# 25. ORGANIC GEOCHEMISTRY OF THE SHALES FROM THE NORTHWESTERN PROTO-ATLANTIC, DSDP LEG 43[1]

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## ABSTRACT

The lipids extracted from Cretaceous samples in the western North Atlantic Ocean (Sites 386 and 387) and Angola Basin (Site 364) were examined for terrigenous components. The distribution patterns of the *n*-alkanes and *n*-fatty acids indicate a mixed autochthonous marine and allochthonous terrigenous origin for the lipids. Minor amounts of diterpenoids are present as a result of a resinous plant component. Sterenes and predominantly 17$\beta$(H)-hopanes constitute the polycyclic molecular markers, and indicate that these sediments are very immature.

The kerogens and humic substances were examined for stable carbon isotope contents. The $\delta^{13}C$ values for the samples from Site 386 are in the range typical for a terrigenous and/or lacustrine origin, while the values for the other samples suggest a more marine origin. The presence of humic substances is a further indication of immaturity.

## INTRODUCTION

Cretaceous black shales have been encountered in the Atlantic Ocean in drill cores from various areas. Some of these areas were anoxic basins with high sedimentation rates and large components of terrigenous organic matter (e.g., Leg 14—Simoneit et al., 1973; Leg 40—Simoneit, 1978; Leg 41—Simoneit, 1978b; and Leg 44—Stuermer and Simoneit, 1978). It was therefore of interest to determine if in the case of the northwestern Atlantic Ocean sediments analysis of the lipid matter would allow a distinction to be made between autochthonous marine and allochthonous terrigenous lipids. In addition, a comparison of the results with similar data from other areas of the Atlantic Ocean was carried out to infer paleoenvironmental conditions of sedimentation.

The samples examined here were obtained from Sites 43-386 (31°11.2′N, 64°14.9′W; 4783 m water depth) and 43-387 (32°19.2′N, 67°40.0′W; 5118 m water depth), located on the central and western Bermuda Rise, respectively (Tucholke et al., 1975). For comparison, further data for a sample from Site 40-364, located on the continental margin of the eastern Angola Basin (11°34.4′S, 11°58.3′E; 2448 m water depth) are also presented. Angola Basin was a sink for terrigenous material during various times of its evolution; it was, however, not necessarily anoxic (Bolli et al., 1975). At both Sites 386 and 387, anoxic basin conditions prevailed during much of the Cretaceous accompanied by a high rate of input of allochthonous organic detritus (Tucholke et al., 1975).

## EXPERIMENTAL

The core samples were freeze-dried and then extracted with toluene and methanol (3:7) in a Soxhlet apparatus (300 cycles of solvent change). The extracts for each sample were concentrated on a rotary evaporator and subjected to gas chromatographic analysis (GC). The extracts were then treated with $BF_3$ in methanol to esterify free acids and subjected to silica gel thin-layer chromatography (TLC) using methylene chloride as eluent. The bands corresponding to hydrocarbons, esters, ketones, and alcohols were scraped off the TLC plate after development iodine vapor, and eluted with ether or ethyl acetate. These fractions were subjected to GC and GC/MS analyses. The alcohol fractions were derivatized to either the acetates or TMSi ethers prior to analysis.

The GC analyses were carried out on a Hewlett-Packard Model 5830 gas chromatograph using a 16-m by 0.75-mm stainless steel SCOT column coated with OV-101, programmed from 110° to 280°C at 4°C per minute using He carrier gas at a flow rate of 3 ml/min.

The GC/MS analyses were carried out on a DuPont Model 21-492-1 mass spectrometer interfaced directly with a Varian Aerograph Model 204 gas chromatograph equipped with a 10-m by 0.75-mm glass column which was packed with Gaschrom Q (80-100 mesh) coated with 1 per cent OV-1. The mass spectrometric data were acquired and processed using a DuPont Model 21-094 data system.

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The stable isotope analyses were carried out by the methods described by Kaplan et al. (1970), using Chicago PDB as reference standard.

## RESULTS AND DISCUSSION

Sample descriptions, carbon analyses, lipid yields, and other results are given in Table 1.

