

36. ORGANIC GEOCHEMISTRY OF TERRIGENOUS MUDS AND VARIOUS SHALES FROM THE BLACK SEA, DSDP LEG 42B¹

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ABSTRACT

The Black Sea is a sink for terrigenous detritus with rapid sediment accumulation, estimated at 16 km thickness in the central basin. Lipid markers of terrigenous origin have been identified in most sediment samples that were examined from Sites 379-381. The molecular indicators of terrigenous lipids were *n*-alkanes (*n*-C₂₅ to *n*-C₃₃, odd-to-even predominance, maximum mainly at *n*-C₂₉), *n*-fatty acids (*n*-C₂₂ to *n*-C₃₀, even-to-odd predominance, maximum at *n*-C₂₄ or *n*-C₂₆) and dehydroabietic acid. Steroidal and triterpenoidal compounds were also identified and they probably originated from primary marine or lacustrine production. Perylene was present in most of the samples and is probably associated with terrigenous lipids. The $\delta^{13}\text{C}$ values for the total lipid fractions were in the range typical of a higher plant and/or lacustrine origin.

INTRODUCTION

Lipid markers of terrigenous origin have been identified in Recent sediments recovered by the *R/V Atlantis II* from the Black Sea (Simoneit, 1974, 1975, in press a). These data, coupled with carbon isotope analyses of lipid fractions, indicated that a major proportion of the lipids were of continental origin. Thus, it is of interest to examine the lipids of the DSDP sediments from the Black Sea in order to assess the input of terrigenous lipids to the older environments. The lithology and palynology reported for the sediment sequences from the three drill sites indicate that terrigenous input occurred during most of the sedimentary history (Ross et al., 1975).

The samples analyzed here were derived from Site 379, located in the central part of the basin (43°0.3'N, 36°0.7'E; water depth 2171 m), Site 380, located at the edge of the basin near the Bosphorus (42°5.9'N, 29°36.8'E; water depth 2115 m), and Site 381, located upslope of Site 380 near the Bosphorus (41°40.3'N, 29°25'E; water depth 1750.5 m) (Ross et al., 1975).

EXPERIMENTAL

The core samples were freeze-dried and then extracted with toluene and methanol (4:1) using ultrasonication. The extracts for each sample were concentrated on a rotary evaporator and subjected to gas chromatographic analysis (GC). The extracts were then treated with diazomethane in ether and subjected to silica gel thin-layer chromatography (TLC) using methylene chloride as eluent. The bands corresponding to hydrocarbons, esters, and ketones were scraped off the TLC plate after development with iodine vapor,

and eluted with ether or ethyl acetate. These fractions were subjected to GC and GC/MS analyses.

The GC analyses were carried out on a Hewlett-Packard Model 5830 gas chromatograph using a 16 m × 0.75 mm stainless steel SCOT column coated with OV-101, programmed from 110-280°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 × 0.75 mm glass column which was packed with Gaschrom Q (80-100 mesh) coated with 1% OV-1. The mass spectrometric data were acquired and processed using a DuPont Model 21-094 data system.

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

RESULTS AND DISCUSSION

The sample descriptions, carbon analyses, lipid yields, and other results are found in Table 1.

The samples from the basin (Hole 379A) are of Pleistocene age and consist of terrigenous and microfossiliferous mud with about 12% carbonate. The organic carbon content and lipid yields are low. The distribution diagrams for the *n*-alkanes and *n*-fatty acids are shown in Figures 1 and 2, respectively. For Sections 379A-25-4 and 379A-30-3 the *n*-alkanes exhibit a hump with a peak at *n*-C₂₂ (no predominance) and a second homolog distribution with a strong odd-to-even carbon number predominance ranging from *n*-C₂₅ to *n*-C₃₃ (maximum at *n*-C₂₉ for Sections 379A-24-5 and at *n*-C₂₇ for 379A-30-3). These second maxima are usually associated with higher plant waxes (Simoneit, 1975, in press). The first maximum, coupled with the low concentration of *n*-C₁₇, is typical of microbially altered algal residues. The *n*-fatty acids exhibits a

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TABLE I
Sample Descriptions, Carbon Analyses, Extract Yields, and Carbon Isotope Values for the Core Sections Examined

