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Perylene and its geochemical significance*

Z. AIZENSHTAT
Department of Geology and the Institute of Geophysics and Planetary Physics,
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(*Received* 1 *June* 1972; *accepted in revised form* 14 *August* 1972)

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INTRODUCTION

PERYLENE (see Fig. 1) has been found in the aromatic hydrocarbon fractions of some sediments and certain petroleum high boiling fractions (SCHNURMANN *et al.*, 1953; CARRUTHERS and COOK, 1954). More recently,

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INTRODUCTION

PERYLENE (see Fig. 1) has been found in the aromatic hydrocarbon fractions of some sediments and certain petroleum high boiling fractions (SCHNURMANN *et al.*, 1953; CARRUTHERS and COOK, 1954). More recently, perylene has been reported in soil (BLUMER, 1961), peat (GILLILAND and HOWARD, 1960; BERGMANN, IKAN and KASHMAN, 1964), marine sediments (ORR and GRADY, 1967), and fresh water lake sediments (HODGSON *et al.*, 1968a). In most cases, only semi-quantitative data have been reported.

This study was prompted by the fact that the results and conclusions reported by ORR and GRADY (1967) may be questioned on the basis of possible oil seeps in the nearby Santa Barbara Channel. As polycyclic and other aromatic compounds are generally not detectable in recent marine sediments, and because perylene can be measured in low concentrations (<1·0 ppm), it was decided to re-investigate the occurrence of perylene in a variety of marine sediments.

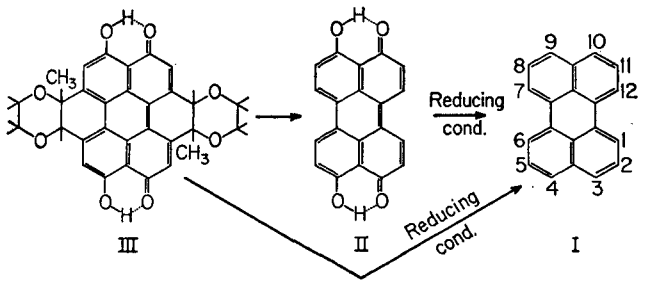

Fig. 1. Perylene (I), 4,9-dihydroxyperylene-3,10-quinone (II), Erythroaphin pigment (III), and hypothetical pathway for perylene synthesis.

EXPERIMENTAL

Sample description

All the marine samples studied consist of clay minerals as a major component. The interstitial waters were studied by our group extensively except for the Bandaras Bay (B.B.-1) sample. For the present study, it is important to establish the redox state of the sediment at

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Table 1.

Sample code number	Location & place	Depth below sea floor* (m)	Sea floor depth (m)	Oxidation state of sediment	% Org. C.	$\delta \frac{^{13}C}{^{12}C}$ (‰)	Perylene† μg/100 g of dry sediment GLC	Perylene† μg/100 g of dry sediment u.v.-Vis	% of org. C × 10^3 GLC	% of org. C × 10^3 u.v.-Vis
	Santa Barbara Basin									
AHF 2622	34°13·5′N 120°01·9′W	0–0·5	600	R	5·8	−21–23	—	7·8	—	0·013
AHF 3503	34°13·5′N 120°02·2′W	0·5–0·8	600	R	5·8	−21–23	—	8·6	—	0·015
FRL 163G	34°11·0′N 120°03·0′W	0·8–1·5	580	R	5·8	−21–23	—	24·4	—	0·042
AHF 2622	34°13·5′N 120°01·9′W	1·2–1·4	600	R	5·8	−21–23	—	26·0	—	0·045
AHF 3504	34°08·9′N 120°01·6′W	0–0·5	493	O(?)	5·8	−21–23	—	<0·02	—	—
	Tanner Basin									
AHF 4696	32°57·4′N 119°44·5′W	0–0·4	1510	R	11·7	−20·5	—	<0·1	—	—
AHF 4696	32°57·4′N 119°44·5′W	0·6–1·5	1510	R	11·7	−20·5	—	<0·1	—	—
AHF 4696	32°57·4′N 119°44·5′W	3–3·3	1510	R	11·7	−20·5	—	<0·1	—	—
T-1	32°56·2′N 119°43·5′W	0–0·2	1472	R	11·1	−23·0	<0·01	<0·1	—	—
T-2	32°56·2′N 119°43·5′W	0·9–1	1472	R	11·2	−22·6	<0·01	<0·1	—	—
	San Clemente Basin									
AHF 3669	32°37·7′N 118°07·5′W	Surface	2060	R	5·7	−21·5	—	<0·02	—	—
Gulf of California	San Pedro Martir Basin									
GC 15–25 Core 3	28°20′N 112°23′W	0·15–0·25	883	R	4·75	−21·0	<0·01	<0·1	—	—
	Saanich Inlet (B.C.)									
3/0-15	48°30·40′N 123°30·06′W	0–0·1	200	R	3·87	−20·2	34·32	32·9	0·088	0·085
3/190-200	48°30·40′N 123°30·06′W	2–2·1	200	R	—	−20·3	74·10	73·0	—	—
3B/1710-1740	48°30·40′N 123°30·06′W	17·1–17·4	200	R	2·82	−21·6	167·58	165·9	0·590	0·588
3B/3450-3480	48°30·40′N 123°30·06′W	34·5–34·8	200	R	2·53	−22·5	237·00	231·0	0·940	0·913
Hole 3 JOIDES	Gulf of Mexico									
J-3-34	23°01·8′N 92°02·6′W	34	3747	R ⇌ O	1·11	−26·6	1·20	n.c.q.	0·01	—
J-3-209	23°01·8′N 92°02·6′W	209	3747	O	0·82	−21·7	<0·01	—	—	—
J-3-324	23°01·8′N 92°02·6′W	324	3747	O	0·47	−22·1	<0·01	—	—	—
J-3-534	23°01·8′N 92°02·6′W	534	3747	O	0·47	−22·2	<0·01	—	—	—
Hole 26 Joides	Vema Fracture Zone									
J-26-100	10°53·55′N 44°02·57′W	100	5168	R	0·87	−25·3	18·46	15·9	0·212	0·182
J-26-230	10°53·55′N 44°02·57′W	230	5168	R	1·00	−27·0	33·13	33·5	0·331	0·335
J-26-478	10°53·55′N 44°02·57′W	478	5168	O	0·51	−25·2	16·07	14·9	0·316	0·292
	Bandaras Bay									
Surface mud										
B.B-1	20°39·9′N 105°16·1′W	Surface	94	R	1·64	−23·41	25·4	25·4	0·155	0·155
England (Avalon)	Glastonbury peat									
P-EG	51°09′N 2°45′W	—	—	R	53·3	−28·1	301·00	315·0‡	0·056	0·059

n.d. = none detected.
n.c.q. = None calculated quantitatively.
R = Reducing.
O = Oxidizing.
* = Depth reported for the JOIDES cores will be ±0·5 m.
† = Perylene detection limit for GLC 0·01 μg/100 g; for u.v.–Vis 0·1 μg/100 g.
‡ = Very rich in other aromatics.
All AHF and FRL coded cores data from ORR and GRADY (1967).

the time of deposition and at present. In the case of the Santa Barbara samples, Core 3 of the Saanich Inlet, and the San Pedro Martir Basin, the negative Eh and sulfate reduction are evident from the surface down the cores, while our samples from Tanner Basin (T_1 and T_2) indicate no sulfate reduction in the first meter, but an extensive reduction below that depth. Core J-26 (JOIDES) exhibits another inconsistency, while the Eh recorded is positive, there is sulfate reduction from 100 m to 230 m. Therefore, we suggest using the total organic matter and the preservation of some specific organic tracers as a criterion for determining the redox history of a given sample (see Results and Discussion Section). Using this criterion, we labelled each sample in Table 1 according to its apparent redox state, either 'R' (reducing) or 'O' (oxidizing).

More detailed descriptions of the samples and their interstitial waters are given in the following references: Santa Barbara, Tanner and San Clemente Basins (EMERY, 1960), Saanich

Inlet (BROWN *et al.*, 1972), Gulf of Mexico and Vema Fracture Zone (JOIDES, holes 3 and 26; KAPLAN *et al.*, 1972); Bandaras Bay (DREVER, 1971).

Perylene: qualitative and quantitative determinations

The extraction and silicic acid chromatography procedures employed for this study were described previously (BROWN *et al.*, 1972, KAPLAN *et al.*, 1972).

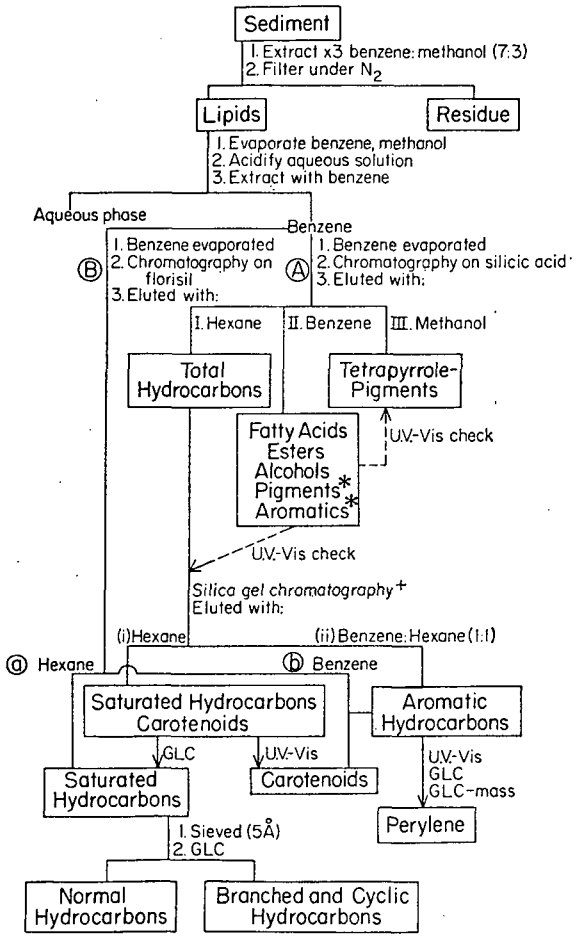

Fig. 2. Flow chart of procedures.

