

44. LIPID GEOCHEMISTRY OF CRETACEOUS BLACK SHALES FROM THE BAY OF BISCAY, SITE 402, AND OF EOCENE MUDSTONE FROM THE ROCKALL PLATEAU, SITE 404¹

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ABSTRACT

The lipids extracted from Cretaceous mudstones from the northern North Atlantic Ocean (Hole 402A). The distribution patterns of the *n*-alkanes, *n*-fatty acids, and *n*-alkan-2-ones indicated a predominant allochthonous terrigenous origin, with a minor autochthonous marine component. Molecular markers of both marine and terrestrial origins were identified. The sedimentation took place under oxic conditions with rapid influx of terrigenous detritus.

The lipids of an Eocene sample from Site 404 were of a predominantly marine origin with only traces of molecular markers from terrestrial sources. This sediment was deposited in oxic deep waters.

The 17 β (H),21 β (H)-hopane series was predominant in all these samples, indicating that these sediments are very immature and have had a mild geothermal history.

INTRODUCTION

The Cretaceous black shales that have been encountered in the Atlantic Ocean had various sedimentary origins. Some were formed in anoxic basins with high sedimentation rates and large components of terrigenous organic matter; other black shales were formed at the continental margins by rapid turbidite influx of oxidized organic matter, in shallow epi-continental and marginal seas with high autochthonous productivity, or under various other paleoenvironmental conditions (e.g., Schlanger and Jenkyns, 1976; Simoneit, in press). Therefore, it was of interest to determine if, in the case of the Bay of Biscay sediments, the analyses of the lipids would allow a distinction to be made between the influx of allochthonous and the production of autochthonous material. Also, a comparison of these results with similar data for samples from other areas of the Atlantic Ocean will contribute to the overall assessment of the paleoenvironment of the proto-Atlantic.

The samples examined here were derived from Hole 402A (47°52.48'N, 08°50.44'W; 2339.5 m water depth), located in a canyon on the mid-continental slope of the Bay of Biscay (Montadert et al., 1976). The Aptian sequence was deposited in less than 200 meters depth in an oxic environment with a high influx rate of terrigenous detritus (Montadert et al., 1976).

An Eocene mudstone from Site 404 (56°03.13'N, 23°14.95'W; 2306 m water depth) also was analyzed for general comparison. This site is located on the rifted southwest margin of the Rockall Plateau and probably represented a near littoral paleoenvironment (Montadert et al., 1976).

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, treated with BF₃ in methanol to esterify free acids, and then subjected to silica-gel thin-layer chromatography (TLC) using methylene chloride as eluent. After development with iodine vapor, the bands corresponding to hydrocarbons and esters with ketones were scraped off the TLC plate and eluted with methylene chloride. These fractions were subjected to gas chromatographic (GC) and GC/MS analyses.

The GC analyses were conducted on a Varian Aerograph Model 1520 gas chromatograph using a 30 m \times 0.25 mm glass capillary column wall-coated with OV-101, programmed from 40-260°C at 6°C/min, then held isothermal for 80 minutes, and using He carrier gas at a flow rate of 2 ml/min (30 cm/s linear velocity).

The GC/MS analyses were conducted on a Finnigan Model 4000 quadrupole mass spectrometer interfaced directly with a Finnigan Model 9610 gas chromatograph equipped with a 30 m \times 0.75 mm glass capillary column (J&W, Inc.) which was wall-coated with OV-101. The GC conditions for the GC/MS analyses were as those for the analytical GC system. The mass spectrometric data were acquired and processed using a Finnigan-Incos Model 2300 data system.

RESULTS AND DISCUSSION

The sample descriptions, carbon and lipid analyses, and other results are given in Table 1. The Cretaceous samples that were examined consist of gray mudstone with an organic carbon content of about 2 per cent, and the Eocene sample consists of green mudstone with about 0.3 per cent organic carbon. The lipid yields for all samples were low.