Sample (Interval in cm)	Depth Below Seabed (m)	Lithology	Geologic Age	Carbon ^a			Pr/Ph (hydrocarbon)	Perylene Presence	$\delta^{13}C^b$ (‰)	Lipid Yields					
				Total (%)	Organic (%)	Carbonate (%)				<i>n</i> - alkanes $\mu\text{g/g}$ CPI	<i>n</i> -fatty acids $\mu\text{g/g}$ CPI		<i>n</i> - ketones $\mu\text{g/g}$ CPI		
379A-25-4, 0-5	230.0	Terrigenous	Pleistocene	2.1	0.6	13	0.8	+++	-29.8	80	1.6	50	5.3	n.d.	-
379A-30-3, 100-105	277.0	Nanno, Diatom. mud	Pleistocene	1.9	0.4	12	-	+	n.d.	6	1.2	10	12.7	10	4.7
380A-3-1, 78-91	352.4	Diatom. mud, dolom. marl	Pleistocene	2.4	0.5	16	n.d. ^c	n.d.	n.d.	n.d.	-	n.d.	-	n.d.	-
380A-21-3, 66-72	526.2	Calcareous ooze and mud	Pleistocene	1.5	0.4	10	-	+	-29.5	10	2.9	3	5.3	1.0	2.9
380A-74-1, 106-112	1017.5	Diatom shale	Pleistocene	2.3	0.9	12	0.2	+	-27.9	40	2.5	8	3.2	7	1.2
380A-78-6, 22-26	1062.2	Black shale	L. Pliocene	2.6	1.1	13	1.4	+	-24.9	75	1.2	13	2.4	n.d.	-
381-1-4, 104-115	5.5	Terrigenous mud	Pleistocene	3.8	2.0	15	0.8	+	-27.5	120	2.7	200	15.1	100	4.4
381-2-3, 67-73	13.2	Terrigenous mud	Pleistocene	1.0	0.5	4	n.d.	n.d.	n.d.	n.d.	-	n.d.	-	n.d.	-
381-6-1 19-30	47.7	Terrigenous mud	Pleistocene	1.5	0.3	10	n.d.	n.d.	n.d.	n.d.	-	n.d.	-	n.d.	-
381-37-3, 32-42	335.9	Diatom. sapropelic mud	Pleistocene	6.8	5.1	15	0.9	-	-27.2	30	4.2	10	4.3	n.d.	-
381-54-5, 94-101	500.9	Shale breccia and siltstone	U. Miocene	1.6	1.4	2	-	+++	-27.9	2	3.5	1.6	4.0	n.d.	-

^aData supplied by G. Bode and S. M. White, Deep Sea Drilling Project, Scripps Institution of Oceanography, University of California at San Diego.

^bvs. PDB standard, all values cited were determined on total lipid extracts.

^cn.d. - not determined.