* The existence of these compounds in fraction II depends on the efficiency of the column and their relative concentration in the lipid extract.

† This chromatography can also be carried out on Florisil.

Fraction I, separated on silicic acid column with hexane as eluant (see path A in flow chart; Fig. 2), contains most of the perylene. In some cases, a portion trails into the benzene fraction (II), and before re-chromatographing on silica gel both fractions should be checked as to their u.v.–Vis spectra. In most samples when carotenoids are present, the second chromatography on silica gel is necessary (see Fig. 3) and will be carried out on the combined fractions I and II. Elution with hexane will separate the carotenoids with the saturated hydrocarbons and hexane: benzene (1:1) will elute the perylene (which displays an intensive fluorescence) with some other

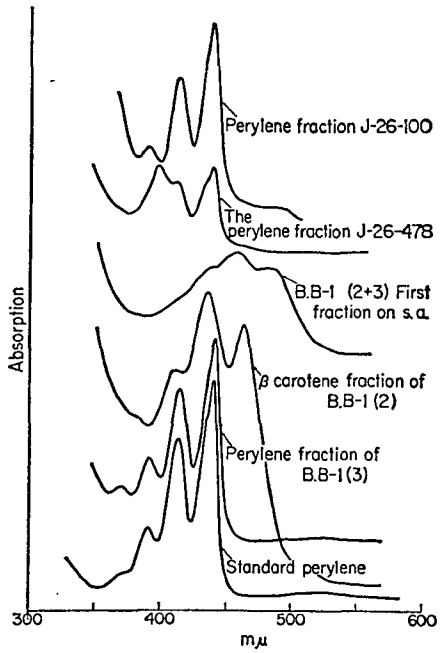

Fig. 3. Ultra-violet spectra of standard perylene, some typical perylene fractions and β-carotene separated from a perylene fraction.

aromatics. For best separation, and to avoid a mixture of compounds that absorb in the same region of the u.v.–Vis as perylene, the change from hexane elution to benzene should be gradual (5, 10, 25, 40, 50 per cent). Although this method gives good qualitative results, in some cases it fails to give quantitative values because other aromatics cover the same region of u.v.–Vis absorption (sample J-3-34 is a good example). In the u.v. technique for identification and quantitative determination, one should note that of the four typical peaks in perylene's u.v.-spectrum, the highest $\lambda_{Max}^{Benzene}$ 440 mμ was selected, $\varepsilon = 4{\cdot}06 \times 10^4$ l/mole/cm (SCHNURMANN *et al.*, 1953).

For those samples where the u.v. method could not be effectively employed, we applied GLC and GLC–mass spectrometry. This technique proved to be simple and precise. In this method, after extraction of the sample, only one liquid column chromatographic separation is required. The extract is evaporated to near-dryness and placed on Florisil column (see path B flow chart, Fig. 2). The first fraction, eluted with hexane, contains aliphatic hydrocarbons and the second, eluted with benzene, contains the aromatics. The benzene fraction is resolved by gas-chromatography on a 6′ × $\frac{1}{8}$″ Ap-L (or OV-17) column, temperature programmed from 200° to 300°C at a rate of 12°/min (see Fig. 4). For further identification, a standard perylene sample is coinjected.

Samples with the highest perylene concentrations were checked by a combination of GLC and medium resolution mass-spectrometry (CEC 21-491). Whereas, the GLC detection limit is 0·01 μg/100 g of dry sediment, the combined technique could not be applied for samples containing less than 25 μg/100 g (if the amount of sediment extracted is <100 g), because of column background and mass-spectrum sensitivity limits. By comparison with standard perylene, the mass spectrum shows that the extracted perylene is at least 95 per cent non-substituted and the 5 per cent probably alkyl derivatives (see Fig. 5).

All packing materials for liquid chromatography were washed in the reversed solvent polarity order of use (methanol, benzene, hexane) and dried at 130–150°C for four hours. The packing materials used were: (1) silicic acid (for lipid chromatography) Bio-SIL-HA, −324 mesh (Bio-Rad. Laboratories); silica gel, 30/60 mesh (Applied Science Laboratory Inc.); Florisil, FX-285-1, −100 mesh (Matheson Coleman & Bell).

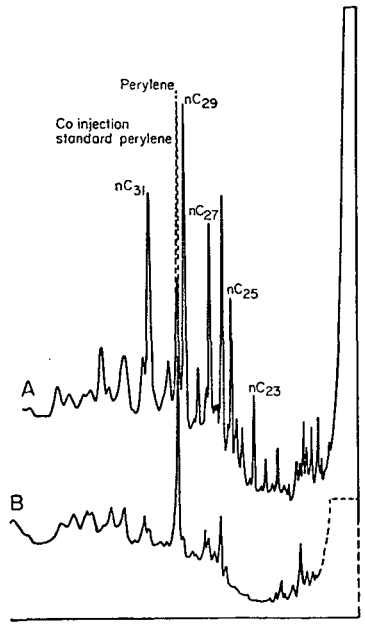

Fig. 4. Gas chromatography of perylene.
A. Total hydrocarbons J-26-230 hexane fraction eluted on silicic acid, chromatographed on Ap-L (200° to 300°C 12°/min); the broken line indicates the coinjection of standard perylene.
B. Total H. C. (A) re-chromatographed on Florisil (aromatic fraction). GLC as described for A.

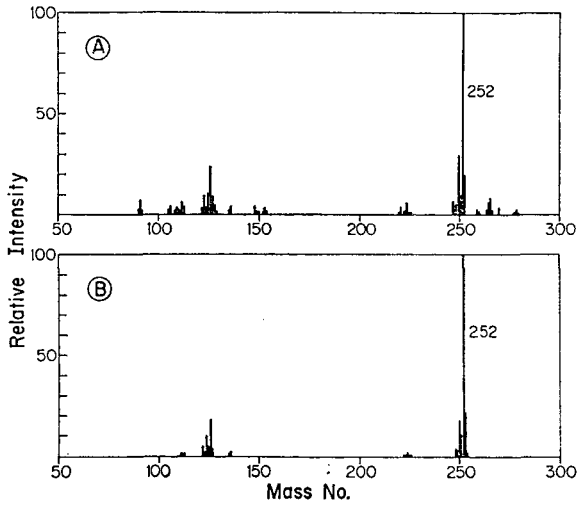

Fig. 5. Mass spectra.
A. Perylene peak from 3B/3450-3480. B. Standard perylene. (Varian 1200 GLC combined with mass-spectrometer CEC-21-491.) Both samples were recorded under same conditions.

RESULTS AND DISCUSSION

The results of the present investigation are summarized in Table 1, and compared with those of ORR and GRADY (1967). In the course of this study, a variety of lithified and unlithified sediments was studied, representing different geographic distribution, terrestrial, neritic, and bathyl environments and depth of burial. The ages of these sediments range from very recent to hundreds of millions of years.

It is apparent that age is not an important criterion for the presence or absence of perylene. From the analysis of 12 deep-sea sediment samples (JOIDES), perylene was only detected in samples from J-26 (JOIDES Hole 26) and in one sample from the Gulf of Mexico (J-3-34). It was present in near-shore sediments such as the Saanich Inlet fjord, British Columbia, and Bandaras Bay, which is fed by flood waters from the Rio Ameca. We were also able to confirm the results of ORR and GRADY (1967) that perylene is absent in the sediment of Tanner Basin (approximately 150 km off the southern California shore). Relatively high concentration of perylene was extracted from a recent English (Glastonbury) peat.

ORR and GRADY (1967) explained the presence of perylene in the Santa Barbara sediments as a result of preservation of organic constituents rapidly deposited under anaerobic conditions from shallow oxygen-poor water. They assumed that the precursors for the hydrocarbon, possibly hydroquinones (shown in Fig. 1), arise from pigments in marine organisms. This would involve step-wise hydrolysis and reduction of the C=O bond leading to dehydration of the phenols (C—OH) to give the aromatic structure as originally proposed by BLUMER (1965). Unfortunately, no precursors of perylene or other polycyclic aromatics extracted from recent sediments, (1,12-benzperylene and coronene; MEINSCHEIN, 1959) have been recognized. It is known, however, that insects (CAMERON *et al.*, 1964) and fungi (THOMPSON, 1957; ALLPORT and BU'LOCK, 1960) do contain several pigments which could be perylene precursors. HODGSON *et al.* (1968b) claim that the u.v. spectrum of some pigments from swiss chard, spinach and lettuce closely resembles that of perylene found in petroleum and sediments. Furthermore, BERGMANN *et al.* (1964) report the isolation of crystalline perylene from peat, derived from land plants and their associated biota.

It appears that the necessary conditions for the formation and preservation of perylene in marine sediments are: (a) source of material (b) deposition history (rapid or slow: mode of transport in water column or turbidity currents, etc.) (c) preservation history (redox conditions, temperature, complexing, etc.). ORR and GRADY (1967) believe that the last two are the controlling factors based on a marine origin of the biological precursors. An alternative explanation can be offered, that the precursors of perylene originate on land and are transported into the ocean. They will only survive if transportation is sufficiently rapid to prevent degradation of biochemicals. For example, 4,9-dihydroxyperylene-3,10-quinone (II) (see Fig. 1) which is considered a possible precursor of perylene, is much more vulnerable to oxidation than perylene, itself. Transformation of these precursors (see Fig. 1) into the aromatic polycyclic hydrocarbons will occur if deposition takes place in a reducing environment. Interpretations based on the environment of deposition and preservation are the same as those suggested by Orr and Grady, but we believe that the source of the precursors may be largely or entirely terrigenous.