The samples that were examined from the Northeastern Atlantic consist of Cretaceous black claystone. The content of organic carbon ranges from 1 to 9 per cent and lipid yields are low. The Cretaceous sample from the Angola Basin consists of sapropelic mudstone with chalk. Organic carbon content is 10.3 per cent and the lipid yield is low. The distribution diagrams for *n*-alkanes and *n*-fatty acids are shown in Figure 1. These distributions reflect various marine sources for the lipids, with an influx of allochthonous higher plant lipids. The ratio of pristane to phytane (Pr/Ph) of $\leq 1$ (cf. Table 1) indicates euxinic depositional conditions (Didyk et al., in press) for all the analyzed sediments. The *n*-alkanes of Sample 386-43-3 (138-141 cm) exhibit a distribution with maxima at *n*-$C_{17}$ and *n*-$C_{27}$ and a strong odd-to-even carbon number predominance $>$ *n*-$C_{23}$. The homologs $>$ *n*-$C_{23}$ can be attributed to an origin from higher plant wax (Simoneit, 1975, in press), and the homologs $<$ *n*-$C_{23}$ are derived from probably autochthonous marine sources (Simoneit, 1975). The *n*-fatty acids for this sample exhibit a distribution with maxima at *n*-$C_{18}$ and *n*-$C_{24}$ and an even-to-odd carbon number predominance. The maximum at *n*-$C_{18}$ (i.e., homologs $<$ *n*-$C_{20}$) appears to be of autochthonous marine origin. The homolog distribution $>$ *n*-$C_{22}$, when considered in conjunction with the *n*-alkane distribution, is further evidence for an input of higher plant lipids (Simoneit, 1975; Hitchcock and Nichols, 1971). Dehydroabietic acid (Structure I) is present as a minor component, indicating some input from resinous higher plants (Simoneit, 1977). The *n*-alkanes from Sample 386-63-1 (142-144 cm) exhibit a maximum at *n*-$C_{23}$ with essentially no carbon number predominance; a branched/cyclic hump which also maximizes at $C_{23}$ is also present. Such a distribution may be attributable mainly to a biodegraded algal residue (Hatcher et al., 1977). There is a significant component of homologs $>$ *n*-$C_{24}$, with a maximum at *n*-$C_{31}$ owing to higher plant wax. Phytane is the most abundant hydrocarbon and Pr/Ph is 0.46. This, coupled with the high content of organic carbon, indicates strongly euxinic paleoenvironmental conditions, where primary productivity and influx of allochthonous material were high (Didyk et al., in press). The *n*-fatty acids exhibit a bimodal distribution maximizing at *n*-$C_{16}$ and *n*-$C_{24}$ with a strong even-to-odd carbon number predominance. The homologs $<$ *n*-$C_{20}$ are of a marine autochthonous origin, and the homologs $>$ *n*-$C_{20}$ are of an allochthonous higher plant origin. Dehydroabietic acid (Structure I) is present as a prominent component, indicating a contribution from resinous higher plants (Simoneit, 1977a).

The *n*-alkane distribution for Sample 387-36-2 (145-150 cm) exhibits maxima at *n*-$C_{22}$ and to a lesser extent at *n*-$C_{31}$; *n*-$C_{1}$- and *n*-$C_{26}$ also are conspicuous. The first maximum exhibits essentially no carbon number predominance (CPI to $C_{25}$ = 1.05) and a branched/cyclic hump is also present which maximizes at the GC retention time of *n*-$C_{23}$. This distribution maximum is typical of a biodegraded algal residue (Hatcher et al., 1977). The second, minor maximum exhibits a strong odd-to-even carbon number predominance (CPI $C_{27}$ to $C_{35}$ = 5.4, overall CPI $C_{12}$ to $C_{35}$ = 1.1) and is typical of higher plant wax. The *n*-fatty acids of this sample have a strong even-to-odd carbon number predominance and a major maximum at *n*-$C_{16}$ with minor even homologs extending to *n*-$C_{30}$. A minor amount of dehydroabietic acid is present. The lipids of this sample appear to be primarily of an autochthonous marine origin with only a minor component of higher plant detritus. The environment of deposition for this sample was probably on the borderline of being euxinic (Didyk et al., in press).

The lipid distributions for Sample 40-364-24-1 (0-10 cm) differ somewhat from those of the Leg 43 sam-

**TABLE 1**
**Sample Descriptions, Carbon Analyses, Extract Yields, and Carbon Isotope Values for the Core Samples Examined**

| Sample (Interval in cm) | Depth Below Sea Bed (m) | Lithology | Geologic Age | Carbon[a] | | | $\delta^{13}C$[b] (‰) | Pr/Ph (hydrocarbons) | Perylene[c] (presence) | Lipid Yields | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | *n*-alkanes | | *n*-fatty acids | | *n*-methylketones | |
| | | | | Total (%) | Organic (%) | Carbonate (%)[a] | | | | µg/g | CPI | µg/g | CPI | µg/g (+ iso-prenoid) | CPI |
| 40-364-24-1, 0-10 | 672.5 | Marly chalk mudstone with sapropel | Cretaceous (Turonian) | 11.5 | 10.3 | 10 | -24.2 (-21.8) [-22.3] | 0.5 | + | 5.2 | 1.8 | 5.3 | 2.3 | 0.15 | 1.4 |
| 43-386-43-3, 138-141 | 740.7 | Black claystone | Cretaceous (Cenomanian) | 8.9 | 8.9 | 0 | -25.2 (-23.9) | 0.96 | tr.[d] | 7.9 | 1.5 | 11 | 1.96 | 3.5 | 0.8 |
| 43-386-63-1, 142-144 | 937.2 | Black claystone | Cretaceous (Aptian) | 4.1 | 3.3 | 7 | -28.9 (-26.0) | 0.46 | +++ | 5.0 | 1.7 | 5 | 3.9 | 2 | 1.3 |
| 43-387-36-2 145-150 | 558.3 | Black claystone | Cretaceous (Barremian or Hauterivian) | 1.0 | 1.0 | 0 | (-19.2) | 0.97 | tr. | 2.4 | 1.1 | 0.6 | 10.8 | 0.08 | 4.3 |
| 43-387-37-2, 142-146 | 577.3 | Black claystone | Cretaceous (Barremian or Hauterivian) | 3.9 | 3.85 | 0.3 | (-26.6) | n.d.[d] | n.d. | n.d. | – | n.d. | – | n.d. | – |