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TABLE 1
Sample Descriptions, Carbon Analyses, and Lipid Yields for the Core Samples Examined From Leg 48

Sample (Interval in cm)	Depth Below Sea Bed (m)	Lithology	Geologic Age	Carbon (%) ^a			HC ($\mu\text{g/g}$)	<i>n</i> -alkanes			<i>n</i> -fatty acids			<i>n</i> -methylketones			Pr/Ph ^d	Perylene
				Total	Org.	CaCO ₃		($\mu\text{g/g}$)	CPI ^b	max. ^c	Total ($\mu\text{g/g}$)	CPI ^b	max. ^c	($\mu\text{g/g}$)	CPI ^b	max. ^c		
402A-21-1, 40-44	327.4	Gray mudstone	Cretaceous (Aptian)	4.64	1.73	24	17	0.30	2.7	19,23,27,33	28.0	3.2	16,28	1.2	1.8	19,25	1.40	0
402A-30-1, 20-27	412.7	Gray mudstone	Cretaceous (Aptian)	5.54	1.95	30	13	0.50	1.7	19,23,27	1.4	3.6	16,28	0.22	2.3	13,19,29	2.00	0
402A-35-4, 13-25	464.7	Gray mudstone	Cretaceous (Aptian)	2.48	0.11	20	n.d. ^e	n.d.	—	—	n.d.	—	—	n.d.	—	—	—	—
404-22-6, 25-50	349.4	Green-gray mudstone	Eocene	0.96	0.25	6	15	0.06	1.1	17,23	0.8	4.9	16,22,28	0.04	1.6	15,27	1.45	0

^aData supplied by S. M. White, DSDP, Scripps Institution of Oceanography, UCSD.

^bCarbon preference index, summed from C₁₀ to C₃₅.

^cThe predominant maximum is underscored.

^dPristane-to-phytane ratio.

^en.d. = not determined.

Samples 402A-21-1, 40-44 cm and 402A-30-1, 20-27 cm

The distribution diagrams for the *n*-alkanes, *n*-fatty acids, and *n*-alkan-2-ones are shown in Figure 1. The *n*-alkanes of both samples exhibit distributions with major maxima at *n*-C₂₃, *n*-C₂₇, and *n*-C₃₃; minor maxima at *n*-C₁₉; and a strong odd-to-even carbon number predominance >*n*-C₂₃. The homologs >*n*-C₂₃ are attributable to an origin from higher plant wax (Simoneit, 1975; 1977a; 1978b), and the homologs >*n*-C₂₂ are probably derived from autochthonous marine sources (Simoneit, 1975; in press). The pristane-to-phytane ratio of both samples is greater than one and both perylene and sulfur are not present in significant amounts, indicating that this sediment accumulated under oxic paleoenvironmental conditions (Didyk et al., 1978). This is corroborated by the preliminary shipboard analysis (Montadert et al., 1976). The *n*-fatty acids of both samples exhibit bimodal distributions with major maxima at *n*-C₂₈, minor maxima at *n*-C₁₆, and a strong even-to-odd carbon number predominance. The homologs >*n*-C₂₂, when considered in conjunction with the *n*-alkane distributions, are further markers of allochthonous higher plant lipids (Simoneit, 1975; in press). The homologs <*n*-C₂₀ appear to be of autochthonous marine origin (Simoneit, 1975). The *n*-alkan-2-ones also exhibit a bimodal distribution, with maxima at C₁₉ and C₂₇ and a strong odd-to-even carbon number predominance. These methylketones are probably derived from *n*-fatty acids by microbial β -oxidation or by microbial oxidation of *n*-alkanes (Arpino, 1973). The ketone distributions reflect a partial terrigenous origin (homologs >C₂₀), as was the case for the samples from the Black Sea (Simoneit, 1978). The isoprenoidal ketones (6,10,14-trimethylpentadecan-2-one and 6,10-dimethylundecan-2-one, cf., Figure 1g,h) are the predominant ketones and reflect oxidative products of phytol (Simoneit, 1973).

The minor molecular markers are comprised of hydrocarbons, acids and ketones. Steranes and sterenes are present only in traces in these two samples. Triterpanes are found as significant components and their relative distributions are shown in Figure 2a,b. The predominant analogs are the 17 β (H),21 β (H)-hopanes, C_nH_{2n-8}, ranging over *n*=27, 29 and 30 (Structure I) and 31-35, with only one diastereomer at C-22 (Structure II). 17 β (H), 21 β (H)-homohopane (II, R=CH₃) is the predominant

triterpane for both samples. Lesser amounts of 17 α (H),21 β (H)-hopanes and various moretanes are also present. Both samples contain some of the aromatized triterpenoids which were characterized in Messel shale and confirmed by synthesis (Greiner et al., 1976) and which were found previously in Samples 40-364-24-1, 0-10 cm, and 41-367-19-4, 10-15 cm (Simoneit, 1977c, 1979). The following compounds were identified by their characteristic mass spectra (Spyckerelle, 1975): 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 III], (3'-ethylcyclopenteno-7,8) 1,1-dimethyltetrahydro (1,2,3,4) chrysene (Structure IV), a higher homolog, C₂₆H₃₀ (IV, with an additional CH₃ in ring A or B), and (3'-ethylcyclopenteno-7,8) 1-methylchrysene (Structure V). These compounds probably represent diagenetic products from hopanes of marine origin.