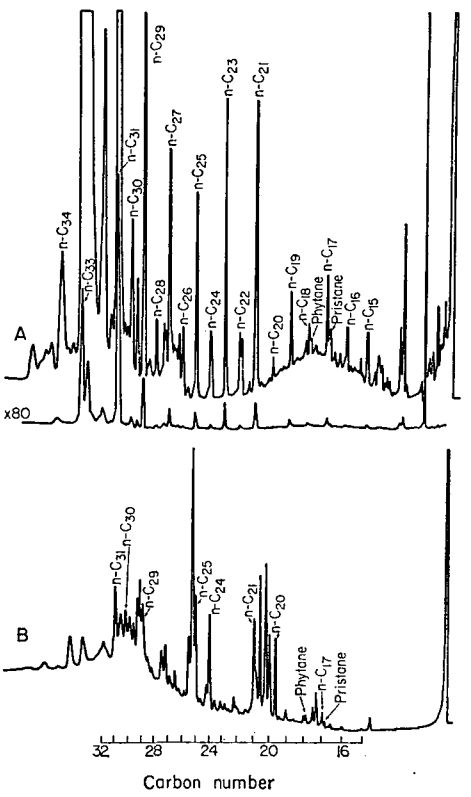

Fig. 6. Total hydrocarbon distribution (P-EG and T_1):
A. Total hydrocarbon fraction from Glastonbury peat (P-EG) chromatographed on Ap-L 8 ft × $\frac{1}{8}$ in. (5 per cent on chromosorb W) 100° to 300°C 4°C/min. B. Total hydrocarbon fraction from Tanner Basin (T_1), GlC under same conditions as A.

Evidence for the presence of land-derived organic components is seen in two properties of the organic matter. First, in all samples where perylene was detected, long-chain hydrocarbons ranging from C_{27} to C_{31} were abundant (see Fig. 4 and 6). Furthermore, the carbon preference index (CPI) of these hydrocarbons was $>1{\cdot}3$. In the case of hydrocarbons from Glastonbury peat, the CPI is above 4 (see Fig. 6A). However, in the case of the Tanner Basin (T_1 and T_2) and other reducing sediments such as the San Pedro Martir Basin (GC-15-25), hydrocarbons in the range C_{18} to C_{24} are most abundant, and there is no apparent odd-over-even predominance (see Fig. 6B). Second, $^{13}C/^{12}C$ measurements of the organic carbon compounds in samples containing perylene indicate some component of higher plant material is present. Marine-derived organic matter generally has $\delta^{13}C$ values of -19 to $-20‰$, whereas land-derived organic matter usually yields $\delta^{13}C$ values between -25 and $-28‰$. The combination of the above two criteria help identify relative sources of organic matter. It is significant to note that samples analysed by MEINSCHEIN (1959) in which polycyclic aromatic hydrocarbons were detected, all came from near

shore (Gulf of Mexico) and, apparently, so did those in which HODGSON (1968a) reported perylene-rich ('type I') aromatics.

The argument of ORR and GRADY (1967) for absence of perylene in Tanner Basin sediment because of the depth of the water column is reasonable; however, it does not explain the presence of perylene in sample J-3-34 from hole 3 (JOIDES) or in the samples from Hole 26. In both these cases, it is apparent that extensive turbidity currents have been responsible for deposition. In the case of Hole 26 (Vema Fracture Zone) the source of the sediment was probably the Amazon River, 1200 km away.

In support of the above argument is the fact that other highly unstable molecules, such as carotenoids and chlorophyll-derived chlorins, were present in Tanner Basin and the Gulf of California sediments. If oxidation, either in the water column during deposition or at the sediment–water interface, was extensive, these molecules would have been degraded. Furthermore, the study of the San Pedro Martir Basin sediments indicates a very close resemblance to the marine-type organic matter in the Tanner Basin. Sample GC 15–25 is very rich in phenophytin and carotenoids, but no perylene was found in this core, despite the fact that sulfate is reduced rapidly at the surface. Once perylene forms, it can be stabilized by π-complexing with transition metals (CLAR, 1964). Hence, even when carotenes can no longer be detected in older sediments, due to degradation (or complexing into humic acids or kerogen-like compounds) perylene can persist once it is formed.

Analysis of two organic-rich Miocene shales from Southern California (Monterey shale and Nicholas Formation shale) indicates the absence of carotenoids in both. However, the Monterey shale contains perylene (150 μg/100 g) and a relatively high concentration of chlorins ($\sim$100 μg/100 g) whereas Nicholas shale contains no perylene or chlorins, but small amounts of a porphyrin (7×10^{-3} μg/100 g, probably Fe-porphyrin) indicating oxidation of organic matter. Both these shales contain long-chain aliphatic hydrocarbons with CPI values higher than 2·0.

It therefore appears that rapid introduction of sediment, probably by turbidity currents, will transform relatively high contents of detrital material into neritic as well as bathyal traps. This rapid deposition will allow reducing conditions to be established and will convert pigment precursors, possibly by hydrolysis and reduction, to relatively stable perylene. Where oxidizing conditions exist at the surface of the sediment, or where the source of organic matter is entirely (or predominantly) marine, perylene will not form in the sediment column during diagenesis.

As stated earlier, perylene is present in small amounts in some petroleum deposits. According to the principles expounded by YEN *et al.* (1961), the molecular configuration of perylene is not compatible with the polynuclear network composed of naphthalene rings and other peri-polycyclic aromatics, therefore, it could not be synthesized under the same conditions. Thus, perylene never becomes an important constituent in aromatic dominated petroleum. Its presence in petroleum arises from extraction out of the source shale or sediment through which oil migrates.

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(Scripps vessel R. V. *Alexander Agassiz*) and collected by E. K. KALIL and R. SWEENEY. The Bandaras Bay mud was presented to us by J. I. DREVER and the San Pedro Martir Basin core was collected by J. BISCHOFF (USC vessel R. V. *Velero*, core 833221).

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C_{18}-Isoprenoid Ketone in Recent Marine Sediment

ISOPRENOID hydrocarbons, fatty acids and alcohols occur in ancient rocks, oil shales, young sediments and living organisms[1,2]. During thermal alteration experiments on a recent marine sediment from Tanner Basin, Southern California continental shelf, we isolated a C_{18}-isoprenoid ketone, namely 6,10,14-trimethylpentadecan-2-one. Samples of sediment from the Tanner Basin were sealed in glass bombs and exposed to temperatures from 60° to 150° C for 7 d, 30 d and 60 d. The sediment was then extracted with benzene-methanol and the extract chromatographed on a silicic acid column. The ketone was found in both the heat-treated and untreated sediment. It was extracted with the fatty acid fraction which had been converted to methyl esters, and was separated with the other branched components by the urea adduction method. For comparative purposes, the C_{18}-isoprenoid ketone was also synthesized[3]. Analytical comparisons by gas-liquid chromatography, using two 5 foot × ⅛ inch columns (3% OV 101 on 100/120 mesh 'Gas Chrom' Q and 3% DEGS on 100/120 mesh 'Gas Chrom' Z), showed the synthetic product to be identical to the sedimental ketone.

We obtained a mass spectrum of the ketone using a gas chromatograph coupled with a CEC-21-491 mass spectrometer. The spectrum showed a molecular ion peak at m/e 268 with fragmentation peaks at m/e 250 (M-18); 235 (M-33); 225 (M-43) and 210 (M-58). Loss of $[CH_3\text{-}CO]^+$ and $[CH_2\text{-}CO\text{-}CH_2]^+$ gave abundant fragments at m/e 43 and 58, respectively (Fig. 1). This pattern is compatible with synthetic C_{18}-isoprenoid ketone reported by Cox *et al.*[4]. Further evidence for ketone structure was also gained from infrared spectroscopic measurements. A weak absorption band (due to small sample size) was observed at 1,714 cm^{-1} (in CCl_4), which is characteristic of a saturated methyl ketone. The NMR spectrum (in CCl_4) showed the expected signals for CH_3CO protons (δ 2.03 p.p.m.), CH_2 protons adjacent to the CH_3CO group (triplet δ 2.25, 2.3, 2.35 p.p.m.), other CH_2 protons as well as CH protons (multiplet centred at δ 1.25 p.p.m.) and $(CH_3)_2$ CH protons (δ 0.82 and 0.9 p.p.m.). The identity of the ketone was further substantiated by *in situ* formation of a yellow 2,4-dinitrophenylhydrazone on thin-layer plates (silica gel GF-254). The measured R_F of 0.66 (triple developed with chloroform-hexane, 3 : 1) was the same as for the synthetic ketone.

The data (Table 1) show the influence of temperature and time of heating upon ketone generation. The ketone

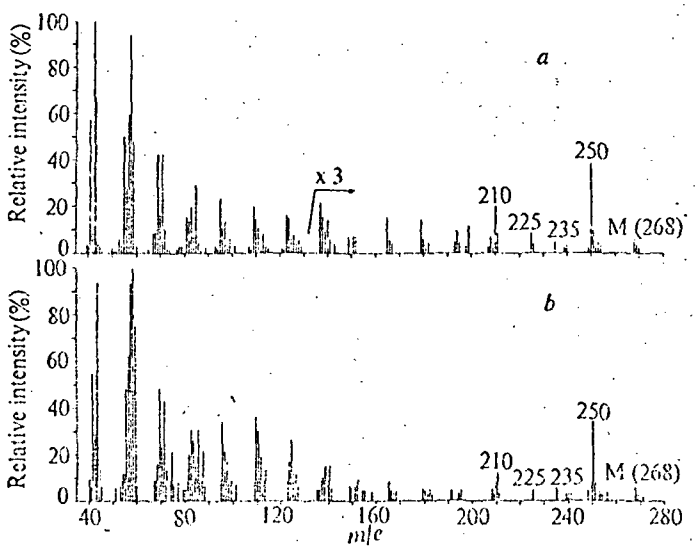

Fig. 1 Mass spectra of, *a*, synthetic C_{18}-isoprenoid ketone; *b*, ketone isolated from sediment.

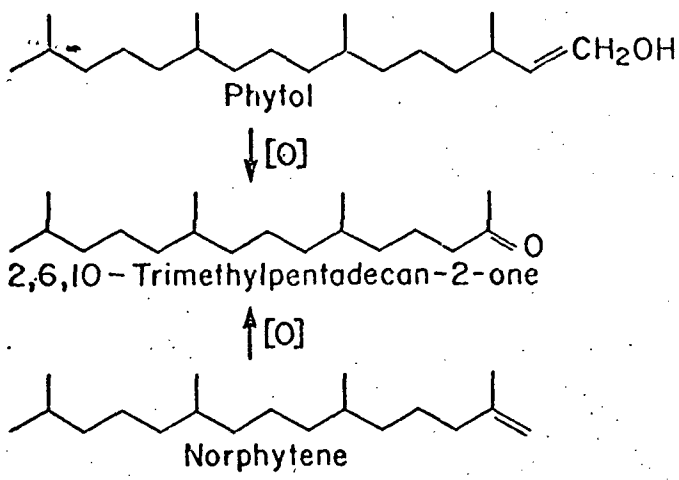

Fig. 2 Possible formation of isoprenoid ketone.

was present initially in the sediment at the concentration of 0.160 p.p.m. The maximum yield was obtained by heating the sample at 150° C for one month. Comparing the quantity of ketone formed from natural and freeze dried samples (150° C, 2 months) indicates considerable inhibition of ketone accumulation in the freeze dried sample.