[a]Data supplied by G. Bode, Deep Sea Drilling Project, Scripps Institution of Oceanography, University of California at San Diego.
[b]Versus PDB standard, determined on total extracted lipids (numbers in parentheses determined for kerogen and in brackets for humic substances).
[c]Determined by UV-visible spectrophotometry.
[d]n.d. = not determined; tr. = trace.

ples; however, their sources appear to be the same. The *n*-alkanes exhibit a complex distribution with maxima at *n*-$C_{15}$, *n*-$C_{23}$, and *n*-$C_{29}$ and an odd-to-even carbon number predominance (CPI overall = 1.8). Again, the homologs $<$ *n*-$C_{20}$ are probably attributable to a marine authochthonous origin and those $>$ *n*-$C_{20}$ are of higher plant derivation. Phytane is the most abundant hydrocarbon and the pristane/phytane ratio (Pr/Ph) is 0.5. This indicates strongly anoxic conditions in an environment of high organic productivity. The *n*-fatty acids exhibit a bimodal distribution, with maxima at *n*-$C_{16}$ and *n*-$C_{24}$ and a strong even-to-odd carbon number predominance. A minor amount of dehydroabietic acid (Structure I) is present, indicating some influx from resinous higher plants. The *n*-fatty acids $<$ *n*-$C_{20}$ are of an autochthonous marine origin and the homologs $>$ *n*-$C_{20}$, when coupled with the *n*-alkane distribution from $C_{20}$ to $C_{33}$, appear to be of higher plant origin.

The distributions of the *n*-methylketones and 6,10,-14-trimethylpentadecan-2-one (Structure II) for these samples are found in Figure 1i-1. The normal series, $C_nH_{2n}O$, ranges from about $n$ = 12 to 27, with a maximum mainly at $C_{17}$. These *n*-methylketones are probably derived from *n*-fatty acids by microbial $\beta$-oxidation or by microbial oxidation of *n*-alkanes (Arpino, 1973). These ketone distributions do not reflect a terrigenous origin as was the case for samples from the Black Sea (Simoneit, 1978b). The analyses of the alcohol fractions have not been completed.

The steroidal and triterpenoidal compounds that have been identified in these sections are listed in Table 2. Steranes, $C_nH_{2n-6}$, ranging from $n$ = 27 to 29 are present in Samples 386-63-1 and 364-24-1 as significant components and in the other two samples as traces. Ster-4-enes, $C_nH_{2n-8}$ (Structure III), ranging from $n$ = 27 to 29 have been identified in Samples 386-43-3 and 364-24-1. The mass spectrum of cholest-4-ene from sample 364-24-1 is shown in Figure 2a. Only traces of these compounds are present in Samples 386-63-1. Backbone rearranged sterenes, first described in sediments by Rubinstein et al. (1975), are found in Samples 386-43-3, 386-63-1, and 364-24-1. The 5$\beta$,14$\beta$-dimethyl-18,19-dinor-8$\alpha$,9$\beta$,10$\alpha$-ster-13(17)-enes, $C_nH_{2n-8}$ (Structure IV), range from $n$ = 27 to 29; the mass spectra of the three homologs from Sample 364-24-1 (0-10 cm) are shown in Figure 2b-d.

The triterpenoidal compounds of these samples consist predominantly of hydrocarbons and acids, with only traces of ketones (cf. Table 2). Trisnorhopane (Structure V), norhopane (Structure VI), hopane (Structure VIII), probably moretane, and extended hopanes (Structure IX), with the 17$\beta$(H) stereochemistry in all cases, are present in Samples 386-43-3, 386-63-1, and 364-24-1. Hop-17(21)-ene (Structure X) is also present as a significant component in these three samples. Sample 387-36-2 (145-150 cm) contains predominantly the 17$\alpha$(H) isomers of trisnorhopane, norhopane, and hopane, with lesser amounts of probably 17$\beta$(H)-normoretane (Structure VII) and 17$\beta$(H)-hopane. No extended hopanes could be detected in this sample. All samples contain triterpenoidal acids, $C_nH_{2n-10}O_2$, ranging from $n$ = 31 to about 35, with $n$ = 32 as maximum. The series has the 17$\beta$(H) stereochemistry (Structure XI) in all cases. The virtual absence of the 17$\alpha$(H) stereoisomers from the samples, excepting 387-36-2, indicates that these Cretaceous sediments are extremely immature. The appearance of the 17$\alpha$(H) stereochemistry, which is thermodynamically more stable with greater depth of burial, has been used as a gage of geologic age and petrogenic maturity of organic matter (Dastillung and Albrecht, 1976).