Other hydrocarbons that have been identified consist of diterpenoids, sesquiterpenoids, and isoprenoids. The predominant diterpenoids are dehydroabietane (VI); dehydroabietin (VII), simonellite (VIII), and retene (IX), with lesser amounts of tetrahydro(1,2,3,4)retene [1-methyl-7-(2'-propyl) tetrahydro(1,2,3,4)-phenanthrene] (X), 17-nordehydroabietane (XI), and various methyl- and dimethylphenanthrenes. (The relative concentrations of these compounds and of the sesquiterpenoids are indicated in Figure 2a,b.) These diterpenoids are molecular markers derived from resinous vascular plants (Simoneit, 1977b). The sesquiterpenoids consist of tetrahydro (1,2,3,4) δ -cadalene (XII) and cadalene (XIII), which may be derived from marine and/or terrigenous sources. Pristane and phytane are present in minor amounts (Pr/Ph >1) and farnesane is not detectable.

The carboxylic acid markers of both samples consist predominantly of triterpenoid and diterpenoid acids. The extended 17 β (H),21 β (H)-hopanoic acids, C_nH_{2n-10}O₂ (XIV), range from *n* = 31 to 33 and their concentrations are summarized in Table 2. These compounds represent oxidation residues from bacteriohopanepolyols (Rohmer, 1975), and their predominantly 17 β (H) stereochemistry indicates geologic immaturity (Dastillung and Albrecht, 1976). Dehydroabietic acid (XV) is present in both samples and is derived from terrigenous resinous plants (Simoneit, 1977b).