Table 1 Concentration of C_{18}-Isoprenoid Ketone in Tanner Basin Heat-treated Sediment (Parts per Thousand Million)*

Time (d)	Temperature (°C)		
	65	100	150
7	140	880	1,240
30	500	1,440	4,700
64	50	730	2,100
64	—	—	820†

* Determined by gas chromatography. Accuracy of total extraction procedure estimated to be ±0.05 p.p.m.
† Freeze dried before heating.

Although other contributors, such as vitamin K_1, α-tocopherol and phospholipids from halophyllic bacteria[5,6] and algae[7] which have been shown to possess a phytyl side chain, are also possible, the most obvious source for the ketone is phytol, originally derived from chlorophyll. A detailed consideration of the processes leading from phytol to the ketone is premature, but various pathways may be invoked to account for the formation of the ketone (Fig. 2). One is the oxidative degradation of norphytene, which was isolated from various plankton, fish and mammalian oils[8], and probably originates from phytol concentrated by zooplankton, followed by dehydration under acid catalysis of the digestive tract of marine animals. The C_{18}-ketone could also be formed during diagenesis, by oxidation of the allylic alcohol phytol, possibly biologically catalysed, during the early stages of sedimentation. We favour the occurrence of the second pathway during heating[4].

R. Ikan*
M. J. Baedecker
I. R. Kaplan

Institute of Geophysics and Planetary Physics,
University of California,
Los Angeles, California 90024

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* Permanent address: Department of Organic Chemistry, Natural Products Laboratory, Hebrew University, Jerusalem.

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Distribution and diagenesis of organic compounds in JOIDES sediment from Gulf of Mexico and western Atlantic*

Z. AIZENSHTAT†, M. J. BAEDECKER and I. R. KAPLAN
Institute of Geophysics and Planetary Physics, University of California at Los Angeles, Los Angeles, California 90024, U.S.A.

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Abstract—Fifteen sediment samples were studied from five drill sites recovered by the 'Glomar Challenger' on Legs I and IV in the Gulf of Mexico and western Atlantic. This study concentrated on compounds derived from biogenic precursors, namely: (1) hydrocarbons, (2) fatty acids, (3) pigments and (4) amino acids.

Carbon isotope (δC^{13}) data (values $< -26‰$ relative to PDB), long-chain *n*-alkyl hydrocarbons ($>C_{27}$) with odd carbon numbered molecules dominating even carbon numbered species, and presence of perylene proved useful as possible indicators for terrigenous contributions to the organic matter in some samples. Apparently land-derived organic matter can be transported for distances over 1000 km into the ocean and their source still recognized.

The study was primarily designed to investigate: (i) the sources of the organic matter present in the sediment, (ii) their stability with time of accumulation and (iii) the conditions necessary for *in situ* formation of new compounds.

INTRODUCTION

UNTIL 1968, when the deep-sea drilling and coring project was initiated by JOIDES, organic geochemical studies on unlithified marine sediments were restricted to samples buried to less than 50 m depth. This work describes the analysis of fifteen samples from five drill sites on Legs I and IV of the JOIDES program. The deepest sample was cored from 534 m (Hole 3) and is Miocene in age; the oldest sample examined came from Hole 6 (153 m) and is Eocene in age.

Other analyses of JOIDES sediment samples have been reported by KOONS (1970), SIMONEIT and BURLINGAME (1971), SIMONEIT *et al.* (1972,1973), MCIVER (1971, 1972), BAKER (1970) and WEHMILLER and HARE (1972). Generally, these reports have each dealt with a restricted group of compounds. Here, an attempt was made to analyze hydrocarbons, fatty acids, pigments (chlorins and porphyrins) and amino acids. The C^{13}/C^{12} ratio was measured on the organic carbon of all sediment samples, and on some extractable and non-extractable residues (e.g. humic acid and kerogen)

EXPERIMENTAL

Sample and site description

A description of the site location, water depth, depth of core penetration below the sediment–water interface, stratigraphic age, a brief lithological description, organic carbon content and δC^{13} in parts per mil, relative to the PDB scale, are given for each sample in Table 1. Detailed descriptions for each core are presented in the Initial Reports of the Deep Sea Drilling Project (EWING *et al.*, 1969; BADER *et al.*, 1970). Some additional notes are listed below, for the purpose of discussion and interpretation of the data obtained in this study.

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† Permanent address: Department of Organic Chemistry, The Hebrew University, Jerusalem, Israel.

Hole 2. Hole 2 was drilled on the Challenger Knoll salt dome. Oil was found in core 5 at 136–138 m depth within porous calcite and gypsum layers. The top sample studied (20 m depth) contained abundant plankton remains and traces of pyrite. The lower sample (103 m) had a strong smell of H_2S when opened. There was no obvious evidence for oil migration into the samples studied here.

Hole 3. This site is about 21 nautical miles S.E. of Hole 2. Four samples were studied, ranging in age from Pleistocene to Miocene. The sediment consists of interbedded turbidites and normal pelagic sediment sequences. The surface cores were reported to be "silty to very silty terrigenous clays, with or without admixture of nanoplankton and foraminifera." A fragment of fossil wood was detected at depth. Evidence of pyrite in the sediment and sulfate reduction in the interstitial water (KAPLAN and PRESLEY, 1969) indicates that this was a reducing environment.

Holes 6A *and* 6. These sites are in deep water on the west flank of the Bermuda Rise. The three samples examined ranged in age from Pleistocene to Eocene. The older Eocene sediments are dominated by turbidity flows. These grade upward to more normal pelagic sediments containing a variety of microfossil remains and volcanogenic debris. The rate of sedimentation was very slow ($<0{\cdot}3$ cm/10^3 yr), allowing oxidation to proceed at the sediment surface.

Hole 26. The site for drilling is the Vema Fracture Zone, a narrow east–west trending trough which cuts through the Mid-Atlantic Ridge. The location has a high heat flow (often associated with mid-ocean ridges). Rapid sedimentation has taken place; apparently all three samples cored (to 478 m) are Quaternary in age. The sediment appears to be turbidites, showing graded

Table 1. Description of samples

Location	Water depth (m)	Sample hole-depth (m)	JOIDES designation*	Age	Description	% Org. C	δC^{13} (‰)
23°27·3′N 92°35·2′W	3572	2-20	1-2 (0-65)	Pleist.	Calcareous mud	0·45	−23·4
		2-103	4-1 (30-90)	Pliocene	Cocc. ooze, H_2S	0·38	−22·8
23°01·8′N 92°02·6′W	3747	3-34	1-2 (0-72)	Pleist.	Calc. silt, clay	1·11	−26·6
		3-209	4-1 (33-100)	Pleist.	Cocc. ooze, clay	0·82	−21·7
		3-324	5-2 (102-150)	Pliocene	Cocc. ooze, clay	0·47	−22·1
		3-534	9-2 (18-60)	Miocene	Grayish-green silty clay	0·47	−22·2
30°50·39′N 67°38·86′W	5125	6A-15	1-2 (10-72)	Pleist.	Brown clay	0·13	−24·0
		6-43	1-1 (90-150)	Pliocene	Brown clay	0·16	−25·4
		6-153	2-2 (0-70)	Eocene	Gray-green clay	0·09	−25·7
10°53·55′N 44°02·57′W	5168	26-100	1-3 (81-130)	Pleist.	Gray silty clay	0·87	−25·3
		26-230	3-2 (100-150)	Pleist.	Olive-gray clay-clay-stone	1·00	−27·0
		26-478	5-1 (89-131)	Pleist.	Dk. olive gray silty clay-stone	0·51	−25·2
15°51·39′N 56°52·76′W	5258	27-143	2-2 (95-150)	Miocene	Lt. olive-gray clay	0·27	−25·0
		27-237	3-2 (0-64)	Miocene	Stiff green-gray clay	0·58	−26·8
		27-249	4-3 (84-150)	Miocene	Green-yellow mottled clay	0·18	−24·5

* Core-section (interval).

bedding with sand at the bottom and clay at the top of each sequence. Detrital silicates, quartz, metal oxides and heavy minerals indicate rapid transport, possibly from the Amazon River which is about 1100 km away. Terrigenous plant fragments were recognized in the sand layers. The sediment was reducing and showed marked sulfate reduction.

Hole 27. The uppermost sample (143 m) consists of silty clay containing glauconite and pyrite. The two bottom samples were sampled in, or adjacent to, recognizable turbidites displaying graded bedding and containing plant fragments. The sediment was reducing (PRESLEY and KAPLAN, 1970), and the lower two samples showed most pronounced sulfate reduction. The age of all samples is Miocene.

Sample storage

Sediment samples received from the Glomar Challenger had been squeezed to remove interstitial water, wrapped in aluminum foil, and frozen; 150 g samples from each location were analyzed.

Analytical procedures

The total organic carbon was determined after reacting a known weight of sediment with 0·2 N HCl to remove carbonate. The residue was washed repeatedly with distilled water to remove all the acid and dried in a vacuum dessicator at 40°C. The dried sample was combusted in an oxygen atmosphere at 1100°C and the volume of CO_2 was measured to calculate the amount of organic carbon in the sediment. The CO_2 was collected and the C^{13}/C^{12} ratio determined on a Nuclide Co. 60° radius mass spectrometer.

A procedure was developed for each sample to determine: hydrocarbons, fatty acids, alcohols, chlorins and porphyrins. In addition, amino acids, fulvic acids, humic acids and kerogen were isolated in samples from Hole 26. A summary of the methods used is shown in Fig. 1. A detailed description of the extraction procedure is given in BROWN *et al.* (1972). Techniques for the separation and analysis of free fatty acids (FFA), hydrolyzable fatty acids (HFA), alcohols and humic and fulvic acids have been described elsewhere (NISSENBAUM *et al.*, 1972a). Kerogen was demineralized by successive treatments with HF, HCl and HNO_3 according to the method developed by SAXBY (1970). Some of the techniques used for the analysis of hydrocarbons, pigments and amino acids were modified slightly for this study.

