | 422 | -24.2 |
| 386-60-5 | Upper Aptian-lower Albian | 914.5-914.6 | 2.65 | 22.08 | 1.80 | 0.053 | 97 | 103 | -29.2 |
| 386-63-1 | Upper Aptian-lower Albian | 937.1-937.2 | 0.10 | .83 | 6.09 | 0.064 | 92 | 2608 | -29.2 |

[a]As determined by the half-Kjeldahl which is representative of ammonium nitrogen only.
[b]As determined by the full-minus the half-Kjeldahl.
[c]Samples obtained from Palmer. This value differs from Palmer's (7.69 percent). The difference can be attributed to either a different portion of the same sample or the method used for the analysis.

**TABLE 2**
**Geochemical Characterization Data for Samples From DSDP Leg 43 for Lipid Fraction**

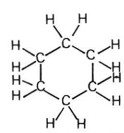
| Site-Core-Section | Lipid/Total Organic C (wt. %) | Total Lipid, Elemental Composition: C | H | N | S | O | H/C | N/C | S/C | Total Lipid: $\delta C^{13}$ PDB | Lipid Fractions: Saturate (wt. %) | Aromatic (wt. %) | Aromatic $\delta C^{13}$ PDB | Asphaltic (wt. %) | Asphaltic $\delta C^{13}$ PDB | OEP |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 386-43-3 | 5.11 | 73.53 | 9.49 | 2.12 | 3.36 | 11.50 | 1.54 | 0.15 | 0.02 | -25.9 | 19.7 | 16.5 | -29.0 | 63.7 | -25.4 | 1.0 |
| 386-54-5 | 9.56 | | | | | | | | | -29.4 | 9.5 | 31.2 | -32.3 | 47.4 | -29.1 | 1.6 |
| 386-56-3 | 1.12 | | | | | | | | | -28.6 | .14.9 | 28.9 | -29.6 | 46.8 | -28.8 | 1.5 |
| 386-57-3 | 0.56 | | | | | | | | | -30.4 | | | | | | |
| 386-58-5 | 0.90 | | | | | | | | | -29.4 | 15.8 | 36.6 | -30.5 | 39.2 | -29.0 | 2.3 |
| 386-60-5 | 2.94 | 77.04 | 10.07 | 0.90 | 7.37 | 4.62 | 1.57 | 0.010 | 0.03 | -31.1 | 13.2 | 38.4 | -30.7 | 41.7 | -30.0 | 2.4 |
| 386-63-1 | 1.05 | 82.48 | 10.92 | 0.83 | 1.57 | 4.20 | 1.59 | 0.009 | 0.001 | -29.3 | 12.0 | 37.4 | -30.4 | 34.6 | -29.3 | a |

The carbon isotopic composition of the lipid fraction indicates the source of the organic matter in the Aptian-Albian samples to be predominantly terrestrial. The contribution from the marine environment was greater in the Cenomanian.

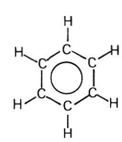
In all cases, the difference between the carbon isotopic compositions of the lipid and kerogen carbon are negative. L-K for core samples -43-3, 60-5, and -63-1 are less than 1. Whereas, the remaining samples are substantially higher, greater than 3.

The chemical composition of the lipid fraction does not vary greatly. For the upper Aptian-lower Albian, middle Albian, and upper Albian samples, the saturates, aromatics, and asphaltic fractions averaged 13 ±7, 35 ±6, and 42 ±7 per cent, respectively. The Cenomanian sample was low in aromatics and high in asphaltics (16.5 and 63.7 percent, respectively).