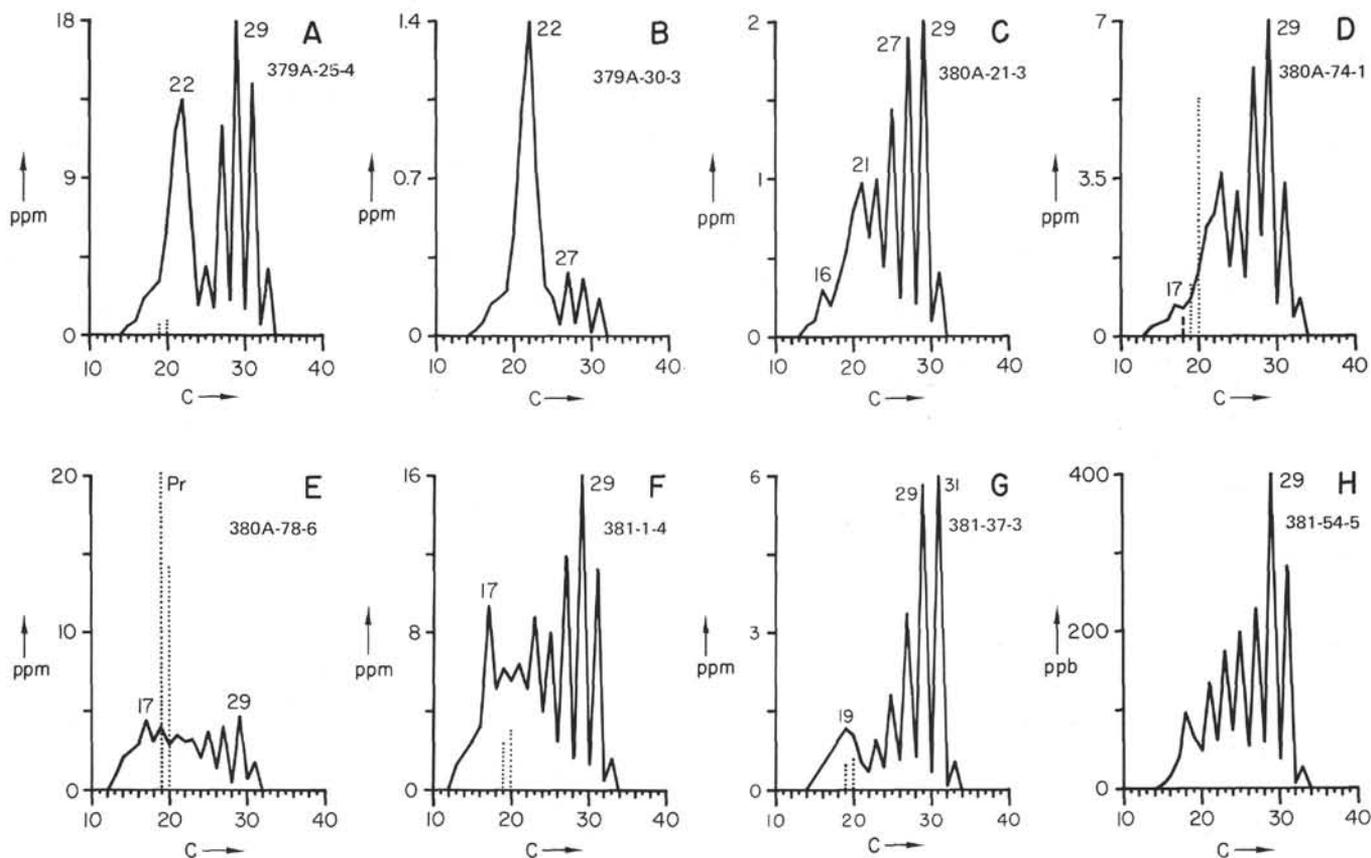


Figure 1. Distribution diagrams for the *n*-alkanes (· · · isoprenoids, - - - diterpenoid)

bimodal distribution with a strong even-to-odd carbon number predominance and modal maxima at *n*-C₁₆ and at *n*-C₂₆ for Section 379A-25-4 and *n*-C₂₄ for Section 379A-30-3 (minor amount only). The maximum at *n*-C₁₆ (i.e., <*n*-C₂₀) appears to be of autochthonous

marine and/or lacustrine origin. The distributions >*n*-C₂₂, when considered in conjunction with the *n*-alkane distributions, are further evidence for higher plant wax inputs (Hitchcock and Nichols, 1971; Simoneit, 1975). The low amount of higher weight fatty acids in the case