The hexane fraction from the silicic acid column (Fig. 1) which contained the hydrocarbons, was evaporated to near-dryness and rechromatographed to separate aliphatic and aromatic hydrocarbons. The total hydrocarbon fraction was applied to a small florisil column and eluted

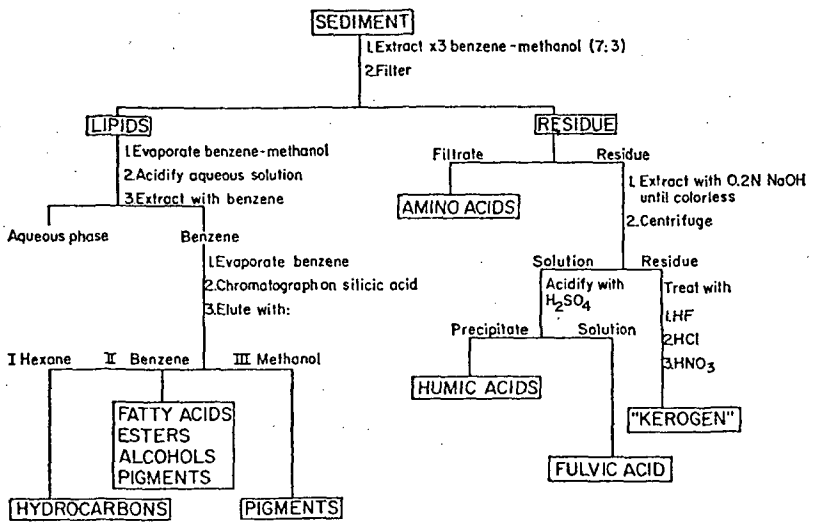

Fig. 1. Flow chart of procedures.

with hexane and then with benzene. The hexane eluent containing aliphatic hydrocarbons and the benzene eluent containing aromatic hydrocarbons were analyzed by gas chromatography. Perylene was analyzed following the procedure of AIZENSHTAT (1973).

Part of the benzene fraction from the silicic acid column was used for the analysis of acids and alcohols and that remaining was used for the study of pigments. Porphyrin and chlorin pigments were found in the benzene and methanol fractions, respectively, from the silicic acid column. Occasionally, some chlorins appeared with the porphyrins, in which case the two fractions were recombined and chromatographed on a silica gel column. The following solvents were used for eluting the pigments: (1) hexane, (2) hexane:benzene (1:1), (3) hexane:benzene (1:4), (4) benzene and (5) 5–20% chloroform in benzene. Porphyrins were in fractions (3) and (4); the latter contained compounds more substituted in carbonyl groups. Fraction (5) contained the chlorins. The fractions were evaporated to dryness, taken up in benzene, and analyzed by ultra-violet and visible spectrometry.

The porphyrin results were calculated by using the Soret peak at 390–408 mμ and the extinction coefficient of $3{\cdot}3 \times 10^5$ l/mole per cm (HODGSON *et al.*, 1968). The data for chlorins were calculated using the 660 mμ peak and $\varepsilon = 3 \times 10^4$ l/mole per cm (GOEDHEER, 1966).

The sediment, after benzene–methanol extraction, was refluxed with 6 N HCl for 12 hours to hydrolyze the amino acids, and then filtered. The filtrate was concentrated by rotary evaporation under vacuum, then diluted with 150 ml water. To this solution 3 N HF was added, and, while stirring, 4 N LiOH was added to bring the pH in the range of 7–9 to precipitate salts. The mixture was filtered and the filtrate, containing the amino acids, was concentrated. The amino acid solution was then applied onto cation exchange resin to complete the desalting procedure. The column was washed with water and, when the eluent was chloride-free, the amino acids were eluted with 2 N NH_4OH. The fractions containing amino acids were concentrated and run on an amino acid analyzer. Optical isomers were determined by gas chromatography on the N-trifluoroacetyl-(+)-2-butyl ester derivatives of the amino acids (KVENVOLDEN *et al.*, 1969).

Reagents and instrumentation

Organic solvents used in the procedure were distilled and the level of solvent contamination was determined to be $<4 \times 10^{-11}$ g/ml for all solvents. The chromatographic packing material: silicic acid (minus 325 mesh), florisil (minus 100 mesh) and silica gel (30–60 mesh), were prewashed with the eluting solvents in reverse order of actual use and oven-dried. The cation exchange resin AG 50W-X8, was washed before use with NaOH, water, HCl and again with water until chloride-free.

Gas chromatographic analyses were carried out on Varian Aerograph Models 204, and 1520 and Hewlett-Packard Model 5750 gas chromatographs. The following columns were used: 5 ft $\times$ $\frac{1}{8}$ in., 3% SE-30 on 100–120 mesh Gas-Chrom Z; 5 ft $\times$ $\frac{1}{8}$ in., 2% Apiezon L on Gas-Chrom Z; 5 ft $\times$ $\frac{1}{8}$ in., 3% DEGS on 100–120 mesh Chromosorb W; 2% carbowax 20 M on Chromosorb W; and 100 ft (0·01 in. i.d.) capillary column coated with Apiezon L. Ultra-violet and visible spectra were obtained on a Cary 15 spectrometer, equipped with a 0·1 cm^3 microcell. A 21-491 CEC mass spectrometer, coupled with a Varian model 1200 gas chromatograph employing a 5 ft $\times$ $\frac{1}{8}$ in., 5% SE-column, was used for structure determinations.

RESULTS

Hydrocarbons

Hole 2. Sample 2-20 contains 17 ppm and sample 2-103 contains 4 ppm of identifiable n-alkanes. The distribution is bimodal; about 97 per cent of the identifiable hydrocarbon is in the range C_{25}–C_{33}, (Figs. 2B and 3) with C_{29} and C_{31} accounting for at least 60 per cent. The remainder fall in short-chain length C_{14}–C_{19}, with no evident dominance of either odd or even numbered carbon compounds. For the range C_{21}–C_{33}, the CPI (carbon preference index; COOPER and BRAY, 1963) equals

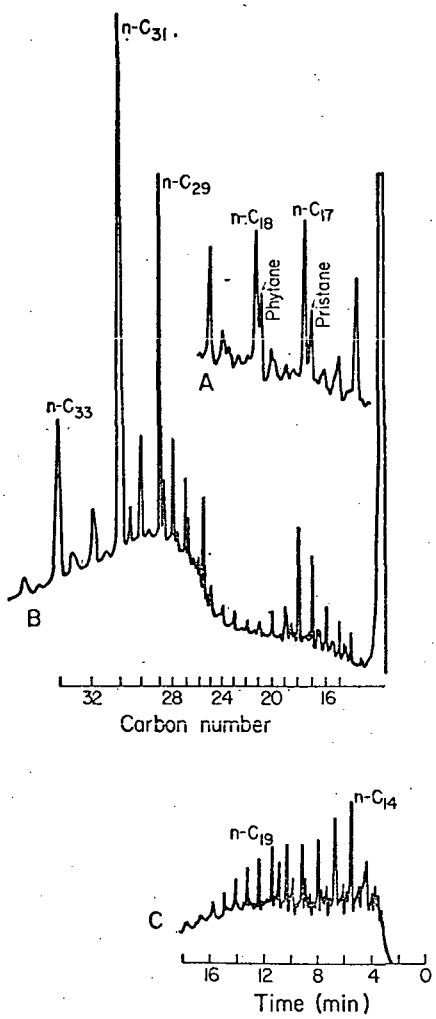

Fig. 2. (A and B) Total hydrocarbon distribution in sample 2-103. (B) shows separation on a 5 ft × $\frac{1}{8}$ in. column packed with 2% Apiezon L on 100-120 mesh Gas-Chrom Z. (A) shows the separation of pristane and phytane from n-C_{17} and n-C_{18}, respectively, on a 200 ft Apiezon L capillary column. (C) Distribution of saturated hydrocarbons in petroleum from Challenger Knoll for comparison (DAVIS and BRAY, 1969).

3·9 in sample 2-20 and 4·6 for sample 2-103. The isoprenoid hydrocarbons pristane and phytane were detected in low abundance (50 ppb) and the ratio pris./phyt. = 0·7 for 2-20 and 0·8 for 2-103 (see Fig. 2A).

Comparison of hydrocarbons extracted from these samples with saturated hydrocarbons from the petroleum at depth of 136–138 m in the same hole, shown in Fig. 2C (DAVIS and BRAY, 1969), indicated a lack of long-chain hydrocarbons in the oil. It is, therefore, unlikely that the petroleum was a source of the hydrocarbons in the overlying sediment. This interpretation is further supported by a lack of aromatic

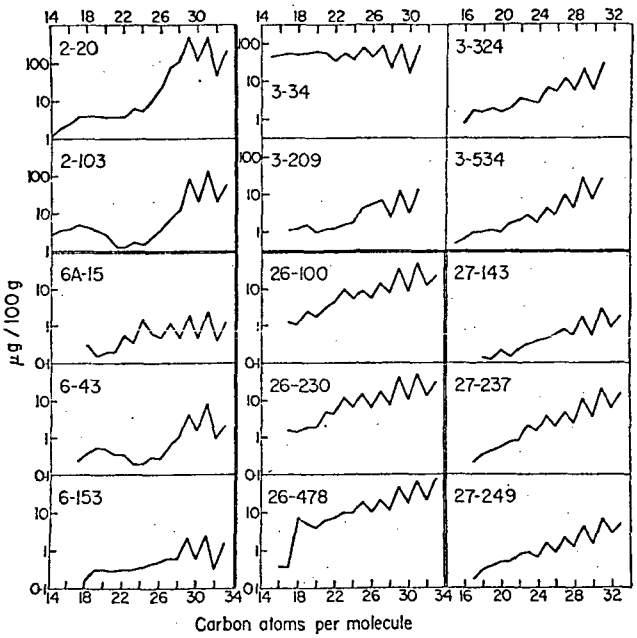

Fig. 3. Comparative distribution of n-alkanes in all samples analyzed.

hydrocarbons in the sample analyzed, in comparison with the petroleum fraction which contained 41 wt. per cent aromatics in the higher molecular weight fraction ($>C_{13}$).