Sample 364-24-1 (0-10 cm) contains two aromatized triterpenoids which have not been previously identified in DSDP samples, but were characterized in Messel shale and confirmed by synthesis (Spyckerelle, 1975). The mass spectrum of the lower homolog is shown in Figure 2e; the fragmentation pattern is identical to that of standard 8,14,18-trisnormethyladianta-8,11,13,15,17-pentaene [(3′-ethylcyclopenteno-7,8)1,-1,15-trimethyloctahydro(1,2,3,4,5,6,7,8)chrysene—Structure XII]. The higher homolog, $C_{27}H_{36}$, has an additional methyl group either in the A or B ring (Structure XIII). The less aromatized analog 14,18-bisnormethyladianta-13,15,17-triene, $C_{27}H_{40}$, has been identified in Sample 41-367-19-4, 10-15 cm (Simoneit, 1978).

Other compounds that have been identified consist of diterpenoid and isoprenoid hydrocarbons, perylene, and minor contaminants. Sample 386-63-1, 142-144 cm contains dehydroabietin (Structure XIV), simonellite (Structure XV) and retene (Structure XVI), and probably minor amounts of fichtelite (Structure XVII), iosene (dihydrokaurene, Structure XVIII), and 15-normethylpodocarpane (Structure XIX). Retene is present in minor amounts in Sections 387-36-2 and 364-24-1; the latter also contains simonellite. These hydrocarbons are diagenetic products of diterpenoids from resinous higher plants (Simoneit, 1977), as in the case for the dehydroabietic acid in the fatty acid fractions. Phytane and pristane are present in all four samples and farnesane (2,6,10-trimethyldodecane) was identified in Sections 364-43-3 and 364-24-1.

Perylene (Structure XX) is present as a major component in Section 386-63-1, a minor component in Section 364-24-1, and in trace amounts in Sections 386-43-3 and 387-36-2 (cf. Table 1). Perylene may be a marker for terrigenous material (Aizenshtat, 1973), since it has been encountered mainly in sediments with lipids of predominantly such an origin (Simoneit, 1975, 1978b).

Contamination from various plasticizers was minor and consists primarily of butyl and octyl phthalates, and dibutyl esters of dicarboxylic acids from the core tubes (Simoneit, 1975).

The humic substances were separated from Sample 364-24-1, 0-10 cm using the procedure of Stuermer et al. (in press). The yield is 1300 $\mu$g/g of dry sediment; that is, 1.25 per cent of the organic carbon consists of humic acids. The $\delta^{13}C$ value for this material is $-22.31‰$. Kerogen was isolated from the remaining sediment using the procedure of Stuermer et al. (in