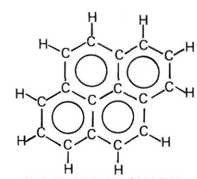
Variations in the proportion of the lipid fraction is reflected in the atomic ratios of hydrogen to carbon for the total lipid fraction. For the two upper Aptian-lower the Cenomanian. Cyclohexane, benzene, and con- Albian samples the ratio is 1.58 ±0.01 versus 1.54 for densed aromatics are indicative of the range of values for this ratio:




CYCLOHEXANE
H/C=2




BENZENE
H/C=1




CONDENSED AROMATIC
H/C=<1

The *n*-alkane distributions are similar for the Aptian and Albian samples, but for the Cenomanian sample differs markedly. The distributions in Figures 9 and 10 for Sections 60-5, 58-5, 56-3, and 54-5, show a predominance of *n*-alkanes at carbon numbers 29, 31, and 33. The average value of the odd-to-even predominance from carbon number 23 through 33, as given by the $\overline{OEP}$ value (Scalen and Smith, 1970), is 2.35 ±0.05 for the upper Aptian-lower Albian samples to middle Albian and 1.55 ±0.05 for the upper Albian samples. The value for the Cenomanian sample is 1.00, indicating a lack of odd-over-even predominance.

The total ammonium nitrogen as determined by the half-Kjeldahl ranges from 34 to 200 ppm with no apparent trends with either depth or organic-carbon content. The organic nitrogen as determined by the full-minus half-Kjeldahl, on the other hand, varies with the organic-carbon content from a low of 100 ppm to a high of 2866 ppm.

## DISCUSSION

The six upper Aptian-lower Albian to upper Albian and the Cenomanian samples studied encompass a depth interval of 740.6 to 937.2 meters. The lithology is relatively constant and consists of grayish black to dark gray organic-carbon-rich claystones or shales with varying amounts of carbonates. The sediments at Site 386 are similar to the reported Cretaceous black and green carbonaceous clays and shales from the northern end of the Hatteras Abyssal plain at Sites 101 and 105 of Leg 11. The upper limit of the carbon-rich zone from Site 105 is Cenomanian and is believed to correspond to Horizon A* (Lancelot et al., 1972). In respect to the properties which can be compared, the lipid fraction of the Cenomanian sample from Site 386 correlates with the Cenomanian from Site 105 (Simoneit et al., 1972).

On the basis of the lipid fraction, the upper Aptian-lower Albian to upper Albian received more terrestrially derived organic matter than did the Cenomanian. This finding is consistent with the concept that during the Aptian and Albian the continents were relatively close together and the marine basin forming between them was receiving a considerable contribution of organic matter from the adjacent land masses. During the Cenomanian the marine basin was more developed and the contribution of organic matter was less.

Average odd-even predominance ($\overline{OEP}$ values, shown in Table 2) increases with depth and age. It is generally accepted that $\overline{OEP}$ declines toward unity with advancing diagenesis. The normal sequence would have been a decrease with depth. In this case just the opposite is true, suggesting either migration of mature oil into this unit, contamination from a refined petroleum product, a high temperature at this depth at some time, or an unusual type of sedimentary organic matter that contained a low initial $\overline{OEP}$ value. The ratio of lipid to total organic carbon for the Cenomanian section is higher than in the lower units by a factor of two to nine, indicating that oil had migrated into this unit. The actual value of 5.1 percent is only slightly larger than the 1 to 3 percent encountered for most oceanic sediments in an early stage of genesis. However, it is not so large as to distinguish between migration, contamination, an advanced stage of petroleum genesis in an unconsolidated rock, or admixture of all three sources of organic matter with indigenous lipid from an early stage of genesis. The presence of both petroporphyrins and porphyrins from an early stage of diagenesis as reported by Palmer et al. (this volume) eliminates all but the migration or contamination source.

## CONCLUSIONS

The upper Aptian-lower Albian through Cenomanian samples studied are exceptionally rich in organic matter. The relatively low lipid to total organic carbon ratios and the high $\overline{OEP}$ values suggest that conversion to petroleum is either in an early stage, or the organic matter has been sufficiently oxidized during or immediately following deposition as to limit or preclude formation of petroleum. The younger Cenomanian sample is anomalous in that it appears to contain lipids or oils representing at least two stages of genesis. Whether one of these oils has migrated into the rock or represents man-made contamination remains to be determined.

## ACKNOWLEDGMENTS

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