Hole 3. The n-alkane hydrocarbon pattern for the uppermost sample 3-34, is different from the three lower samples (Fig. 3). Samples 3-209, 3-324 and 3-534 contain 0·6, 1·1 and 1·0 ppm n-alkanes, whereas 3-34 contains 9·3 ppm. Furthermore, the lower samples have a distribution similar to those in Hole 2, with 80 per cent of the n-alkanes having a chain length $>C_{24}$, whereas 3-34 has 50 per cent of the n-alkanes lighter than C_{24}. In all cases, the hydrocarbons heavier than C_{26} display a marked odd carbon number dominance, with CPI_{21-29} falling in the range 2–3·5.

Isoprenoid hydrocarbons in 3-209, 3-324 and 3-534 are present in trace amounts only (<10–20 ppb), whereas in 3-34, the pristane concentration is 665 ppb and the phytane concentration is 383 ppb. There is also evidence from u.v. spectroscopy for a greater aromatic hydrocarbon concentration in 3-34.

Hole 6. The n-alkane contents of the samples from 6A-15, 6-43 and 6-153 are 130, 240 and 120 ppb, respectively, and no pristane or phytane was identified. C_{29}, C_{31} and C_{33} (Fig. 3) are strongly dominant, and account for ~50 per cent of the total n-alkanes.

Hole 26. The concentration of n-alkanes increases in samples from this site with depth, from 2·0 ppm in 26-100 to 2·4 ppm in 26-230 to 3·4 ppm in 26-478. Again, as in other samples, C_{29}, C_{31} and C_{33} predominate (Fig. 3) and the CPI for C_{25}–C_{31} is 3·3, 3·7 and 2·2 in the three samples, respectively. However, unlike the other samples at least half of the extracted hydrocarbons were branch-chained. They showed a complex distribution over the entire hydrocarbon range (C_{15}–C_{33}) and no attempt was made to identify individual compounds.

Hole 27. The n-alkane content of the three samples at this site is very low (120 ppb for 27-143, 810 ppb for 27-237 and 320 ppb for 27-249). Again, there is a strong odd-to-even relationship with $CPI_{21-31} = 2{\cdot}2$, 3·3 and 2·5 in the three samples, respectively. The long-chain hydrocarbons C_{25} to C_{33} predominate (Fig 5). Branched hydrocarbons are only present at concentration 1/50 of the straight-chain components, and pristane is less abundant than phytane in all cases (pris./phyt. = 0·19, 0·43 and 0·43, respectively).

Perylene

Perylene ($C_{20}H_{12}$) was the only aromatic hydrocarbon identified quantitatively in this study. It was present in trace amounts in sample 3-34 of Hole 3 and in all three samples analyzed in Hole 26 in quantities of 185 ppb for 26-100, 331 ppb for 26-230 and 161 ppb for 26-478. This compound was not detected in the other samples.

Fatty acids and alcohols

Hole 2. Sample 2-20 contained 600 ppb of hydrolyzable fatty acids (HFA) and sample 2-103 only 70 ppb. No free fatty acids (FFA) were detected. The dominant components in each case were n-C_{16}, C_{28} and C_{30}. No C_{16} unsaturated HFA was detected, and the ratio Δ-C_{18}/C_{18} was <1 for both samples (Table 2). In both samples, HFA $> C_{20}$ were the most abundant.

It was estimated that <70 ppb alcohols were present in each sample; even-numbered carbon members, from C_{14} to C_{26} were detected.

Hole 3. Whereas no FFA were detected, HFA were identified in all the four samples from this site. The highest concentration (900 ppb) was found in the top sample. The dominant acids were n-C_{16} and C_{18}. Saturated C_{16} was always more abundant than Δ-C_{16} (Table 2), whereas, in 3-324 and 3-534 Δ-C_{18} was more abundant than C_{18}. These were the only two samples in the present study, which showed Δ-$C_{18}/C_{18} > 1$.

Alcohols were detected in all four samples in concentrations equal to ~25 per cent of HFA. The identified alcohols were even-numbered compounds, the dominant

Table 2. Hydrolyzable fatty acids

Hole-depth (m)	Total μg/100 g*	% > C_{20}	% Unsaturated	Δ16/16	Δ18/18
2-20	60	67	5	—	0·69
2-103	7	71	4	—	0·75
3-34	90	15	14	0·12	0·60
3-209	29	11	14	0·08	0·78
3-324	36	8	30	0·10	2·64
3-534	41	15	23	0·13	1·35
26-100	279	83	3	0·14	0·53
26-230	149	76	3	0·07	0·40
26-478	58	70	2	—	0·27
27-143	3	—	22	0·17	0·78
27-237	250	53	8	0·08	0·77
27-249	28	15	13	0·12	0·52

* Fatty acids identified range in carbon number from C_{14} to C_{20} with the exception of Hole 3 which ranges from C_{14} to C_{24}.

alcohol was generally n-C_{20}; however, higher molecular weight compounds which were not identified constitute the bulk of this fraction. In sample 3-34, phytol was tentatively identified on the basis of retention time data from a 2 per cent carbowax 20 M column, at the concentration level of 9 ppb, but no dihydrophytol could be found.

Hole 6. Only traces of HFA (<50 ppb) were measured and no alcohols were detected in samples analyzed at this site.

Hole 26. This site is the only one in which FFA were identified. Concentrations in the three samples were 150 ppb in 26-100, 1000 ppb in 26-230 and 140 ppb in 26-478. The high concentration of FFA in 26-230 is mainly due to large amounts of even carbon-numbered fatty acids: C_{24}, C_{26}, C_{28} and C_{30}. The HFA, however, showed a gradual decrease from 2790 ppb in 26-100 to 580 ppb in 26-478 (Fig. 4). In all cases, even carbon-numbered acids from C_{16} to C_{30} dominate over the odd carbon-numbered acids. Small quantities of Δ-C_{16} were present in the upper two samples, but could not be detected in 26-478 (Table 2). The ratio Δ-C_{18} to C_{18} was lower at this site than any other (Table 2).

The alcohol fractions consisted mainly of long straight-chained alcohols in the C_{20}–C_{30} range, with only trace amounts of C_{16} and C_{18} (Fig. 4). The even carbon-numbered alcohols were dominant with a maximum at C_{24}. A CPI $\sim$ 10 was calculated for the alcohols, applying a similar notation suggested by KVENVOLDEN (1966)

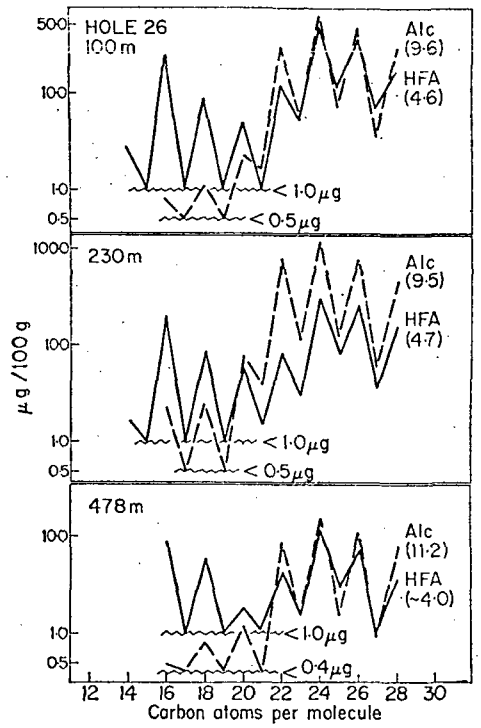

Fig. 4. Distribution of hydrolyzable fatty acids (HFA) and alcohols (Alc) in Hole 26. Carbon preference indices are given in parentheses for the range C_{20}–C_{28}.

Table 3. Concentration of identified compounds from benzene–methanol extract (μg/100 g)

Hole	Depth (m)	n-Alkanes	(CPI)*	Isoprenoid hydrocarbons	Perylene	FFA†	HFA‡	Alcohols	Chlorins	Porphyrins
2	20	1700	(3·9)	5	a	a	60	~7	a	2·3
2	103	403	(4·6)	5	a	a	7	~7	a	0·8
3	34	930	(2·1)	105	t	a	90	23	8·1	8·6
3	209	59	(2·1)	3	a	a	29	5	4·9	1·1
3	324	114	(2·1)	3	a	a	36	3	0·8	1·2
3	534	102	(3·6)	2	a	a	41	9	a	2·8
6A	15	13	(1·8)	a	a	a	<5	a	a	a
6	43	24	(3·5)	a	a	a	<5	a	a	a
6	153	12	(2·5)	a	a	a	<5	a	a	a
26	100	191	(3·3)	a	19	15	279	233	56·8	a
26	230	242	(3·7)	a	33	100	149	407	14·6	a
26	478	344	(2·2)	a	16	14	58	60	a	2·2
27	143	12	(2·2)	<1	a	a	3	9	a	0·2
27	237	81	(3·3)	<1	a	a	250	136	1·2	a
27	249	32	(2·5)	<1	a	a	28	4	a	1·0

a = none detected; t = trace.

* Carbon preference index for C_{21} through C_{31} hydrocarbons, except Hole 3 which is for C_{21} through C_{29} (COOPER and BRAY, 1963).

† Free fatty acids.

‡ Hydrolyzable (bound) fatty acids.

for fatty acids. Again, as in the case of the FFA, 26-230 contained the greatest concentration of alcohols (4·1 ppm, Table 3); this amount surprisingly exceeded the combined concentration of FFA and HFA (2·5 ppm) in this sample. Samples 26-100 (2·3) and 26-478 (0·6 ppm) contained significantly less alcohols than 26-230. No isoprenoid alcohols could be identified in these sediments.

Hole 27. No FFA were found at this site. In both 27-143 and 27-249 C_{14}–C_{18} even carbon numbered straight-chained HFA dominate. The distribution in 27-237 is bimodal, with approximately equal quantities in the range C_{16}–C_{18} and C_{24}–C_{28}. Sample 27-143 has the greatest percentage content of unsaturated fatty acids. The Δ-C_{18}/C_{18} is 0·78 (Table 2). Sample 27-237 has about the same ratio of 0·77. However, in this sample the HFA concentration (2·5 ppm) is an order of magnitude greater than that in 27-249 and nearly two orders of magnitude greater than the HFA in 27-143.