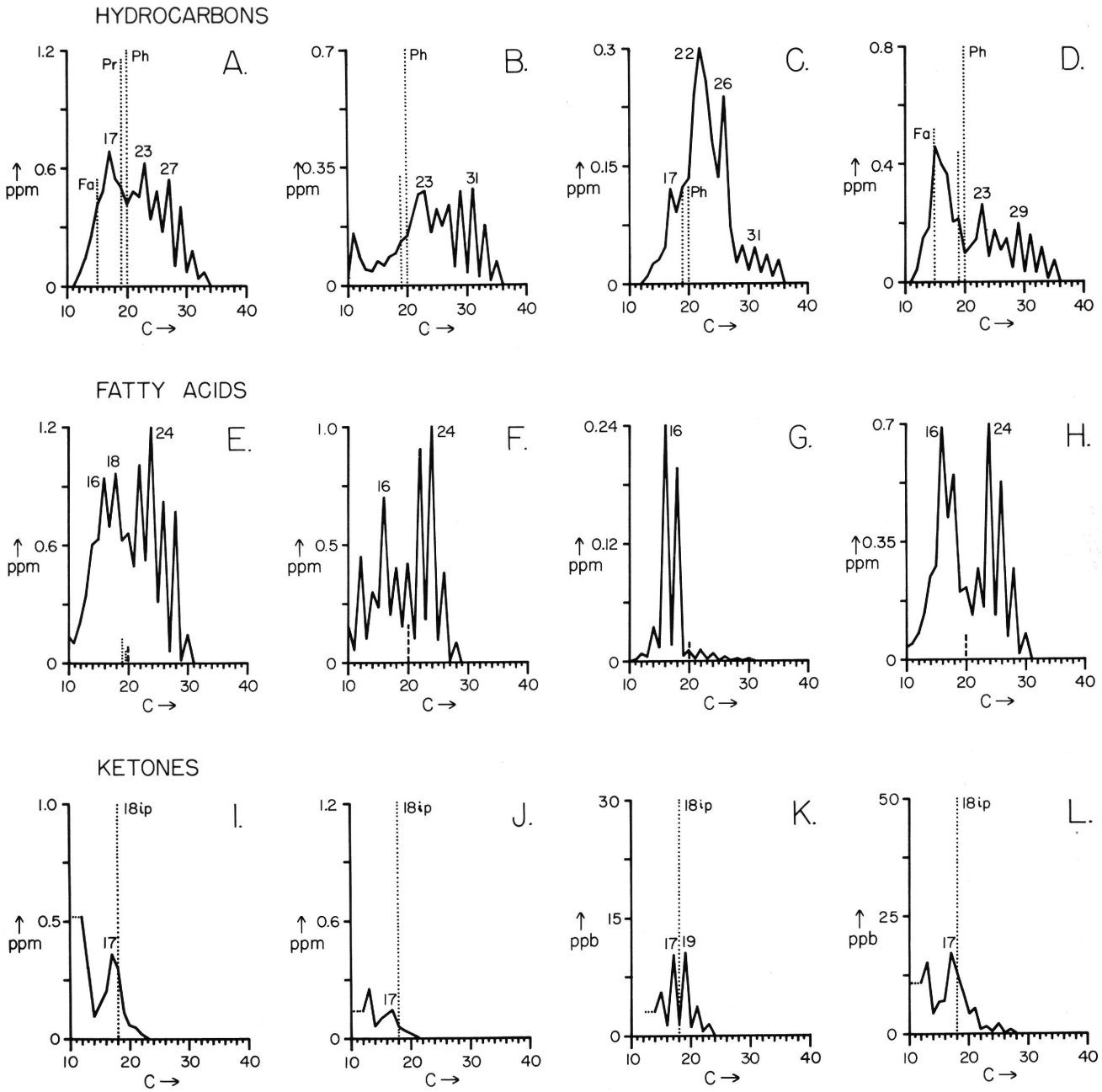


Figure 1. *Distribution diagrams for the* n-*alkanes,* n-*fatty acids and ketones (. . . isoprenoids; - - - diterpenoids, the line height indicates relative concentration).* n-*alkanes: (A) Sample 386-43-3, 138-141 cm; (B) Sample 386-63-1, 142-144 cm; (C) Sample 387-36-2, 145-150 cm; (D) Sample 364-24-1, 0-10 cm;* n-*fatty acids: (E) Sample 386-43-3, 138-141 cm; (F) Sample 386-63-1, 142-144 cm; (G) Sample 387-36-2, 145-150 cm; (H) Sample 364-24-1, 0-10 cm;* n-*methyl and isoprenoid (. . . .) ketones: (I) Sample 386-43-3, 138-141 cm; (J) Sample 386-63-1, 142-144 cm; (K) Sample 387-36-2, 145-150 cm; (L) Sample 364-24-1, 0-10 cm.*

press); it has a $\delta^{13}C$ value of –21.8‰. The $\delta^{13}C$ values for the lipids and kerogens from the other samples are listed in Table 1. The kerogens are isotopically heavier than the lipids. The $\delta^{13}C$ values for Sections 386-43-3 and 386-63-1 are in the range typical of a terrigenous (and/or lacustrine) origin (Degens, 1969). Section 364-24-1 is a borderline case, and Sections 387-36-2 and 387-37-2 have $\delta^{13}C$ values for kerogen typical of marine sources (Degens, 1969).

## CONCLUSIONS

The distributions of the *n*-alkanes and *n*-fatty acids reflect a mixed origin from autochthonous marine and allochthonous terrigenous sources. In the case of Sample 387-36-2, 145-150 cm the marine lipid component predominates over the allochthonous component. The excess of pristane over phytane (Pr/Ph $<1.0$) confirms anoxic conditions of sedimentation (Didyk et al., in