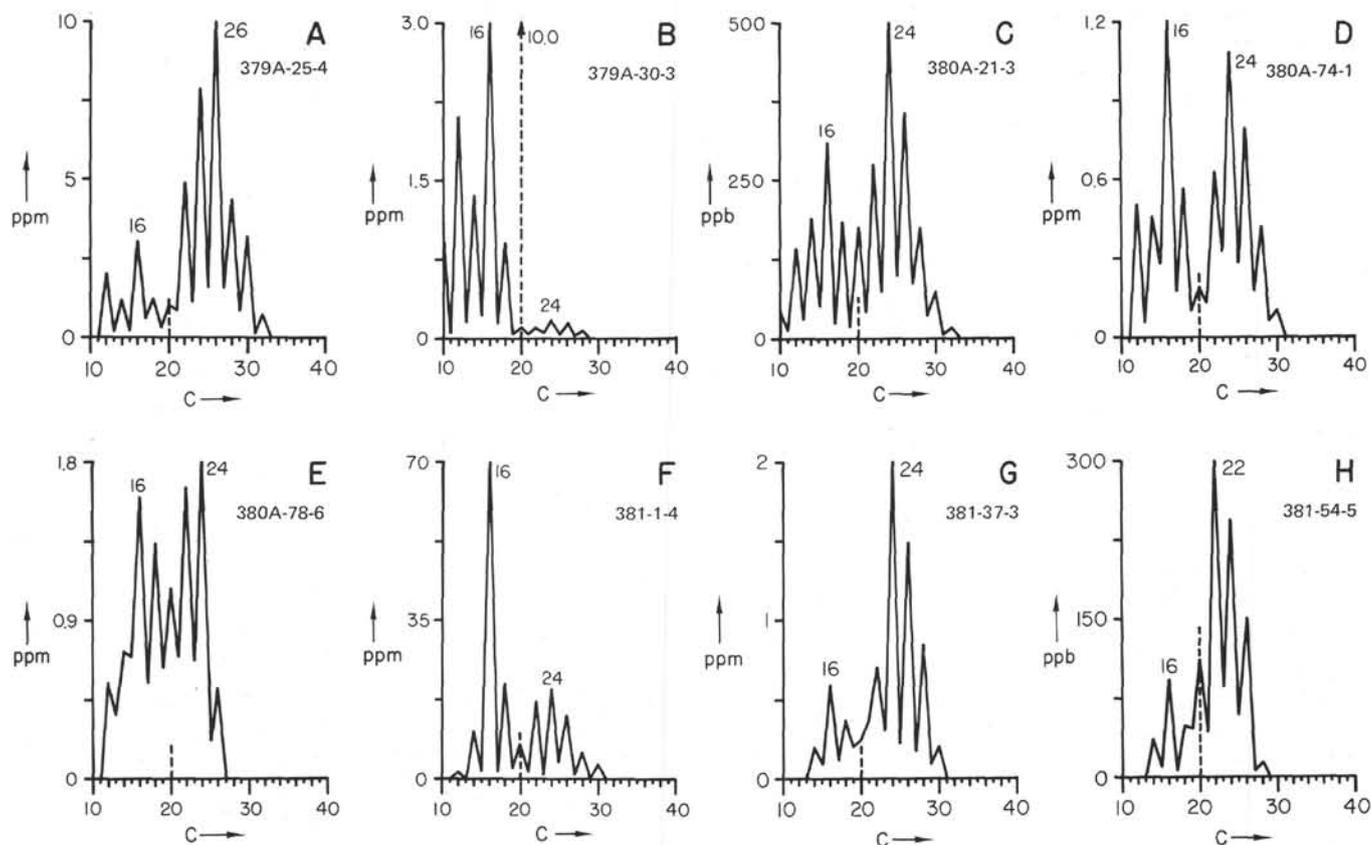


Figure 2. Distribution diagrams for the *n*-fatty acids (--- diterpenoid)

of Section 379A-30-3 may be due to removal by microbial activity. The diterpenoid, dehydroabietic acid (Appendix, Structure I) is present in both samples. This compound is a marker of terrigenous resinous plants (Simoneit, 1977). The ketone fraction of Section 379A-30-3 consists predominantly of normal methylketones, $C_nH_{2n}O$, ranging from $n = 14$ to 31, with a strong odd-to-even carbon number predominance and a maximum at n -C₂₇ (Figure 3a). 6, 10, 14-Trimethylpentadecan-2-one (Structure II) is also present in this fraction. The normal ketones are probably derived from *n*-fatty acids by microbial β -oxidation or by microbial oxidation of *n*-alkanes (Arpino, 1973). Thus, this distribution pattern also reflects a terrigenous origin. Perylene (Table 1) is present in both samples.

The samples from the western Black Sea (Hole 380A and Site 381) range in age from Pleistocene to late Miocene and they are predominantly of terrigenous lithology with 2%-15% carbonate (Table 1). The organic carbon contents range from 0.3% to 5%, but the lipid yields are relatively low.

The *n*-alkanes of all samples (380A-21-3, 380A-74-1, 381-1-4, 381-37-3, and 381-54-5) exhibit a distribution where the homologs from n -C₂₃ to n -C₃₃ predominate (maxima at n -C₂₉ or n -C₃₁) and a minor maximum is observed in the range from n -C₁₇ to n -C₂₁ (Figure 1). These higher weight *n*-alkanes are derived from plant wax sources (Simoneit, 1975, in press) and are dominant over autochthonous components ($<n$ -C₂₂) in the paleoenvironments closer to shore. The *n*-fatty acids of the samples from Hole 380A and Site 381