Apart from sample 27-237 where the alcohol concentration was 1·4 ppm, the other two samples had <100 ppb alcohol (Table 3). The extracted alcohols are dominated by straight-chain C_{22}–C_{28} even carbon numbered species.

Chlorins and porphyrins

In samples from all sites, except Hole 3, chlorins and porphyrins were either absent (Hole 6) or mutually exclusive (Table 3). In Hole 2, only porphyrins were present (23 and 8 ppb), and from the spectrum shown in Fig. 5, it was deduced by comparison with spectra from known porphyrins (HODGSON *et al.*, 1968), that the compound is a vanadyl porphyrin. In Holes 26 and 27, it was not possible to determine the porphyrin type with any confidence. The Soret absorption peaks for porphyrin from samples 26-478, 27-143 and 27-249 lay between 395 and 408 mμ.

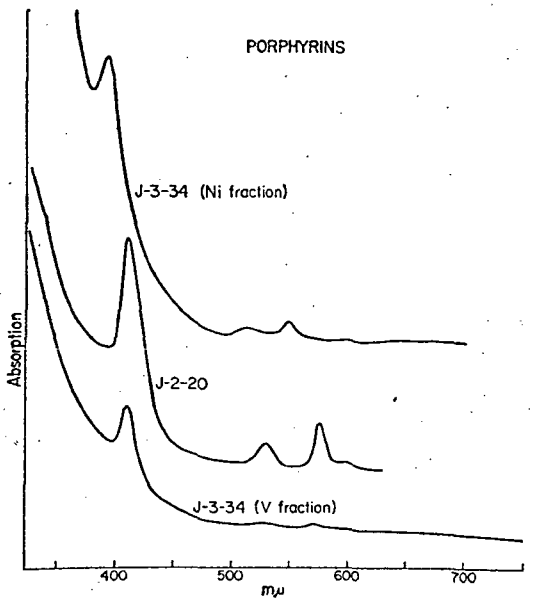

Fig. 5. Absorption spectra of porphyrins from selected samples, Holes 2 and 3.

However, the peaks were not very sharp due to superposition of other absorption peaks, probably aromatic hydrocarbons, which co-eluted with the porphyrins and chlorins. The non-Soret peaks for samples from Hole 27 were very shallow, whereas in sample 26-478, two non-Soret peaks at 555 and 585 mμ were measured, indicating a possible mixture of at least two specific porphyrins.

Best resolution was obtained in samples from Hole 3, especially 3-34. Here, it was possible to separate two compounds with absorption properties similar to Ni-porphyrin (392, 512 and 549 mμ) and the other with an absorption spectrum (405–407, 530, 570 mμ) similar to V-porphyrin (see Fig. 5). Two porphyrins with similar absorption characteristics were also separated from sample 3-534, indicating a V-porphyrin and Ni-porphyrin mixture. In this sample, the ratio of V/Ni complex = 13, whereas in 3-34, V/Ni complex = 4.

When present, the chlorin content decreases with depth. Chlorins can be recognized by their absorption peak at 663–665 mμ, as shown for 3-34 in Fig. 6. However, the concentration of chlorins was found to be very great in sample 26-100 (568 ppb) and it was possible to determine other non-Soret peaks at 668, 610, 535 and 505 mμ (Fig. 6). These absorption peaks were also measured by BAKER (1970) in Hole 26 from a sample at 120 m depth, and interpreted by him as typical of pheophytin. Hence, the chlorins in sample 26-100 and 26-230 apparently still contain the phytol side chain.

Amino acids and racemization

Because of the relatively high concentration of organic carbon and the relatively good preservation of the chlorins and fatty acids in the sediment at site 26, the three

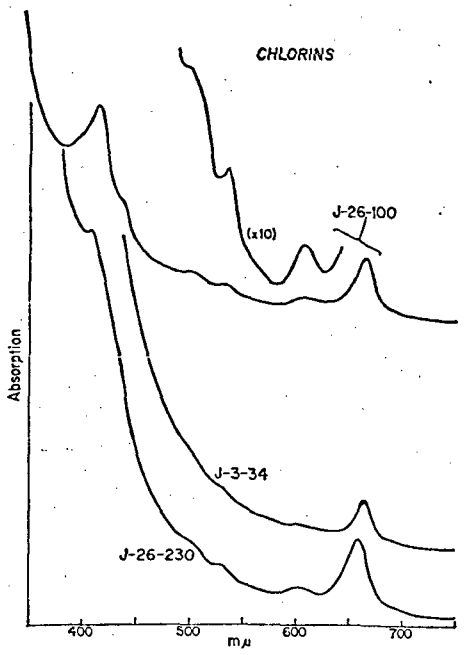

Fig. 6. Absorption spectra of chlorins from selected samples, Holes 3 and 26.

samples obtained from Hole 26 were analysed for hydrolysable amino acids (a.a.). The concentration was greatest in sample 26-100 (500 n-moles/g and decreased with depth (390 n-moles/g for 26-230 and 75 n-moles/g for 26-478. The acidic a.a. (e.g. glutamic acid and aspartic acid) decreased most rapidly followed by hydroxy-amino acids. The neutral acids were more stable. The general pattern of degradation shown in Fig. 7 confirms studies by BROWN *et al.* (1972) on sediment from a fjord.

Although degradation in the sediment column probably results from microbiological alteration, amino acids have a defined lifetime even under sterile conditions, which may be predictable (ABELSON, 1963). Racemization of the enantiomers is another measure of alteration (HARE and ABELSON, 1967; BADA *et al.*, 1970;

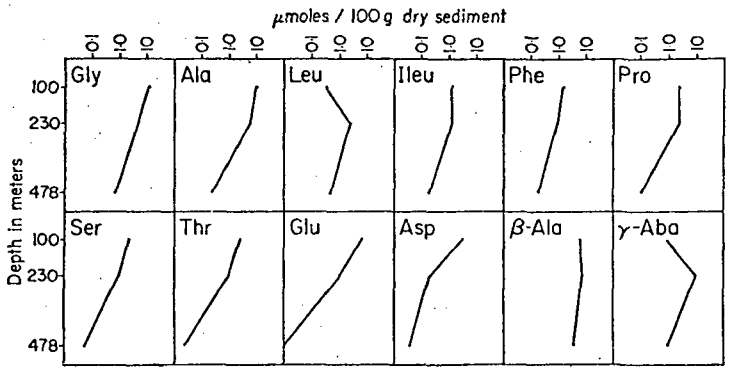

Fig. 7. Depth distribution of amino acids in Hole 26.

Table 4. %D enantiomer of amino acids from hole 26

Amino acid	Sample depth (m) 100	230	478	Difference 478–100
Ala	21	19	47	26
Val	6*	13*	23	17
Aileu	5*	7*	14*	9
Leu	8	15	29	21
Pro	12*	14*	25*	13
Phe	11	15	32	21
Glu	19*	24*	35*	16

Results are an average of data from analyses on two capillary columns coated with different liquid phases—UCON 75H-90,000 and XE-60. (KVENVOLDEN *et al.*, 1970)

* Results obtained through the use of only one capillary column.

WEHMILLER and HARE, 1971), and was shown to occur in a.a. from reducing sediment of a fjord by KVENVOLDEN *et al.* (1970). The data in Table 4 show that in sample 26-100, alanine and glutamic acid already are very significantly racemized. The greatest change is seen in sample 26-478, where alanine shows 47 per cent of the D-form. At this depth, phenylalanine, leucine, valine and proline also show significant conversion.

Using the method of BADA *et al.* (1970) for calculating sediment age by the rate of epimerization of L-isoleucine to D-alloisoleucine (estimated by plotting ln [1 + alloisoleucine/isoleucine] vs depth of burial), one obtains an age for 26-478 = $1{\cdot}2 \times 10^6$ yr. This agrees with the general stratigraphic age of the sediment (Upper-Middle Pleistocene; BADER *et al.*, 1970). However, many pitfalls exist in the application of this method for dating sediments (WEHMILLER and HARE, 1971). It can further be seen from Table 4 that the degree of racemization does not progress smoothly down the core. For example, the sediment from 26-230 shows less L–D interconversion for alanine than is found in the overlying sample 26-100. In part, this maybe due to source material (whether planktonic or terrigenous) and partly due to the conditions of accumulation. Furthermore, new a.a. are being generated in the sedimentary column. For example, the non-protein amino acids, β-alanine and γ-amino-butyric acid, are present in higher concentration at depth 230 m than at 100 m. These acids could conceivably have been introduced at the surface by diverse plant remains. However, the percent of β-alanine and γ-aminobutyric acid relative to the total amino acids increases dramatically down the sediment column (13 per cent at 100 m, 44 per cent at 230 m and 70 per cent at 478 m). They were probably derived by decarboxylation from other amino acids such as aspartic and glutamic acids. Eventually, death of the indigenous microflora will also release new L-amino acids into the sediment.

Diagenetic pathway of carbon compounds

It is apparent from results in Fig. 7 that the protein-derived amino acids generally decrease in the sediment column. However, with the exception of chlorins, the lipid associated compounds do not show any systematic decrease with depth. The combined contribution of recognizable lipids and amino acids to the organic carbon in

Table 5. Organic constituents identified in JOIDES samples (% of total org. C × 10^2)

Hole	Depth (m)	n-Alkanes	Perylene	FFA	HFA	Alc.	Chlorins	Porphyrins
2	20	32·16	a	a	1·04	~0·13	a	0·04
2	103	9·03	a	a	0·14	~0·15	a	0·01
3	34	7·14	a	a	0·63	0·17	0·05	0·06
3	209	0·61	a	a	0·28	0·05	0·04	0·01
3	324	2·06	a	a	0·60	0·05	0·01	0·02
3	534	1·85	a	a	0·68	0·16	a	0·05
6A	15	0·85	a	a	<0·30	a	a	a
6	43	1·28	a	a	<0·30	a	a	a
6	153	1·14	a	a	<0·30	a	a	a
26	100	1·87	0·20	0·13	2·50	2·19	0·49	a
26	230	2·06	0·32	0·78	1·16	3·32	0·11	a
26	478	5·38	0·30	0·21	0·89	0·96	a	0·04
27	143	0·38	a	a	0·09	0·27	a	0·01
27	237	1·19	a	a	3·35	1·91	0·02	a
27	249	1·51	a	a	1·21	0·18	a	0·04

a = none detected.

the sediment is less than 1 per cent (Tables 5 and 6). In the organic extractable fraction (Table 5) the hydrocarbons become the most abundant component, except for relatively young sediment (as in Hole 26) which has been rapidly deposited. Here, free fatty acids and chlorins can also be detected. The total content of the extractable fraction was found to be less than 0·1 per cent of the total organic carbon in the samples analyzed. Only in sample 2-20, where 17 ppm n-alkanes were extracted, was there an increase above this relative concentration.