TABLE 2
Steroidal and Triterpenoidal Compounds Identified in the Lipids

| Compound Name | Structure Number | Composition | Sample[a] 386-43-3, 138-141 cm | 386-63-1, 142-144 cm | 387-36-2, 145-150 cm | 364-24-1, 0-10 cm |
|---|---|---|---|---|---|---|
| Cholestane | – | $C_{27}H_{48}$ | tr.[c] | 80 | tr. | 17 |
| Cholest-4-ene | III | $C_{27}H_{46}$ | 50 | tr. | n.d. | 40 |
| 5β,14β-dimethyl-18,19-dinor-8α,9β,10α-cholest-13(17)-ene | IV | $C_{27}H_{46}$ | 30 | 45 | n.d. | 90 |
| 17α(H)-trisnorhopane | V | $C_{27}H_{46}$ | n.d.[c] | n.d. | 30 | n.d. |
| 17β(H)-trisnorhopane | V | $C_{27}H_{46}$ | 40 | 100 | 20 | 27 |
| Sterane | – | $C_{28}H_{50}$ | tr. | 25 | tr. | 8 |
| Ster-4-ene | III | $C_{28}H_{48}$ | 25 | tr. | n.d. | 15 |
| 5β,14β-dimethyl-18,19-dinor-8α,9β,10α-ster-13(17)-ene | IV | $C_{28}H_{48}$ | 15 | 55 | n.d. | 46 |
| Sterane | – | $C_{29}H_{52}$ | tr. | 65 | tr. | 20 |
| Ster-4-ene | III | $C_{29}H_{50}$ | 70 | tr. | n.d. | 50 |
| 5β,14β-dimethyl-18,19-dinor-8α,9β,10α-ster-13(17)-ene | IV | $C_{29}H_{50}$ | 50 | 70 | n.d. | 95 |
| 17α(H)-norhopane | VI | $C_{29}H_{50}$ | n.d. | n.d. | 100 | n.d. |
| 17β(H)-norhopane | VI | $C_{29}H_{50}$ | 15 | 50 | n.d. | tr. |
| 17β(H)-normoretane | VII | $C_{29}H_{50}$ | n.d. | n.d. | 20 | n.d. |
| Hop-17(21)-ene | X | $C_{30}H_{50}$ | 55 | 28 | n.d. | 30 |
| Triterpene | – | $C_{30}H_{50}$ | 70 | tr. | n.d. | 40 |
| 17α(H)-hopane | VIII | $C_{30}H_{52}$ | n.d. | tr. | 80 | tr. |
| Hopane | VIII | $C_{30}H_{52}$ | 60 | 65 | 35 | 80 |
| Moretane (17α/β) | – | $C_{30}H_{52}$ | 100 | 40 | n.d. | 100 |
| 17α(H)-homohopane | IX | $C_{31}H_{54}$ | n.d. | n.d. | 20 | n.d. |
| 17β(H)-homohopane | IX | $C_{31}H_{54}$ | 80 | 55 | 47 | 90 |
| 17β(H)-homohopanoic acid[b] | XI | $C_{31}H_{52}O_2$ | tr. | tr. | tr. | 0.1 |
| 17β(H)-bishomohopane | IX | $C_{32}H_{56}$ | 10 | 5 | n.d. | 20 |
| 17β(H)-bishomohopanoic acid[b] | XI | $C_{32}H_{54}O_2$ | 0.8 | 0.4 | 0.03 | 1.0 |
| 17β(H)-trishomohopane | IX | $C_{33}H_{58}$ | 5 | tr. | n.d. | 15 |
| 17β(H)-trishomohopanoic acid[b] | XI | $C_{33}H_{56}O_2$ | tr. | 0.1 | tr. | 0.3 |
| 17β(H)-tetrakishomohopane | IX | $C_{34}H_{60}$ | tr. | n.d. | n.d. | 8 |
| 17β(H)-tetrakishomohopanoic acid[b] | XI | $C_{34}H_{58}O_2$ | n.d. | tr. | n.d. | 0.1 |
| 17β(H)-pentakishomohopane | IX | $C_{35}H_{62}$ | n.d. | n.d. | n.d. | 4 |
| 17β(H)-pentakishomohopanoic acid[b] | XI | $C_{35}H_{60}O_2$ | n.d. | n.d. | n.d. | 0.03 |

[a]The concentrations are expressed approximately on a relative scale based on the mass spectrum base peak intensity.
[b]These values are expressed as approximate yield in μg/g of dry sediment.
[c]tr. = trace; n.d. = not detected.

press), especially when considered in conjunction with the absence of bioturbation and the excellent preservation of fossil plant detritus (Bolli et al., 1975; Tucholke et al., 1975).

The presence of sterenes and 17β(H)-hopanes indicates that Samples 386-43-3, 386-63-1, and 364-24-1, are very immature and the lipids have undergone essentially no diagenesis. The presence of a hump and 17α(H)-hopanes in Section 387-36-2 indicates that this sample has undergone some maturation. The absence of higher molecular weight ketones may be due to the rapid influx and sedimentation of plant detritus into the euxinic basin without biodegradation, thus fixing the *n*-alkanes and *n*-fatty acids from waxes essentially unaltered. The presence of various diterpenoids in minor amounts can be used as a marker for some influx of detritus from resinous vascular plants.

The $\delta^{13}C$ data for the lipids are isotopically lighter than for the kerogens and humic substances. Since these sediments are immature on the basis of the lipid data, the $\delta^{13}C$ values reflect the isotopic compositions of the original materials. These include a partially terrigenous and/or lacustrine origin for the lipids and a probably allochthonous recycled component of older (mature) kerogen with some autochthonous sources of both lipids and kerogen.

## ACKNOWLEDGMENTS

I thank the National Science Foundation for making the core samples available, R. P. Philp and S. C. Brown for GC/MS data, D. Winter for stable isotope analyses, and I. Venkatesan for technical assistance. Financial assistance from the National Science Foundation (Grants OCE 76-21506 and OCE 76-23390) and from the Energy Research and Development Administration, Grant E(04-3)-34 P.A. 134, are gratefully acknowledged. I thank Dr. Shmuel Brenner and Dr. Ansis Kaneps for the review of the manuscript.