exhibit a bimodal distribution with strong even-to-odd carbon number predominances and maxima at n -C₁₆ and n -C₂₄ and n -C₂₂ (Section 381-54-5) (Figure 2). The maximum at n -C₁₆ is derived from autochthonous lacustrine and/or marine production. The distributions $>n$ -C₂₀, when considered with the *n*-alkanes $>n$ -C₂₃, are further indications of higher plant lipid input. Dehydroabietic acid (Structure I) is present in all samples and is an indicator of input from resinous plants (Simoneit, 1977). The ketone fractions (Sections 380A-21-3, 380A-74-1, and 381-1-4) consist of normal methyl and isoprenoidal ketones (Figure 3) and triterpenoidal ketones. The normal series, $C_nH_{2n}O$, range from $n = 11$ to 33, with odd-to-even carbon number predominances and bimodal distributions. These ketones are microbial alteration products (Arpino, 1973), and thus the distributions $>n$ -C₂₁ reflect a terrigenous origin. The isoprenoidal ketones consist of predominantly 6,10,14-trimethylpentadecan-2-one (Structure II) and in Sections 380A-74-1 and 381-1-4 lesser amounts of 6,10-dimethylundecan-2-one (Structure III).

The alicyclic compounds found in this sample suite consist principally of steroidal and triterpenoidal compounds. The shallower samples contain predominantly sterenes, C_nH_{2n-8} for $n = 27$ to 29 (Structure IV, R = H) and minor amounts of stanones, $C_nH_{2n-8}O$ for $n = 27$ to 29. The deeper samples (e.g., 381-54-5 and 380A-74-1) contain primarily steranes, C_nH_{2n-6} for $n = 27$ -29 (Structure V), with the 5 α stereochemistry. Section 380A-74-1 also contains minor

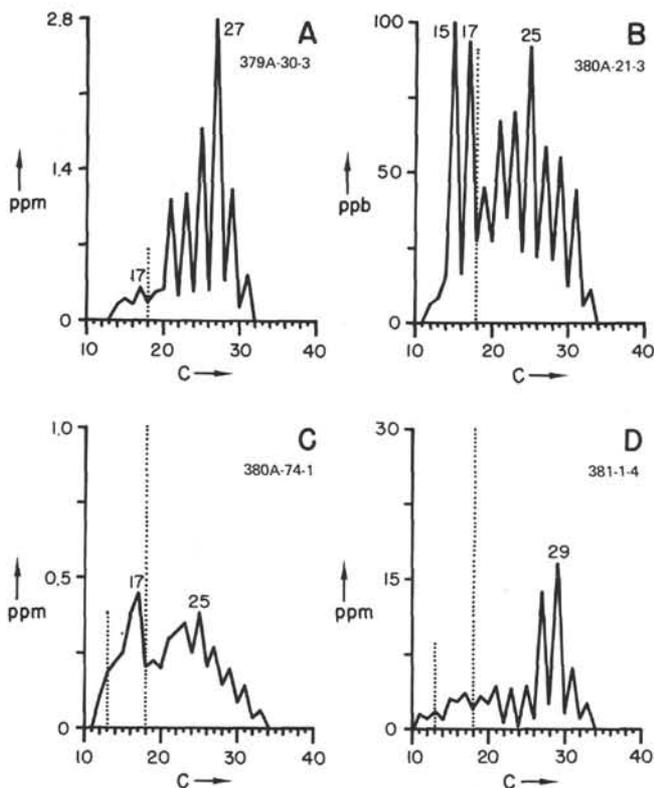


Figure 3. Distribution diagrams for the *n*-ketones (..... isoprenoids)

amounts of 4-methylsterenes (Structure IV, $R = CH_3$), C_nH_{2n-8} for $n = 28$ and 29 ; the double bond position is uncertain. The ketone fractions from Sections 381-1-4 and 380A-74-1 contain significant amounts of probably 4-methylstan-3-ones, $C_nH_{2n-8}O$ for $n = 28$ to 30 . The triterpenoids consist mainly of the hopane and moretane skeleton. In the shallower samples the predominant species are diploptene (Structure VI), adiantanes (Structure VII) and hopane or moretane (Structure VIII). Standard compounds were not coinjected, therefore the stereochemistry of the $C_{30}H_{52}$ species cannot be assigned. In the deeper samples (e.g., 380A-74-1) the major triterpenoids are comprised of adiantanes (Structure VII), hopane or moretane (Structure VIII), the predominant species $17\beta(H)$ -homohopane (Structure IX), and a minor amount of its stereoisomer $17\alpha(H)$ -homohopane (Structure X). Section 380A-74-1 also contains about 10 ppm of triterpenoidal acids. The major species is $17\beta(H)$ -bishomohopanoic acid (Structure XI, $R = CH_2COOH$) and the minor homologs are $C_nH_{2n-10}O_2$, with $n = 31$ [both 17α and $\beta(H)$, Structures XI and XII], $n = 32$ [$17\beta(H)$, Structure XII], and $n = 33$ [$17\beta(H)$, Structure XI]. The triterpenoidal ketones are composed of mainly trisnorhopan-21-one (Structure XIII), adiantones (Structure XIV) and a C_{30} ketone (probable Structure XV).