It is, therefore, obvious that biogenic-derived organic matter rapidly transforms to stable polymeric configurations or else degrades. That carbon compounds are degraded in the sediment is known, in part because of a small decrease with depth of burial, but also because of excess CO_2 liberated into the interstitial water (Presley and Kaplan, 1968) and release of ammonia, methane and hydrogen sulfide (Nissenbaum *et al.*, 1972b). Previous studies on very young near-shore reducing sediment (Brown *et al.*, 1972) have shown that the humic acid fraction (0·2 N NaOH-soluble and acid-insoluble) may contain 40 per cent of the total carbon and another 30 per cent is present in the fulvic acid fraction. The fulvic acid content decreases with

Table 6. Organic groups identified in Hole 26 (% of total org. C and δC^{13})

Sample (δC^{13})*	Benzene soluble	Amino acids	Humic acids (δC^{13})	Kerogen (δC^{13})	Remainder
26-100 (−25·3)	<0·1	0·3	28 (−24·7)	11 (−25·1)	61
26-230 (−27·0)	<0·1	0·2	43 (−25·8)	10 (−26·6)	47
26-478 (−25·2)	<0·1	0·1	27 (−24·4)	14 (−25·6)	59

* ‰ relative to PDB standard.

depth of burial, and in sediment nearly 10,000 years old, it represents ~9 per cent of the total carbon. In the present study (Table 6) the humic acid fraction represents from 27–43 per cent of identifiable carbon. The fulvic acid content analyzed varied from 5–18 per cent, but because of difficulty in purification (during removal of salt) reproducible values could not be obtained and are, therefore, not recorded in Table 6. The non-extractable fraction (kerogen) represents only 10–14 per cent of the total carbon. Therefore, about 50 per cent or more of the carbon has not been accounted for. To test where this loss occurred, total organic carbon remaining in the sediment was measured by combustion on a small aliquot, after each extraction. It was found that the carbon was lost, in part, during acid hydrolysis but mostly during alkali extraction. Cleavage of small soluble molecules from the complex humic acid has occurred. Those with a molecular weight of several thousands, the fulvic acids, may amount to 10 or 20 per cent of these unaccountable compounds. Those which can pass through a dialysis membrane (mol. wt. <2000) but resemble components of the fulvic and humic acids are lost. These are probably peptide, carbohydrate and aromatic constituents with hydrophylic groups.

DISCUSSION

Several conclusions have emerged from the study. First, it is apparent that burial under conditions where heat flow is insufficient to raise the temperature beyond 30 or 40°C, causes disappearance (removal) of much of the labile biochemical components originally deposited in the sediment. There is some evidence, however, based on the presence of free fatty acids, unsaturated fatty acids and non-protein amino acids, that some biochemical compounds are being generated in the sediment column, probably by bacterial activity. There is no evidence that petroleum can from under these conditions, although small quantities of hydrocarbons (in the ppm range) may be generated (as appears to be happening in Hole 26).

The major sink for the non-decomposed, buried carbon compounds in unlithified sediment is humic acid and, to a lesser extent, kerogen. Some compounds are strongly complexed and will precipitate with the humic acid polymer. Others will be solubilized on acid treatment of the alkaline humic acid solution (the fulvic acids), whereas less complexed groups will become soluble in distilled water or weak brine. It is probable that continued dehydration during lithification would convert proportionately more of the humic acid fraction to kerogen, although we have no proof for this, in the present study.

The environment of deposition and accumulation is most important for the preservation of organic matter. Slow deposition in deep water of pelagic sediment, or exposure to surface currents after rapid deposition, for example, by turbidity currents, could lead to destruction of most of the labile molecules prior to effective burial. This has probably occurred at site 6 and 6A and to a lesser extent, site 2. Oxidation would rapidly remove free fatty acids, carotenoids (which could not be identified in this study) and chlorophyll derivatives.

Porphyrins would form under mild oxidizing conditions, preceded by loss of the phytyl group from chlorophyll. The presence of porphyrins in the relatively young sediment of Hole 2 and Hole 3 may suggest an external source rather than generation *in situ*. This is particularly true for sample 3-34, which contains both chlorins and porphyrins.

Although this study and that by KOONS (1970), do not show a clear relationship between the hydrocarbons identified from sediment of Holes 2 and 3 and the petroleum removed from Hole 2 above Challenger Knoll, there may be horizontal or vertical migration from various reservoirs. The hydrocarbon content in sample 2-20 is 4 times greater than in 2-103, and that of sample 3-34, 9 times greater than the other samples in Hole 3, which argues against a simple upward migration. However, the n-alkane fractions here are greater in concentrations than in most other unconsolidated Quaternary sediments. These samples differ from young sediments in two other respects: the presence of porphyrins, as stated earlier, and the presence of aromatic hydrocarbons.

Of particular interest is the sedimentological evidence for detrital minerals in many of the organic-rich cores. Evidence was also produced for plant debris in Hole 26 and turbidity current deposits associated with Hole 27. Both of these sites are about 1000 km from land. The geochemical evidence obtained here indicates that land-derived organic matter may be more common at great distance from continents than previously assumed.

Data shown in Tables 1 and 6 for C^{13}/C^{12} ratios indicate that samples 3-34, 26-230 and 27-237 have δC^{13} ratios typical of land plants (see NISSENBAUM and KAPLAN, 1972). The light isotopic values of about $-27‰$ for the total organic carbon in samples 26-230 and 27-237 are also reflected in the humic acids and kerogen (Table 6). Carbon isotope values for plankton-derived organic matter is more normally -18 to $-22‰$. It had been suggested that organic matter in marine sediment with light isotopic ratios (approaching $-30‰$ PDB) may be due to growth of plankton in cool water (ROGERS and KOONS, 1969); however, this interpretation is speculative and may only be applicable in very specific environments (SACKETT and RANKIN, 1970; PLUCKER, 1970).

The presence of long-chain n-alkanes (C_{25}–C_{32}) and also long-chain alcohols suggests that plant waxes may have been the contributing source. In fact, the n-alkanes of all the samples analysed in this study had high CPI's (1·8–4·6), which suggests terrigenous contribution. A particularly interesting index is perylene $C_{20}H_{12}$. AIZENSHTAT (1973) suggested that this molecule probably originates from soil as the precursor 4,9-dihydroxy-perylene-3, 10-quinone. This compound is highly susceptible to oxidation, and therefore must be rapidly deposited under reducing conditions. Marine sediment primarily receiving planktonic organic matter does not contain perylene. Near-shore sediments deposited under oxidizing conditions also do not contain perylene (AIZENSHTAT, 1973).

CONCLUSIONS

The results of the study indicate that degradation and diagenesis of organic matter occurs in steps. The important factors to be considered are the following:

1. *Environment of deposition*

Initially, this factor is of overriding importance. Irrespective of the quantity and nature of organic matter being deposited under natural conditions, if the path through which it deposits permits exposure to oxygen, a great majority of the organic matter will be decomposed. This generally occurs during settling through a long

water column to abyssal or haedal depths. Furthermore, pelagic sedimentation in the bathyal environment is generally very slow (<1 cm/1000 yr) and permits deposited material to be degraded once it has settled. Site 6 described in the present study falls into this category of environment.

2. *Source of material*

If deposition is relatively rapid and the environment of deposition allows organic matter to be buried, its alteration path will depend on the nature of the initial organic matter. Land-derived higher plant material containing lignins and waxes are probably not degraded to CO_2 as effectively as plankton-derived organic matter. The terrigenous contributions to starting material may be recognized by several combined indices described in this paper: (i) δC^{13} values $< -26‰$, (ii) long-chain alcohols and hydrocarbons ($>C_{27}$), (iii) CPI > 2 in these hydrocarbons and (iv) presence of the aromatic hydrocarbon perylene.

3. *Environment of accumulation*

Deposition on the sea floor by means of turbidity or density currents may be rapid. However, these currents may occur at infrequent periods, so that re-working of the surface sediment by bottom currents and benthonic organisms may prevent the preservation of 'delicate' components such as unsaturated fatty acids, chlorins or the quinoid precursors of perylene. In such an event, evidence for source origins based on presence or absence of ephemeral compounds may be misleading. This explanation can probably be applied to the organic matter of site 27.

4. *Alteration pathway*

The two most pronounced patterns are: (a) degradation of recognizable biological polymers (e.g. cellulose, proteins) and (b) formation of new condensed components enriched in hydrophylic groups and probably aromatic compounds. Carotenoids disappear early; chlorophyll alters to phaeochlorins which may almost disappear; extractable amino acids amount to <1 per cent of the total organic reservoir. The humic and fulvic acid components assume 50 per cent of the total extractable organic material. In fact, they represent 80 per cent+ of the organic matter, but are hydrolyzed during alkaline extraction, at which time the smaller more soluble fragments are lost. Many unaltered or partially altered compounds may be either complexed or strongly adsorbed to these high-molecular weight components. Kerogen appears to constitute <20 per cent of the organic matter in the unlithified sediment. New molecules, such as perylene or porphyrins, may appear.

5. *Alteration during lithification*

Diagenesis during lithification will involve dehydration and possibly heating. The humic acid complexes may begin to degrade, releasing their constitutive compounds. The remainder may become less soluble and will then be termed kerogen. The alteration from humic acid to kerogen is not understood, and few examples have yet been studied in sediment passing the phase transition from mud to shale.

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