## REFERENCES

Aizenshtat, Z., 1973. Perylene and its geochemical significance: *Geochim. Cosmochim. Acta*, v. 37, p. 559-567.

Arpino, P., 1973. Les lipides des sédiments lacustres éocènes: Thèse, l'Université Louis Pasteur de Strasbourg, France.

Bolli, M. H., Ryan, W. B. F., McKnight, B. K., Kagami, H., Melguen, M., Siesser, W. G., Natland, J., Longoria, J. F., Proto-Decima, F., Forsman, J. B., and Hottman, W. E., 1975. Basins and margins of the eastern South Atlantic *Geotimes*, v. 20 p. 22-24.

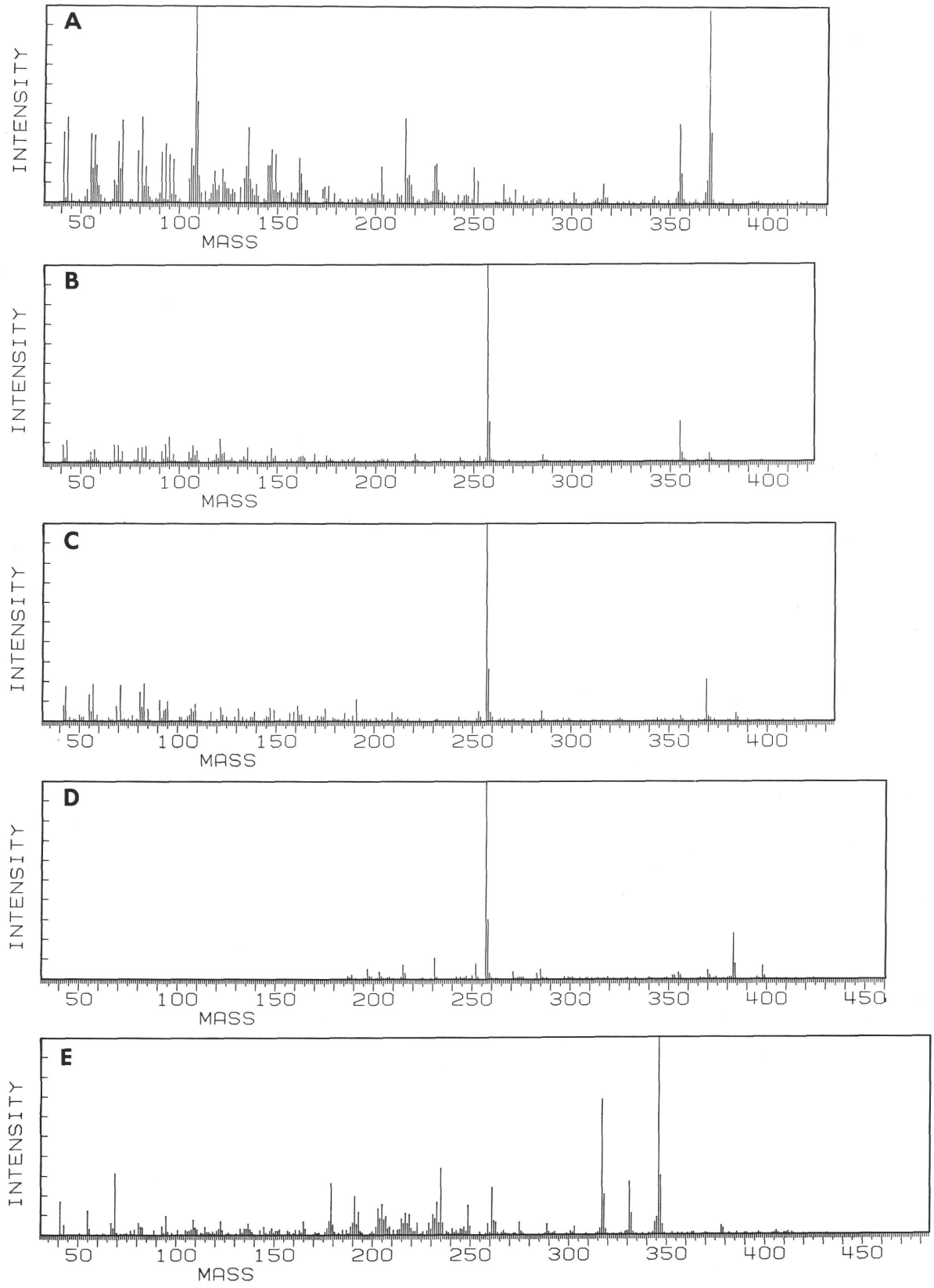


Figure 2. *Mass spectra of various compounds from the hydrocarbon fraction of Sample 364-24-1, 0-10 cm (GC/MS data): (A) cholest-4-ene; (B) 5β, 14β-dimethyl-18, 19-dinor-8α, 9β, 10α-cholest-13 (17)-ene; (C) 5β, 14β-dimethyl-18, 19-dinor-8α, 9β, 10α-ster-13 (17)-ene, $C_{28}$ $H_{48}$; (D) 5β, 14β-dimethyl-18, 19-dinor-8α, 9β, 10α-ster-13 (17)-ene, $C_{29}$ $H_{50}$; (E) 8, 14, 18-trisnormethyladianta-8, 11, 13, 15, 17-pentaene, $C_{26}$ $H_{34}$.*