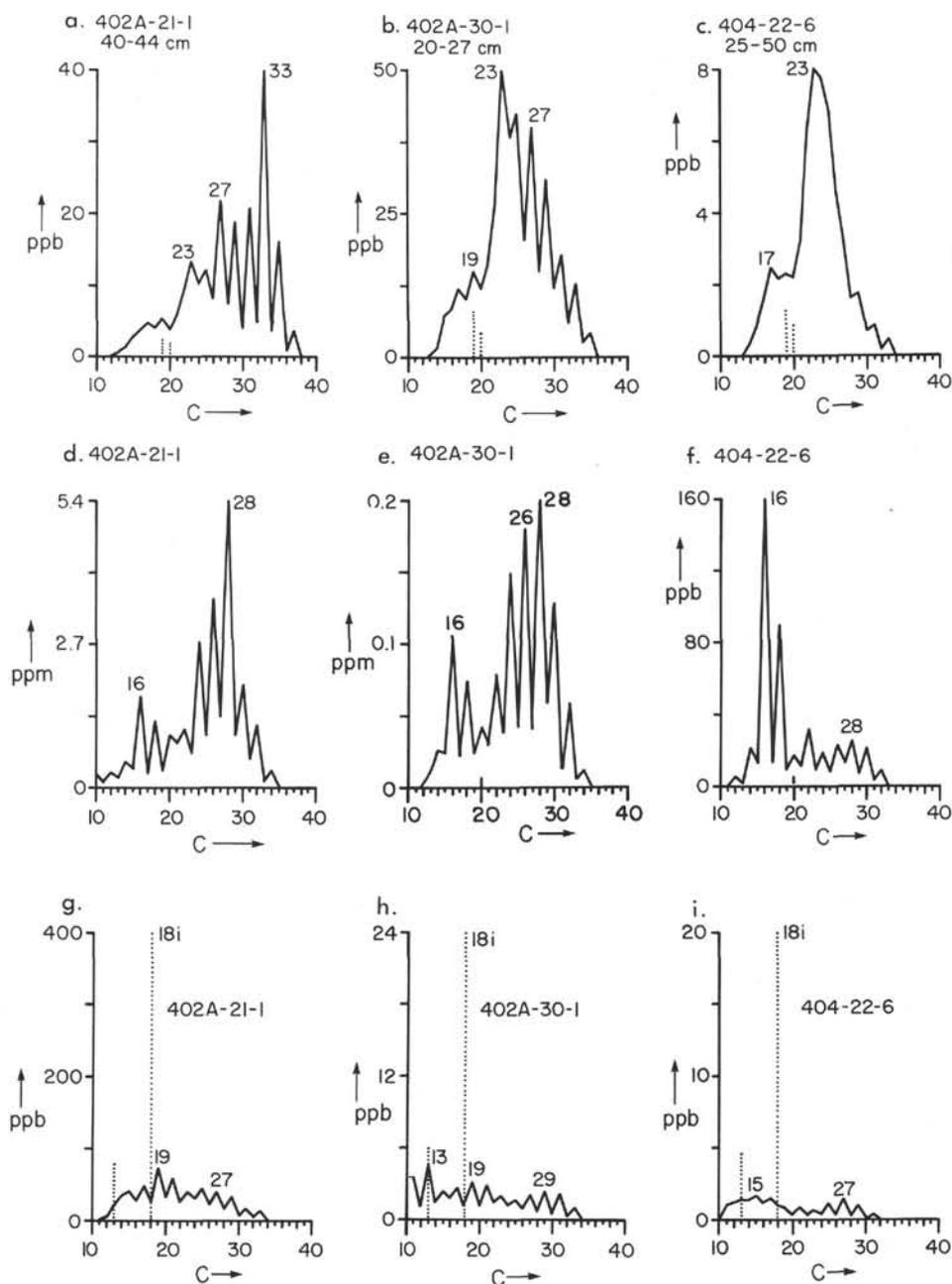


Figure 1. Concentrations of *n*-alkanes (a-c), *n*-fatty acids (d-f) and *n*-alkan-2-ones (g-i). Isoprenoids (.....) and dehydroabietic acid (-----) are also indicated.

The ketone markers of both samples consist mainly of triterpenoids. The major analogs are $17\beta(\text{H})$ -trisorhopan-21-one (XVI) and probably $17\beta(\text{H})$ - $21\beta(\text{H})$ -norhopan-22-one (XVII) (Simoneit, 1978), with lesser amounts of the $17\alpha(\text{H})$ structures and several isomers of a $\text{C}_{31}\text{H}_{52}\text{O}$ ketone. The mass spectra of the two predominant isomers of the $\text{C}_{31}\text{H}_{52}\text{O}$ ketone are shown in Figure 3. The fragmentation scheme, shown in Figure 4, best fits significant ions at m/e 147, 191, 219, 355, 368, 422, 425 and the molecular ion, 440. Thus, the proposed structure for these ketones is homohopan-29-one (XVIII), and the stereochemistry at C-17 and C-21 needs to be confirmed with authentic standards. The mass spectrometric

fragmentation pattern does not fit for a nonhopane skeleton or for homohopan-31-one. These homohopan-29-ones have not been identified before in any sample and may represent diagenetic products of bacteriohopanepolyols. The norhopanones have been characterized in sediments from the Black Sea (Simoneit, 1978) and may represent degradation products of the bacteriohopanepolyols.

Sample 404-22-6, 25-50 cm

The *n*-alkanes of this sample exhibit an essentially unimodal distribution (Figure 1c) with a maximum at *n*-C₂₃ and no carbon number predominance. This distribution is typical of a microbially degraded, algal-lipid residue (e.g.,