Retene (Structure XVI), a diterpenoidal dehydrogenation product (Simoneit, 1977), is present in Sections 381-37-3 and 380A-74-1. Most samples contain perylene ($C_{20}H_{12}$) (Table 1), which elutes on TLC as a bright yellow band just below the hydro-

carbons. An example of a UV-visible spectrum of this component is shown in Figure 4 which corresponds well with that of the standard compound (Simoneit, 1975). Perylene may be a terrigenous marker (Aizenshtat, 1973) since it has been mainly encountered in sediments with lipids of predominantly such an origin (Simoneit, 1975). The perylene of these samples appears to be of a terrigenous origin.

The analyses of the stable carbon isotopes support a terrigenous and/or lacustrine origin for the total lipids. The $\delta^{13}C$ values observed for the lipids range from -24.9 to -29.8‰ (Table 1). These values fall within the ranges typical of terrestrial plants, some lacustrine higher plants and fresh water plankton (Degens, 1969). They are, however, outside the typical range of values observed for marine organic matter, which is within $\delta^{13}C = -12$ to -23‰ (Degens, 1969).

Contamination from various plasticizers and lubricants is minor and consists predominantly of dibutyl, dioctyl, and heptyl nonyl phthalates.

CONCLUSIONS

The lipid extracts from Pleistocene to upper Miocene samples from the Black Sea (Sites 379A, 380A, and 381) have *n*-alkanes, *n*-fatty acid, and *n*-methylketone distributions typical for a terrigenous and/or lacustrine origin. Potamic transport appears to have brought in the allochthonous component of the lipids. The lipids of samples from Hole 380A and Site 381 reflect predominantly higher plant wax distributions and dehydroabietic acid, the molecular marker of resinous plants, is also present. The samples from the basin (Hole 379A) have a lipid content reflecting a microbial component of lacustrine and/or marine origin and a

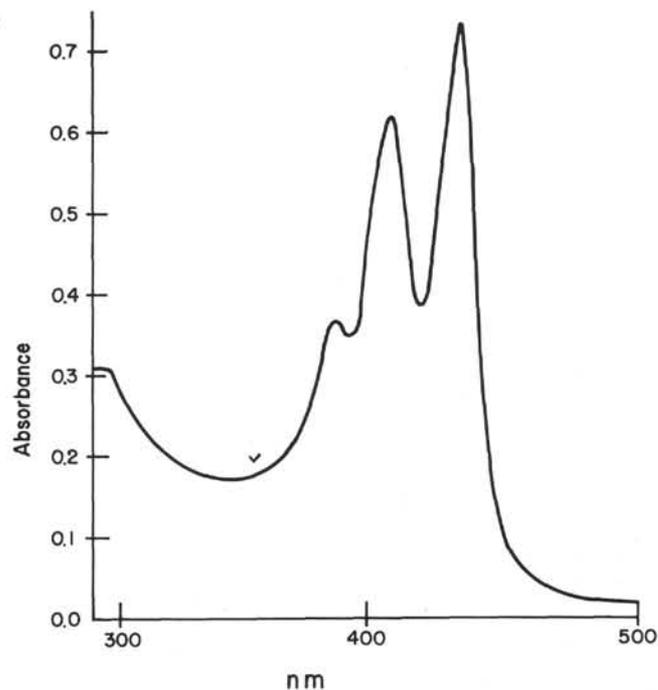


Figure 4. UV-Visible spectrum of perylene from Section 381-54-5 (Cary Model 15 spectrophotometer, pathlength 1 cm, in CH_2Cl_2).

higher plant wax component. Dehydroabietic acid is also present in these samples. The $\delta^{13}\text{C}$ values for the total lipids are in the range typical of a higher plant and/or lacustrine origin. The steroidal and triterpenoidal compounds in the lipids probably originate from primary autochthonous production. The perylene appears to be associated with terrigenous lipids. Based on these data it can be concluded that the paleo-environment of the Black Sea (at these sampling points) was lacustrine, with a high potamic influx of terrigenous higher plant lipids. Some of the Pr/Ph values (Table 1) are <1 , which may indicate anoxic paleoenvironmental conditions (Didyk et al., in press).

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