Dastillung, M. and Albrecht, P., 1976. Molecular test for oil pollution in surface sediments, *Mar. Poll. Bull.*, v. 7, p. 13-15.

Degens, E. T., 1969. Biogeochemistry of stable carbon isotopes. *In* Eglinton, G. and Murphy, M. T. J. (Eds.), *Organic geochemistry, methods and results:* Berlin (Springer-Verlag), p. 304-329.

Didyk, B. M., Simoneit, B. R. T., Brassell, S. C., and Eglinton, G., in press. Geochemical indicators of paleoenvironmental conditions of sedimentation, *Nature.*

Hatcher, P. G., Simoneit, B. R., and Gerchakov, S. M., 1977. The organic geochemistry of a Recent sapropelic environment: Mangrove Lake, Bermuda. *In* Campos, R., and Goni, J. (Eds.), *Advances in organic geochemistry 1975*: Madrid (Enadimsa), p. 469-484.

Hitchock, C. and Nichols, B. W., 1971. *Plant lipid biochemistry*: London (Academic Press).

Kaplan, I. R., Smith, J. W., and Ruth, E., 1970. Carbon and sulfur concentration and isotopic composition in Apollo 11 lunar samples. *In Proc. Apollo 11 Lunar Sci. Conf.—Geochim. Cosmochim. Acta, Suppl. 1 (Pergamon),* v. 2, p. 1317-1329.

Rubinstein, I., Sieskind, O., and Albrecht, P., 1975. Rearranged sterenes in a shale: Occurrence and simulated formation: *J. Chem. Soc., Perkin Trans. I,* p. 1833-1836.

Simoneit, B. R. T., 1975. Sources of organic matter in oceanic sediments: Ph.D. Thesis, University of Bristol, England.

_____, 1977. Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance: *Geochim. Cosmochim. Acta*, v. 41, p. 463-476.

_____, 1978. Leg 41 sediment lipids – Search for eolian organic matter in Recent samples and examination of a black shale. *In* Lancelot, Y. Seibold, E., et al., *Initial Reports of the Deep Sea Drilling Project,* v. 41: Washington (U. S. Government Printing Office), p. 855-858.

_____, 1978a. Lipid analyses of sediments from Site 364 in the Angola Basin DSDP Leg 40. *In* Bolli, H. M., Ryan, W. B. F., et al., *Initial Reports of the Deep Sea Drilling Project,* v. 40: Washington (U. S. Government Printing Office), p. 659-662.

_____, 1978b. Organic geochemistry of terrigenous muds and various shales from the Black Sea, DSDP Leg 42B. *In* Ross, D., Neprochnov, Y., et al., *Initial Reports of the Deep Sea Drilling Project,* v. 42B, Part 2: Washington (U. S. Government Printing Office), p. 749-754.

_____, in press. The Black Sea, a sink for terrigenous lipids, *Deep-Sea Res.*

Simoneit, B. R., Scott, E. S., and Burlingame, A. L., 1973. Preliminary organic analysis of DSDP cores, Leg 14, Atlantic Ocean. *In* van Andel, T. H., Heath, G. R., et al., *Initial Reports of the Deep Sea Drilling Project,* v. 16: Washington (U. S. Government Printing Office), p. 575-600.

Spyckerelle, C., 1975. Constituants aromatiques de sédiments: Ph.D. Thesis, l'Université Louis Pasteur de Strasbourg, France.

Stuermer, D. H. and Simoneit, B. R. T., 1978. Varying sources for the lipids and humic substances at Site 391, Blake-Bahama Basin DSDP Leg 44. *In* Benson, W. E., Sheridan, R. E., et al., *Initial Reports of the Deep Sea Drilling Project,* v. 44: Washington (U. S. Government Printing Office), p. 587-592.

Stuermer, D. H., Peters, K. E., and Kaplan, I. R., in press. Source indicators of humic acid and kerogen, *Geochim. Cosmochim. Acta.*

Tucholke, B., Vogt, P., McCave, I. N., Murdmaa, I. O., Rothe, P., Houghton, R. L., Galehouse, J., Kaneps, A., McNulty, C., Okada, H., Kendrick, J., and Demars, K., 1975. *Glomar Challenger* drills in the North Atlantic, *Geotimes,* v. 20, p. 18-21.