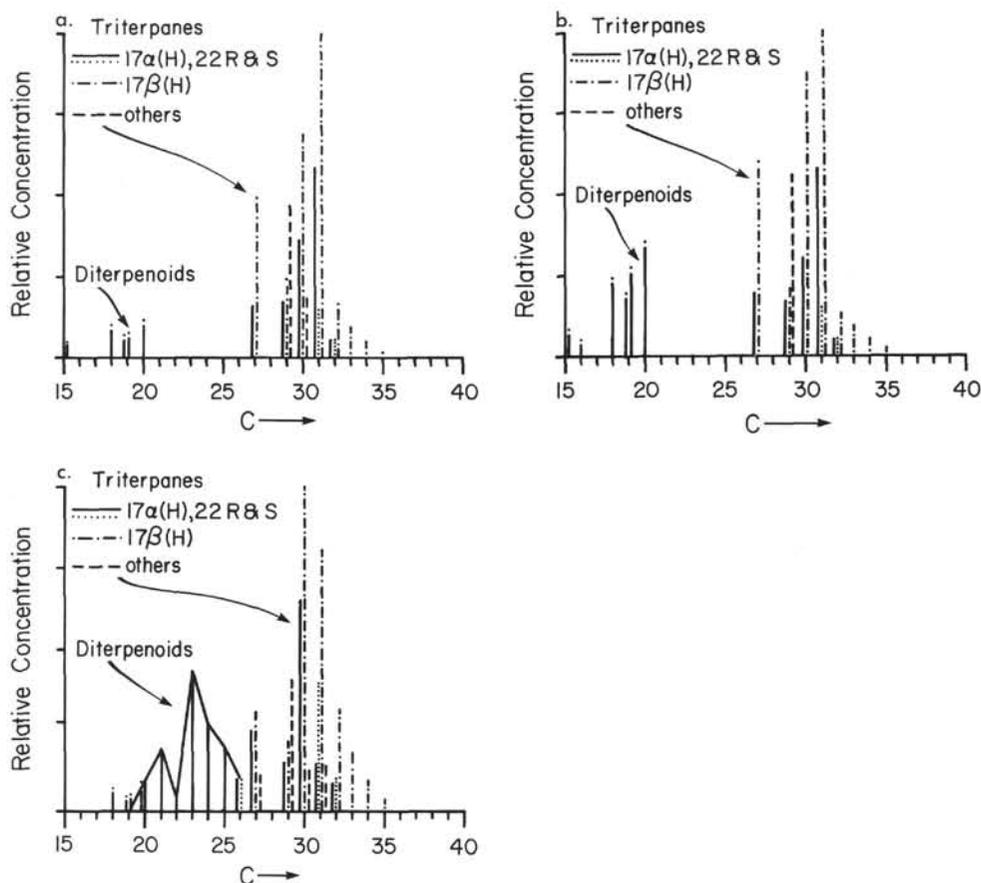


Figure 2. Relative concentrations of triterpanes and diterpenoids: (a) Sample 402A-21-1, 40-44 cm; (b) Sample 402A-30-1, 20-27 cm; (c) Sample 404-22-6, 25-50 cm.

TABLE 2
Concentrations of Triterpenoidal Acids

Compound	Kovats Index (methyl esters on OV-101)	Sample (Interval in cm)		
		402A-21-1, 40-44	402A-30-1, 20-27	404-22-6, 25-50
17β(H),21β(H)-Homohopanoic acid	3304	2 μg/g ^a	48 ng/g ^a	4 ng/g ^a
17β(H),21β(H)-Bishomohopanoic acid	3428	10 μg/g	200 ng/g	20 ng/g
17β(H),21β(H)-Trishomohopanoic acid	—	1 μg/g	20 ng/g	3 ng/g
17α(H),21β(H)-Bishomohopanoic acid (R,S)	3280/3317	1/1 μg/g	10/8 ng/g	n.d. ^b

^aConcentration based on dry weight of sediment.

^bn.d. = not detected.

Hatcher et al., 1977). Only traces of *n*-alkanes (>*n*-C₂₇, odd C predominance) derived from higher plant wax are present. The isoprenoids pristane and phytane are present as minor components and farnesane is not detectable. Their ratio (Pr/Ph) is 1.45, and the sulfur content is low, which indicates oxic paleoenvironmental conditions of sedimentation (Didyk et al., 1978). The *n*-fatty acids exhibit a bimodal distribution, with a major maximum at *n*-C₁₆, a minor one at *n*-C₂₈ and a strong even-to-odd carbon number predominance (Figure 1f). The homologs <*n*-C₂₀ are of an autochthonous marine origin and the homologs >*n*-C₂₂ represent a minor influx of allochthonous terrigenous matter derived from higher plants (Simoneit, 1975, in press). The

n-alkane-2-ones also exhibit a bimodal distribution with maxima at C₁₅ and C₂₇ and an odd-to-even carbon number predominance (Figure 1i). The isoprenoidal ketones are dominant. The ketones reflect oxidative degradation products from alkanes or fatty acids (Arpino, 1973) and phytol, respectively (Simoneit, 1973).

The minor molecular markers are comprised of hydrocarbons, acids, and ketones. Steranes are present as minor components in a complex mixture of various isomers. The relative distribution of the triterpanes and diterpenoids is shown in Figure 2c. The predominant analogs are the 17β(H),21β(H)-hopanes, C_nH_{2n-8}, with *n* = 27,29,30 (I) and 31-35 (one diastereomer only at C-22, II). 17β(H),21β(H)-homohopane (II, R = CH₃) is the major analog present, and 17α(H),21β(H)-hopanes and moretanes are lesser constituents. Aromatized triterpenoids are found as minor components, and (3'-ethylcyclopenteno-7,8) 1,1-dimethyltetrahydro(1,2,3,4)-chrysene (Structure IV) and (3'-ethylcyclopenteno-7,8)1-methylchrysene (Structure V) are confirmed. These triterpenoids probably represent diagenetic products from hopanes of autochthonous origin. Diterpenoid and traces of sesquiterpenoid hydrocarbons are present. The predominant diterpenoids consist of diterpanes, C_nH_{2n-4}, ranging from *n* = 20 to 26 (XIX) (Figure 2c), where the C₂₆H₄₈ homolog is resolved into the R and S diastereomers. These diterpanes have been identified in petroleum and some Recent algal sediments (Simoneit and

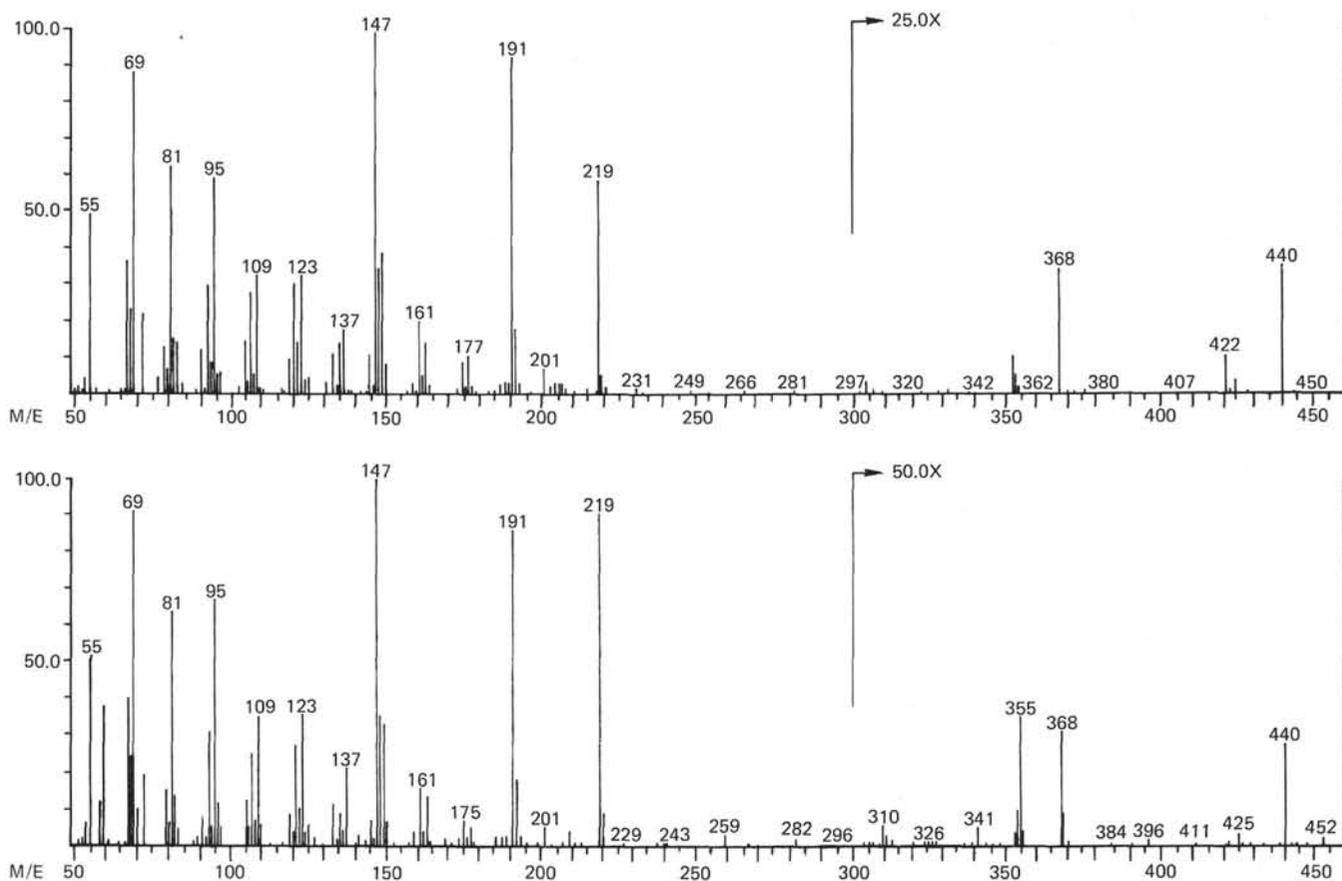


Figure 3. Mass spectra (GC/MS Finnigan Model 4000 quadrupole) of two isomers of homohopan-29-ones from Sample 402A-21-1, 40-44 cm.

Kaplan, in press) and may be molecular markers with a marine origin. Minor amounts of the allochthonous terrigenous diterpenoids are also present: they are dehydroabietane (VI), dehydroabietin (VII), retene (IX), and traces of simonellite (VIII) and the sesquiterpenoids cadalene (XIII) and tetrahydrocadalene (XII). A trace of dehydroabietic acid (XV) is present in the acid fraction. The extended $17\beta(H), 21\beta(H)$ -hopanoic acids, $C_nH_{2n-10}O_2$ (XIV), range from $n = 31$ to 33 and their concentrations are given in Table 2. These acids represent oxidation products from autochthonous bacteriohopanepolyols, and their $17\beta(H)$ stereochemistry indicates geologic immaturity (Dastillung and Albrecht, 1976). Significant amounts of $17\beta(H)$ -trisorhopan-21-one (XVI) and probably $17\beta(H)$ - $21\beta(H)$ -norhopan-22-one (XVII) and traces of two isomers of homohopan-29-one are present. These ketones may reflect the degradation products of autochthonous bacteriohopanepolyols.

CONCLUSIONS

The lipids of the two Cretaceous mudstones are of a predominantly terrigenous-allochthonous origin. This is indicated by the distributions of the n -alkanes ($>n-C_{23}$), n -fatty acids ($>n-C_{22}$), and n -alkan-2-ones ($>C_{21}$) and is supported by the presence of molecular markers of terrestrial origin, which are comprised of diterpenoids and sesquiterpenoids. The paleoenvironmental conditions of

sedimentation were controlled by rapid influx of terrigenous detritus, superimposed on autochthonous productivity in oxic waters. This observation is based on the pristane-to-phytane ratio greater than about one, the absence of sulfur and perylene, and the presence of oxidation products from autochthonous precursors such as bacteriohopanepolyols.

The lipids of the Eocene mudstone are of a predominantly autochthonous marine origin. This is indicated mainly by the distributions of the n -alkanes (maximum at $n-C_{23}$) and n -fatty acids (maximum at $n-C_{16}$) and the presence of the only minor amounts of molecular markers of a terrigenous origin. These data, the pristane-to-phytane ratio of 1.45, the absence of perylene and sulfur, and the presence of autochthonous triterpenoidal oxidation products indicate that this Eocene mudstone is from an oxic, deep water paleoenvironment, with little terrestrial influx.

These inferences are in agreement with the preliminary description of the sedimentary record that has been presented (Montadert et al., 1976). The predominance of the $17\beta(H), 21\beta(H)$ -hopane series in all three samples indicates the geologic immaturity of the sediments.

ACKNOWLEDGMENTS

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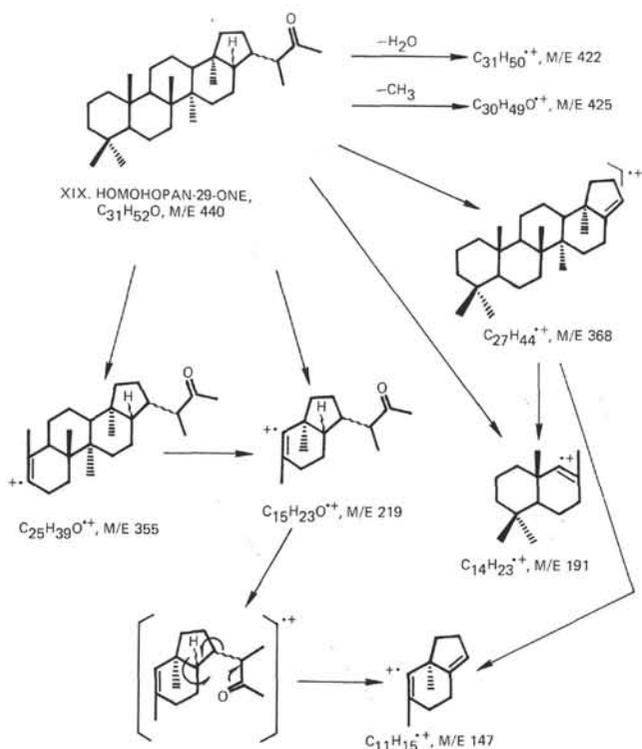


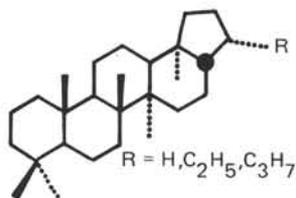
Figure 4. Mass spectrometric fragmentation pattern for the homohopan-29-ones.

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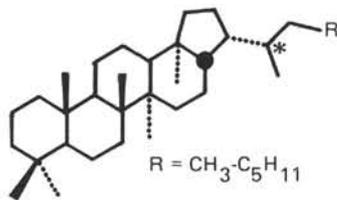
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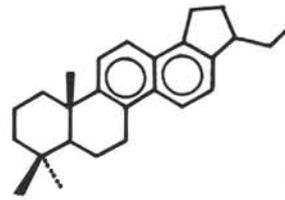
APPENDIX
Chemical Structures Cited in Text



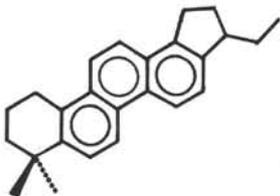
I. 17β(H),21β(H)-hopanes



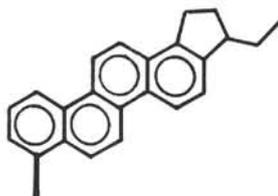
II. extended 17β(H),21β(H)-hopanes



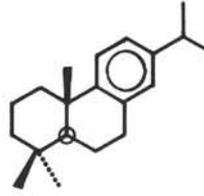
III. ethylcyclopentenotrimethyloctahydrochrysene



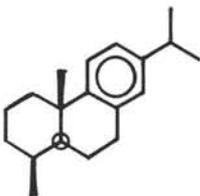
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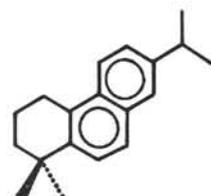
V. ethylcyclopentenomethylchrysene



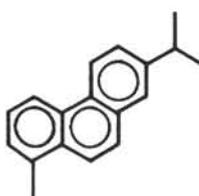
VI. dehydroabietane



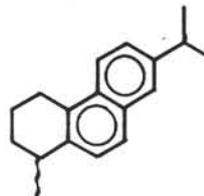
VII. dehydroabietin



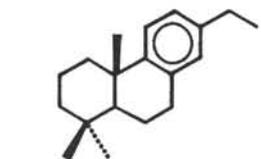
VIII. simonellite



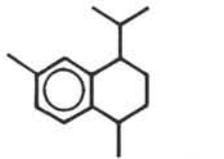
IX. retene



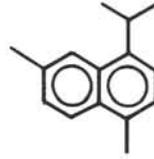
X. tetrahydroretene



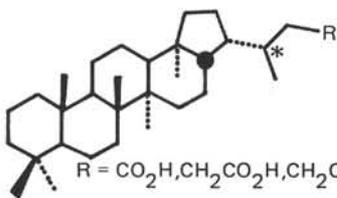
XI. 17-nordehydroabietane



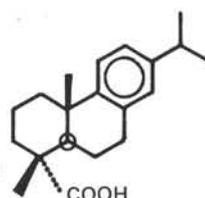
XII. tetrahydrocadalene



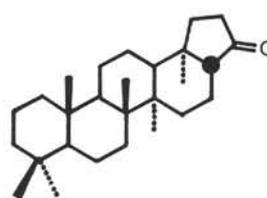
XIII. cadalene



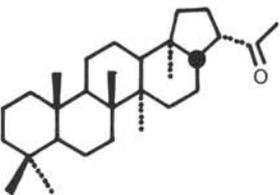
XIV. extended 17β(H),21β(H)-hopanoic acids



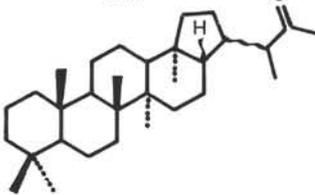
XV. dehydroabietic acid



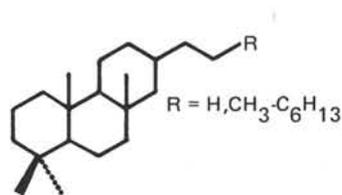
XVI. 17β(H)-trisnorhopan-21-one



XVII. 17β(H),21β(H)-norhopan-22-one



XVIII. homohopane-29-one



XIX. diterpanes